STUDIES IN

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THESIS

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By

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A C K N O W L E D G E M E N T S

The work in this thesis was carried out in the Department of Inorganic and Physical Chemistry of the Imperial College of Science and Technology between February 1950 and July 1953.

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A B S T R A C T

Measurements of hydrogen over potential on silver and tungsten cathodes in 0.1N, 0.4N and 1N hydrochloric acid solutions were carried out between 10^{-7} and 10^{-2} amps. cm.$^{-2}$ approximately. The major part of this work was devoted to obtaining successful results at low current densities and the following improvements in technique were found to be necessary:-

1. Oxide and particularly sulphide films on the silver electrode surface require uniform reduction at temperatures above that possible with glass.

2. Carbon or carbide films on tungsten must be removed by flashing tungsten at 3000°C approximately.

3. More rigorous pre-electrolysis conditions, than had been hitherto realised, must be applied. The continuous passage of a high pre-electrolysis current for long period was made possible only by a continuous water-cooling technique on the taps across which the current passed.

Tafel lines obtained with the above conditions are termed simple Tafel lines. For both silver and tungsten, these exhibit two well defined slopes, in the linear, logarithmic section, of b_1 = 0.06 v. and b_2 = 0.10 v. approximately (in 0.1N and 0.4N HCl.)

When the solution was not sufficiently purified or when the metal surface was not thoroughly cleaned, Tafel lines with a complex nature were observed.

Measurements of the electron number (from simple Tafel lines) indicate that its most probable value, for silver and tungsten in the above given concentrations, is 2. The mechanism would, therefore, be an electrochemical or a catalytic desorption. The catalytic mechanism is excluded since the experimental values of b_1 and b_2 are not 0.029 v. and there is no indication

for the occurence of a limiting current. The simple electrochemical desorption, however, is associated with a slope of $b_1 = 0.04$ v. From this, together with the evidence from the measurements of the electron number, it is concluded that the mechanism of hydrogen evolution on silver and tungsten (in 0.1N and 0.4N HCl) involves as the rate-dtermining step a complex electrochemical desorption in which the specific adsorption of H_3O^+ ions is an important part.

Studies on the effect of electropolishing on hydrogen overpotential indicate that the nature of the electropolishing solution plays an important role in directing the change of overpotential with electropolishing.

Equations for the heat of activation were deduced taking into considerations the change of the reversible potential $\Delta\phi_r$, the zeta potential ζ and the transfer coefficient α with temperature. The result indicates that if α and ζ are taken as constants, the heat of activation A_0 at the reversible potential, is identical with that deduced by Bockris and Potter taking $\Delta\phi_r$ as temperature independent.

For the calculations of the dielectric constant in the diffuse double layer as a function of distance, a method was developed for the integration of Poisson's equation (with a variable dielectric constant). Results of such calculations show that the concept of assuming a dielectric constant in the diffuse layer equal to that of the bulk of the solution is incorrect. This conclusion has an important effect on the numerical calculations of the double layer properties.

C O N T E N T S

Part ∝

KINETICS OF THE HYDROGEN EVOLUTION REACTION

Section I

PREVIOUS WORK ON THE KINETICS OF HYDROGEN EVOLUTION

		Page No.
1.	Introduction	1
2.	Activation Overpotential	
	a. Equations relating Current and Potential	3
3.	Reaction Paths for Hydrogen Evolution	
	a. Kinetics of Hydrogen Evolution when Discharge is rate-determining and Catalytic is desorptive ..	14
	b. Kinetics of Hydrogen Evolution when Catalytic Desorption is rate-determining	17
	c. Kinetics of Hydrogen Evolution when Electrochemical Mechanism is rate-determining	18
4.	Diagnostic Criteria for Hydrogen Evolution	19
5.	Observations on Experimental Techniques	
	a. State of the Metal Surface ..	21
	b. Design of the electrolytic cell	24
	c. Purity of the Solution ..	26
	d. Purity of Hydrogen ..	30
6.	Reasons for the Present Work ..	31

Page No.

SECTION II

EXPERIMENTAL WORK ON HYDROGEN ELECTRODE KINETICS

A. SOLID CATHODES

1. Introduction 33

2. Electrode Preparation
   a. Silver 33
   b. Tungsten 34
   c. Magnitude of Current necessary for reaching sufficient Temperature in Tungsten Wire .. 36

3. Conductivity Water .. 37
   a. Measurement of Conductivity 39
   b. Distillation under Hydrogen 40
   c. Purification of Nitrogen .. 41

4. Purification of Hydrogen .. 41

5. Preparation of Hydrogen Chloride .. 44

6. The electrolytic Cell .. 44

7. Apparatus for Electrical Measurements
   a. Measurement of Current .. 46
   b. " " Potential .. 46
   c. Source of Polarisation .. 47

8. The Hydrogen Electrode .. 48

9. Water-sealed Tap 49

10. Cleaning Mixture 52

11. Conditions for Pre-electrolysis .. 52

12 Method of Establishing the Tafel Line 55

B. EFFECT OF ELECTROPOLISHING ON OVERPOTENTIAL

1. Introduction 58

2. The electrolytic Cell .. 58

3. Purification of Hydrogen .. 59

4. Electrode Preparation .. 60
   a. Tin and Aluminium
   b. Iron

5. Conditions for Electropolishing .. 61

SECTION III

EXPERIMENTAL RESULTS

1. Complex Tafel Lines
   a. Silver 63
   b. Tungsten 64

2. Simple Tafel Lines 64

3. The Electron Number 68

4. Effect of Electropolishing .. 71

SECTION IV

DISCUSSION OF EXPERIMENTAL RESULTS

1. Complex Tafel Lines
   a. Effect of Depolarisers .. 73
   b. Effect of Platinum .. 77
   c. Effect of Carbide Formation 78

2. Simple Tafel Lines
   a. Observations on Experimental Technique necessary to obtain Results at very low current densities -
      (i) Purification of Hydrogen 81
      (ii) Electrode Preparation 82
      (iii) Pre-electrolysis .. 83
   b. Comparison with Previous Work 84
   c. The Mechanism of Hydrogen Evolution on Silver and Tungsten .. 88
   d. Complex Electrochemical Desorption
      (i) Possibility I .. 90
      (ii) " II
      (iii) Conclusion .. 94

Page No.

3. The Heat of Activation
   a. Method using i_c and i_o .. 96
   b. Method using $(\partial\eta/\partial T)$ .. 100

4. Effect of Electropolishing .. 102

PART β

THE DIELECTRIC CONSTANT IN THE DIFFUSE DOUBLE LAYER

1. Introduction 104

2. Work of Grahame
   a. General Equations .. 104
   b. Relation between S and D .. 107

3. Theory of Dielectric Constant near a charged Surface
   a. Introduction .. 111
   b. General Equations .. 112
   c. Graphical Method of Solution 116

4. Discussion 124

APPENDIX I

PREPARATION OF ALKALINE SOLUTIONS

1. Introduction 128

2. Purification of Sodium Hydroxide 128

APPENDIX II

IMPROVEMENTS IN THE EXPERIMENTAL TECHNIQUE OF HYDROGEN OVERPOTENTIAL STUDIES.

1. Purification of Hydrogen .. 132

2. The electrolytic Cell .. 133

3. Tap to withstand High Vacuum in the Presence of Electrolytic Solutions easily contaminated by Grease 135

PART α.

KINETICS OF

THE HYDROGEN EVOLUTION REACTION.

S E C T I O N I.

PREVIOUS WORK ON
THE KINETICS OF HYDROGEN EVOLUTION.

1. INTRODUCTION

When a metal is inserted in a solution containing hydrogen ions, and a current is allowed to flow through the metal solution interface, hydrogen ions are discharged forming molecular hydrogen. A change in potential (to a more negative value) which depends on the metal and the current density, is observed. At a given current density this change in potential is greater for mercury than it is for platinum. The difference between the potential of the electrode, at a given current density, and the reversible potential, termed hydrogen overpotential (η) was found by Tafel[1] to be connected with the current density by the empirical equation,

$$\eta = a - b \log_{10} i_c , \qquad (I 1.)$$

where a and b are independent of the current density but may depend on the metal.

Hydrogen overpotential is divided into three sections:

(a) activation overpotential η_A ,

(b) resistance overpotential η_B ,

(c) concentration overpotential η_C .

The term hydrogen overpotential usually refers to the activation overpotential of hydrogen at a given current density, it being assumed that care has been taken to reduce the other contributions to the overpotential to negligible amounts.

Consider a galvanic cell of a metal C and platinum dipped in the same solution and at the same temperature. To measure the potential of this cell a potentiometer is connected to C and to the platinum electrode with two pieces of wire of the same material as C. If the galvani p.d. between the bulk of C and the bulk of the solution is designated by $\Delta\phi_C$ that between the bulk of platinum and the bulk of the solution by $\Delta\phi_{Pt}$ and the contact potential between C and platinum by $\Delta\Phi$, then the potential measured with the potentiometer, ΔE is given by

$$\Delta E = \Delta\phi_C - \Delta\phi_{Pt} + \Delta\Phi \cdot \qquad (I2)$$

But,

$$\Delta\Phi = \Phi_C - \Phi_{Pt} , \qquad (I3)$$

where Φ_C , Φ_{Pt} are the thermionic work functions of the metal C and platinum respectively. The galvani p.d. $\Delta\phi_C$ is, therefore, given by

$$\Delta\phi_C = \phi_m - \phi_S = \Delta\Psi + \zeta + \Delta\chi_1 + \Delta\chi_2$$
$$= \Delta\phi + \zeta , \qquad (I4)$$

where ϕ_m , ϕ_S are the inner potentials in the bulk of the metal and the solution respectively, $\Delta\Psi$ is the p.d. due to excess charge between the surface of the metal and the centre of ions forming the Helmholtz double layer, $\Delta\chi_1$ is the p.d.

between the bulk of the metal and its surface, ζ is the p.d. between the bulk of the solution and the Helmholtz layer, and $\Delta\chi_2$ is p.d. due to dipoles adsorbed on the metal surface. From (I 2) and (I 3), in the case of hydrogen overpotential,

$$\Delta E = \Delta\phi_C - (\Delta\phi_{Pt} + \Phi_{Pt} - \Phi_C)$$
$$= \Delta\phi_C - \Delta\phi_r = \eta \,, \qquad (I\,5)$$

where $\Delta\phi_r$ is the galvani p.d. for the reversible hydrogen electrode in the same solution as metal C.

2. ACTIVATION OVERPOTENTIAL

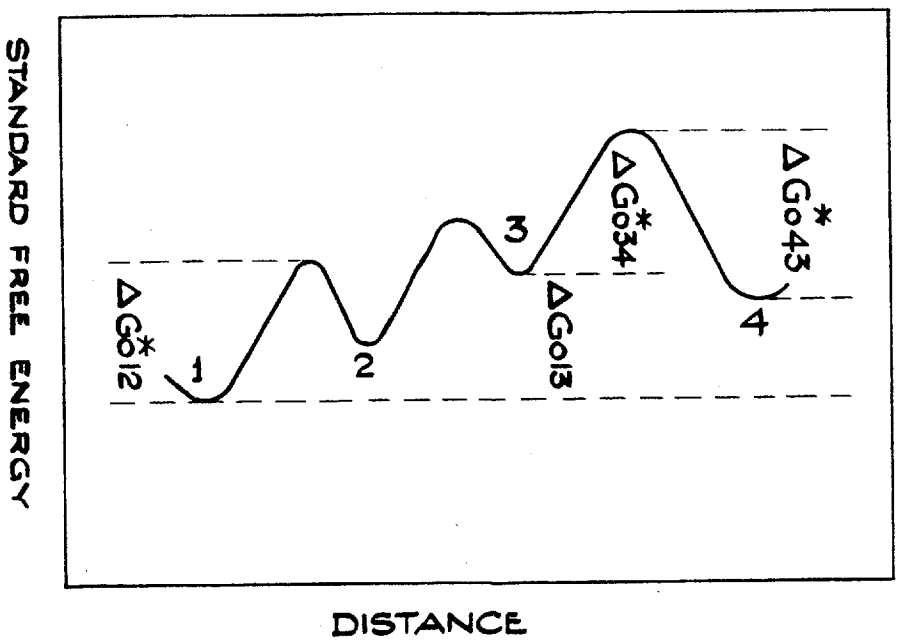
a. Equations relating Current and Potential.

The cathodic hydrogen evolution is represented by the overall reaction,

$$2\,BH^+ + 2\,e_0 \rightleftharpoons H_2 \,, \qquad (I\,6)$$

where BH^+ is the solvated hydrogen ion. This reaction, like other electrode reactions, is characterised by its consecutive nature, the overall rate of the reaction being governed by the slowest step. A schematic diagram of such a reaction is shown in Fig. (I_1). The initial state is represented by 1, and the final state by 4. In crossing the energy barrier from 1 to 2, the rate of this step according to the theory of

FIG (I1)



absolute reaction rates[2] is given by

$$V_{12} = K_{12} \frac{kT}{h} \pi a_1 \bar{e}^{\frac{\Delta G^*_{o12}}{RT}} , \qquad (I\ 7)$$

where K_{12} is the transmission coefficient for the forward direction of this step, k is the Boltzman's constant, T is the absolute temperature, h is Planck's constant, πa_1 is the product of activities for the reactants in state 1, and ΔG^*_{o12} is the standard free energy of activation for the forward direction of this step. For the reverse direction, the rate is given by

$$V_{21} = K_{21} \frac{kT}{h} \pi a_2 \bar{e}^{\frac{\Delta G^*_{o21}}{RT}} . \qquad (I\ 8)$$

Similarly for the energy barrier between states 2 and 3,

$$V_{23} = K_{23} \frac{kT}{h} \pi a_2 \bar{e}^{\frac{\Delta G^*_{o23}}{RT}} , \qquad (I\ 9)$$

and,

$$V_{32} = K_{32} \frac{kT}{h} \pi a_3 \bar{e}^{\frac{\Delta G^*_{o32}}{RT}} . \qquad (I\ 10)$$

Since according to the theory of absolute reaction rates, states 1, 2 and 3 can be assumed to be in equilibrium,[3]

$$\nu_{12} = \nu_{21} \quad \text{and,} \quad \nu_{23} = \nu_{32} ,$$

$$\therefore \frac{\pi a_2}{\pi a_1} = \frac{K_{12}}{K_{21}} \; e^{-\frac{(\Delta G^*_{o12} - \Delta G^*_{o21})}{RT}} , \qquad (I\ 11)$$

and,

$$\frac{\pi a_3}{\pi a_2} = \frac{K_{23}}{K_{32}} \; e^{-\frac{(\Delta G^*_{o23} - \Delta G^*_{o32})}{RT}} . \qquad (I\ 12)$$

The product of the activities of the reactants in state 3 is given by

$$\pi a_3 = \pi a_1 \times \frac{\pi a_2}{\pi a_1} \times \frac{\pi a_3}{\pi a_2} . \qquad (I\ 13)$$

Substituting (I 11) and (I 12) in (I 13) one gets

$$\pi a_3 = \pi a_1 \, \pi_K \, e^{-\frac{(\Delta G^*_{o12} - \Delta G^*_{o21} + \Delta G^*_{o23} - \Delta G^*_{o32})}{RT}}$$

$$= \pi a_1 \, \pi_K \, e^{-\frac{\Delta G_{o13}}{RT}} , \qquad (I\ 14)$$

where π_K is the product of the transmission coefficients and ΔG_{o13} is the standard free energy difference between state 1 and state 3.

Since the energy barrier between states 3 and 4 is the highest with respect to the initial state 1, then the rate of this step governs the rate of the overall reaction and is given by

$$v_{34} = \vec{v} = K_{34} \frac{kT}{h} \pi a_3 \, \bar{e}^{\frac{\Delta G^*_{o34}}{RT}} , \qquad (I\ 15)$$

where $\vec{v}$ is the rate of the overall reaction in the forward direction. Substituting (I 14) in (I 15) one gets,

$$\vec{v} = \pi K' \frac{kT}{h} \pi a_1 \, e^{-\frac{(\Delta G_{o13} + \Delta G^*_{o34})}{RT}}$$

$$= K \frac{kT}{h} \pi a_1 \, e^{-\frac{\vec{\Delta G}^*_o}{RT}}$$

$$= \vec{k} \, \pi a_1 , \qquad (I\ 16)$$

where $\pi K'$ is another product of transmission coefficients, $\vec{\Delta G}^*_o$ is the standard free energy of activation of the rate-determining step in the forward direction with respect to the initial state 1, i.e., the standard free energy of activation of the overall reaction in the forward direction, and $\vec{k}$ is the specific reaction rate in the forward direction. Since all transmission coefficients in this case are equal to one,[2] $\pi K'$ is replaced by K.

Since the activated state having the highest free energy referred to the initial state will also have the highest free energy referred to the final state, the reverse reaction must follow the same path as the forward reaction in the opposite direction. This is so because if a reaction path with a lower energy of activation is available for the reverse

reaction, it will also be available for the forward reaction. The rate of the overall reaction in the reverse direction is, therefore, given by

$$\overleftarrow{v} = \kappa \frac{kT}{h} \pi a_f \, e^{-\frac{\overleftarrow{\Delta G_o^*}}{RT}}$$

$$= \overleftarrow{k} \, \pi a_f \,, \qquad (I\,17)$$

where πa_f is the product of activities of the reactants in state 4, $\overleftarrow{\Delta G_o^*}$ is the standard free energy of activation of the rate-determining step, and hence of the overall reaction between the final state and the highest energy barrier, and $\overleftarrow{k}$ is the specific reaction rate in the reverse direction.

Let us define a quantity, λ, called the electron number as the number of electrons which must be given up by the electrode to complete one act of the rate-determining step. Let the initial state be taken as λ gram ions of hydrogen in the Helmholtz layer and λ gram electrons in the surface of the metal. Let the final state be taken as $\lambda/2$ gram moles of hydrogen molecules in the gas phase. When a potential, $\Delta\phi_c$, exists between the bulk of the metal and the bulk of the solution, part of this potential will help the forward reaction and another part will retard the reverse reaction. These parts of the potential are evaluated in the

following way:

The terms $\overrightarrow{\Delta G_o^*}$ and $\overleftarrow{\Delta G_o^*}$ in (I 16) and (I 17), when a potential ($\Delta\phi - \Delta\chi_1$) is applied between initial and final states, are identical with the standard electrochemical potentials of activation $\overrightarrow{\Delta\bar{\mu}_o^*}$ and $\overleftarrow{\Delta\bar{\mu}_o^*}$ respectively. The standard electrochemical potential of any ionic component is related to its standard chemical potential with the following relation:

$$\bar{\mu}_o = \mu_o + \lambda z F \phi \,, \qquad (I\ 18)$$

where ϕ is the inner potential of the phase in which this component exists, z is the valence of this component, $\bar{\mu}_o$ and μ_o are the standard electrochemical and chemical potentials for λ gram ions. z is one in the case of hydrogen evolution. The standard electrochemical potential of the initial state is, therefore, given by

$$\bar{\mu}_{o1} = \mu_{o1} + \lambda F (\phi_s + \zeta) - \lambda F (\phi_m - \Delta\chi_1), \qquad (I\ 19)$$

where μ_{o1} is the chemical potential of ions and electrons in the initial state. The standard electrochemical potential of the activated state is given by

$$\bar{\mu}_{oAc} = \mu_{oAc} + \lambda F(\phi_+) - \lambda F(\phi_-) \,, \qquad (I\ 20)$$

where (ϕ_+) , (ϕ_-) are the inner potentials for the hydrogen ions and electrons in the activated state.

Assuming that the electrons taking part in the reaction,

$$H^+ + e_0 \longrightarrow MH \ ,$$

remain in the metal surface, i.e., proton transfer rather than electron transfer occurs, then,

$$\phi_- = \phi_m - \Delta\chi_1 \ . \qquad (I\ 21)$$

The electrical potential of hydrogen ions in the activated state, ϕ_+ , is more negative than their potential in the initial state so that,

$$\phi_+ = (\phi_s + \xi) + \beta\,(\Delta\phi - \Delta\chi_1) \ , \qquad (I\ 22)$$

where

$$\beta = \frac{\text{distance between activated and initial states}}{\text{" " initial and final states}}$$

Substituting (I 22) and (21) in (I 20) one gets,

$$\bar{\mu}_{oAc} = \mu_{oAc} + \lambda F\left[(\phi_s+\xi) + \beta(\Delta\phi - \Delta\chi_1) - (\phi_m - \Delta\chi_1)\right] \qquad (I\ 23)$$

From (I 23) and (I 19) the standard electro-chemical potential of activation for the forward direction is given by

$$\Delta\vec{\bar{\mu}}_o^{\,*} = \bar{\mu}_{oAc} - \bar{\mu}_{oi} = \mu_{oAc} - \mu_{oi} + \lambda\beta F(\Delta\phi - \Delta\chi_1) \ . \qquad (I\ 24)$$

Since $\Delta\chi_1$, which represents the p.d. between the bulk of the metal and its surface, remains constant with changing the applied potential, the term $\lambda\beta F\Delta\chi_1$ can be included in the constant term in (I.24). Therefore one gets,

$$\overrightarrow{\Delta\bar{\mu}_o^*} = \overrightarrow{\Delta\mu_o^*} + \lambda\beta F\Delta\phi \,. \qquad (I\,25)$$

Since the final state is composed only of neutral components, the electrochemical potential of any of these components is equal to its chemical potential, so that:

$$\bar{\mu}_{of} = \mu_{of} \,. \qquad (I\,26)$$

From (I 26) and (I 23),

$$\overleftarrow{\Delta\bar{\mu}_o^*} = \mu_{oAc} - \mu_{of} - \lambda(1-\beta)F(\Delta\phi - \Delta\chi_1)$$

$$= \overleftarrow{\Delta\mu_o^*} - \lambda(1-\beta)\Delta\phi F \,, \qquad (I\,27)$$

where $\overleftarrow{\Delta\mu_o^*}$ is the standard electrochemical potential of activation for the reverse direction, i.e., the dissolution of molecular hydrogen into hydrogen ions.

Substituting (I 25) and (I 27) in (I 16) and (I 17) respectively one gets,

$$\overrightarrow{v} = K\frac{kT}{h}\pi a_1 \, e^{-\overrightarrow{\Delta\mu_o^*}/RT} \, e^{-\lambda\beta\Delta\phi F/RT} \,, \qquad (I\,28)$$

and,

$$\overleftarrow{V} = K \frac{kT}{h} \pi a_f \, e^{-\overleftarrow{\Delta\mu_0^*}/RT} \, e^{+\lambda(1-\beta)\Delta\phi F/RT} \,. \qquad (I\,29)$$

The forward and the reverse currents, i.e., the cathodic and anodic transfer currents are given by

$$\overrightarrow{i} = \lambda F \overrightarrow{V} = \lambda F K \frac{kT}{h} \pi a_i \, e^{-\overrightarrow{\Delta\mu_0^*}/RT} \, e^{-\lambda\beta\Delta\phi F/RT} \,, \qquad (I\,30)$$

and,

$$\overleftarrow{i} = \lambda F \overleftarrow{V} = \lambda F K \frac{kT}{h} \pi a_f \, e^{-\overleftarrow{\Delta\mu_0^*}/RT} \, e^{\lambda(1-\beta)\Delta\phi F/RT} \,. \qquad (I\,31)$$

From (I 4) and (I 5),

$$\eta = \Delta\phi_c - \Delta\phi_r = \Delta\phi + \zeta - \Delta\phi_r \,. \qquad (I\,32)$$

When $\Delta\phi_c$ is equal to $\Delta\phi_r$, $\eta = 0$ and the cathodic and anodic transfer currents are equal, thus,

$$\overrightarrow{i} - \overleftarrow{i} = 0 \,, \quad \overrightarrow{i} = \overleftarrow{i} = i_0 \,,$$

where i_0 is called the exchange current.

Substituting (I 32) in (I 30) and (I 31) one gets,

$$\overrightarrow{i} = \left[\lambda F K \frac{kT}{h} \pi a_i \exp.\left(-\frac{\overrightarrow{\Delta\mu_0^*}}{RT}\right) \exp.\left(-\frac{\lambda\beta F(\Delta\phi_r - \zeta)}{RT}\right)\right]$$

$$\times \exp.\left(-\frac{\lambda\beta\eta F}{RT}\right) = i_0 \exp.\left(-\frac{\lambda\beta\eta F}{RT}\right) \,, \qquad (I\,33)$$

and similarly,

$$\overleftarrow{i} = i_o \exp.\left(\frac{\lambda(1-\beta)\eta F}{RT}\right). \qquad (I\,34)$$

The net cathodic current in amps $cm.^{-2}$ is given by

$$i_c = \overrightarrow{i} - \overleftarrow{i} = i_o\left[e^{-\frac{\lambda\beta\eta F}{RT}} - e^{\frac{\lambda(1-\beta)\eta F}{RT}}\right]. \qquad (I\,35)$$

At high cathodic polarisation the second term in brackets in (I 35) becomes very small, thus,

$$i_c = i_o\, e^{-\lambda\beta\eta F/RT}. \qquad (I\,36)$$

$$\therefore \eta = 2.303\frac{RT}{\lambda\beta F}\log_{10} i_o - 2.303\frac{RT}{\lambda\beta F}\log_{10} i_c. \qquad (I\,37)$$

Equation (I 37) is identical with the Tafel equation (I 1). From (I 37) and (I 1) one gets,

$$a = 2.303\frac{RT}{\lambda\beta F}\log_{10} i_o, \qquad (I\,38)$$

and,

$$b = 2.303\frac{RT}{\lambda\beta F}. \qquad (I\,39)$$

$$\therefore \frac{a}{b} = \log_{10} i_o. \qquad (I\,40)$$

At very small cathodic polarisation, the exponential terms in (I 35) may be expanded approximately, so that:

$$i_c = - i_o \frac{\lambda \eta F}{RT} . \qquad (I\,41)$$

$$\therefore \left(\frac{\partial i_c}{\partial \eta}\right)_{\eta \to 0} = - \frac{i_o \lambda F}{RT} .$$

$$\therefore \lambda = - \frac{RT}{i_o F} \left(\frac{\partial i_c}{\partial \eta}\right)_{\eta \to 0} \qquad (I\,42)$$

It is evident from (I 41) that, at low overpotential values, there is a linear relation between i_c and η. The slope of the line giving the relation between i_c and η is of tremendous importance for the evaluation of the electron number λ as shown in (I 42). The electron number is an important parameter for elucidating the mechanism of hydrogen evolution. Thus for the slow discharge mechanism,

$$H_3O^+ + e_0 \longrightarrow H_2O + MH \qquad \lambda = 1 ,$$

for the electrochemical,

$$H_3O^+ + MH + e_0 \longrightarrow H_2O + H_2 + M \qquad \lambda = 2 ,$$

and for the catalytic,

$$MH + MH \longrightarrow 2M + H_2 \qquad \lambda = 2 .$$

3. REACTION PATHS FOR HYDROGEN EVOLUTION[4]

In aqueous acid solutions the possible paths for hydrogen evolution are,

a. $H_3O^+ + e_o \xrightarrow{slow} MH + H_2O$, $MH + MH \xrightarrow{fast} H_2 + 2M$

b. $MH + MH \xrightarrow{slow} H_2 + 2M$, $H_3O^+ + e_o \xrightarrow{fast} H_2O + MH$

c. $H_3O^+ + e_o \xrightarrow{slow} MH + H_2O$, $MH + e_o + H_3O^+ \xrightarrow{fast} H_2 + H_2O + M$

d. $MH + e_o + H_3O^+ \xrightarrow{slow} H_2 + H_2O + M$, $H_3O^+ + e_o \xrightarrow{fast} H_2O + MH$

It is impossible that hydrogen is discharged from water molecules in acid solutions.[5] In alkaline solutions hydrogen is probably discharged from water molecules,[6] not from hydroxonium ions, owing to the fact that the overwhelmingly large number of water molecules overcomes the energetics to make this the faster of the two discharge steps.

a. Kinetics of Hydrogen Evolution when Discharge is rate-determining and catalytic is desorptive.

The following equations represent the forward and reverse rates of the slow discharge and that of the catalytic respectively*;

$$v_1 = k_1 (a_{H^+})_{d.l.} (1-x)\, e^{-\Delta\phi F/2RT}, \qquad (I\,43)$$

---

* The dissolution of molecular hydrogen is neglected because of the very large heat of dissociation of hydrogen.

$$v_2 = k_2 (a_H) e^{+\Delta\phi F/2RT}, \qquad (I\,44)$$

$$v_3 = k_3 (a_H)^2, \qquad (I\,45)$$

Where $\Delta\phi$ is the potential difference between the bulk of the cathode and the Helmholtz double layer, $(a_{H^+})_{d.l.}$ is the activity of hydrogen ions in the double layer, x is the fraction of the available surface covered with adsorbed hydrogen atoms and (a_H) is the activity of adsorbed hydrogen atoms. Since there are 10^{15} spaces available for adsorption per cm.^{2}, and taking the activity coefficient of adsorbed hydrogen to be one, the following relation is thus obtained,

$$(a_H) = \frac{x\,10^{15}}{N} \simeq x\,10^{-9}, \qquad (I\,46)$$

where N is Avogadro's number and (a_H) is in gram atoms per cm.^{2}

In the steady state,

$$v_1 - v_2 - 2v_3 = 0 . \qquad (I\,47)$$

From (I 43), (I 44), (I 45), (I 46) and (I 47),

$$x = \frac{-(a_1+a_2) + \sqrt{(a_1+a_2)^2 + 8a_1a_3}}{4a_3}, \qquad (I\,48)$$

where,

$$\left.\begin{aligned} a_1 &= k_1 (a_{H^+})_{d.l.} \exp.(-\Delta\phi F/2RT) \\ a_2 &= k_2 (10^{-9}) \exp.(+\Delta\phi F/2RT) \\ a_3 &= k_3 (10^{-18}) \end{aligned}\right\} \quad (I\,48a)$$

The current will therefore be,

$$i_c = 2F v_3 = 2F a_3 x^2. \quad (I\,49)$$

The slow discharge is rate-determining when ,

$$a_3 > 10\, a_1 \quad , \quad a_1 > 10\, a_2 . \quad (I\,50)$$

Then from (I 50),

$$a_1 a_3 > 10 (a_1)^2 \; , \; (a_1)^2 > 10\, a_1 a_2 \; , (a_1)^2 > 100 (a_2)^2. \quad (I\,51)$$

Substituting (I 50) and (I 51) in (I 48), the coverage of the surface when the slow discharge is rate-determining is,

$$x = \sqrt{\frac{a_1}{2a_3}} . \quad (I\,52)$$

From (I 49) and (I 52) the current is,

$$i_c = 2F a_3 x^2 = F k_1 (a_{H^+})_{d.l.} e^{-\Delta\phi F/2RT} . \quad (I\,53)$$

Therefore α for the slow discharge is 0.5, and since $\lambda = 1$ β is 0.5.

b. Kinetics of Hydrogen Evolution when Catalytic Desorption is rate-determining.

Using the condition $a_1 > 10 a_3$, and with the help of (I 48), the coverage of the surface when the catalytic combination is rate-determining is,

$$x = \frac{a_1}{a_1 + a_2} \qquad (I54)$$

[In the derivation of (I 54) it is necessary to use the approximation: $\sqrt{1+n} = 1 + n/2$ where n is small.] Substituting (I 54) in (I 49) the relation for the overall current results as:

$$i_C = 2Fk_3 10^{-18} \left[\frac{1}{1 + \frac{k_2 10^{-9}}{k_1 (a_{H^+})_{d.l.}} e^{\Delta\phi F/RT}} \right]^2 \qquad (I55)$$

Therefore,

$$\left(\frac{d\Delta\phi}{d \ln i_C}\right) = \frac{-b}{2.303} = \frac{1 + \frac{k_2 10^{-9}}{k_1 (a_{H^+})_{d.l.}} e^{\Delta\phi F/RT}}{\frac{2Fk_2 10^{-9}}{RTk_1 (a_{H^+})_{d.l.}} e^{\Delta\phi F/RT}} . \qquad (I56)$$

In the case when,

$$\frac{k_2 10^{-9}}{k_1 (a_{H^+})_{d.l.}} e^{\Delta\phi F/RT} > 10 , \qquad (I57)$$

the slope of the Tafel line is given by (cf equation I 56),

$$\frac{2.303 RT}{2F} = 0.029 \text{ V. at } 20^\circ C .$$

Therefore α is 2, and since λ is 2, β is one. From (I 57) and (I 55),

When $\Delta\phi$ tends to $-\infty$, b tends to ∞ so that $\alpha \longrightarrow 0$ and $\beta \rightarrow 0$; also the term between brackets in (I 55) tends to unity so that,

$$i_c = 2F k_3 10^{-18}. \qquad (I59)$$

Equation (I 59) indicates that at high cathodic polarisation the current becomes constant for the atomic combination mechanism. This is termed the limiting current.

c. Kinetics of Hydrogen Evolution when the Electrochemical Mechanism is rate-determining.

The rate of the electrochemical desorption is,

$$V_4 = k_4 (10^{-9} x)(a_{H^+})_{d.l.} e^{-\Delta\phi F/2RT}. \qquad (I60)$$

At the steady state one gets,

$$V_1 - V_2 - V_4 = 0 . \qquad (I61)$$

Therefore,

$$x = \frac{a_1}{a_1 + a_2 + a_4}, \qquad (I62)$$

where a_1 and a_2 are given by (I 48a) and,

$$a_4 = k_4 (10^{-9})(a_{H^+})_{d.l.} e^{-\Delta\phi F/2RT}. \qquad (I63)$$

The current is, therefore, given by,

$$i_c = 2F v_4 \cdot \qquad (I64)$$

The conditions for the electrochemical mechanism to be rate-determining are,

$$a_1 > 10\, a_2 \quad , \quad a_2 > 10\, a_4 \qquad (I65)$$

or,

$$a_2 > 10\, a_1 \quad , \quad a_1 > 10\, a_4 \qquad (I66)$$

From (I 65) x is one and the current is,

$$i_c = 2F k_4 (10^{-9}) (a_{H^+})_{d.l.} \, e^{-\Delta\phi F/2RT} \, , \qquad (I67)$$

from which α is 0.5 and since λ is 2, β is 0.25. From (I 66) $x = a_1/a_2$ and the current is,

$$i_c = 2F \frac{k_1 k_4}{k_2} (a_{H^+})^2_{d.l.} \, e^{-3\Delta\phi F/2RT} \, , \qquad (I68)$$

From (I 68) α is 1.5 and since λ is 2, β is 0.75.

4. DIAGNOSTIC CRITERIA FOR HYDROGEN EVOLUTION.

The rate-determining step in the process of cathodic hydrogen evolution is ascertained with a knowledge of the parameters α, β, λ and b. Table (I 1) gives their values for different mechanisms.

TABLE (I 1)

Parameters of the Hydrogen Evolution Reaction

Mechanism	α	β	λ	b
Slow discharge	0.5	0.5	1	0.116
Catalytic (low polarisation)	2	1	2	0.029
" (high ")	0	0	2	∞
Electrochemical ($x = 1$)	0.5	0.25	2	0.116
" ($x = a_1/a_2$)	1.5	0.75	2	0.039

5. OBSERVATIONS ON EXPERIMENTAL TECHNIQUES.

Irreproducibility previously observed in the results of various authors may be attributed to the lack of uniformity in the procedures used, particularly to the lack of appreciation of impurity effects. The factors influencing the work on hydrogen overpotential are as follows:

a. State of the metal surface,

b. Design of the electrolytic cell,

c. Purity of the solution,

d. Purity of hydrogen.

a. State of the Metal Surface.

Owing to the fact that hydrogen overpotential is dependent on the surface properties of the metal, the cathode has to be thoroughly cleaned. Oxide and sulphide films on the surface cause depolarisation (the tendency of the potential to become anodic) at low current densities, the hydrogen evolved being consumed in the reduction of these films. At high current densities these films may also have a resistance high enough for an appreciable contribution from ohmic overpotential to be observed. Organic impurities also vitiate the kinetics of the hydrogen evolution reaction, probably owing to the effect on the heat of adsorption of hydrogen on the metal. Thus the preliminary treatment of the cathode

effects overpotential, in so far as it either cleans the surface or adds more impurities to it.

Platonova and Levina[7] working on hydrogen overpotential on iron, cleaned the iron electrode in hot alkali to remove organic impurities. This was followed by treating the electrode with sulphuric acid. The pre-treatment of the electrode with acids or alkalis, which contain a considerable amount of impurities such as metallic cations, is best avoided.

Bockris and Parsons[8] prepared platinum, palladium, gold and silver electrodes by electrodepositing these metals on platinum substrate. This method is not reliable, specially for low current density work, unless the solution used for electrodeposition is of the same standard of purity as the solution used for overpotential measurements.

Mechanical methods of cleaning the surface, such as cutting it with a knife or a razor, or rubbing it with emery paper,[13] cause the contamination of the surface with metallic or sand particles. In the first case hydrogen will be evolved preferentially on the metal of lowest overpotential, which may be the particles of the knife. In the second case, the true area of the cathode changes and impurities from the sand may be adsorbed on the surface.

Bockris[9] has shown that it is erroneous to use grease, organic or inorganic cements[14] for fixing the electrode to glass. These cements tend to dissolve in the solution and even if this dissolution is of very small extent, the resulting

impurities may affect the kinetics of the reaction.

Platonova and Levina[7] prepared the electrodes by reducing them in an atmosphere of hydrogen at high temperatures, and keeping them sealed in ampoules under an atmosphere of hydrogen. These ampoules were broken a short time before the experiment and the electrodes were exposed to the atmosphere. However short this time is, an oxide or sulphide film, varying in thickness from one metal to another, is formed on the surface.

Other workers, e.g., Lukovstev, Levina and Frumkin[10][11] tried to reduce the oxide on nickel electrodes after fixing them in the electrolytic cell by filling the cell with hydrogen and using an external heater. Since hydrogen becomes moist after introducing it into the cell, the water vapour sets up an equilibrium with the oxide-covered metal and retards its complete reduction. Furthermore if the electrode is originally covered with a sulphide film, sulphur compounds such as hydrogen sulphide may be formed by this treatment and these cause the deviation from linearity of the Tafel line at high current densities.[20]

Some authors, e.g. Hammett[12], cleaned the cathode surface by anodic polarisation in the same solution used for over-potential measurements. The results obtained for platinum treated in this way, were found to be reproducible. The only difficulty attached to this method is that it leads to the presence of depolarising gases, dissolved in the solution. These are of lesser account for metals of very low overpotential,

such as platinum. However, for metals such as silver and nickel they would lead to depolarisation. Furthermore, surface films of, e.g., silver chloride would be formed.

The most reliable method for the preparation of solid electrodes has been given by Bockris and Conway.[15] This consists of cleaning the spectroscopically pure metal by heating it in a stream of dried and purified hydrogen and then sealing it in a glass bulb containing the same gas. This bulb is broken in the de-oxygenated, purified solution directly before the measurements are started.

For mercury cathodes the most appropriate method of obtaining a clean surface is to distill it twice in an all glass apparatus under a partial vacuum, after subjecting it to electrolytic purification, the mercury undergoing purification being the anode as described by Naray-Szabo.[16] The mercury is then stored in a reservoir attached to the electrolytic cell, and is finally distilled to the cathode compartment of the cell under vacuum.

b. Design of the electrolytic Cell.

The main requirements in an ideal electrolytic cell for hydrogen overpotential studies are,

(i) The cell must be air-tight.

(ii) It must be designed in a manner to prevent the diffusion of anodic products to the cathode.

(iii) It must not contain any greased taps in contact with the solution.

(iv) The cathode must be capable of being adjusted to touch the tip of the Luggin capillary.

(v) The cell must be constructed of arsenic-free glass. A brand of borosilicate glass commercially called Hysil is the most suited for this purpose.

The use of ungreased vacuum taps is unsatisfactory since air diffuses into the cell through the barrel and the stopcock. This type of tap is replaced by a water-sealed tap where a thin film of equilibrium water, between the barrel and the stopcock, hinders the inward diffusion of air. Connections between various parts of the apparatus and the cell are made with the help of ground glass joints surrounded by glass jackets filled with equilibrium water which also hinders air diffusion.

To prevent the diffusion of anodic products to the cathode a sintered glass disc and a water-sealed tap are inserted between the anode and the cathode compartments. Grew[17] used an external anode in a beaker containing a solution of the same strength as that inside the cell. A bulb of lead conductivity glass was connected to the cathode and hydrogen electrode compartments, and was dipped into the beaker. The transfer of current through the wall of this bulb takes place by lead ions in the glass and the oxygen evolved on the anode escapes to the atmosphere. A cell having the above requirements

was designed by Levina and Silberfarb.[18] Such cells have been extensively developed by Frumkin and by Bockris.[9]

c. Purity of the Solution.

Various methods for preparing solutions for hydrogen overpotential work are recorded in the literature. That based on using solutions of acids as obtained from the bottle, and diluting these appropriately without any further purification, is not recommended since most of these acids contain appreciable quantities of heavy metals, such as lead and arsenic compounds. Arsenic compounds have a poisoning effect on hydrogen overpotential. Bockris and Conway[19] studied the effect of poisoning the surface of platinised platinum and nickel with arsenic trioxide at constant current density. For platinised platinum they found an increase in the overpotential with the increase of arsenic trioxide added. On nickel electrodes they noticed a decrease in the overpotential when the concentration of As_2O_3 was as little as 10^{-10} mole per litre. Similar sensitivity was noticed with carbon monoxide and potassium cyanide.

The appropriate method of preparing the solution is to start with conductivity water refluxed under purified hydrogen for a long time to ensure the removal of all traces of oxygen. Hydrogen chloride gas or sulphuric acid crystals prepared by fractional crystallisation in an atmosphere of hydrogen, are

dissolved in water with a stream of purified hydrogen. The solution is then extensively purified by pre-electrolysis[20][18] on a separate cathode of the same material as the test electrode. The appropriate current density for pre-electrolysis varies from one metal to another. Bockris and Watson,[21] working with mercury obtained reproducible results using a current density of 10^{-4} amps. per cm.^{2} for pre-electrolysis. Bockris and Conway[22] found that, to get satisfactory results on silver, the current density for pre-electrolysis should be 10^{-1} amps. per cm.^{2} in 0.001 N hydrochloric acid solution. The conditions of pre-electrolysis depend on the nature and concentration of the depolarisers and other impurities present in the solution. Those conditions must be determined by trial and error and the criterion of the "pure" solution being reached when further increase in pre-electrolysis makes no further difference to the measured overpotential.

The concentration of depolarisers in the solution determines the lowest current density below which depolarisation is effective. The limiting current of diffusion of a depolariser is given by[23],[24]

$$i_L = \frac{DzFC}{\delta}$$

where D is the diffusion coefficient in cm.^{2} per second, F is the faraday in coulombs, δ is the thickness of the diffusion layer in cm., z is the number of faradays used

up for the electrolysis of one mole of the depolariser, and C is the concentration of the depolariser in gram mole per cc. In unstirred solution δ is approximately equal to 0.05 cm.[25] The limiting current of diffusion is, thus given by

$$i_L = 1.93 \times 10^{-3} D z C'$$

where C' is the concentration in gram mole per litre. For oxygen[23] $Z = 4$ and $D = 1.8 \times 10^{-5}$, thus

$$(i_L)_{O_2} \simeq 0.14 C'$$

If C' is 1×10^{-5} mole O_2 per litre, the depolarisation by oxygen will therefore be effective at a current density of 1.4×10^{-6} amps per cm.^{2} and below it.

Owing to the extreme sensitivity of hydrogen overpotential to poisons, it is necessary to use hysil glass in all parts of the apparatus that come in contact with the solution (pyrex glass contains arsenic).

The use of platinum in the cell as anode or conductivity electrodes is not recommended for overpotential work in high acid concentrations.[22] Platinum dissolves, either anodically or through the attack of acids, specially hydrochloric acid, and is then deposited on the cathode causing a decrease in overpotential. Spectroscopically pure carbon anodes and conductivity electrodes are therefore preferable and can be equally effective.[6][22][26]

Some workers, e.g. Kabanov and Jofa,[27] working on lead electrodes, used the same electrode both for pre-electrolysis and actual measurements. This is obviously not satisfactory because of the impurities deposited during the pre-electrolysis. Others[7] pre-electrolysed the solution in one compartment and transferred it to the cathode compartment where the measurements were made. This is also unsatisfactory since in the process of transferring, the solution may be contaminated with impurities from the walls of the cathode compartment.

For the preparation of sodium hydroxide solutions Lukovstev and co-workers[11] prepared sodium amalgam by the electrolytic polarisation of a sodium salt solution using mercury as cathode. The amalgam was then decomposed in conductivity water previously saturated with hydrogen. The disadvantage of this method is that if the solution of the sodium salt is not pre-electrolysed, the amalgam formed will contain some impurities. The resulting sodium hydroxide solution contains, therefore, foreign cations in addition to mercury ions. The method of preparing sodium hydroxide solutions used by Kenyon,[28] and Kenyon and Bowden consists of redistilling sodium metal and then dissolving it in conductivity water. This method is inconvenient owing to the practical difficulty of sodium distillation.

Bockris and Potter[6][29] prepared NaoH solutions by fractional crystallisation of analar NaoH in conductivity

water and under an atmosphere of hydrogen. This was followed by pre-electrolysis of the solution between two platinum electrodes.

d. Purity of Hydrogen

Electrolytic hydrogen is prepared commercially in two grades; the commercial grade and the oxygen-free grade. The commercial grade contains impurities such as carbon dioxide, carbon monoxide, oxygen, water vapour, and traces of methane, ethane and other hydrocarbons. The oxygen-free grade contains a much lesser quantity of oxygen than the commercial grade and practically the same quantities of other impurities. In the design of a hydrogen purification train, it is important to have only solid reagents otherwise it is possible that some of the liquid components may be carried over into the cell in the form of a spray. The train must be able to withstand a vacuum to allow the removal of oxygen and parts of it which are subject to heat must be of hysil glass.

6. THE REASON FOR THE PRESENT WORK.

The mechanisms of hydrogen evolution on metals of high overpotential, e.g., mercury[30] and lead[27] and on metals of low overpotential, e.g., platinum[12][31] and palladium[32] were established with some degree of certainty. However, for metals of intermediate overpotential, the electron number λ has been measured for nickel cathodes in alkaline solutions by Bockris and Potter[6] and for copper in alkaline solutions by Bockris and Pentland.[33] In acid solutions measurements of λ for nickel and copper were found to be impractical owing to the dissolution of these two metals, thus causing the Tafel line to become horizontal to the logic axis, at potentials negative with respect to the potential of the reversible hydrogen electrode. Thus, hitherto, the mechanism of hydrogen evolution on metals of intermediate overpotential in acid solutions has not been established.

It was, therefore, necessary to choose, for the measurements of λ in acid solutions, two metals of intermediate overpotential which do not dissolve easily in aqueous solutions of hydrochloric acid. Furthermore, these two metals must be capable of being cleaned easily and must make a tight seal to hysil glass. Silver and tungsten were found to have the above mentioned properties. Part α of this thesis is, therefore, concerned with measurements of λ in aqueous solutions of hydrochloric acid for silver and tungsten as well as the effect

of electropolishing the electrode surface on hydrogen over-potential. The choice of cathodes for the study of the effect of electropolishing on hydrogen overpotential was limited by the availability of data on electropolishing. Tin, aluminium and iron were chosen for this particular reason.

Although the temperature effect on hydrogen overpotential has not been investigated in the present work, it was necessary to include in Section IV a theoretical deduction for the heat of activation for future reference.

SECTION II.

EXPERIMENTAL WORK ON

HYDROGEN ELECTRODE KINETICS.

A. SOLID CATHODES.

1. INTRODUCTION.

The difficulty attached to hydrogen overpotential studies at low current densities is the elimination of all traces of oxygen and other impurities, which cause depolarisation. Special care should also be taken to get rid of oxide and sulphide films from the surface of the electrode.

2. ELECTRODE PREPARATION.

a. Silver.

Spectroscopically pure silver was used in the form of a wire 1 m.m. in diameter. The appropriate length of wire was cut and spot-welded to a piece of platinum by heating the ends of the two wires in an oxygen coal gas flame and then pressing them together by means of a platinum-tipped forceps. A piece of hysil tubing 0.5 cm. in diameter was cleaned in a mixture of 50% analar sulphuric and nitric acids (in later experiments chromic-sulphuric mixture was used). This was followed by washing in equilibrium water. The tube was then dried in an oxygen flame and a thin bulb[15] was blown at the end. The tube was then constricted near the bulb and a hysil cone, previously cleaned with acid and washed with conductivity

FIG (II 1)



FLEXIBLE
POLYTHENE TUBE

QUARTZ FURNACE
(700 °C)

QUARTZ SOCKET
HYSIL CONE

ELECTRODE STEM

PLATINUM

SILVER

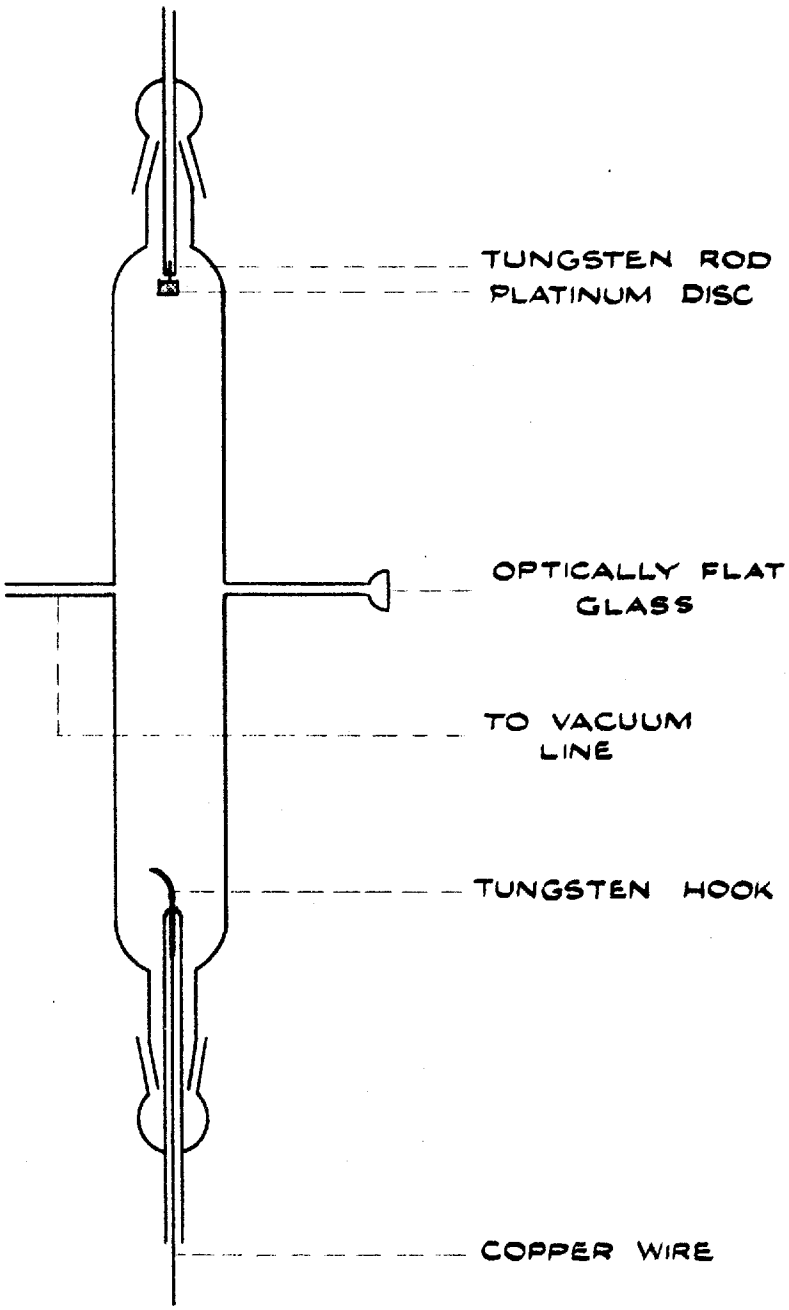
JET (H_2)

water, was fixed to the free end of the tube. A quartz furnace, consisting of a quartz tube joined by one end to a quartz socket and by the other end to a source of pure hydrogen, was used for the reduction of oxide and sulphide films on the metal. It was kept at a temperature of 700°C. The electrode was inserted in the furnace and the hysil tube was joined to the furnace via the ground glass joint. Pure dry hydrogen was passed through the furnace, with the help of a polythene tubing, and was allowed to escape to the atmosphere through a jet. After passing hydrogen for 5-10 minutes to replace the air in the furnace, the latter was switched on. The electrode was heated for 20 minutes at least, and the hysil tube was carefully flamed to remove all traces of water which, if not removed, would oxidise the electrode surface. After sufficient heating, the tube was sealed beyond the bulb and the wire was slid through the constriction, the silver section being in the bulb. The metal-glass seal was made on the silver-platinum junction so that platinum was not brought in contact with the solution. The electrode stem was washed with equilibrium water before fixing it in the electrolytic cell. A detailed scheme of the furnace arrangement is shown in Fig. (II 1).

b. Tungsten.

Owing to the stability of the oxides of tungsten this

FIG (II2)


TUNGSTEN ROD
PLATINUM DISC
OPTICALLY FLAT GLASS
TO VACUUM LINE
TUNGSTEN HOOK
COPPER WIRE

metal was cleaned in a different way. Spectroscopically pure tungsten wire, 1 m.m. in diameter, was prepared by passing the thick wire or rod through a die using a lubricant. This lubricant and other impurities which contaminated the wire (including oxide) were volatalised by heating the wire electrically to a high temperature in vacuum (see below).

The apparatus used is shown in Fig. (II 2). A pyrex tube about 18" long and 3" in diameter was joined at both ends to a B19 cone. On the upper cone was fitted a socket with a pyrex tube sealed in the middle. A tungsten rod several m.ms. thick and spot-welded to a platinum disc was sealed to the bottom of this tube. To the lower cone was fitted a socket with a tungsten rod in the shape of a hook, sealed to a tube in the middle. Electrical contact with the upper tungsten rod was made through mercury, with the lower one through a thick copper wire silver-soldered to tungsten. The 1 m.m. tungsten wire was spot-welded to the platinum disc, and the tungsten hook was rotated to make contact with the free end of this wire. Picien was used to seal the top and bottom of the tube. A two-stage mercury diffusion pump was used to attain a vacuum of 10^{-5} m.m. Hg, which was recorded with the help of a McLeod gauge. The appropriate current was then passed and the temperature of the wire (about 3000°C), was measured by an optical pyrometer (through optically flat glass, cf. Fig.II 2), and the emissivity corrections were applied. After flashing

the wire, it was left to cool in vacuum and air was then introduced in the system. The piclen was melted and the tungsten wire was removed without touching the side of the upper cone. The wire was cut into pieces of 2 cm. long and each piece was used to prepare an electrode, in a manner similar to that used in silver except that spot-welding to platinum was dispensed with since tungsten makes a good seal with hysil glass.

a. Magnitude of Current necessary for reaching sufficient Temperature in Tungsten Wire.

The quantity of heat gained by the Tungsten wire per second is given by

$$\frac{i^2\sigma(1+\alpha\Delta t)\ell}{4.2\ A} \quad \text{cals.} \qquad (\text{II } 1)$$

where i is the current in amps., σ is the resistivity of tungsten and is equal to 5.51×10^{-6} ohms cm. at 20°C according to Langmuir;[34] α is the temperature coefficient of resistance taken to be 0.0041 approximately at 20°C,[35] ℓ is the length of the wire, A is the cross-sectional area, and Δt is the temperature difference between room temperature and the temperature of the wire after 1 second. Now,

$$\frac{i^2\sigma(1+\alpha\Delta t)\ell}{4.2\ A} = A.\ell.\rho.C_p.\Delta t, \qquad (\text{II}_2)$$

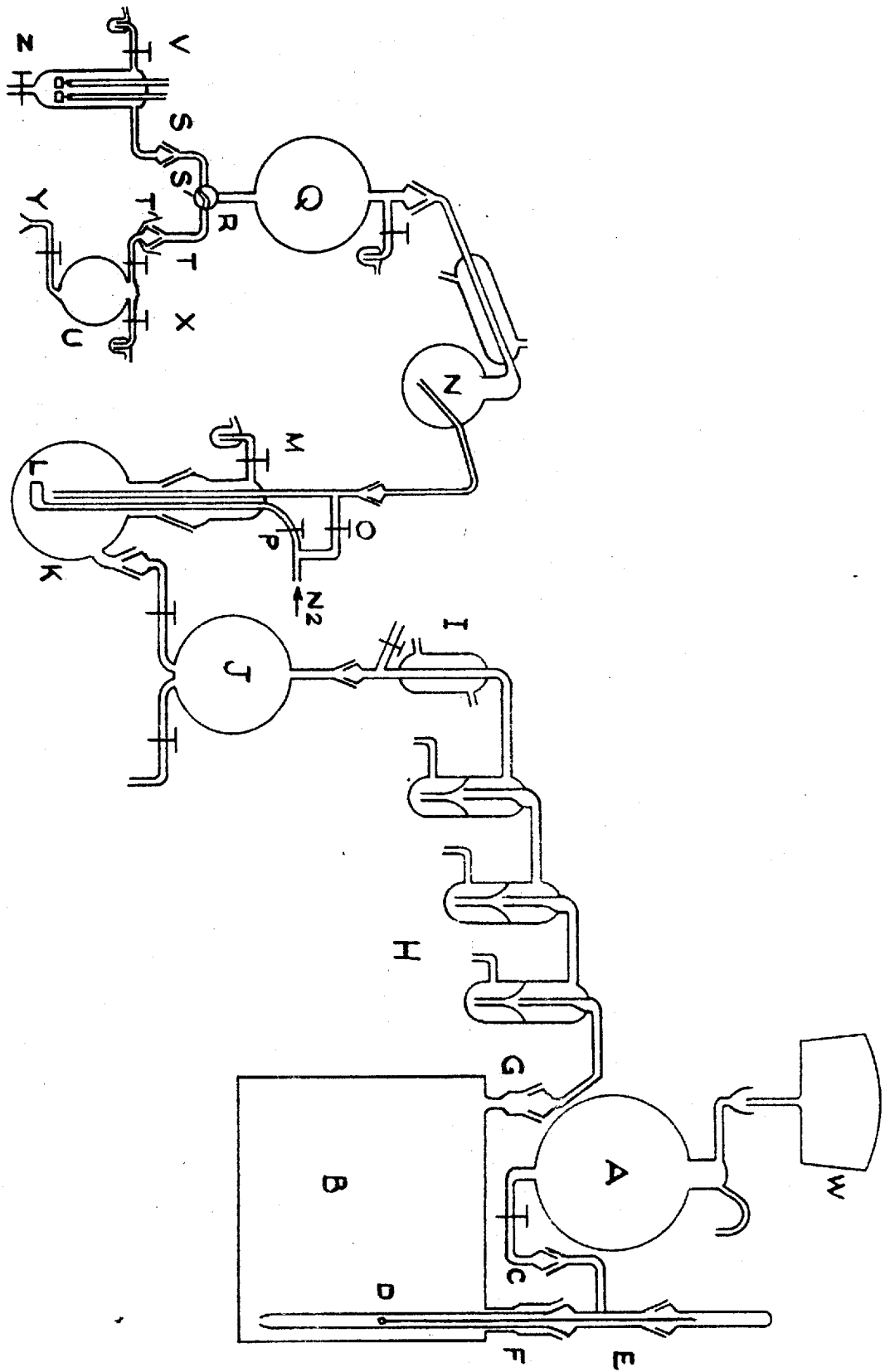
where ρ is the density and C_p is the mean specific heat over the temperature range Δt. From this relation one gets the minimum current necessary to produce a temperature difference of Δt between the wire and its surroundings, in the absence of heat loss by radiation, in a time of one second. Thus, this equation was used to give some orientation as to the value of i necessary to produce the required temperature and then the current was adjusted so that it created in the wire a temperature of 3000°C, as indicated by an optical pyrometer.

3. CONDUCTIVITY WATER

Ordinary distilled water was again distilled with alkaline permanganate in a stainless steel tank to get rid of organic impurities. This still is shown in Fig. (II 3).

Distilled water from the still W was stored in A and then introduced in the stainless steel tank B, containing a dilute solution of equal quantities of potassium permanganate and potassium hydroxide, through a tap and a ground glass joint C. (It is preferable to use alkaline rather than acid solutions of potassium permanganate owing to the lesser volatility of the products of oxidation in alkaline solutions). The level of the water in the tank was judged by means of a glass float D. This was allowed to move upwards and downwards in a channel provided by a tube E constricted at the bottom

FIG (II 3)

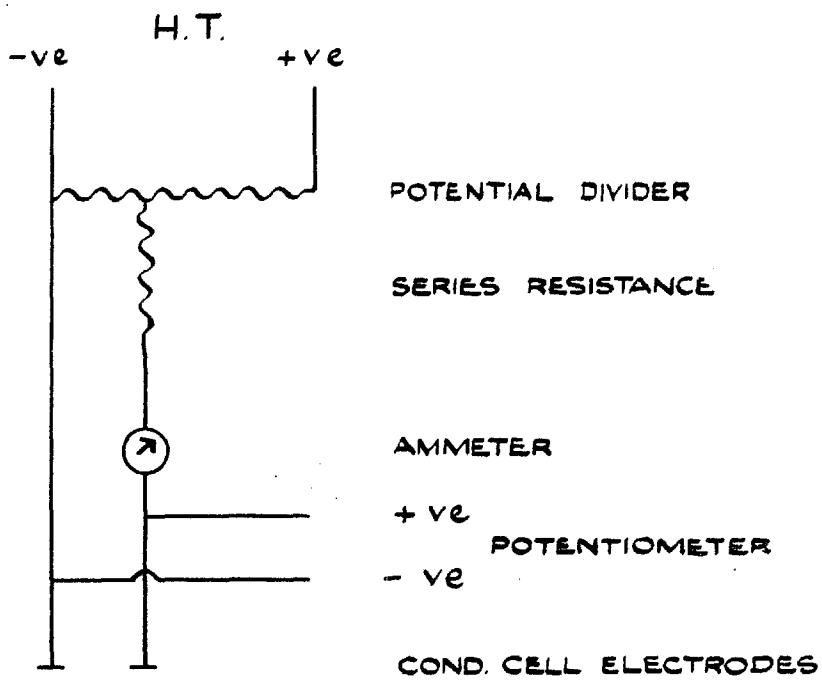


to keep the float in the guiding tube. E was joined to another tube F by means of a ground glass joint so that E could be lifted upwards and the float replaced if necessary. The tubes F and G were fixed to the top of the tank by means of copper to glass seals. The vapour was partially condensed in a series of three traps,* H. The water thus condensed was rejected through waste pipes. The remaining vapour was then condensed by a water condenser I into a reservoir J from which water, having a specific conductivity of 2-3 x 10^{-6} $ohms^{-1}$ $cm.^{-1}$, was drawn. This grade of water was generally used for washing of cells, etc. To obtain water of lesser conductivity, water from J was introduced into K through a tap and a ground glass joint. This water was then heated under a stream of purified nitrogen for 30 hours at a temperature of 90°C, the nitrogen being passed through a sintered glass disc L and driven out through a tap and a bubbler M. This process eliminates carbon dioxide. Water from K was pushed under a stream of nitrogen to the flask N. From N water was distilled with nitrogen passing through O, taps P and M being closed. The distillate was collected in a reservoir Q and was either introduced to the conductivity cell or the conductivity water vessel (U).

---

* The object of these traps is to remove spray, containing potassium permanganate, etc., and also to condense heavier components of the distillate from B.

FIG (II 4)


H.T.
-ve
+ve
POTENTIAL DIVIDER
SERIES RESISTANCE
AMMETER
+ ve
POTENTIOMETER
- ve
COND. CELL ELECTRODES

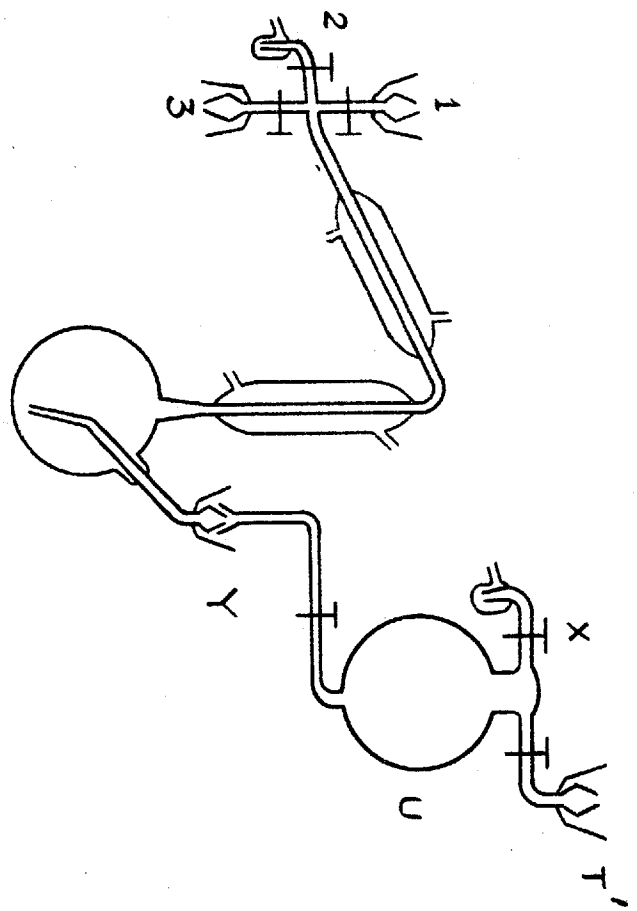
This was done with the help of a two-way tap R with two sockets S and T joined to it. The ventils S′ and T′ fit to the sockets S and T respectively. Water from Q was pushed with a stream of nitrogen through the conductivity cell and out through Z, tap V being closed, to wash the cell several times (about 12) before the conductivity measurement was taken. After ascertaining the value of the conductivity, water from Q was pushed through TT′ and out through Y, X being closed, to wash the vessel U several times. After this Y was closed and the vessel U was filled with water under nitrogen and the gas was passed through the tap X and a bubbler. To prevent the contamination of conductivity water with air originally present in this vessel, this was evacuated through Y to several centimeters of mercury before introducing water from Q into it.

Water from this vessel was then distilled under purified hydrogen in a still (Fig. II 5) attached to the electrolytic cell. The specific conductivity of the last stage water varies from 9×10^{-8} to 2×10^{-7} mhos cm^{-1}. It must be noted that apart from A, F and G the rest of the apparatus was made of hysil glass.

(i) Measurement of Conductivity.

An approximate method was used. A source of potential, usually an H.T. battery, was applied across a potential divider

FIG (II 5)



(see Fig. II 4), and with the help of a series resistance the current passing through the conductivity cell was kept below 10^{-5} amps., to diminish the effect of polarisation on the measurement, since the polarisation of platinised platinum becomes appreciable above 10^{-5} amps. per cm^2. The potential between the electrodes of the conductivity cell was measured with a G.E.C. valve potentiometer. From the value of the current I, the potential V and the cell constant C, the specific conductivity was calculated according to the following equation,

$$\kappa = \frac{IC}{V} . \qquad (II\ 3)$$

(ii) Distillation under Hydrogen.

Another still, shown in Fig. (II 5), was used for the distillation of conductivity water under hydrogen. This is essential to get rid of most of the oxygen remaining in the conductivity water, and which might have leaked through the conductivity water vessel(4). The still was evacuated with the water pump to several millimeters of mercury through the ventil 1, all the taps being closed. Purified hydrogen was then passed through T', thus pushing the water from the conductivity water vessel U (which is transferable from the conductivity still of Fig. II 3 and attachable to the main apparatus) into the still via the socket Y and the gas was

let out through the bubbler 2. Water was then refluxed for four hours and distilled through the ventil 3 into the electrolytic cell.

(iii) Purification of Nitrogen.

Nitrogen from the cylinder was passed through two copper furnaces kept at 500°C to get rid of the traces of oxygen in the gas. The gas was then passed over soda lime to absorb carbon dioxide.

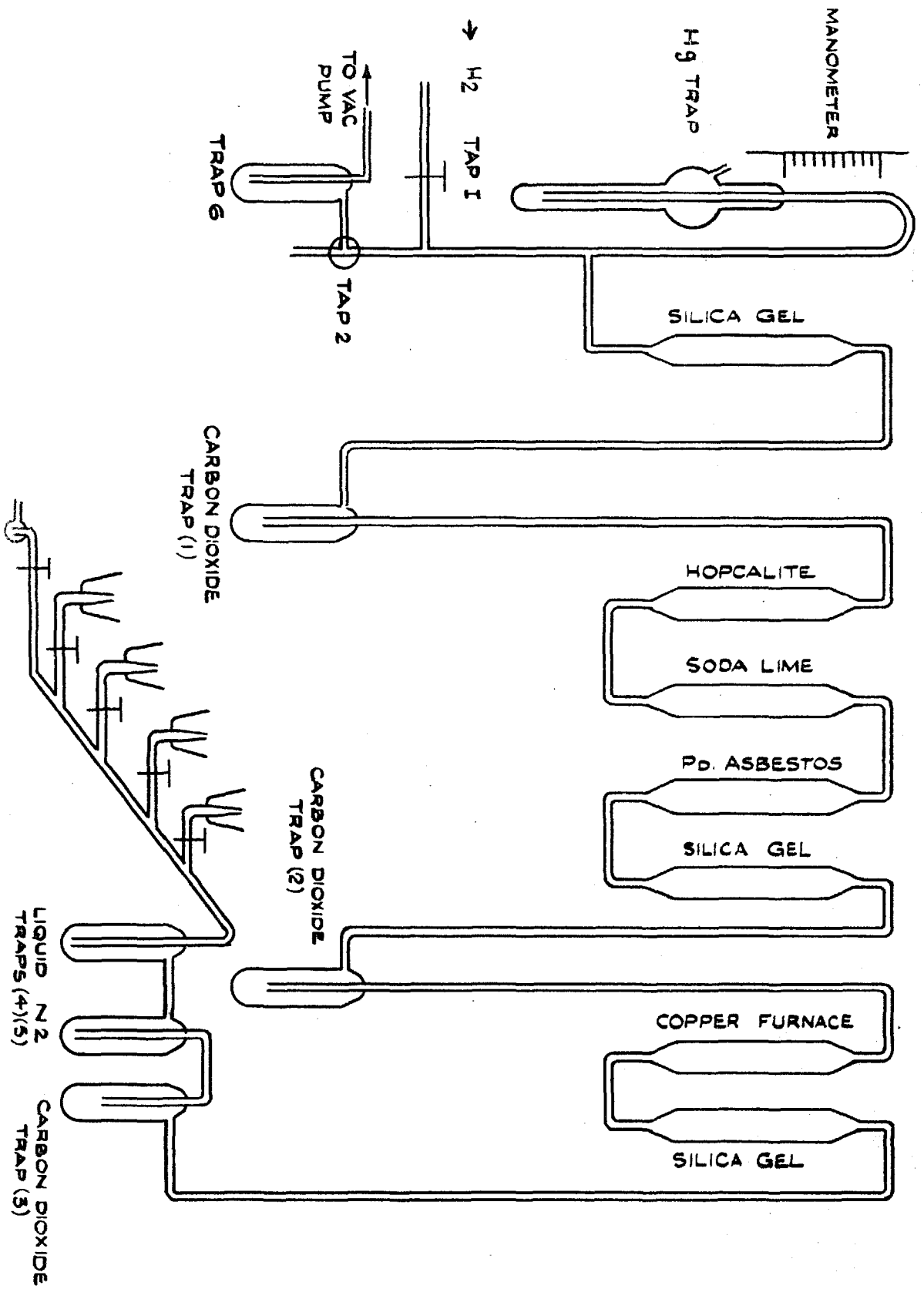
4. PURIFICATION OF HYDROGEN.

Commercial hydrogen, supplied by the British Oxygen Co., has the following composition (by volume) :

Hydrogen	99.95 %
Oxygen	0.001 %
Carbon Monoxide	0.001 %
Carbon Dioxide	nil
Methane and Ethane	0.048 %

Oxygen was removed by passing hydrogen in a palladised asbestos furnace heated to 400°C. This catalysed the combination between oxygen and hydrogen to form water. To ensure that the highest possible proportion of oxygen was

FIG (II 6)


MANOMETER
Hg TRAP
H2
TAP 1
TO VAC PUMP
TRAP 6
TAP 2
SILICA GEL
CARBON DIOXIDE TRAP (1)
HOPCALITE
SODA LIME
Pd. ASBESTOS
SILICA GEL
CARBON DIOXIDE TRAP (2)
COPPER FURNACE
SILICA GEL
LIQUID N2 TRAPS (4)(5)
CARBON DIOXIDE TRAP (3)

removed, hydrogen was then passed into another furnace containing reduced copper, heated to 400°C. These two furnaces were made of hysil glass. Carbon monoxide was catalytically oxidised to carbon dioxide by the use of hopcalite. This is a mixture of manganese dioxide, cupric oxide, and some other metallic oxides.[36,37,38]

The catalytic effect of hopcalite depends on the particle size and on the number and type of metallic oxides present. It has been found[38] that the presence of water vapour poisons the catalyst. For this reason hydrogen had to be dried before passing it over hopcalite. The poisoning effect is temporary, since the catalyst could be recovered by drying. Hopcalite is used at room temperature in the case of hydrogen, since it is reduced by this gas if heated. In the presence of air or oxygen the catalytic activity of hopcalite is increased with rise of temperature. In this case the mechanism of the catalyst is as follows:

$$2CO + O_2 = 2CO_2 .$$

In presence of hydrogen (from cylinder) either this mechanism or the following,

$$MnO_2 + 2CO = Mn + 2CO_2 ,$$

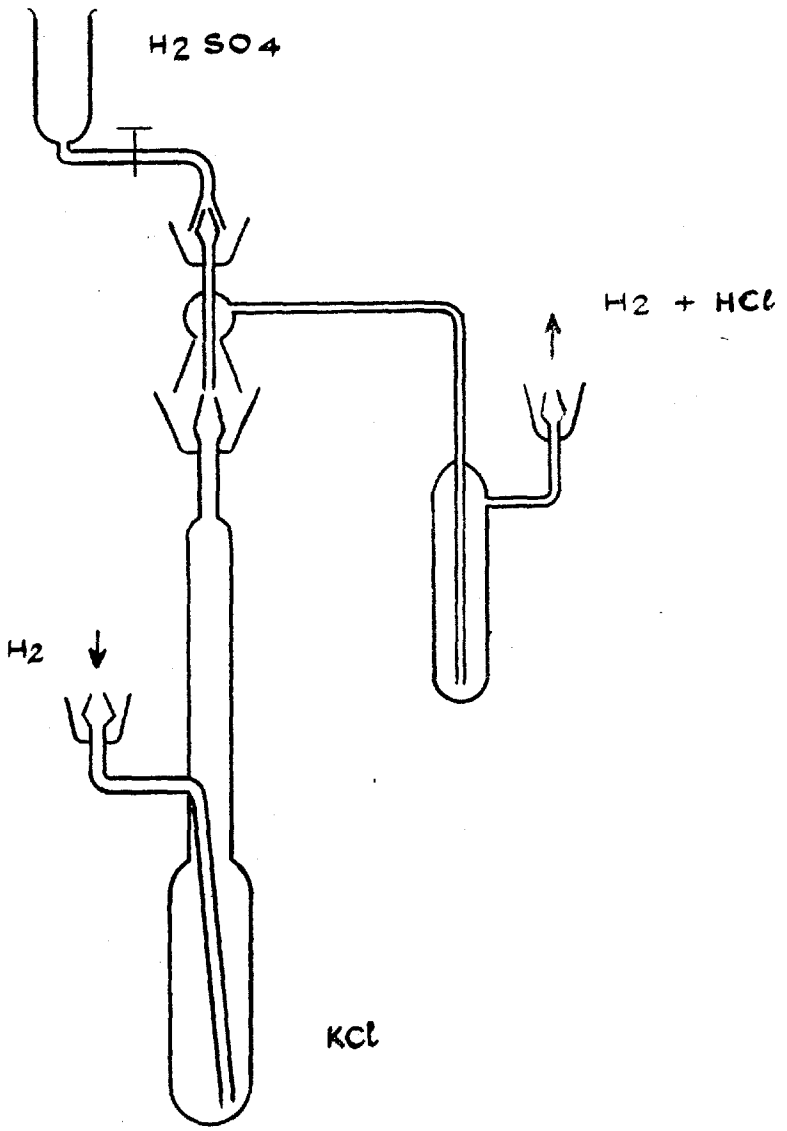
or both, take place. The oxygen required for the first

mechanism is present in the cylinder hydrogen. In the second mechanism the catalyst is exhausted. For this reason hopcalite had to be renewed often.

Ethane and Methane were removed by passing hydrogen over activated charcoal cooled to liquid nitrogen temperature. Fig. (II 6) shows the general arrangement of the purification train.

Hydrogen from a cylinder was passed over a combined manometer mercury trap. This helped to release the excess pressure of the gas when the train was blocked. From this, hydrogen was passed over silica gel and then into trap 1. This trap was cooled in solid carbon dioxide to solidify all the water vapour in the gas. Dry hydrogen was then passed over hopcalite at room temperature, then over soda lime to absorb the carbon dioxide formed. This was followed by the palladised asbestos and copper furnaces, hydrogen being dried after passing in each furnace. The inner tubes of traps 1, 2 and 3 should be about 3" from the bottom to ensure enough space for the ice formed, thus preventing any blockage in the train. From trap 3 hydrogen was passed over charcoal cooled in liquid nitrogen in traps 4 and 5, and then to a tube sloping downwards. This tube carried a number of water-sealed taps and ventils from which purified hydrogen could be passed to different parts of the apparatus. Any water present in this tube was pushed downwards with a stream of hydrogen to a bubbler. Before passing hydrogen, tap 1 was closed and the

FIG (II 7)



train was evacuated to the water vapour pressure, and then tap 2 was closed, tap 1 was opened and hydrogen was passed into the train.

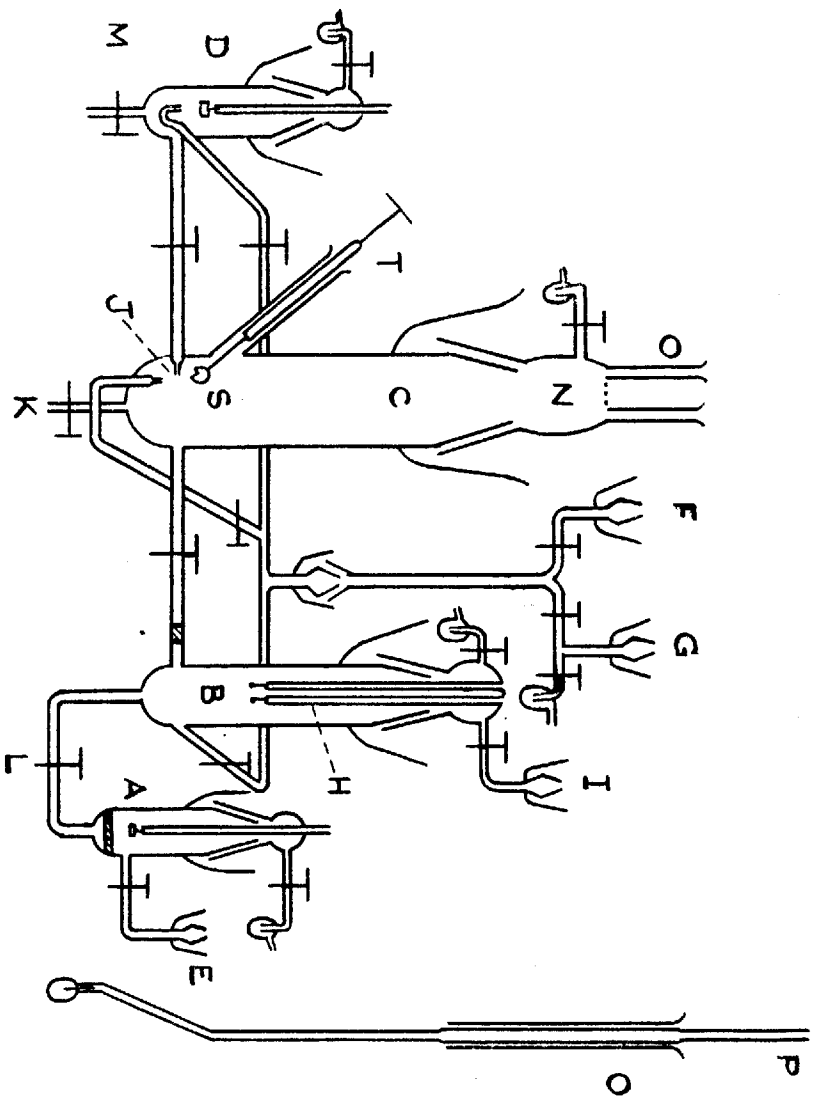
5. PREPARATION OF HYDROGEN CHLORIDE.

Hydrogen chloride was prepared from analar potassium chloride and analar sulphuric acid. Potassium chloride was baked in a stream of hydrogen at 400°C, for several hours to remove organic impurities. After cooling, analar sulphuric acid was dropped on potassium chloride and hydrogen chloride formed was carried with a stream of hydrogen through an empty trap cooled in a mixture of solid carbon dioxide and alcohol, to condense sulphuric acid vapour. The gas stream was then passed to the electrolytic cell. The diagram of the HCl preparation vessel is shown in Fig. (II 7).

6. THE ELECTROLYTIC CELL.

The cell, shown in Fig. (II 8), was composed of four compartments: the anode compartment A, the solution preparation compartment B, the cathode compartment C and the hydrogen electrode compartment D. The anode used was a platinum disc, 1 cm^2, in area, sealed to glass. To prevent the anodic products from diffusing towards the cathode a sintered glass disc (porosity 1) was fixed to the bottom of A. Purified hydrogen was introduced through E to bubble over

FIG (II8)



the anode, thus carrying oxygen and chlorine formed electrolytically to the atmosphere. A tap L inserted between A and B was kept closed whenever the polarising current was on. The use of a sintered glass disc between B and C helped to prevent the diffusion of anolyte to catholyte. The solution was prepared by passing conductivity water, refluxed under hydrogen, through I, and its conductivity was approximately checked with the help of two platinum electrodes H. A stream of hydrogen carrying hydrogen chloride gas was passed through G to B and the concentration was then determined conductimetrically.

In earlier experiments carbon (spectroscopically pure) was used for the anode and conductivity electrodes. This was found to disintegrate in presence of cleaning mixture. Furthermore, it was observed that when a potential, higher than 110 volts, was applied for pre-electrolysis, colloidal carbon was observed on the surface of the pre-electrolysis electrode. For the above reasons the use of platinum was satisfactory as long as the concentration of hydrochloric acid was not high.

Hydrogen from the train was introduced through F to B, C or D. The cathode compartment C had a multi-electrode cap N, five electrodes being used together (only two are shown in diagram). The middle electrode was used for pre-electrolysis while the other four were used as test electrodes. Each electrode was fixed to the bottom of a piston P of a hypodermic syringe, the barrel O being fixed to the top of

the cathode cap. A breaker S was used for breaking the bulb of the electrode and was fixed to a piston T similar to that used for the electrode. A tap K, fixed to the bottom of the cathode compartment was used for rejecting the water with which the cell was washed. A Luggin capillary, J, 1 m.m. in diameter was used between C and D. The hydrogen electrode was a platinised platinum sheet, 1 cm. square. It was kept in conductivity water and this water was rejected through the tap M and replaced with solution before taking the measurements.

7. APPARATUS FOR ELECTRICAL MEASUREMENTS.

a. Measurement of Current.

A Cambridge multirange microammater was used for the range 1.4×10^{-6} to 1.2×10^{-1} amps. Below 1.4×10^{-6} amps., the current was measured by passing it through a standard resistance (1 megohm), and the potential drop across this resistance was measured by a G.E.C. valve potentiometer. From the value of the potential and the resistance, the current was calculated.

b. Measurement of Potential.

The overpotential was measured with a G.E.C. valve potentiometer. It had the range of 0 to 1400 millivolts, and

drew less than 10^{-11} amps. The potential was read with an accuracy of 0.5 millivolts. A double pole double throw switch was used to connect the potentiometer either to the cathode hydrogen electrode circuit or to the ends of the megohm resistance.

(c) Source of Polarisation.

For pre-electrolysis a D.C. generator giving 400 V. was used. During the measurement the polarising current was drawn from two batteries, a 120 V. H.T. battery for the high current density range, and a 4.5 V. one for the lower range. The use of H.T. batteries was necessary to avoid the fluctuations in the D.C. main. The polarising current was varied with the help of two 10,000 ohm wire wound potentiometers and the final adjustment of the current was made with a megohm variable carbon resistance in series with the electrolytic cell. The appropriate switches and resistances were mounted on a paxolin board. This board together with the microammeter, the valve potentiometer and the polarising batteries were kept on a table covered with paraffin wax. This was necessary to prevent current leaks to earth.

Screened copper wire with earthed screen and covered with an insulation was used for all connections. A knife switch was used to change from one battery to the other without cutting the polarising current. To prevent leakage of current

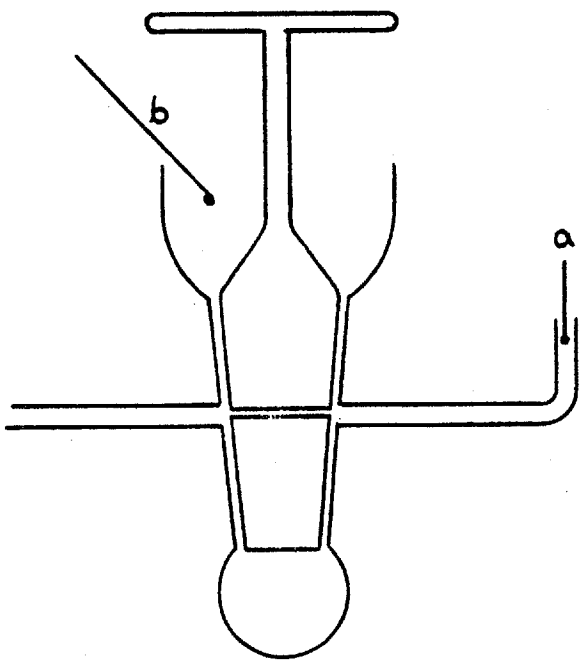
through the electrolytic cell to earth, a special stand was furnished for the cell. This consisted of a paxolin board mounted on paraffin wax and covered with a layer of the same wax.

8. THE HYDROGEN ELECTRODE.

The method used for preparing the hydrogen electrode was based on Ellis's work.(39) A sheet of platinum, 1 cm. square, was welded to a platinum wire sealed in a hysil tube. The electrode was washed with chromic acid and then with equilibrium water. This was followed by heating the platinum in oxygen flame to ensure the removal of all organic impurities. The platinising solution was prepared by dissolving 1 gram of chloroplatinic acid in 100 c.c. of equilibrium water to which was added a drop of analar conc. hydrochloric acid. The hydrogen electrode was platinised with the help of a subsidiary platinum electrode at a current of 10-20 milliamps, for more than one hour. The current was reversed every 10 minutes. The electrode was then washed several times with equilibrium water and then kept in a closed vessel containing conductivity water.

In some cases it was observed that the Tafel line became horizontal, in the low current density region, at a potential more negative than the potential of the reversible hydrogen electrode (taken as zero in the same solution as the test

FIG (II 9)



electrode). A check of the hydrogen electrode against a calomel electrode was necessary before any conclusions were made. In all these cases the potential of the hydrogen electrode was found to be more negative than the reversible potential by a quantity corresponding to the upward shift of the Tafel line and hence allowance was made for this false zero in calculating the Tafel constants.

9. WATER-SEALED TAP.

All taps used in the apparatus were sealed with water. A diagram of one of them is shown in Fig. (II 9). Such a tap was covered with water on the top, to prevent diffusion of oxygen inside the system. Water formed a thin film between the stopcock and the barrel. The concentration of oxygen C in the water on top of the tap, was calculated taking the absorption coefficient, α, for oxygen in water as 0.025 cc. of oxygen per cc. of water at N.T.P.

$$\therefore \quad C = \frac{0.025}{5 \times 22.4} \,, \qquad (II\,4)$$

where C is in gram moles of oxygen, per lite of water under a partial pressure of oxygen of 0.2 atmos. The dimensions of the thin water film around the stopcock were calculated by measuring the resistance R of the tap between two points a and b (cf. Fig. II 9) in a solution of known specific

conductivity such as 0.5 N hydrochloric acid. The specific conductivity K of 0.5 N hydrochloric acid was taken as 0.163 mhos cm^{-1}. at 25°C, and the average value of the resistance R was found to be 6.3×10^5 ohms. The ratio ℓ/A of the thin water film was, therefore, given by,

$$\frac{\ell}{A} = KR = 0.163 \times 6.3 \times 10^5 \simeq 10^5 \qquad (II\,5)$$

Using Fick's diffusion equation,

$$Q = -D \frac{dC}{d\ell} A = -D \frac{C}{\ell} A, \qquad (II\,6)$$

where Q is the quantity of oxygen that diffuses through the tap per second, D is the diffusion coefficient, $dC/d\ell$ is the concentration gradient, A is the cross-sectional area, ℓ is the length of the film and substituting (II 4) and (II 5) in this equation (II 6), using $D = 2.0 \times 10^{-5}$ cm^2. $sec.^{-1}$

$$Q = 4 \cdot 10^{-4} \quad mole\ O_2 / Sec.$$

Taking the total number of taps (and ground glass joints) in the system as 50, the total rate of diffusion of oxygen in the system was

$4 \times 10^{-14} \times 50 = 2 \times 10^{-12}$, gram molo of oxygen per second.

From the amount of hydrogen consumed during one experiment and the time during which hydrogen was passed, a rough estimate of the rate of flow of hydrogen was found to be 4×10^{-4} gram mole of hydrogen per second. Therefore the partial pressure of oxygen entering the apparatus through diffusion was,

$$\frac{2 \times 10^{-12}}{4 \times 10^{-4}} = 5 \times 10^{-9} \text{ atmos.}$$

The concentration of oxygen in the solution was calculated from the absorption coefficient, the partial pressure of oxygen and the volume occupied by 1 gram mole of the gas as,

$$\frac{0.025 \times 5 \times 10^{-9}}{22.4} = 5.6 \times 10^{-12} \text{ gram mole/litre}$$

With silver and tungsten the lowest current density attained was 10^{-8} amps. cm^{-2}. Therefore, the limiting current of diffusion for oxygen (i_L) should be at least ten times less than 10^{-8}, i.e., it should be less than 10^{-9}, to avoid depolarisation. The limiting current of diffusion is related to the concentration of oxygen in gram moles per litre, by [23] the following approximate equation,

$$i_L = 0.14 C_1$$

$$\therefore \quad C_1 = 7 \times 10^{-9} \qquad (\text{II } 8)$$

where C_1 is the maximum permissible concentration of oxygen. It is clear that the concentration of oxygen in the solution, due to diffusion, as given by (II 7) is much smaller than the value of C_1 given by (II 8). From this it is concluded that the use of water-sealed taps is a satisfactory method of avoiding the ingress of oxygen into the system.

10. CLEANING MIXTURE.

A cleaning mixture composed of equal parts of analar sulphuric and nitric acids was used to clean the electrolytic cell and other detachable parts of the apparatus. The cleaning mixture was left over night in the vessel and was then sucked out. The vessel was then washed with small amounts of tap water followed by thorough washing with equilibrium water (the use of considerable amounts of tap water should be avoided, since this water contains appreciable quantities of impurities).

In later experiments chromic-sulphuric mixture was used. This was prepared by grinding analar chromic oxide and adding analar sulphuric acid to it. This mixture was effective in getting rid of grease.

11. CONDITIONS FOR PRE-ELECTROLYSIS.

The process of electrolytic purification of the solution, called pre-electrolysis, was found to be of large importance for obtaining satisfactory Tafel lines. The conditions

(20)

(current and amount of electricity passed) for pre-electrolysing any solution depend on the concentration of the solution and the method of its preparation; the higher the concentration of the solution the bigger is the amount of electricity required for pre-electrolysis. Table (II 1) below shows the behaviour of Tafel lines obtained with different pre-electrolysis conditions for silver electrodes in hydrochloric acid solutions.

Table (II 1)

conc.	c.d. (Acm^{-2})	coulombs	behaviour of T.line
0.05 N	1×10^{-2}	900	depolarised
0.05 N	1×10^{-1}	9000	"
0.05 N	1×10^{-2}	9500	"
0.05 N	2×10^{-1}	16000	satisfactory
0.1 N	1×10^{-2}	1450	depolarised
0.1 N	6×10^{-2}	4750	"
0.1 N	4×10^{-2}	5050	"
0.1 N	2×10^{-1}	20000	satisfactory
1.0 N	1	30000	"

It can be seen from table (II 1) that satisfactory conditions for pre-electrolysis in 0.05 N, 0.10 N and 1 N HCl are attained when passing 16000, 20000 and 30000 Coulombs

respectively. These conditions were, therefore, applied during the latter part of this work.

Pre-electrolysis was carried out between the platinum anode and a cathode of the same material as the test electrode using a 400 V D.C. generator. For low concentrations (below 0.1 N) the tap between the solution preparation compartment B (Fig. II 8) and the cathode compartment C was partially opened while the tap between the anode compartment A and B was always closed during pre-electrolysis. It was observed that bubbles tend to form in the vicinity of these taps, due to overheating of the taps, thus cutting down the pre-electrolysis current. To avoid this, a jet of water was applied on both sides of these two taps thus enabling the establishment of better conditions for pre-electrolysis.

The condition of the pre-electrolysis electrode, after pre-electrolysis, gives a preliminary information as to the probable success or failure of the run. A contaminated pre-electrolysis electrode is accompanied, in most cases, by an unsuccessful run.

Before pre-electrolysis was commenced, allowance was made for the decrease of hydrochloric acid concentration during pre-electrolysis by means of a calculation based on Faraday's laws of electrolysis.

12. METHOD OF ESTABLISHING THE TAFEL LINE.

The direct method and the rapid technique were used. After pre-electrolysis the pre-electrolysis electrode was drawn out of the solution with hydrogen still passing through the cathode compartment and current still on. The pre-electrolysis current was then switched off and part of the pre-electrolysed solution was pushed with a stream of hydrogen from the cathode compartment to the hydrogen electrode compartment, from which the water had been previously removed by means of hydrogen pressure. To avoid increasing the diffusion of any depolariser still present in the solution, the bubbling of hydrogen was then stopped in the cathode compartment and commenced in the hydrogen electrode compartment where it was allowed to continue for 20 minutes at least, after which bubbling continued only over the anode.

The first test electrode was connected to the polarising circuit and the value of the current density was approximately adjusted (with the help of a potential divider calibrated in a blank experiment) to 10^{-5} amps. $cm.^{-2}$. The current density was chosen so that it was low enough to avoid the deposition of impurities at high current densities, and high enough so that it was on the linear section of the Tafel line, thus enabling a value of i_0 to be obtained from the first readings. The electrode was inserted into the solution and after breaking the bulb, it was adjusted to touch the tip of the Luggin

capillary. The electrode was left polarised at 10^{-5} amps.cm.$^{-2}$ till a constant potential was attained. During this time (about 10 minutes) the potential increased with time and approached a constant value.

The Tafel line was traversed down to the potential of the reversible hydrogen electrode, measurements being taken as quickly as possible at potential intervals of 5 millivolts down to 30 mV and then at intervals of 0.5 - 1 millivolt. This was necessary in order that an accurate value of $(\partial\eta/\partial i)_{\eta\to 0}$ could be obtained (cf. Section I). Once the potential of the reversible electrode was attained, the Tafel line was quickly traversed upwards to a current density of 10^{-3} - 10^{-2} amps cm.$^{-2}$, after which hydrogen was bubbled into the cathode compartment before the electrode was drawn out of the solution. It was necessary to bubble hydrogen into the cathode compartment before the electrode was drawn out of the solution to eliminate the possibility of air diffusing into this compartment during the process of removal of the electrode. The other test electrodes were treated in the same way.

Owing to the increased possibility of deposition of impurities on the electrode at high current densities, any one electrode was used only once for measuring a Tafel line. Also for this reason the best representation of the Tafel line was considered to be the first up line. This is defined as the line traversed for the first time, starting with the potential

of the reversible hydrogen electrode in the direction of high current densities.

The area of most of the electrodes used was in the range of 0.2 to 0.4 $cm.^2$.

B. EFFECT OF ELECTROPOLISHING ON HYDROGEN OVERPOTENTIAL

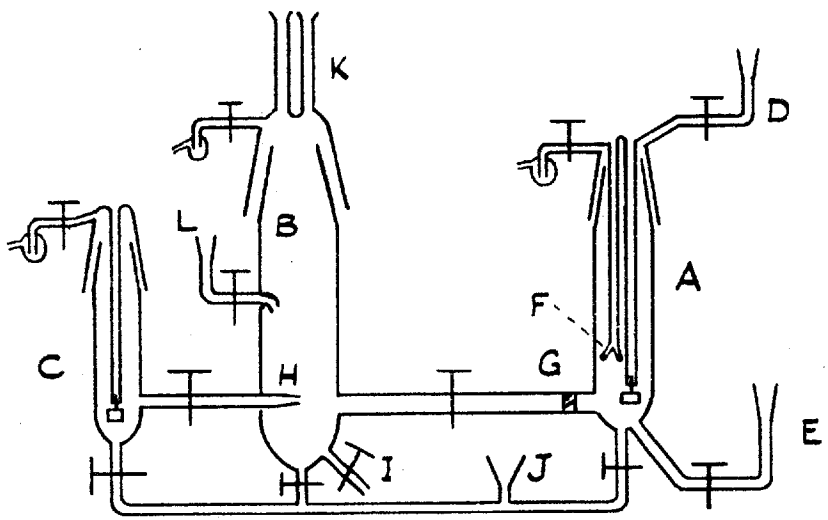
1. INTRODUCTION

The apparatus used for measuring hydrogen overpotential on electropolished surfaces was designed on the same principle as that used for silver and tungsten work. It was only necessary, for the sake of comparing the overpotential values of the electropolished and non-electropolished metals, to confine the measurements to the current density range 10^{-4} to 10^{-1} amps. cm.$^{-2}$. For this reason, stringent purification of the solution and removal of oxygen from the system were not necessary, since according to Hickling,(40) oxygen depolarisation takes place at 10^{-3} and 10^{-4} amps. cm.$^{-2}$ for stirred and unstirred solutions respectively. Special care was therefore taken not to stir the solution during the measurements.

2. THE ELECTROLYTIC CELL.

A diagram of this cell is shown in Fig. (II 10). It was composed of three compartments: the anode compartment A, the cathode compartment B, and the hydrogen electrode compartment C. The solution was prepared in A. Conductivity water was distilled with a stream of hydrogen through D and hydrogen chloride gas was passed through E to prepare the required concentration which was checked by measuring the

FIG (II 10)

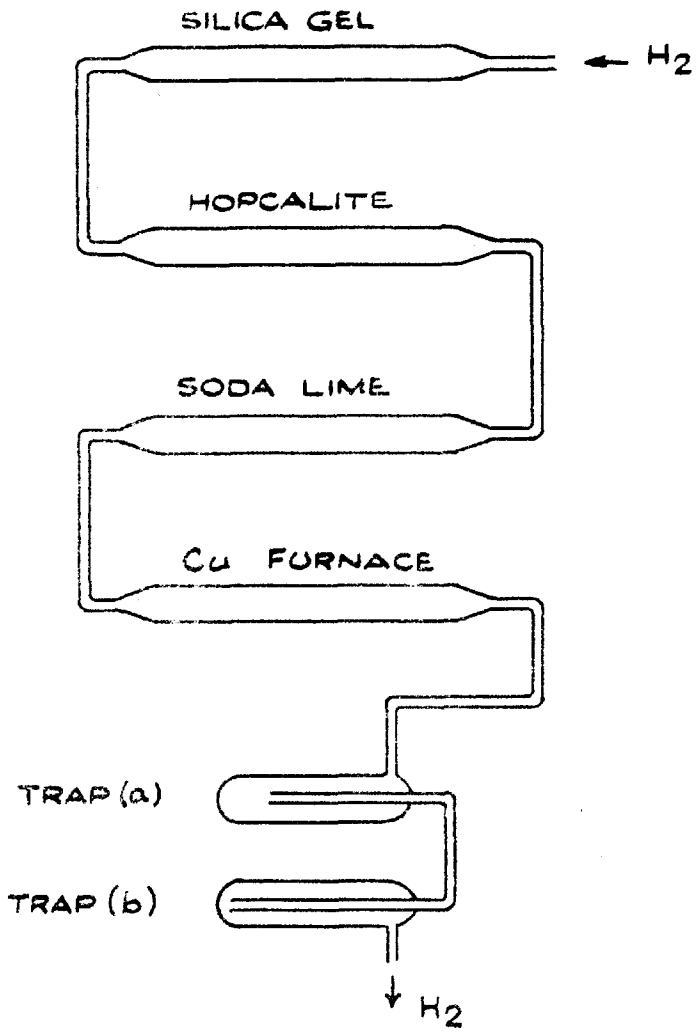


conductivity between the two platinum electrodes F (or by means of a glass float). The anode used was a piece of platinum about 1 cm.^{2} in area. A sintered glass disc G inserted between A and B helped to prevent the diffusion of anodic products to the catholyte. The cathode compartment had a Luggin capillary H connecting it with the hydrogen electrode compartment, and a tap I to reject the water used for washing the cathode compartment. The cathode cap K contained two ground pieces of glass tubing in the form of a barrel of a hypodermic syringe through which the electrode, fixed to a stem in the form of a piston, was moved upwards and downwards. A ground glass joint and a tap L were fixed to the side of the cathode compartment to help in filling this compartment with equilibrium water which was displaced by hydrogen through J. Hydrogen from J was divided between A, B and C with the help of three taps and was released to the atmosphere through three bubblers. All taps used in this cell and in other parts of the apparatus were ungreased vacuum taps.

3. PURIFICATION OF HYDROGEN

A simple purification train was used, the diagram of which is given in Fig. (II 11). Hydrogen from the cylinder was passed over silica gel to dry it, and then over hopcalite and soda lime tubes. A copper furnace heated at 400°C was

FIG (II 11)



used for the removal of oxygen through its combination with copper to form an oxide. Water was also collected in an empty trap (a) cooled in a mixture of solid carbon dioxide and methylated spirit. Another trap (b) containing activated charcoal was used to adsorb organic impurities.

4. ELECTRODE PREPARATION

The metals used were tin, aluminium and iron.

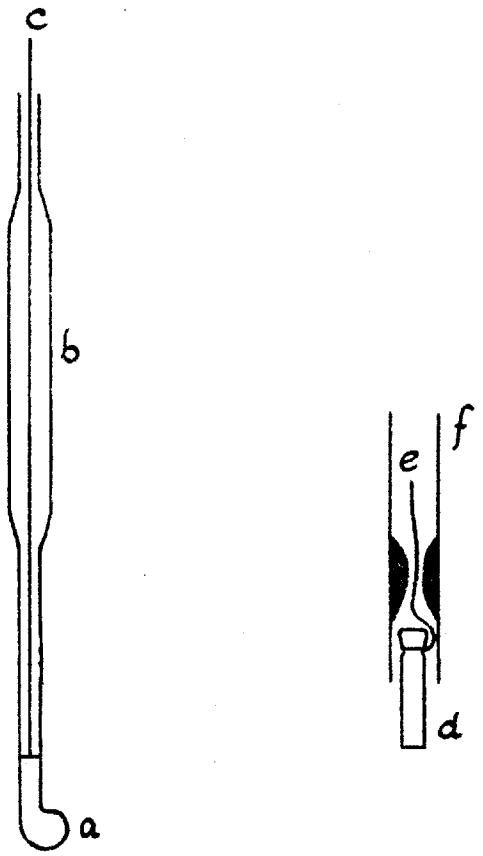
a. Tin and Aluminium.

Analar tin and aluminium were used. A diagram of one of these electrodes is shown in Fig. (II 12). A glass tube about 0.5 cm. in diameter was bent and a thin bulb (a) was blown at the end. This tube was fixed to the barrel (b) of a hypodermic syringe. The molten metal was poured into the tube and a piece of copper wire (c) was inserted in the melt to ensure electrical contact. The metal was left to solidify and the bulb was broken.

b. Iron.

A piece of spectroscopically pure iron rod (d) Fig.(II 12), 1 cm. long and about 0.5 cm. in diameter was used. A groove was sawn around one end and a platinum wire (c) was wrapped around it. This was introduced through the end of a glass tube (f) and glass was melted over the platinum wire as well

FIG (II 12)



as the end of the iron rod. Electrical contact was made with the help of a drop of mercury on top of (e). This electrode was sealed to the end of the barrel (b).

Two electrodes of the same metal were prepared in the previous way. They were cleaned with chromic sulphuric mixture, followed by washing with equilibrium water. One of them was electropolished and the other left unpolished for comparison.

The rest of the apparatus, including water distillation and preparation of hydrogen chloride, was similar to that used for silver and tungsten work.

5. CONDITIONS FOR ELECTROPOLISHING. (47)

Metal	C.D. or V.	Time	Solution
Sn	2 - 3 amps cm.$^{-2}$	4 minutes	144 c.c. ethyl alcohol 10 grams $AlCl_3$ 45 " $ZnCl_2$ 32 c.c. water 16 c.c. butyl alcohol
Al	0.5 amps cm.$^{-2}$	1 minute	200 c.c. methyl alcohol 100 c.c. nitric acid
Fe	10 A.C.Volt	30 seconds	110 c.c. orthophosphoric acid (1.75 sp. gravity) 90 c.c. water

During electropolishing the solution was cooled in cold water. After electropolishing the metal was washed with boiling equilibrium water to remove any loose oxide from the surface.

S E C T I O N III

EXPERIMENTAL RESULTS

1. COMPLEX TAFEL LINES *

a. Silver.

Measurements were made in a nonpre-electrolysed solution of 0.06 N aqueous hydrochloric acid and the Tafel line is shown in Fig. (III 1). From this figure it is evident that the line has three slopes, i.e., values of $(d\eta/d\log i_c)$ corresponding to 0.14 V., 0.06 V. and 0.088 V. The change of slope occurs at about 3×10^{-6} and 1.2×10^{-4} amps $cm.^{-2}$ respectively. The lower slopes (0.06 and 0.088) occur in the linear logarithmic part of the Tafel line. Similar lines were obtained in solutions which were not extensively purified by pre-electrolysis (cf. Section II). Fig. (III 2) shows a Tafel line for silver in a solution of 0.2 N HCl, which was purified by passing 4000 coulombs only. This line has two slopes of 0.065 V. and 0.095 V. and the change takes place at 3×10^{-6} amps $cm.^{-2}$.

In solutions contaminated with platinum Tafel lines with much smaller slopes than the ones recorded above, were also obtained. Fig. (III 3) shows a typical example of such lines. The change of slope in the linear logarithmic part from 0.024 V. to 0.048 V. takes place at a current density of

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* This signifies lines having abnormal parameters (abnormal in the sense that they deviate to a considerable extent from simple lines reported in the following sub-section).

FIG (III 1)

Ag IN 0·06 NH Cl (No PRE-ELECTROLYSIS).

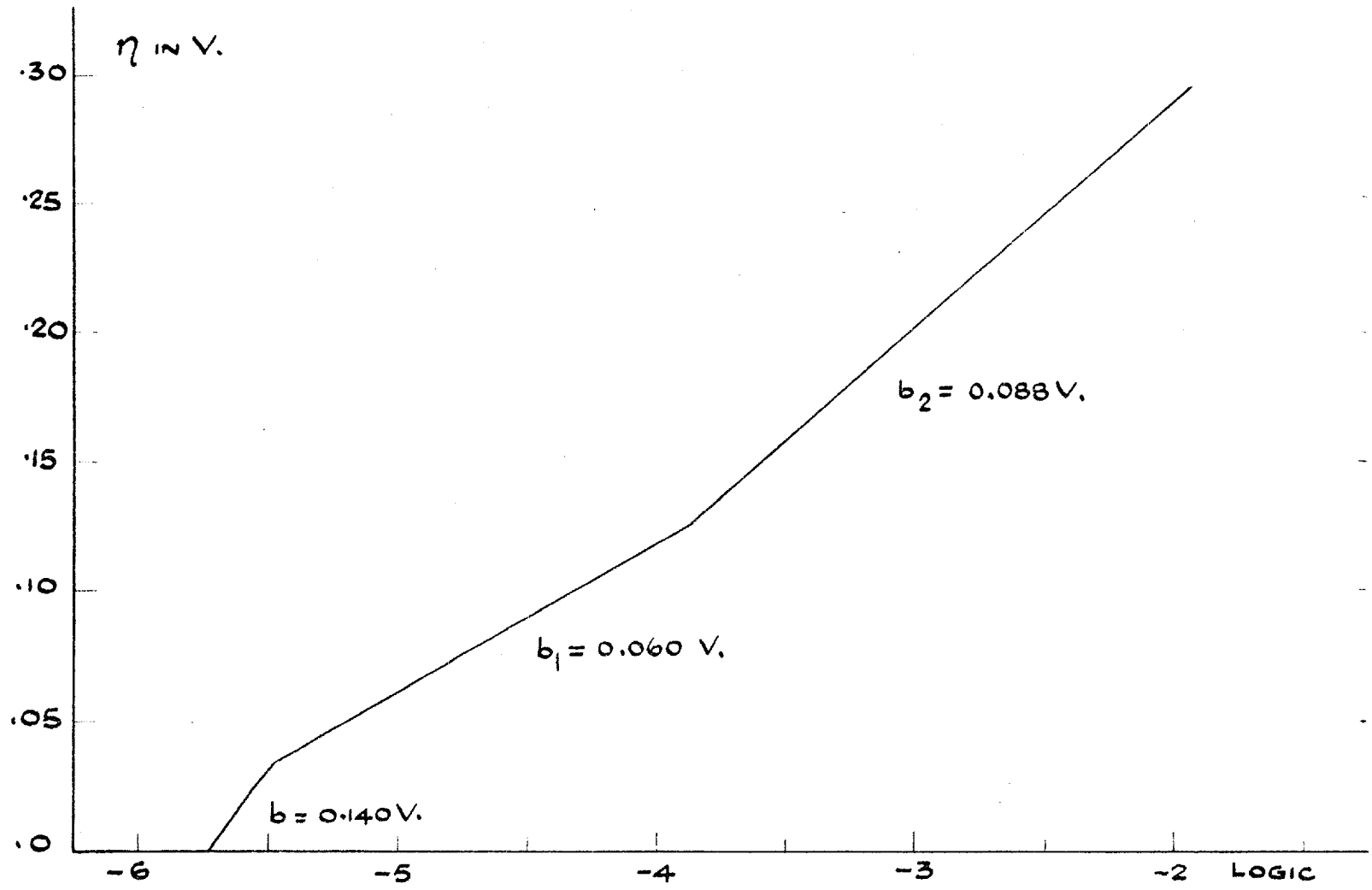


FIG (III 2)

Ag IN 0·2 N H Cl (PRE-ELECTROLYSIS: 4000 COULOMBS)

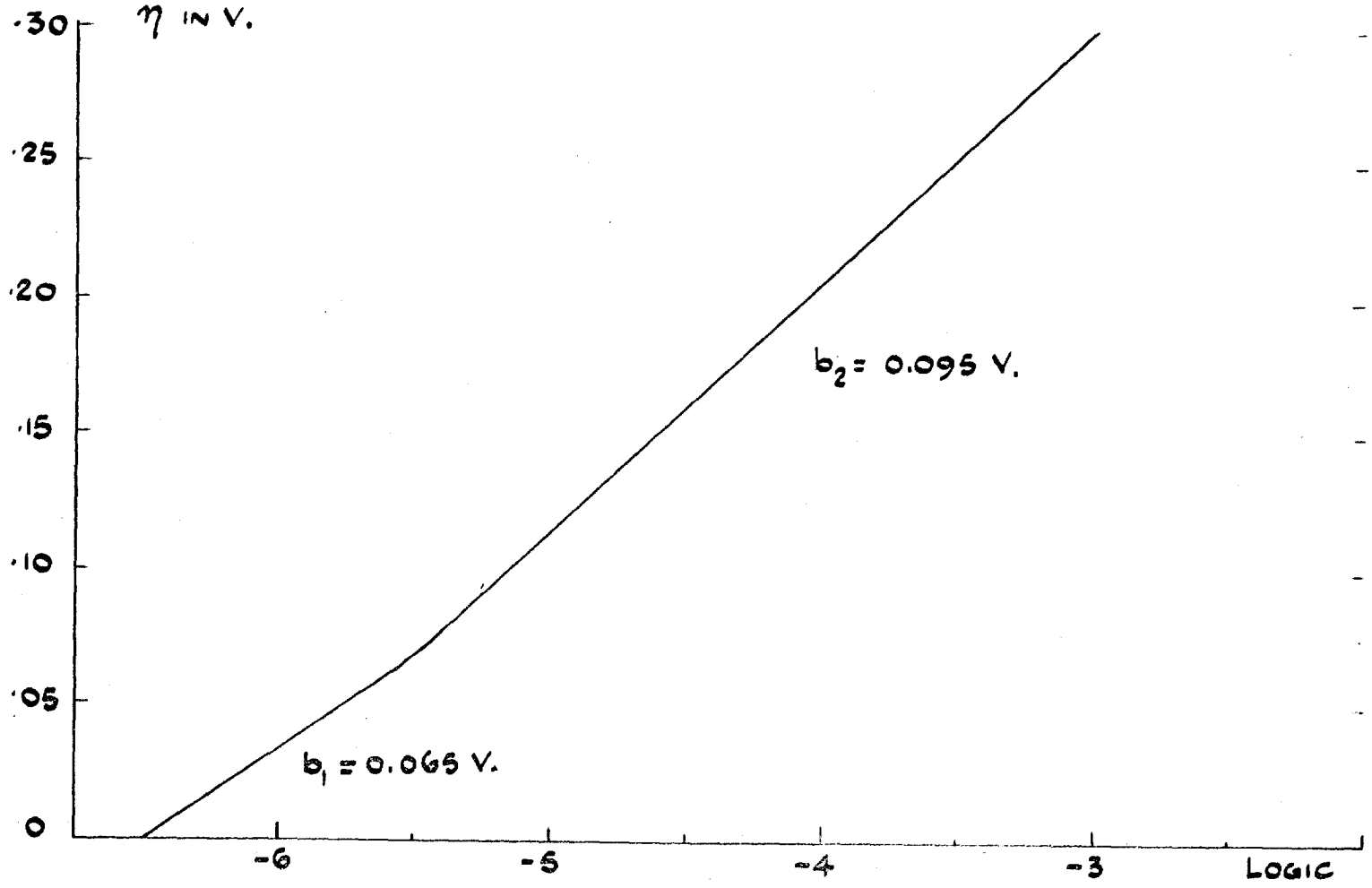


FIG (III 3)

Ag IN 0.1 NHCl (Pt CONTAMINATION)

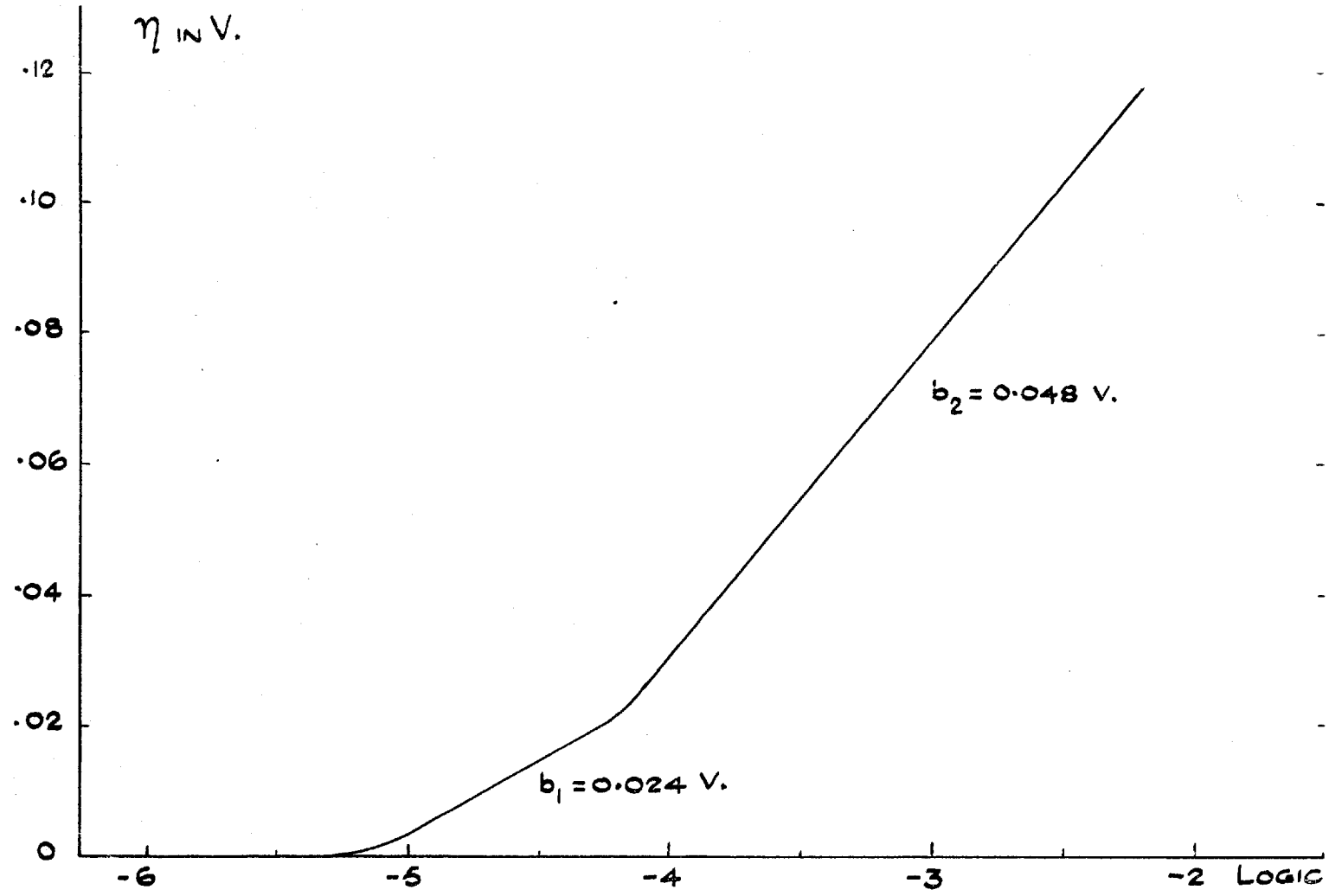


FIG (III 4)

W IN 0.10 NH Cl (CARBON CONTAMINATION)

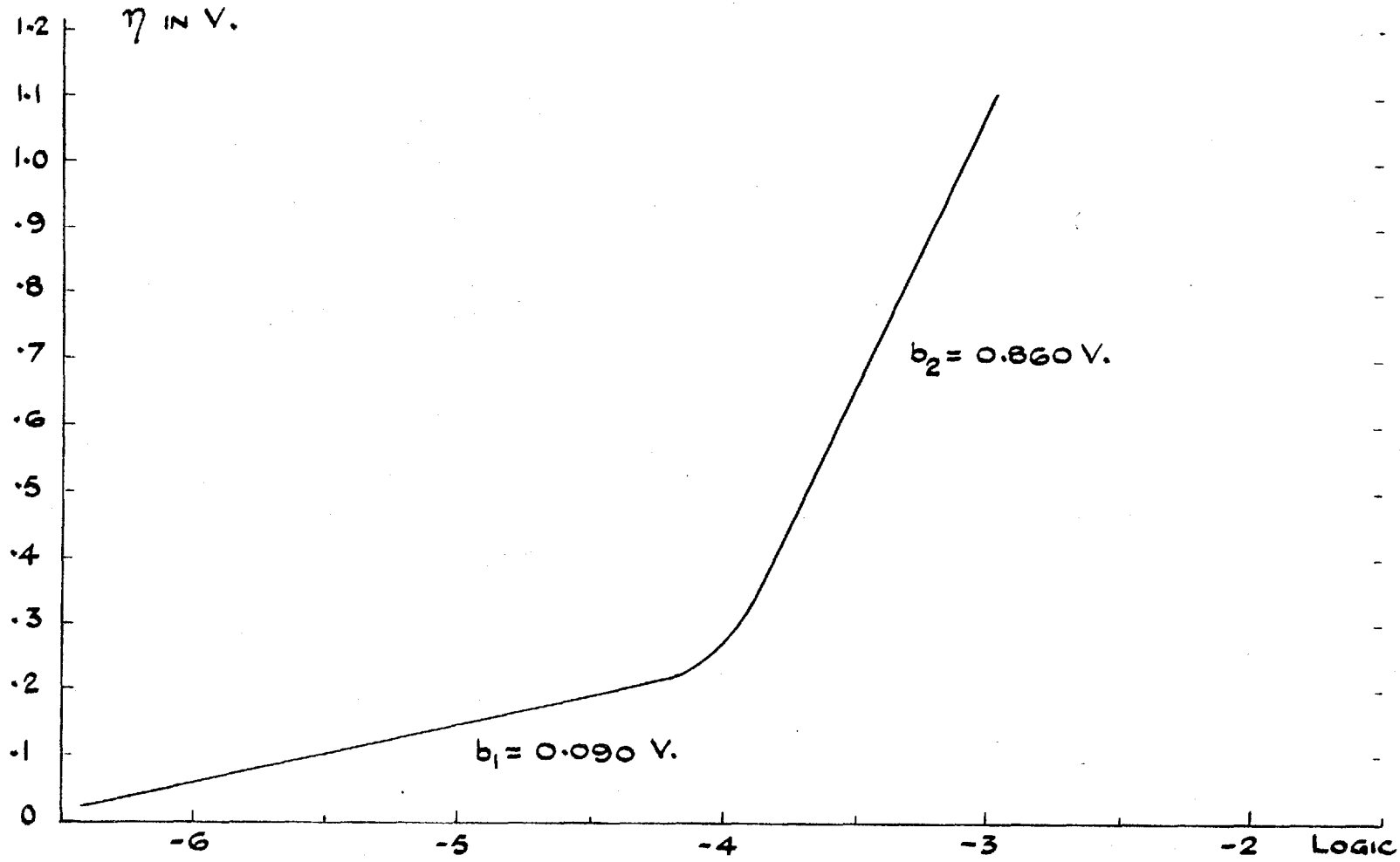
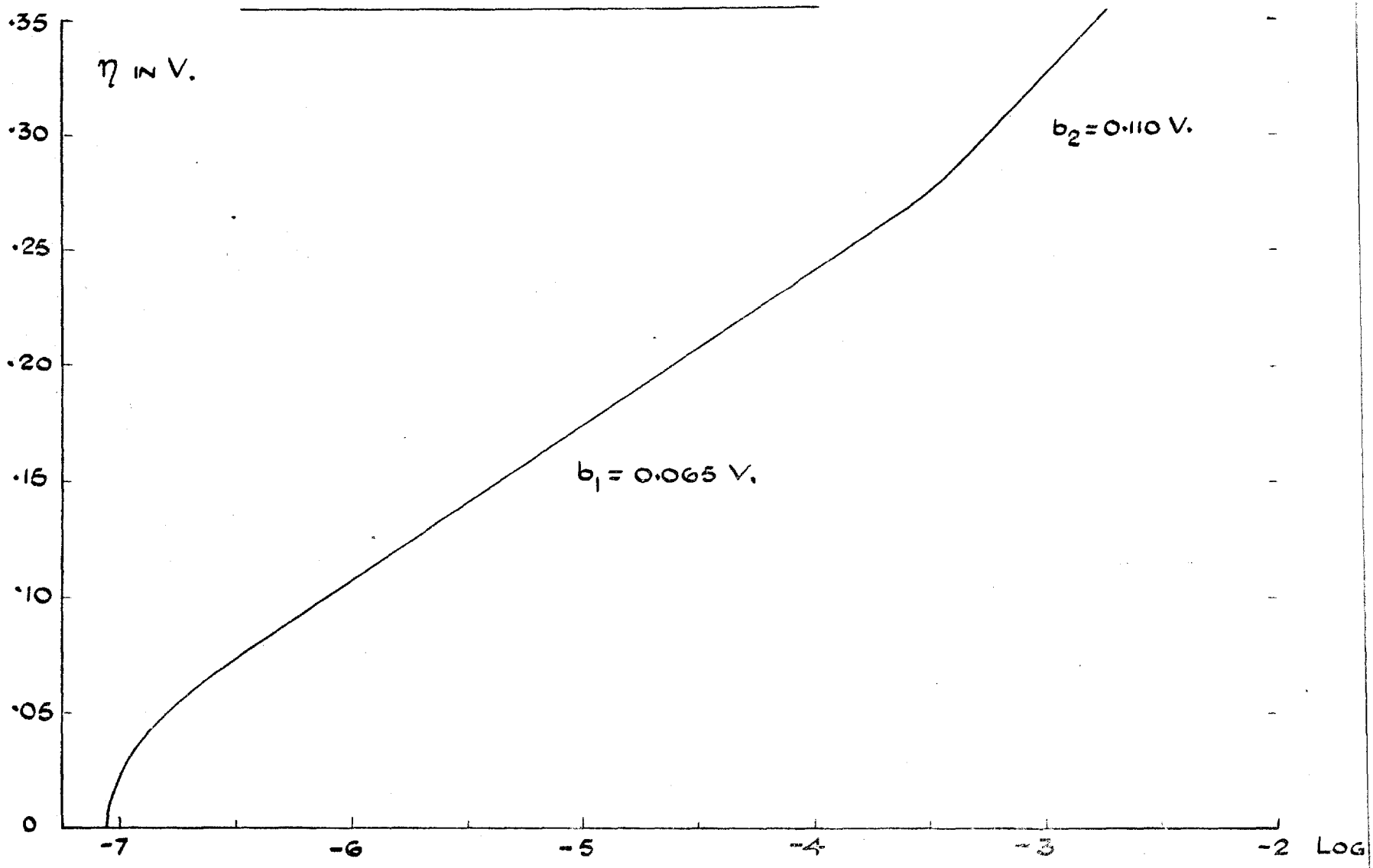


FIG. (III 5)

W IN 0.06 N H Cl (NO PRE-ELECTROLYSIS)



6.3×10^{-5} amps $cm.^{-2}$. It is to be noted that the lower slope (0.024) approaches in magnitude other slopes (0.029) obtained for platinum.[12][31]

b. Tungsten

Complex Tafel lines (cf. Fig. III 4) with slopes higher than 0.12 V. were observed for tungsten electrodes which were not extensively cleaned from carbon contamination.

The effect of impurities on the Tafel line constants is indicated by Fig. (III 5) where the solution was not purified by pre-electrolysis.

2. SIMPLE TAFEL LINES.

A simple Tafel line is defined as a line with parameters corresponding to well established mechanisms, and which is devoid of effects due to depolarisation and resistance over-potential. Such lines were obtained for silver and tungsten in rigorously purified solutions, on extremely clean electrode surfaces and with numerous precautions (cf. Section II) in the procedure of carrying out the experiment and taking the measurements. It was observed for the concentration range covered (between 0.1 N to 1 N HCl for silver and 0.1 N HCl for tungsten) that the Tafel line has two well defined slopes in the linear logarithmic parts (cf. Fig. III 6 and Fig. III 8).

FIG (III 6)

W IN 0.1 N H Cl

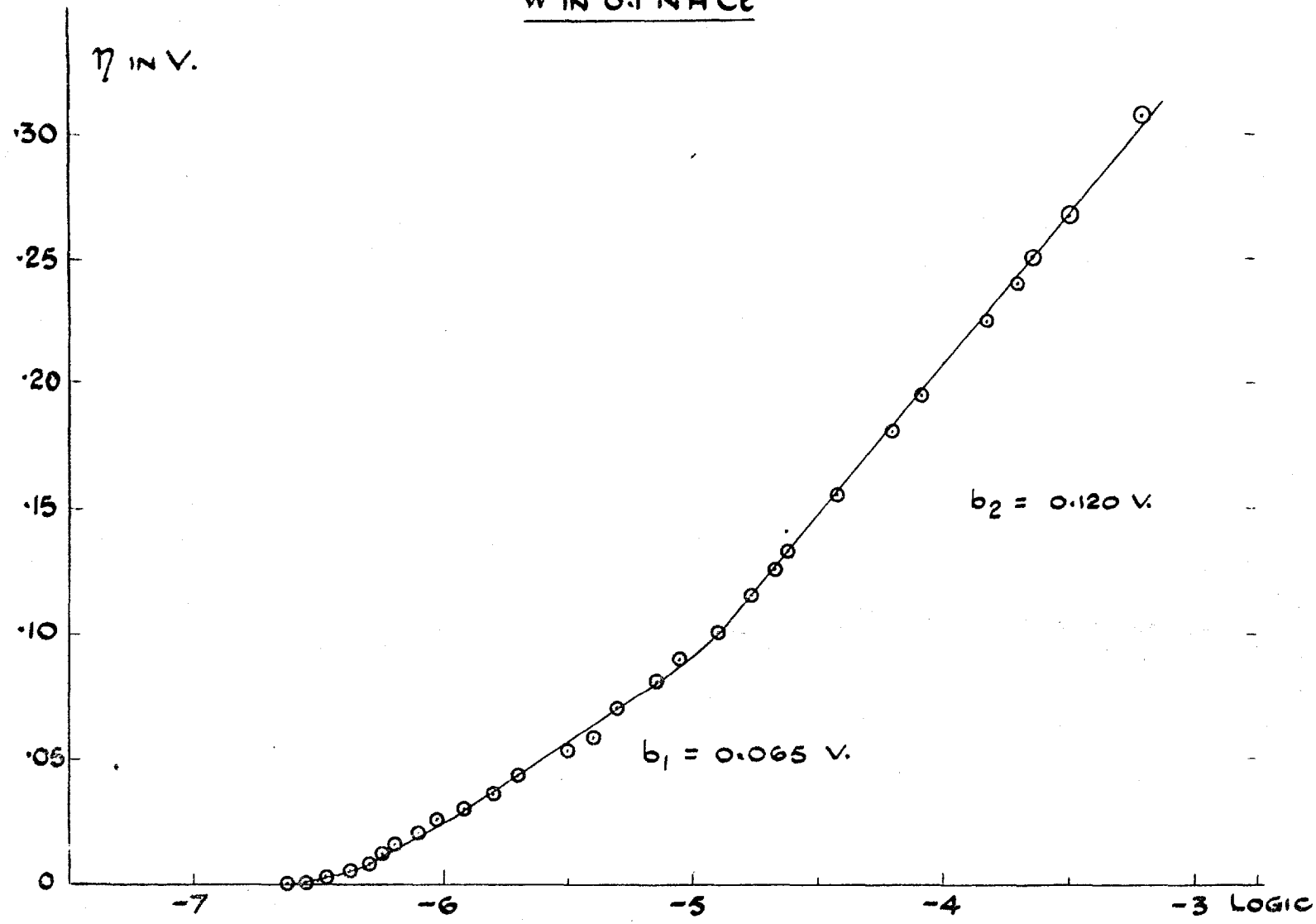


FIG (III 7)

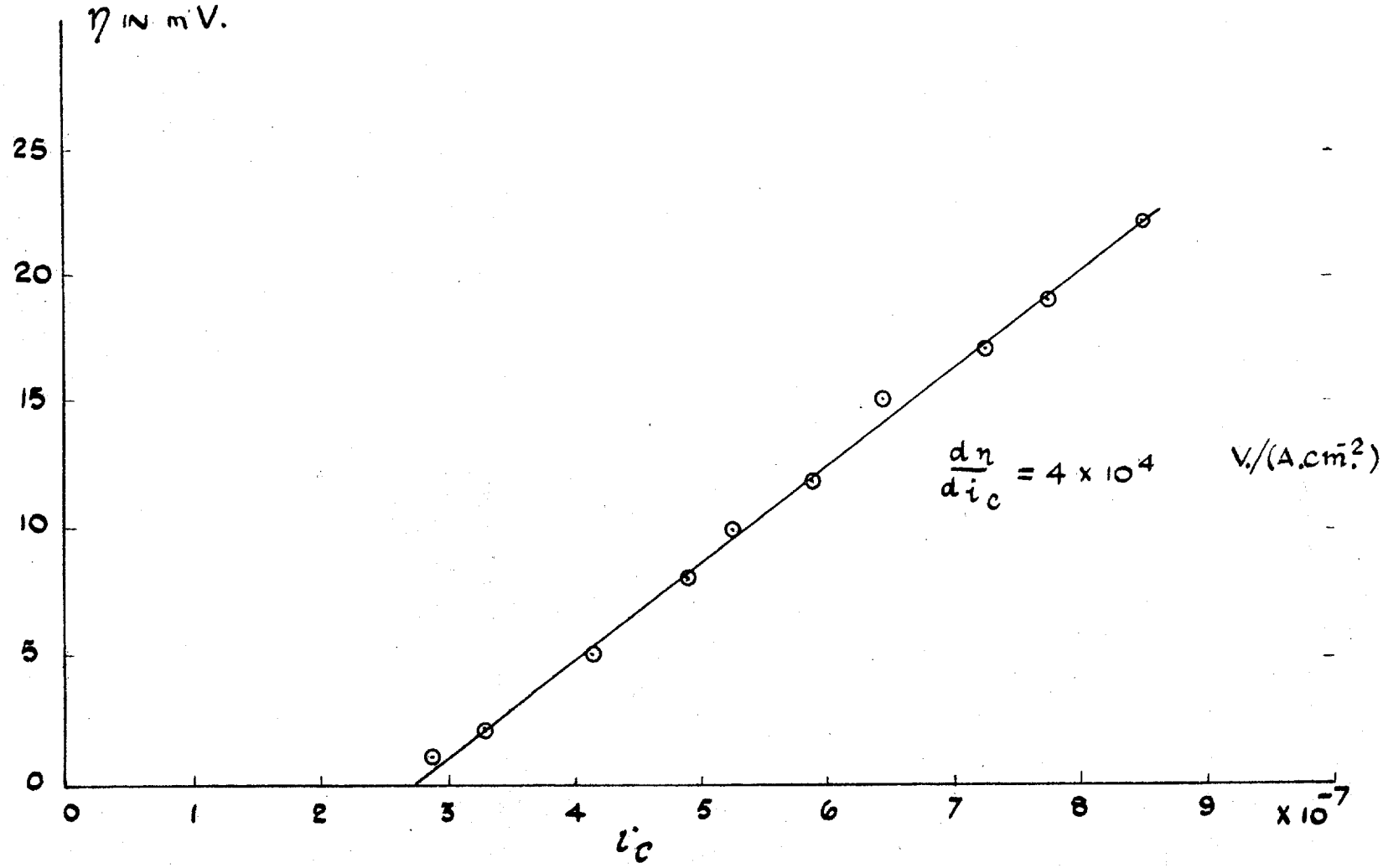

η IN m V.
25
20
15
10
5
0
0
1
2
3
4
5
6
7
8
9
X 10⁻⁷
i_c
$\frac{d\eta}{di_c} = 4 \times 10^4$ V./(A.cm⁻²)

FIG (III 8)

Ag IN 0.4 N H Cl

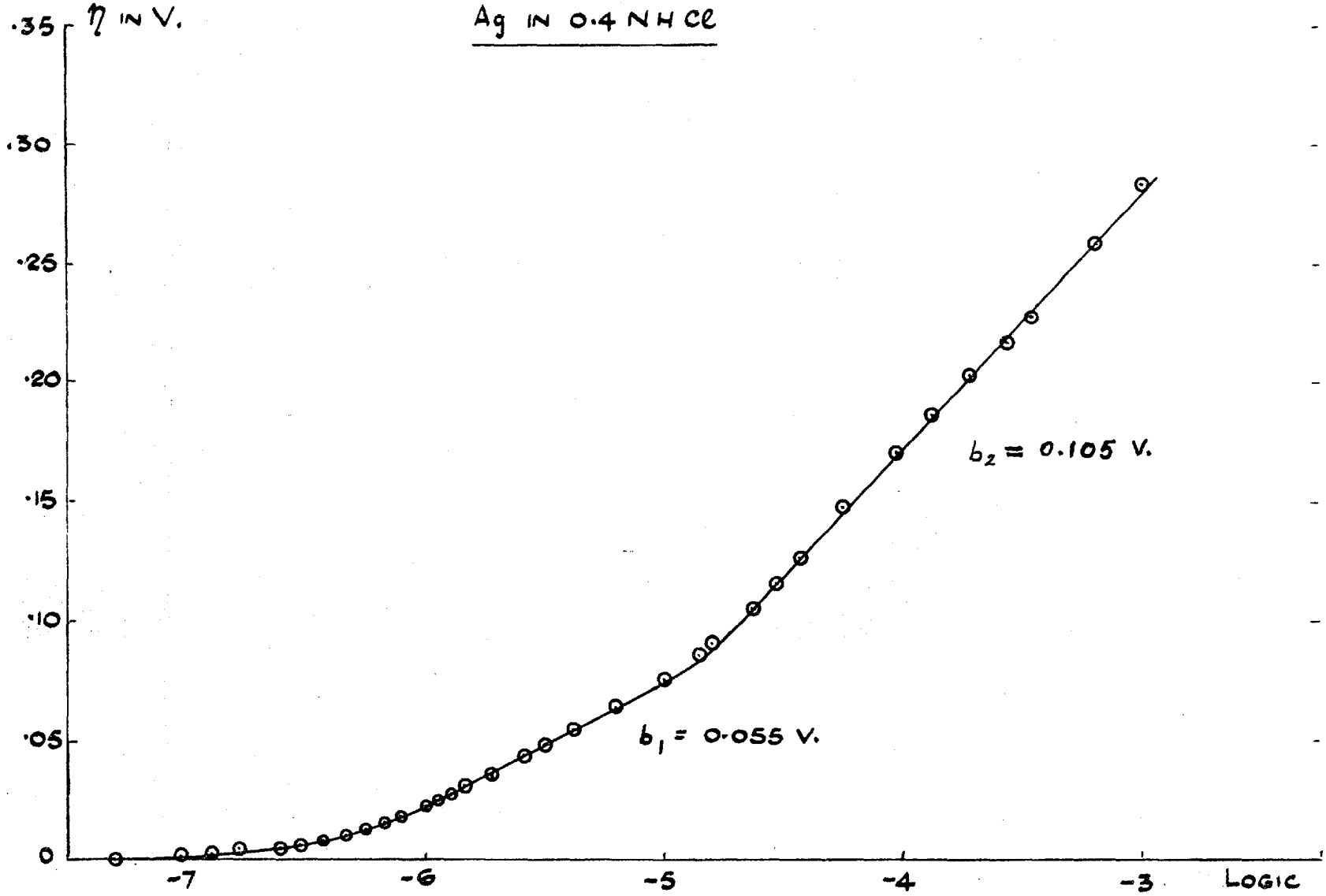
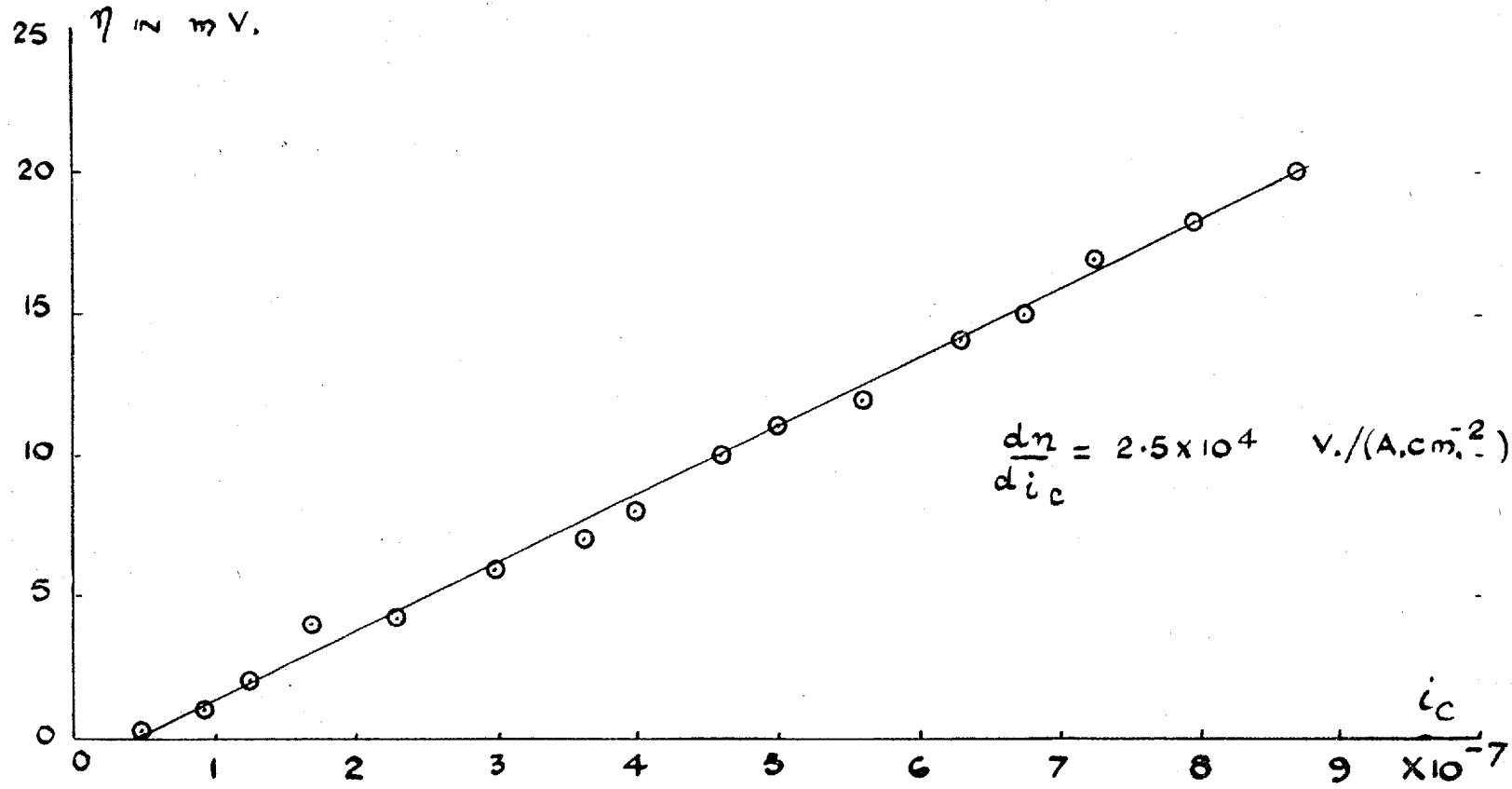


FIG. (III 9)


η in mV.
25
20
15
10
5
0
0
1
2
3
4
5
6
7
8
9
X10⁻⁷
i_c
$\frac{d\eta}{di_c} = 2.5 \times 10^4$ V./(A.cm.⁻²)

In tables (III 1) and (III 2), the slopes as well as the current density range, io values, concentration and the potential at which the Tafel line changes its slope, are given for silver and tungsten.

Tables (III 3) and (III 4) give the mean results on silver and tungsten respectively.

TABLE (III 1)

Parameters of Hydrogen Evolution on Silver in aqueous HCl Solutions

Conc.	c.d. range for lower linear section $A cm^{-2}$	b_1 V.	io_1 $A cm^{-2}$	c.d. range for higher linear section $A cm^{-2}$	b_2 V.	io_2 $A cm^{-2}$	η at which line changes its slope V.
0.1 N	$1 \times 10^{-6} - 1.6 \times 10^{-7}$	0.060	6.3×10^{-8}	$1 \times 10^{-6} - 3 \times 10^{-3}$	0.100	1.78×10^{-7}	0.100
	$1 \times 10^{-5} - 1 \times 10^{-6}$	0.060	5.75×10^{-7}	$1 \times 10^{-5} - 2 \times 10^{-4}$	0.100	2.0×10^{-6}	0.090
	$3 \times 10^{-6} - 3 \times 10^{-7}$	0.055	1.78×10^{-7}	$3 \times 10^{-6} - 10^{-3}$	0.090	3.55×10^{-7}	0.070
0.4 N	$1.4 \times 10^{-5} - 1 \times 10^{-6}$	0.055	4×10^{-7}	$1.4 \times 10^{-5} - 10^{-3}$	0.105	2.50×10^{-6}	0.090
	$1.4 \times 10^{-5} - 1 \times 10^{-6}$	0.055	2×10^{-7}	$1.4 \times 10^{-5} - 10^{-3}$	0.080	7.08×10^{-7}	0.100
	$3 \times 10^{-4} \times 1 \times 10^{-6}$	0.060	1.78×10^{-7}	$3 \times 10^{-4} - 3 \times 10^{-3}$	0.100	3.55×10^{-6}	0.175
	$5.6 \times 10^{-5} - 1 \times 10^{-6}$	0.060	3.16×10^{-7}	$5.6 \times 10^{-5} - 3 \times 10^{-3}$	0.110	2.80×10^{-6}	0.140
	$3 \times 10^{-4} - 1 \times 10^{-6}$	0.055	3.16×10^{-7}	$3 \times 10^{-4} - 3 \times 10^{-3}$	0.110	1.26×10^{-5}	0.150
1 N	$5.6 \times 10^{-5} - 3 \times 10^{-6}$	0.040	7.08×10^{-7}	$5.6 \times 10^{-5} - 3 \times 10^{-3}$	0.120	1.26×10^{-5}	0.075

TABLE (III 2)

Parameters of Hydrogen Evolution on Tungsten in 0.1 N HCl Solution.

c.d. range for lower linear section $Acm.^{-2}$	b_1 V.	io_1 $Acm.^{-2}$	c.d. range for higher linear section $Acm.^{-2}$	b_2 V.	io_2 $Acm.^{-2}$	η at which line changes its slope V.
$2.2 \times 10^{-5} - 3 \times 10^{-6}$	0.060	1.78×10^{-6}	$2.2 \times 10^{-5} - 10^{-3}$	0.115	6.3×10^{-6}	0.060
$1 \times 10^{-5} - 10^{-6}$	0.065	4×10^{-7}	$1.3 \times 10^{-5} - 10^{-3}$	0.095	1.2×10^{-6}	0.095
$1 \times 10^{-5} - 10^{-6}$	0.065	4×10^{-7}	$1.4 \times 10^{-5} - 10^{-3}$	0.120	2×10^{-6}	0.100
$3 \times 10^{-5} - 2 \times 10^{-6}$	0.060	5.6×10^{-7}	$3 \times 10^{-5} - 10^{-3}$	0.090	2×10^{-6}	0.110

TABLE (III 3)

Mean Results on Silver in aqueous HCl Solutions

Conc.	b_1 (V.)	io_1 ($Acm.^{-2}$)	b_2 (V.)	io_2 ($Acm.^{-2}$)
0.1 N	0.058 ± 0.002*	$(2.72 \pm 2.02) 10^{-7}$	0.097 ± 0.004	$(8.44 \pm 7.70) 10^{-7}$
0.4 N	0.057 ± 0.002	$(2.82 \pm 0.74) 10^{-7}$	0.101 ± 0.009	$(4.43 \pm 3.27) 10^{-6}$

* mean deviation from the mean.

TABLE (III 4)

Mean Results on Tungsten in

0.1 N HCl Solution

b_1 (V.)	io_1 ($Acm.^{-2}$)	b_2 (V.)	io_2 ($A\ cm.^{-2}$)
0.063 ± 0.003	(7.85 ± 4.98) 10^{-7}	0.105 ± 0.013	(2.88 ± 1.72) 10^{-6}

3. THE ELECTRON NUMBER λ

As has been indicated in Section I, the electron number plays an important part in elucidating the mechanism of electrode reactions. λ was evaluated using the following expression,

$$\lambda = -\frac{RT}{i_o F}\left(\frac{\partial i_c}{\partial \eta}\right)_{\eta \to 0}$$

A linear relation between overpotential (η) and current density (i_c) was obtained for all successful runs on silver and tungsten cathodes, at low current densities in hydrochloric acid solutions. Fig. (III 7) and Fig. III 9) show the relation between η and i_c corresponding to Fig. (III 6) and Fig. (III 8) respectively.

Tables (III 5) and (III 6) give values of λ for the successful runs on silver, calculated from first up and first down Tafel lines respectively. Values of λ for tungsten are given in Table (III 7).

TABLE (III 5)

The Electron Number λ

For Silver in aqueous HCl solutions

First Up Tafel Lines

conc.	$\left(\frac{\partial \eta}{\partial i_c}\right)_{\eta \to 0}$ V/(A cm^{-2})	i_o, (A cm^{-2})	λ
0.1 N	2.25 x 10^5	6.3 x 10^{-8}	1.78
	2.50 x 10^4	5.75 x 10^{-7}	1.75
	1.0 x 10^5	1.78 x 10^{-7}	1.41
mean value of λ =		1.65 $\pm$ 0.16	
0.4 N	2.5 x 10^4	4 x 10^{-7}	2.52
	7.5 x 10^4	2 x 10^{-7}	1.68
	6.5 x 10^4	1.78 x 10^{-7}	2.18
	4.2 x 10^4	3.16 x 10^{-7}	1.90
	3.5 x 10^4	3.16 x 10^{-7}	2.28
mean value of λ =		2.11 $\pm$ 0.26	
1 N	1.8 x 10^4	7.08 x 10^{-7}	1.98

TABLE (III 6)

The Electron Number λ

For Silver in aqueous HCl Solutions

First Down Tafel Lines

conc.	$\left(\frac{\partial \eta}{\partial ic}\right)_{\eta \to 0}$ V/(A cm^{-2})	i_{o_1} (A cm^{-2})	λ
0.4 N	2.25 x 10^4	5.01 x 10^{-7}	2.23
	9.0 x 10^4	1.59 x 10^{-7}	1.76
	3.0 x 10^4	4.0 x 10^{-7}	2.10
mean value of λ = 2.03 ± 0.18			
1 N	1.4 x 10^4	7.94 x 10^{-7}	2.27

TABLE (III 7)

The Electron Number λ

For Tungsten in 0.1 N HCl Solution

T. line	$\left(\frac{\partial \eta}{\partial i_c}\right)_{\eta \to 0}$ V/(A cm^{-2})	i_{o_1} (A cm^{-2})	λ
first up	8×10^{3}	1.78×10^{-6}	1.77
" "	4.2×10^{4}	4.0×10^{-7}	1.50
" "	4.0×10^{4}	4.0×10^{-7}	1.57
" "	3.0×10^{4}	5.6×10^{-7}	1.50
first down	1.6×10^{4}	1.0×10^{-6}	1.57
" "	3.0×10^{3}	3.16×10^{-6}	2.66

mean value of λ = 1.76 ± 0.30

4. EFFECT OF ELECTROPOLISHING ON HYDROGEN OVERPOTENTIAL.

The effect of electropolishing the cathode surface on hydrogen overpotential was studied for iron, aluminium and tin, in 1 N hydrochloric acid solution. For iron cathodes (cf. Fig. III 10) the electropolished electrode shows a decrease of overpotential of about 12.5 mV., from the non-polished one, below 10^{-4} amps. cm.$^{-2}$. Above 10^{-3} amps. cm.$^{-2}$ electropolishing of iron has very little effect on its hydrogen

FIG(III 10)

Fe IN 1.0 N HCl

x NONELECTROPOLISHED

⊙ ELECTROPOLISHED

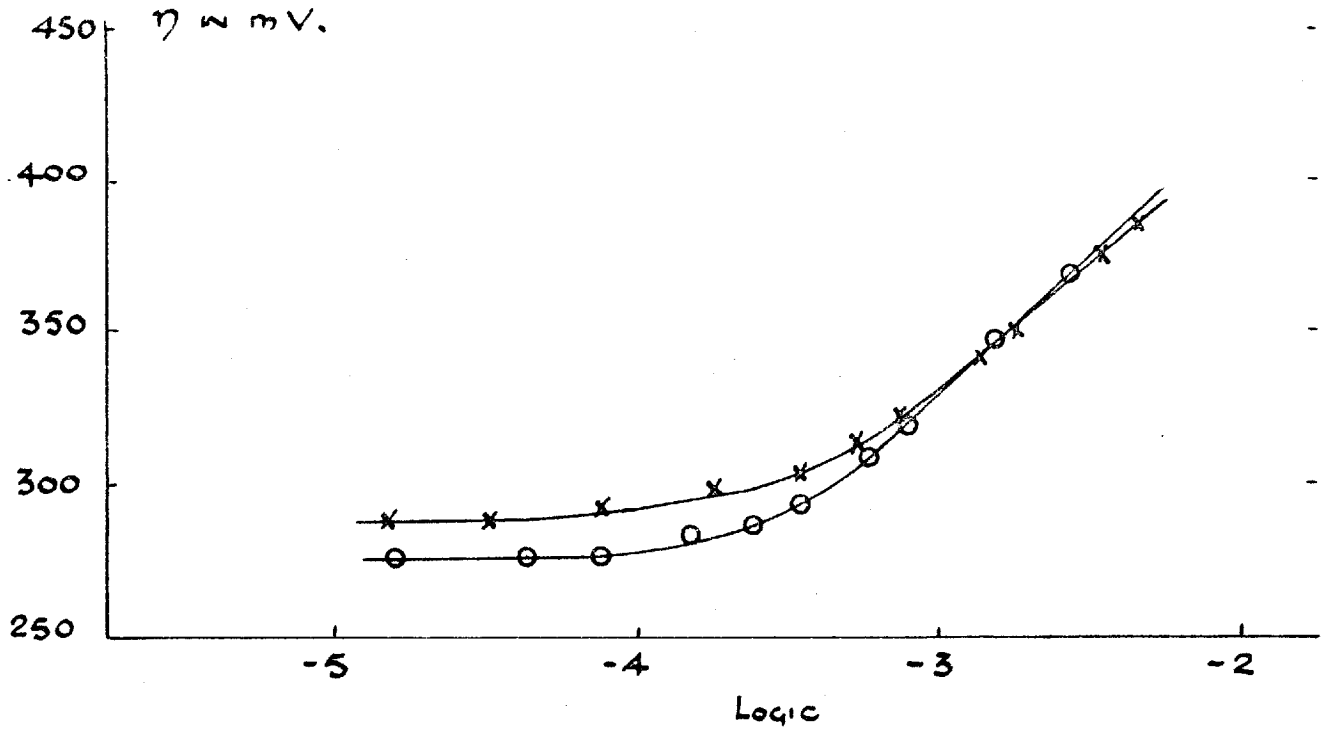


FIG (III 11)

Al IN 1·0 N H Cl

× NONELECTROPOLISHED

⊙ ELECTROPOLISHED.

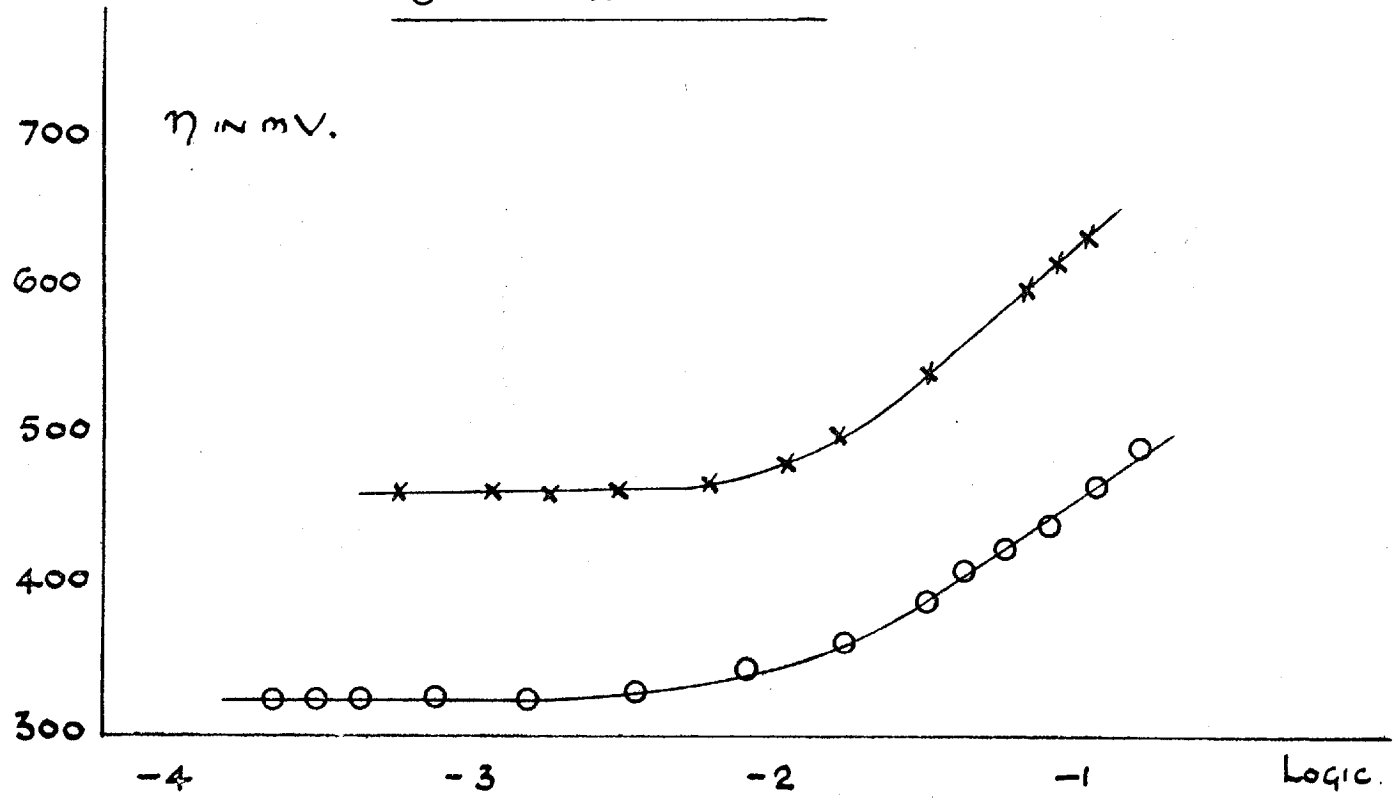
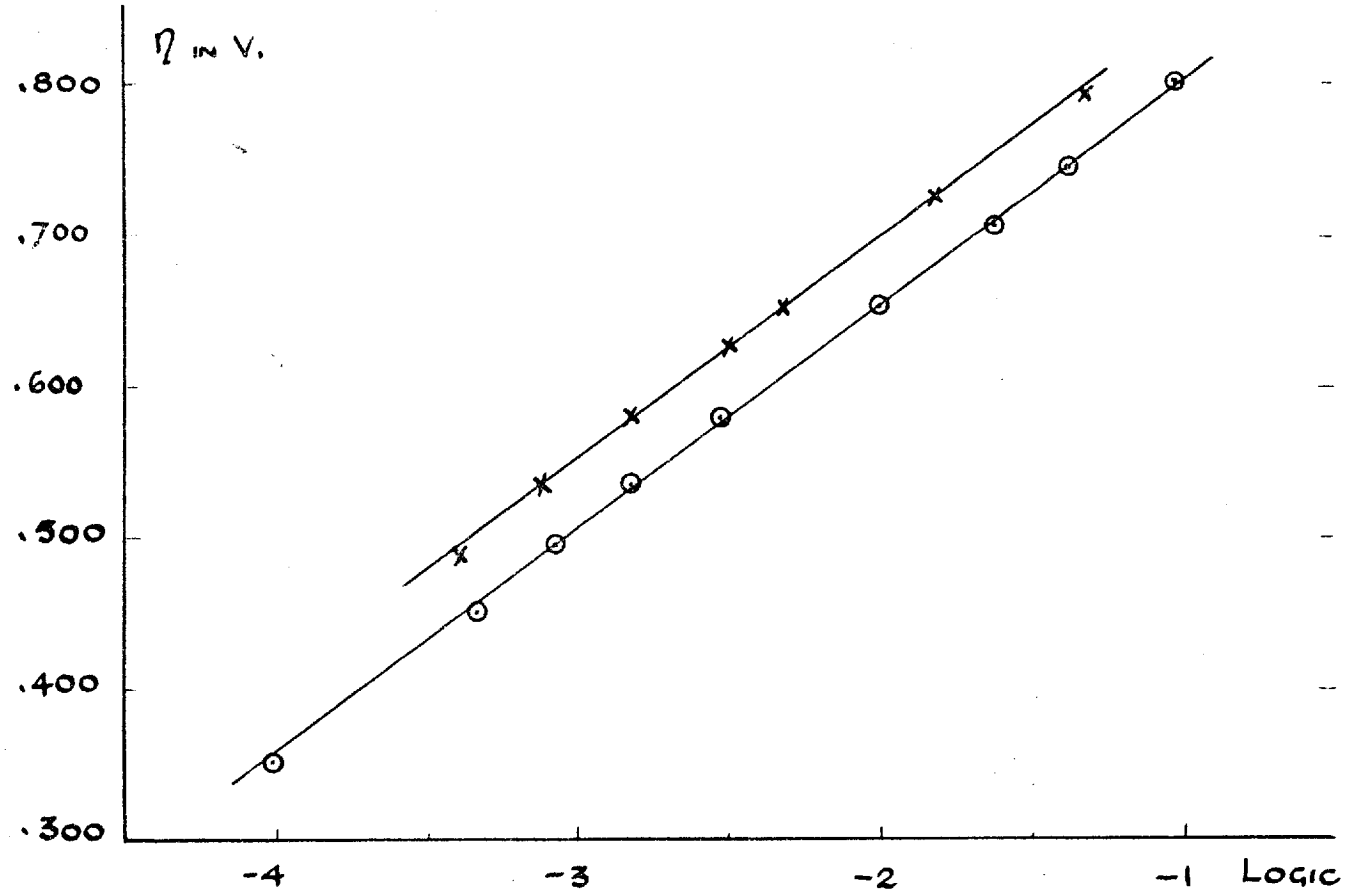


FIG. (III 12)

Sn IN 1·0 N H Cl

x NON ELECTROPOLISHED

⊙ ELECTROPOLISHED.



overpotential.

For aluminium, electropolishing lowers the Tafel line by about 130 - 140 mV. The effect of electropolishing of aluminium on hydrogen overpotential is shown in Fig.(III 11).

For tin cathodes electropolishing also lowers the Tafel line (cf. Fig. III 12) by about 50 mV. in the current density range $3 \times 10^{-4} - 10^{-1}$ amps. $cm.^{-2}$.

S E C T I O N IV

DISCUSSION

OF EXPERIMENTAL RESULTS

1. COMPLEX TAFEL LINES.

a. Effect of Depolarisers

It is clear from Fig. (III 5) that the Tafel line for tungsten in a nonpre-electrolysed solution of 0.06 N HCl, changes to the anodic side at a current density of about 10^{-7} amps. $cm.^{-2}$. The behaviour of this line at low current densities is similar to that observed for mercury cathodes in solutions containing oxygen.(20) The effect of oxygen on the Tafel line for mercury was attributed to the electroreduction of molecular oxygen.(41) The processes involved in the electroreduction of oxygen are :

(i) The diffusion of oxygen towards the cathode.

(ii) The combination of an oxygen molecule with a hydrogen ion and an electron,

$$O_2 + H^+ + e_o \longrightarrow O_2H$$

(iii) The discharge of a hydrogen ion on HO_2 to form a hydrogen peroxide molecule on the electrode surface,

$$HO_2 + H^+ + e_o \longrightarrow H_2O_2$$

Steps (ii) and (iii) are potential dependent and if one of these two steps is rate-determining for the electroreduction process the Tafel line must have a definite slope in the region where depolarisation takes place. The rate of

the electroreduction of oxygen on mercury cathodes assuming step (ii) to be rate-determining is given by,[20]

$$i = k\, a_{O_2}\, (a_{H^+})_{d.l.}\, e^{-\xi F/RT}\, e^{-\alpha \Delta\phi F/RT}, \qquad (IV\ 1)$$

Where a_{O_2} is the activity of oxygen and $(a_{H^+})_{d.l.}$ is the activity of hydrogen ions in the double layer. From (IV 1),

$$\frac{d\,\Delta\phi}{d\,\ln i} = -\frac{RT}{\alpha F}, \qquad (IV\ 2)$$

and since α is 0.5 for mercury, the slope of the Tafel line in the region where depolarisation by oxygen takes place is 0.116 V. This result is in good agreement with experiment.[20]

However, the case for tungsten is different from these results (cf Fig. III 5) since the Tafel line has no definite slope in the depolarisation region. This suggests that if the depolariser is oxygen, the rate-determining step is the diffusion of oxygen towards the cathode.

The relation between overpotential η, the net cathodic current i_C and the limiting current of diffusion of oxygen i_L is given by,[42]

$$\eta = \frac{RT}{nF} \ln\left(\frac{i_L}{i_L - i_C}\right), \qquad (IV\ 3)$$

where n is the number of faradays necessary for the electrolysis of one mole of oxygen. Taking i_L as a constant, one gets for the slope of the Tafel line in the depolarisation region,

$$\frac{d\eta}{d\ln i_c} = -\frac{RT}{nF}\left(\frac{i_c}{i_c - i_L}\right). \qquad (IV\ 4)$$

Thus equation (IV 4) gives a limiting slope of $-RT/nF$ when $i_c \gg i_L$, so that the expected slope would be $2.303\ \frac{RT}{nF} = 0.029$ V. at ordinary temperatures (n is 2 when H_2O_2 is formed as shown above). In the present experiment, however, the experimental values of $d\eta/d\log i_c$ at low current densities are a function of current density. Hence it must be assumed that i_c in the region of breakdown of the Tafel equation is of the same order as i_L, whereupon from (IV 4) it is clear that the rapidly increasing numerical values of b (cf. Fig. III 5) would be expected.

The limiting current of diffusion of oxygen is related to the concentration of oxygen in the solution by,[23]

$$i_L \simeq 0.14\,C, \qquad (IV\ 5)$$

where C is in gram moles per litre. Taking i_L as 2×10^{-7} amps. $cm.^{-2}$. (cf. Fig. III 5) one gets from (IV 5),

$$C = 1.4 \times 10^{-6} \text{ mole } O_2\text{/litre solution} \qquad (IV\ 6)$$

Taking the absorption coefficient of oxygen in water at room temperature as approximately equal to 0.025 c.c. of oxygen per c.c. of water under a partial pressure of oxygen of one atmosphere, the above concentration (IV 6) corresponds to a partial pressure of oxygen of,

1.25×10^{-3} atmos. (IV 7)

There are several possibilities for the origin of oxygen responsible for the depolarisation of the Tafel line in Fig. (III 5),

(i) The vacuum obtained in the hydrogen purification train (the water vapour pressure) is not sufficient for the removal of all traces of oxygen.

(ii) The time (about two hours) allowed for the passage of hydrogen in the hydrogen chloride preparation apparatus is not sufficient for the complete removal of oxygen.

(iii) The presence of a pinhole in the apparatus. Possibilities (i) and (ii) are excluded since undepolarised Tafel lines were obtained with the same treatment, i.e., evacuation of the hydrogen train to the water vapour pressure and passage of hydrogen in the HCl preparation apparatus for two hours. The most probable cause of depolarisation by oxygen is, therefore, the presence of a pinhole, too small to be detected, which during pre-electrolysis (usually 40-50 hours) allows a certain amount of oxygen to contaminate the solution. Confirmation of this view was obtained when Tafel lines devoid of depolarisation were obtained when certain glass bridges (connecting different parts of the apparatus were replaced.

For silver (cf. Fig. III 1) the Tafel line in the depolarisation region has a slope of 0.140 V. This shows that, if the depolariser is oxygen, either,

$$H^+ + e_o + O_2 \longrightarrow HO_2 \quad , \qquad \text{(IV 8)}$$

or,

$$2HO_2 \longrightarrow H_2O_2 + O_2 \quad , \qquad \text{(IV 9)}$$

or,

$$HO_2 + e_o + H^+ \longrightarrow H_2O_2 \quad , \qquad \text{(IV 10)}$$

is the rate-determining step for the electroreduction of oxygen. Measurements of the stoichiometric number μ (the number of acts of the rate-determining step necessary for one act of the overall reaction, $2H^+ + O_2 + 2e_o \longrightarrow H_2O_2$), where $\mu = 2/\lambda$, from the relation between η and i_c at low current densities for the Tafel line in Fig. (III 1), gave a value of 1.8. This shows that the most probable rate-determining step in the oxygen depolarisation reaction on silver cathodes is the discharge of hydrogen ions on oxygen molecules (probably adsorbed on the electrode surface) to form HO_2 as given by equation (IV 8), where $\mu = 2$. For (IV 9) and (IV 10) μ is one.

b. Effect of Platinum in the Solution.

Fig. (III 3) shows a Tafel line obtained for a silver cathode in 0.1 N HCl. The slope of this line at intermediate current densities is 0.024 V. This slope corresponds to the catalytic recombination mechanism (cf. table I 1), which is known to occur for platinum[12,43] and palladium cathodes.[32] The occurrence of a slope of 0.024 V. for silver cathodes indicate

the presence of platinum in the solution since platinum is used for the anode and the conductivity electrodes.

Previous authors[21] have observed that the use of platinum in the cell vitiated the hydrogen overpotential results obtained for mercury. However, it is noteworthy that in the solution in which the Tafel line in Fig. (III 3) was obtained, some difficulties had been experienced with regard to the constant level of the solution in the anode compartment and irregular bubbling of hydrogen had caused momentary loss of contact between the anode and the solution during pre-electrolysis. This caused sparking* at the anode-solution contact and it seems likely that this was the process leading to the dissolution of platinum in the anolyte. Platinum would be transferred to the cathode compartment by diffusion and would be deposited on the cathode surface, thus lowering the slope of the Tafel line and causing the catalytic recombination to be rate-determining.

c. Effect of Carbide Formation.

At the beginning of the present work on hydrogen overpotential on tungsten, the electrodes were prepared in a manner similar to that described by Bockris and Conway.[15] A piece of tungsten wire, 2 cm. long and 1 m.m. in diameter,

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* p.d. applied during pre-electrolysis was 400 V.

was reduced in a hysil tube (connected to the fragile bulb, cf. Section II) with a stream of hydrogen passing over it. Furthermore, for the overpotential measurements, the Tafel line was traced downwards starting with a high current density (about 10^{-2} amps. $cm.^{-2}$). With these conditions Tafel lines similar to that in Fig. (III 4) were obtained. Such a line has two slopes of 0.86 V. and 0.090 V. at high and intermediate current densities respectively. The higher slope corresponds to that obtained by Bowden and Rideal[44] for carbon cathodes. This suggests that the tungsten cathodes, prepared as mentioned above, were covered with carbide (or carbon) when the polarisation was first started and on tracing the Tafel line downwards the carbide (or carbon) was reduced and evaporated in the form of volatile organic compounds. This view is supported by the fact that for the preparation of thin tungsten wire, thick tungsten rods are drawn through a die using colloidal graphite as a lubricant. For this reason, it was necessary to change the method of electrode preparation and the procedure of flashing the tungsten wire, to a temperature of about 3000°C, was adopted (cf. Section II).

The detailed theory of the considerable change in slope brought about by the presence of carbide (or carbon) on the surface is difficult to evaluate in the absence of knowledge of the effect of carbide and carbon on the adsorption energy of hydrogen on tungsten. It must be presumed that the

presence of carbide or carbon alters the constants of the Morse function representing the adsorption energy and that this causes a change in the relative slopes of the Morse equations for the final state in the hydrogen discharge reaction compared with that of the initial state.

2. SIMPLE TAFEL LINES.

a. Observations on the Experimental Technique necessary to obtain Results at very low Current Densities.

At the beginning of the present work, Tafel lines with complex nature (cf. Section III) were obtained. Certain improvements of the experimental technique were therefore necessary for the success of establishing the Tafel line at very low current densities. Thus, it is necessary to discuss the alterations in the technique which lead to the above mentioned result.

(i) Purification of Hydrogen.

Hydrogen was first purified by a method similar to that used by Bockris et al.[19] The disadvantage of this method, where the train is not evacuated, is that the purity of hydrogen will depend on the time allowed for hydrogen to displace air in the train. This difficulty is overcome by evacuating the train to the water vapour pressure, before filling it with hydrogen (cf. Section II). As an added precaution, particularly during fast passage of hydrogen, an additional deoxygenation stage in the form of a tube (36" long) at a temperature of 400°C, containing reduced CuO wire, was used. Silica gel was also used in place of magnesium

perchlorate as a drying agent, since the latter is decomposed by heat (during the process of drying the train) and becomes functionless. Tubes of silica gel were used after each section of the train in which water could be produced, and these tubes were followed by empty traps cooled in a mixture of carbon dioxide and methylated spirit to ensure the complete drying of hydrogen.

(ii) Electrode Preparation.

The method of electrode preparation (developed by Bockris and Conway[15]), which was used in the first part of this work is unsatisfactory for metals, e.g., tungsten whose surface oxide or carbide films are not reduced by heating (to the temperature of the oxygen coal gas flame) in hydrogen. For such cases, the surface films are best volatalised by flashing the metal in vacuum (cf. Section II). Although Bockris and Conway's method is satisfactory for metals of lower melting point (cf. Bockris and Potter[6]), it probably results in a non-homogeneous reduction of the surface films. This conclusion is drawn from the fact that the slopes of the Tafel lines obtained in the present work on silver are different from those obtained by Bockris and Conway.[22] The homogeneous reduction of the surface films is carried out by heating the metal in a uniformly heated quartz furnace (with hydrogen passing into it) to a temperature depending on the

metal (cf. Section II).

(iii) Pre-electrolysis.

The stringent conditions of pre-electrolysis which were determined for silver electrodes by Bockris and Conway[22] could not at first be reproduced in the present work, because of interruption of the high current density needed for pre-electrolysis (1×10^{-1} amps. $cm.^{-2}$) by bubbles formed near the main tap between the cathode and the anode. This difficulty was overcome by projecting a stream of water over the tap, thus maintaining this at room temperature.

b. Comparison with Previous Work.

Bockris and Conway[22] obtained two slopes for the Tafel lines on silver in aqueous hydrochloric acid solutions of strength greater than 0.1 N and their mean results are given in table (IV 1).

Table (IV 1)

conc.	0.1 N	1.0 N	5.0 N	7.0 N
b_1	0.09	0.06	0.07	0.09
b_2	0.12	0.13	0.12	0.11
io_1	5×10^{-7}	4×10^{-6}	2×10^{-7}	8×10^{-8}
io_2	3×10^{-6}	2×10^{-4}	6×10^{-6}	2×10^{-7}

A comparison between table (IV 1) and tables (III 1) and (III 3) shows that the values of b_1 and b_2 obtained by Bockris and Conway are higher than those obtained in the present work although io values are approximately the same. The discrepancy between b_1 values could be attributed to the following reasons:

(i) Purity of the solution.

(ii) State of the electrode surface.

Since there is virtually no difference between the present work and that of Bockris and Conway with regards to

the solution purity, it is unlikely that the difference between b_1 values is caused by any solution factor. The only obvious reason, for the discrepancy of b_1 values, is therefore the difference between the state of the electrode surface obtained in the present work and that obtained by Bockris and Conway. Since silver is always covered with an oxide or a sulphide film (which are reduced during the electrode preparation), the state of the metal surface depends on the method used for the reduction of these films. A comparison between the method used in the present work (cf Section II) and that used by Bockris and Conway,[22] shows that the former method is more reliable for obtaining a standard purity of the electrode surface. However, it is clear that in Bockris and Conway's work there is no vitiating effects due to the presence of any oxide or sulphide films on the electrode surface. The difference between b_1 values is most probably attributed to the extent of the surface heterogenity. The inadequate uniformity of heating, manifest in Bockris and Conway's method, was avoided in the present work (cf. Section II).

From the effect of neutral salts at constant pH, Bockris and Conway concluded that the process of discharge of hydrogen ions takes place from hydroxonium ions rather than from water molecules. Also from the single observation of the electron number for silver in 0.075 N HCl, made by Potter,[45] where λ was one, they concluded that the rate-determining step is the slow discharge of hydroxonium ions. From the pH effect on

hydrogen overpotential and from the observation of Drake and Benton[46] that activated adsorption of hydrogen occurs on silver at high temperatures and remains at low temperatures, they assumed that it is possible for specific adsorption of hydroxonium ions on silver to take place. The p.d. due to specific adsorption of H_3O^+, assuming that these ions form a condenser with the electrode surface is,

$$x = \frac{4\pi\mu}{d} C_o e^{-\zeta_o F/RT} , \qquad (IV\ 11)$$

where μ is the dipole moment of $A\bar{g} - H_3O^+$, Co is the bulk concentration of H_3O^+, ζ_o is the standard zeta potential at the plane of the Helmholtz double layer, and d is the dielectric constant in this layer. However, equation (IV 11) is oversimplified, since there is no evidence that, even if specific adsorption of H_3O^+ takes place on silver, the resulting structure is a perfect condenser. Moreover, if equation (IV 11) is correct, it would be expected that specific adsorption of H_3O^+ ions is independent of the p.d. between initial and final states ($\Delta\phi$). This is clearly incorrect since, for the case of specific adsorption of iodide ions on mercury Butler[48][24] found that the concentration of specifically adsorbed ions is related to the potential by,

$$C = C_o e^{-\alpha e_o V/kT} , \qquad (IV\ 12)$$

where Co is the concentration of the specifically adsorbed ions at a potential V = 0, and α is the part of potential

which helps specific adsorption.

Assuming specific adsorption of H_3O^+ ions, and that the mechanism is the slow discharge of H_3O^+, and using the expression for the slope of the Tafel line,[49][50][51]

$$b = -2.303 \frac{RT}{\beta F}, \qquad \text{(IV 13)}$$

where β is a factor of symmetry of the energy barrier, Bockris and Conway's results (cf. table IV 1) show that β decreases with increase of cathodic polarisation. They concluded from this that at high cathodic polarisation, the initial state is displaced towards the cathode in virtue of the increased attraction due to specific adsorption.

From table (IV 1) and equation (IV 13), β at intermediate current densities is more than 0.5 and is apparently equal to one in 1.0 N HCl solutions. It is unlikely that a simple slow discharge process would be associated (in absence of specific adsorption of H_3O^+ at low and intermediate current densities as indicates by Bockris and Conway) with a distorted energy barrier. In all cases where a slow discharge mechanism involving hydrogen ions is well established (cf. Frumkin[30] and also Bockris and Potter[4]) an approximately symmetrical energy barrier is found to exist.

c. The Mechanism of Hydrogen Evolution on Silver and Tungsten

As has been indicated in Section I, a knowledge of the electron number together with other parameters helps to elucidate the mechanism of cathodic hydrogen evolution. Tables III 5, III 6 and III 7 show clearly that the most probable value of λ for the cathodic hydrogen evolution on silver (in 0.1 - 1 N HCl) and tungsten (in 0.1 N HCl) is two. This (cf. table I 1) shows that the rate-determining step is either a catalytic or an electrochemical process. The catalytic mechanism is associated with a slope of 0.029 V. at low cathodic polarisation[1][12] and a limiting current (giving a slope of ∞ for the Tafel line) exists for this mechanism at high cathodic polarisation[4][52] when the surface is completely covered with adsorbed hydrogen. The electrochemical mechanism as given by,

$$MH + H_3O^+ + e^- \longrightarrow M + H_2O + H_2, \qquad \text{(IV 14)}$$

gives a slope of 0.04 V. at low cathodic polarisation, and a slope of 0.116 V. at high cathodic polarisation.[4]

From tables III 3 and III 4 it is seen that the observed slopes, at low cathodic polarisation, do not agree well with the above prediction. Thus, the average value of b_1 for silver (cf. table III 3) is about 0.058 and comparing this with the theoretical slope for mechanism (IV 14) at low cathodic polarisation, it is seen that,[53]

$$0.058 = 2.303 \frac{R\,T}{(1+\beta)F},$$

hence, $\beta \simeq 0$ and this is an unlikely result.

However, the slopes of 0.058 (for silver) and 0.063 (for tungsten) correspond most nearly to an electrochemical mechanism and therefore, together with the evidence just given, indicate a complex electrochemical mechanism.

d. Complex Electrochemical Desorption

There are two possibilities to account for the slope (b_1) of 0.057 V. to 0.063 V. obtained for silver and tungsten in concentrations less than 1.0 N HCl solutions.

(i) Possibility I.

Assuming that the initial state for the electrochemical desorption is composed of hydroxonium ions specifically adsorbed on the electrode surface, hydrogen atoms and electrons on the electrode surface, the rate of this process is given by,

$$v_4 = k_4 (a_H)(a_{H^+})_{ads.} e^{-\beta_1 \Delta\phi F/RT}, \qquad (\text{IV } 15)$$

where $(a_{H^+})_{ads.}$ is the concentration of specifically adsorbed hydroxonium ions. As has been shown before (cf. Section I) the activity of atomic hydrogen is,

$$(a_H) = \chi 10^{-9} \qquad (\text{IV } 16)$$

where χ is the fraction of the available surface covered with atomic hydrogen. The activity of specifically adsorbed hydroxonium ions is related to the activity of hydroxonium ions in the double layer and the potential by an equation similar to that given by Butler[24] for the specific adsorption of iodide ions. Therefore,

$$(a_{H^+})_{ads.} = (a_{H^+})_{d.l.}\, e^{-\beta_2 \Delta\phi F/RT}, \qquad (\text{IV } 17)$$

where β_2 is the part of potential which helps specific adsorption of H_3O^+ ions.

From (IV 15), (IV 16) and (IV 17) one gets,

$$V_4 = k_4 (x10^{-9})(a_{H^+})_{d.l.}\, e^{-(\beta_1+\beta_2)\Delta\phi F/RT} \qquad (\text{IV } 18)$$

The net cathodic current, when the electrochemical mechanism (whose rate is given by IV 15) is rate-determining, is

$$i_c = 2FV_4 = 2Fk_4 (x10^{-9})(a_{H^+})_{d.l.}\, e^{-(\beta_1+\beta_2)\Delta\phi F/RT} \qquad (\text{IV } 19)$$

When x is one, the slope of the Tafel line, from (IV 19), is given by,

$$\frac{d\Delta\phi}{d\log i_c} = -\frac{2.303\,RT}{(\beta_1+\beta_2)F} \qquad (\text{IV } 20)$$

Since metals of intermediate overpotential, e.g., silver and tungsten adsorb hydrogen well (cf. Bockris and Conway;[22] Drake and Benton[46]), it is possible to assume that the fraction of the available surface covered, i.e., x at intermediate current densities in unity. Equation (IV 20), therefore, represents the slope of the Tafel line at intermediate current densities. Comparing the slope of the Tafel line as given by (IV 20) with the experimental values of b_1 (cf. tables III 3 and III 4) it is concluded that, at intermediate current densities,

$$\beta_1 \simeq \beta_2 \simeq 0.5, \qquad (\text{IV } 21)$$

and the energy barriers associated with the specific adsorption of H_3O^+ ions as well as those associated with the electrochemical mechanism (as described above) are symmetrical.

At high cathodic polarisation, the concentration of specifically adsorbed H_3O^+ ions reaches a maximum, after which it is no longer dependent on the potential. In this range of potential equation (IV 17), is no longer applicable. From (IV 15), (IV 16) and taking $(a_{H^+})_{ads.}$ as constant, it results, at high current density that,

$$i_c = 2F k_5 (\varkappa 10^{-9}) e^{-\Delta\phi F \beta_1 / RT} . \qquad (IV\,22)$$

From (IV 22) for silver and tungsten (where $\varkappa$ is one as shown above), the slope of the Tafel line at high cathodic polarisation is,

$$\frac{d\Delta\phi}{d \log i_c} = - \frac{2.303 RT}{\beta_1 F} \qquad (IV\,23)$$

Equation (IV 23) gives the slope (b_2) of approximately 0.12 V. (cf. tables III 3 and III 4) when β_1 is 0.5.

(ii) <u>Possibility II.</u>

Consider a dual electrochemical-catalytic mechanism with the two steps taking place simultaneously. The rate of the simple electrochemical desorption (assuming symmetrical energy barriers) is given by (cf. Section I),

$$V_4 = k_4 (\varkappa 10^{-9})(a_{H^+})_{d.l.} \exp.\left(-\frac{\Delta\phi F}{2RT}\right) = a_4 \varkappa . \qquad (IV\,24)$$

The rate of the catalytic desorption is,

$$V_3 = k_3 x^2 10^{-18} = a_3 x^2. \qquad (\text{IV } 25)$$

For a dual electrochemical-catalytic mechanism the two rates V_4 and V_3 are equal. Thus,

$$a_4 x = a_3 x^2.$$

$$\therefore \quad x = \frac{a_4}{a_3}. \qquad (\text{IV } 26)$$

Since the total rate of desorption is equal to the sum of the electrochemical and catalytic rates, the net cathodic current is given by,

$$i_c = 4F V_4, \qquad (\text{IV } 27)$$

or by,

$$i_c = 4F V_3. \qquad (\text{IV } 28)$$

From (IV 27), (IV 26), (IV 25) and (IV 24),

$$i_c = \frac{4F(k_4)^2(a_{H^+})^2_{d.l.} e^{-\Delta\phi F/RT}}{k_3}. \qquad (\text{IV } 29)$$

Equation (IV 29) is also obtained from (IV 28), (IV 26), (IV 25), and (IV 24). From (IV 29), the slope of the Tafel line for a dual electrochemical catalytic mechanism is,

$$\frac{d\Delta\phi}{d \log i_c} = -\frac{2.303 RT}{F}. \qquad (\text{IV } 30)$$

The slope of the Tafel line as given by (IV 30) corresponds to that obtained for silver and tungsten at intermediate

current densities (cf. Section III).

With increase of cathodic polarisation,

$$V_3 \neq V_4$$

and when $V_3 \gg V_4$, the rate-determining process is the electrochemical desorption. When $V_4 \gg V_3$, the rate-determining step is the catalytic desorption. It is unlikely that, for silver and tungsten, $V_4 \gg V_3$ since this results in a slope of 0.029 V. or a limiting current at high cathodic polarisation. It is, therefore, possible that at high cathodic polarisation, the dual electrochemical-catalytic mechanism is replaced by a simple electrochemical desorption, and the resulting slope b_2 (cf. Section I) is given by,

$$b_2 = - \frac{2.303\ (2\ RT)}{F} \qquad \text{(IV 31)}$$

Values of b calculated from (IV 31) agree with those experimentally obtained for silver and tungsten (cf. Section III).

(iii) Conclusion.

The possibility of a dual electrochemical catalytic mechanism, accounting for the slope of 0.057 V. to 0.063 V., is not great since it is unlikely that the two rates V_3 and V_4 are equal over the range of potential where $b_1 = 0.057$ V. or

0.063 V. This is so, because the expressions for V_3 and V_4 contain an expression for $\mathcal{X}$ and since $\mathcal{X}$ is dependent on potential, V_3 and V_4 will only be equal over a very short range of potential. Even when $\mathcal{X}$ is one [as has been suggested in part (i) above] the same argument will apply since in this case V_4 is still dependent on potential while V_3 is not.

It is, therefore, concluded that the slopes at intermediate current densities are best accounted for by assuming specific adsorption of H_3O^+ ions. Even if the assumption of the existence of specifically adsorbed H_3O^+ ions has not yet been experimentally verified, there is good indirect evidence that it takes place (cf. the theory of pH effects at high concentration by Bockris and Conway.[22])

Anomalous results have been obtained for silver in 1.0 N HCl where b_1 was found to be 0.04 V. (cf. table III 1). Potter[45] also obtained one slope (0.105 V.) for silver in 0.075 N HCl. Both cases are unreliable since only one measurement was carried out in each case.

3. THE HEAT OF ACTIVATION. (54, 55, 56, 57, 58, 5)

a. Method using ic and io.

From equations I 33 and I 36 (Section I) the net cathodic current is given by,

$$i_c = \lambda F K \frac{kT}{h} \pi a_1 \, e^{-\Delta G_o^*/RT} \, e^{-\frac{\lambda \beta \Delta \phi F}{RT}} .$$

Since,

$$\Delta G_o^* = \Delta H_o^* - T \Delta S_o^* ,$$

where ΔH_o^* is the heat of activation at the absolute zero of potential, i.e., when $\Delta \phi = 0$ Taking πa_1 as a constant,

$$i_c = C_1 \, e^{\frac{(\Delta H_o^* + \alpha \Delta \phi F)}{RT}} = C_1 \, e^{-W/RT}, \qquad (IV\,32)$$

Where C_1 is a constant including ΔS_o^* and W is the heat of activation at constant $\Delta \phi$, i.e., the ideal heat of activation.(56) This cannot be determined because of the lack of information as to the magnitude of $\Delta \phi$ and its variation with temperature.

However,

$$\eta = \Delta \phi_c - \Delta \phi_r = \Delta \phi + \xi - \Delta \phi_r ,$$

and substituting this expression in (IV 32) one gets,

$$i_c = C_1 e^{-[\Delta H_0^* + \alpha F(\eta + \Delta\phi_r - \xi)]/RT}$$

$$\therefore \ln i_c = \ln C_1 - \frac{\Delta H_0^*}{RT} - \frac{\alpha\eta F}{RT} - \frac{\alpha\Delta\phi_r F}{RT} + \frac{\alpha\xi F}{RT} \quad (\text{IV } 33)$$

$\therefore (\partial \ln i_c/\partial T)_{\eta,m}$ where m indicates the composition of the electrolyte, is given by,

$$\left(\partial \ln i_c/\partial T\right)_{\eta,m} = \frac{\Delta H_0^*}{RT^2} - \frac{\eta F}{RT^2}\left(T\frac{\partial\alpha}{\partial T} - \alpha\right)$$

$$- \frac{\alpha F}{RT^2}\left(T\frac{\partial\Delta\phi_r}{\partial T} - \Delta\phi_r\right) - \frac{F\Delta\phi_r}{RT}\left(\frac{\partial\alpha}{\partial T}\right)$$

$$+ \frac{\alpha F}{RT^2}\left(T\frac{\partial\xi}{\partial T} - \xi\right) + \frac{F\xi}{RT}\left(\frac{\partial\alpha}{\partial T}\right)$$

$$= [\Delta H_0^* - \eta F\{T(\partial\alpha/\partial T) - \alpha\} - \alpha F\{T(\partial\Delta\phi_r/\partial T) - \Delta\phi_r\}$$

$$- FT\Delta\phi_r(\partial\alpha/\partial T) + \alpha F\{T(\partial\xi/\partial T) - \xi\}$$

$$+ F\xi T(\partial\alpha/\partial T)]/RT^2. \quad (\text{IV } 34)$$

When α and ξ are temperature independent,

$$\left(\frac{\partial \ln i_c}{\partial T}\right)_{\eta,\alpha,\xi,m} =$$

$$[\Delta H_0^* + \alpha F(\eta - \xi) - \alpha F\left(T\frac{\partial\Delta\phi_r}{\partial T} - \Delta\phi_r\right)]/RT^2 \quad (\text{IV } 35)$$

By comparison with Arrhenius equation,[59] for the change of the rate constant with temperature, the nominators on the right hand side of (IV 34) and (IV 35) represent the heat of

activation for the cathodic hydrogen evolution at an over-potential η.

From Thermodynamics, the electrochemical free energy (electrochemical potential) of the overall reaction of cathodic hydrogen deposition at the reversible potential is given by,

$$\left.\begin{aligned} \Delta\bar{G} &= \Delta G + F\Delta\phi_r = 0 \\ \therefore \Delta G &= \Delta H - T\Delta S = -F\Delta\phi_r \\ \therefore \left(\frac{\partial \Delta G}{\partial T}\right) &= -\Delta S = -F\left(\frac{\partial \Delta\phi_r}{\partial T}\right), \end{aligned}\right\} \quad (\text{IV } 36)$$

taking ΔH (for the overall reaction as temperature independent. From (IV 35) and (IV 36) one gets,

$$\left(\frac{\partial \ln i_c}{\partial T}\right)_{\eta,\alpha,\xi,m} = [\Delta H_o^* - \alpha\Delta H + \alpha F(\eta - \xi)]/RT^2. \quad (\text{IV } 37)$$

When excess neutral salts are added to the solution ξ becomes zero,[60] thus,

$$\left(\frac{\partial \ln i_c}{\partial T}\right)_{\eta,\alpha,m,\xi=0} = [\Delta H_o^* - \alpha\Delta H + \alpha\eta F]/RT^2 \quad (\text{IV } 38)$$

When $\eta = 0$, $i_c = i_o$

$$\therefore \left(\frac{\partial \ln i_o}{\partial T}\right)_{\alpha,m,\xi=0} = [\Delta H_o^* - \alpha\Delta H]/RT^2, \quad (\text{IV } 39)$$

Where $[\Delta H_o^* - \alpha\Delta H]$ is the heat of activation at the reversible potential $\Delta\phi_r$ when the solution is saturated with neutral salts, and is usually given the

symbol Ao. Thus the heat of activation, A, at an over-potential η (when $\xi = o$) is related to Ao (cf. equation IV 38) by,

$$A = A_o + \alpha F \eta . \qquad (IV\ 40)$$

Since,

$$\frac{d(1/T)}{dT} = - \frac{1}{T^2}$$

$$\therefore \left[\frac{\partial \ln i_o}{\partial (1/T)}\right]_{\alpha, m, \xi=o} = - \frac{A_o}{R} . \qquad (IV\ 41)$$

Also,

$$\left[\frac{\partial \ln i_c}{\partial (1/T)}\right]_{\eta, \alpha, m, \xi=o} = - \frac{A}{R} . \qquad (IV\ 42)$$

The term Ao is identical with the heat of activation developed by Bockris and Potter.(4)

The above derivation is based on the assumption that C_1 is independent of temperature (cf. IV 32). However, since C_1 is given by the expression,

$$C_1 = \lambda F K \frac{kT}{h} \pi a_1 \, e^{\Delta S_o^*/R} = C_2 T , \qquad (IV\ 43)$$

it varies with temperature in the following way,

$$\frac{\partial \ln C_1}{\partial T} = \frac{1}{T} .$$

Therefore (cf. IV 43, IV 33 and IV 34),

$$\left(\frac{\partial \ln i_c}{\partial T}\right)_{\eta,\alpha,m,\xi=0} = \frac{RT + \Delta H_o^* - \alpha\Delta H + \alpha\eta F}{RT^2} = \frac{RT + A}{RT^2}$$

$$\left(\frac{\partial \ln i_o}{\partial T}\right)_{\alpha,m,\xi=0} = \frac{RT + A_o}{RT^2} \qquad \text{(IV 44)}$$

The term RT in (IV 44) is exceedingly small in comparison with the experimentally observed values of A and Ao and could, therefore, be neglected.

b. Method using $\partial\eta/\partial T$

From the Tafel equation,

$$\eta = \frac{RT}{\alpha F}\ln i_o - \frac{RT}{\alpha F}\ln i_c ,$$

at constant ic and composition (m),

$$\left(\frac{\partial \eta}{\partial T}\right)_{i_c,m} = \frac{R}{\alpha^2 F}(\ln i_o)\left(\alpha - T\frac{\partial \alpha}{\partial T}\right) + \frac{RT}{\alpha F}\left(\frac{\partial \ln i_o}{\partial T}\right) - \frac{R}{\alpha^2 F}(\ln i_c)\left(\alpha - T\frac{\partial \alpha}{\partial T}\right). \qquad \text{(IV 45)}$$

Substituting in (IV 45) the value of $(\partial \ln i_o/\partial T)_{m,\xi=0}$ as obtained from (IV 34) one gets,

$$\left(\frac{\partial \eta}{\partial T}\right)_{i_c,m,\xi=0} = \frac{RT\ln(i_o/i_c) - (RT^2/\alpha)(\partial\alpha/\partial T)\ln(i_o/i_c)}{\alpha F T} + \frac{A_o - FT\Delta\phi_r(\partial\alpha/\partial T)}{\alpha F T}.$$

If we put $(\partial\alpha/\partial T) = 0$ then,

$$\left(\frac{\partial \eta}{\partial T}\right)_{i_c, m, \alpha, \xi=0} = \frac{R T \ln (i_0/i_c) + A_0}{\alpha F T} .$$

But from the Tafel equation,

$$RT \ln (i_0/i_c) = \alpha \eta F$$

$$\therefore \left(\frac{\partial \eta}{\partial T}\right)_{i_c, m, \alpha, \xi=0} = \frac{\alpha \eta F + A_0}{\alpha F T}$$

$$= \frac{A}{\alpha F T} . \qquad (IV\ 46)$$

It is to be noted that in the deduction of (IV 34) the term C_1 is considered as temperature independent, therefore, the same approximation applies to (IV 46).

4. THE EFFECT OF ELECTROPOLISHING.

Previous authors [43][44] noticed that electropolishing either increases the hydrogen overpotential or does not change it. The increase of η (to more negative values) with electropolishing is attributed to the decrease of the true surface area. Thus, the true and apparent areas become nearly identical after electropolishing.

However, in the present work, electropolishing was found to decrease the overpotential at high current densities in the case of aluminium and tin, while it has practically no effect in the case of iron cathodes. It is to be noted that the electropolishing solutions for aluminium and tin contain organic alcohols.

According to Hoar and Mowat, [61] electropolishing in acid media results in the formation of an oxide layer on the surface of the anode and the dissolution of the metal takes place in a random manner through the lattice defects of this oxide. By studying the potential time behaviour of the anodically polarized nickel electrodes, they concluded that during the period when oxygen is evolved, the oxide is formed. This is followed by another period during which the evolution of oxygen ceases and the oxide is dissolved.

It is possible to assume that, if the metal is anodised in solutions containing organic alcohols, products of oxidation of these alcohols (probably containing aldehydic or carboxylic

groups) are formed. The dissolution of the metal, will therefore result in the formation of salts with the products of organic oxidation. These salts will probably form a thin film (together with an oxide film) on the surface of the anodically polarised metal and the random dissolution of the metal will take place through this film. If the anodic polarisation is carried out over a long period of time, a deposit (similar to that suggested by Müller for passivity)[62] composed of salts and oxides is detached from the surface into the electropolishing solution leaving a thin film of the same structure on the surface. This film is not affected by washing the electrode with water and when cathodic polarisation is started, the organic alcohols are regenerated through the reduction of these salts by hydrogen. These alcohols are produced near to the electrode surface and consequently form the main constituent of the layer near the electrode. It can reasonably be expected, therefore, that near to this electrode, the constitution of the solution is largely alcoholic. However, it is known[63] that in an alcoholic solution of high alcohol content, the overpotential is much lower than in aqueous solutions. Consequently, a reduction in overpotential will be observed.

The horizontal part in the Tafel line is due to the dissolution of the metal. This view is supported by the fact that such behaviour is not observed for tin in the range of potential covered.

PART β

THE DIELECTRIC CONSTANT

IN THE DIFFUSE DOUBLE LAYER

1. INTRODUCTION

When a charged metal is placed in an electrolytic solution, a double layer is formed in the vicinity of the metal. This double layer according to Stern's theory,[64] is formed of a compact layer of ions usually called the Helmholtz double layer, and a diffuse layer extending to the bulk of the solution.[65] [66] Many authors using Stern's model considered the dielectric constant in the diffuse double layer as equal to that of the bulk. This is clearly incorrect owing to the approach to saturation of the dielectric under the high field strength of the electrode. According to Webb[67] the dielectric constant would be expected to decrease towards the metal, reaching a limiting value in the Helmholtz double layer.

Grahame[68] used Webb's value of three for the dielectric constant in the Helmholtz double layer, and derived several relationships between the field strength, the surface charge density, the dielectric constant and the potential of the diffuse double layer.

2. WORK OF GRAHAME.

a. General Equations

Poisson's equation in one dimension is,

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi\rho}{DD_o}\,, \qquad (1)$$

where ψ is the electrical potential at a point the charge density of which is given by ρ, D is the differential dielectric constant (the rate of change of the dielectric displacement with intensity) also termed the dielectric coefficient and Do is a constant equal to 1.1128×10^{-12} coulomb/volt cm. and is called diabittivity by Grahame. If D is taken as a constant the integration of (1) becomes,

$$\int_{\infty}^{x} d\frac{d\psi}{dx} = \int_{\infty}^{x} -\frac{4\pi\rho}{D D_o}\, dx$$

$$= \frac{4\pi\eta}{D D_o}, \qquad (2)$$

where the limits of integration ∞ and x refer to the bulk of the solution and a distance x from the metal surface respectively. The term η is the surface charge density per cm^2, at the plane to which x refers, and is given by,

$$\eta = \int_{x}^{\infty} \rho\, dx \qquad (3)$$

If D is a function of the field strength, Poisson's equation is therefore written as,

$$D\frac{d}{dx}\left(\frac{d\psi}{dx}\right) = D\frac{dS}{dx} = -\frac{4\pi\rho}{D_o}, \qquad (4)$$

where the negative field strength S is given by

$$S = \frac{d\psi}{dx}.$$

Therefore,

$$\int_{S=o}^{S^o} D\, dS = -\int_{x=\infty}^{x} \frac{4\pi\rho}{D_o}\, dx = \frac{4\pi}{D_o}\,\eta^d \qquad (5)$$

If x is taken to refer to the outer plane of the Helmholtz double layer, η^d therefore is the surface charge density at this plane, i.e., the charge of a column of solution of a cross-sectional area of 1 cm.^{2} extending from the bulk of the solution to the outer plane of the Helmholtz double layer.

From experiments on the double layer, Grahame found that the surface charge density of the diffuse layer (η^d) is independent of concentration and has a value of 26 μ coulombs/cm.^{2}. The corresponding value of field strength S^o, at the outer plane of the Helmholyz layer will, therefore, be independent of concentration.

The charge density ρ is given by,

$$\rho = \sum n_{oi} z_i e_o e^{-z_i e_o \psi / kT}, \qquad (6)$$

where n_{oi} is the number of ions i per c.c. in the bulk of the solution, zi is the valence of the corresponding ion and e_o is the electronic charge. Introducing (6) in (1) and using the identity,

$$\frac{1}{2} \frac{d}{d\psi} \left(\frac{d\psi}{dx}\right)^2 = \frac{d^2\psi}{dx^2}, \qquad (7)$$

one gets,

$$\int_{S=o}^{S^o} D\, dS^2 = -\frac{8\pi}{D_o} \int_o^{\psi^o} \sum n_{oi} z_i e_o e^{-z_i e_o \psi / kT} \cdot d\psi$$

$$= \frac{8\pi kT}{D_o} \sum n_{oi} \left(e^{-z_i e_o \psi^o / kT} - 1\right), \qquad (8)$$

where ψ^o is the potential at the outer plane of the Helmholtz double layer. Since for electrolytes with symmetrical valence,

$$\rho = -2 n_o e_o z \sinh \frac{z e_o \psi}{kT}, \qquad (9)$$

where $|z|$ is the valence without any sign, equation (8) therefore becomes,

$$\int_{S=o}^{S^o} D \, dS^2 = \frac{8\pi kT n_o}{D_o}\left(e^{\frac{z e_o \psi^o}{kT}} + e^{\frac{-z e_o \psi^o}{kT}} - 2\right)$$

$$= \frac{32\pi kT n_o}{D_o} \sinh^2\left(\frac{z e_o \psi^o}{2kT}\right). \qquad (10)$$

b. Relation between S and D.

According to Malsch,[69] the dielectric constant is related to S by the empirical equation,

$$D = \frac{A}{\left(1 + (b/m) S^2\right)^m} + C, \qquad (11)$$

where C is the limiting value of D at high field strength and is taken by Grahame[70] (following Debye and Webb[67]) as 3, b is a constant given by Malsch as 1.2×10^{-13} cm^2/volt^2, and m is a parameter related to the decrease of dielectric constant with field strength. The parameter A is given by,

$$A = \varepsilon - C, \qquad (12)$$

where $\mathcal{E}$ is the dielectric constant at zero field strength. The rapidity with which the dielectric constant decreases to the saturation value, increases with increase of m. When m is zero, the dielectric constant in the double layer has a value the same as that in the bulk of the solution.

Grahame takes m = 0.5, although without apparent justification. Therefore,

$$D = \frac{A}{(1+2bS^2)^{1/2}} + C \,. \tag{13}$$

Substituting (13) in (8), one gets,

$$\int_{S=0}^{S^0} \left(\frac{A}{(1+2bS^2)^{1/2}} + C \right) dS^2 = \frac{8\pi kT}{D_0} \sum n_{0i} \left(e^{\frac{-z_i e_0 \psi^0}{kT}} - 1 \right)$$

Therefore,

$$\frac{A}{b}(1+2bS^{0^2})^{1/2} - \frac{A}{b} + CS^{0^2} = \frac{8\pi kT}{D_0} \sum n_{0i} \left(e^{-z_i e_0 \psi^0 / kT} - 1 \right) . \tag{14}$$

And for electrolytes with symmetrical valence from (13) and (10),

$$\frac{A}{b}(1+2bS^{0^2})^{1/2} - \frac{A}{b} + CS^{0^2} = \frac{32\pi kT n_0}{D_0} \sinh^2\left(\frac{z e_0 \psi^0}{2kT}\right) . \tag{15}$$

Substituting (13) in (5) one gets,

$$\int_{S=0}^{S^0} \left[\frac{A}{(1+2bS^2)^{1/2}} + C \right] dS = \frac{4\pi \eta^d}{D_0} \tag{16}$$

The integration of (16) is carried out as follows:

$$\int_{S=0}^{S^o}\left(\frac{A}{\sqrt{(1+2bS^2)}}+C\right)dS=\int_{S=0}^{S^o}\left[\frac{A}{\sqrt{2b}\sqrt{(1/2b)+S^2}}+C\right]dS$$

$$=\left(\frac{A}{\sqrt{2b}}\sinh^{-1}(S\sqrt{2b})+CS\right)_{S=0}^{S^o} \qquad (17)$$

Putting,

$$y=\sinh^{-1}(S\sqrt{2b})$$

Therefore,

$$(S\sqrt{2b})=\sinh y=\frac{1}{2}\left(e^{y}-e^{-y}\right)$$

and,

$$e^{y}-e^{-y}-2S\sqrt{2b}=0 \qquad (18)$$

Multiplying both sides of (18) by e^{y},

$$e^{2y}-2(S\sqrt{2b})\,e^{y}-1=0 \qquad (19)$$

From (19),

$$e^{y}=S\sqrt{2b}+\sqrt{2bS^2+1}\,.$$

$$\therefore\ y=\sinh^{-1}(S\sqrt{2b})=\ln\left(S\sqrt{2b}+\sqrt{2bS^2+1}\right). \qquad (20)$$

From (20) and (17)

$$\int_{S=0}^{S^o}\left(\frac{A}{\sqrt{(1+2bS^2)}}+C\right)dS=\frac{4\pi\eta d}{D_o}$$

$$=\frac{A}{\sqrt{2b}}\ln\left(S^o\sqrt{2b}+\sqrt{2bS^{o2}+1}\right)+CS^o. \qquad (21)$$

From (21) Grahame computed S^o for any value of η^d. Also from (21) and (15) or (14) he calculated ψ^o for different values of η^d. Similarly from (21) and (11) the dielectric constant at the outer plane of the Helmholtz double layer was calculated as a function of η^d. Table I gives the result of such calculations for $\eta^d = 26\ \mu$ coulomb/cm^2 in 0.1 N solution of 1:1 electrolyte.

TABLE I

m	o	$\frac{1}{2}$	1	2	∞
S^o	3.74	5.94	8.23	17.58	33.5
D	78.49	27.53	11.27	3.2	3.0
ψ^o	135.9	142.3	145.4	153.0	168.8

S^o in megavolts/cm.

ψ^o in millivolts.

From Table I it is clear that the dielectric constant at the outer plane of the Helmholtz double layer is less than the bulk value for values of m greater than zero.

2. THEORY OF DIELECTRIC CONSTANT NEAR A CHARGED SURFACE.*

a. Introduction

In Grahame's work the empirical equation (11) is used to relate the dielectric constant and field strength. The use of such an equation (that of Malsch) depends on the choice of the proper value of m. Grahame used m = 0.5, although he indicated that the most probable value lies between 0 and 2. He also confirmed that the dielectric constant at the outer plane of the Helmholtz double layer is less than that of the bulk. However, he pointed out that the properties of the double layer (such as the variation of the potential with distance) calculated on the assumption of a value of D in the Helmholtz double layer equal to that of the bulk, do not vary from those calculated on the assumption of a value of D in the Helmholtz double layer approaching the saturation value.

Grahame, however, did not consider the change of the dielectric constant with distance in the diffuse double layer.

It was, therefore, necessary that the dependence of the dielectric constant on distance should be investigated from a priori considerations, i.e., by methods not based upon an empirical equation.

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* This was deduced in collaboration with Conway and Bockris.

b. General Equations.

The dielectric constant near an ion is a function of the distance from the ion. The mean (cf. Table II) of the data of Webb,[67] Debye and Sohwartzenbach[72] and Schwartzenbach[73] is used for the present calculation.

TABLE II

Mean Values of D corresponding to a Distance x from a univalent Ion assumed to be a Point Charge

x (Å)	D	x (Å)	D
1	4.7	11	60.8
2	7.8	12	64.3
3	13.0	13	67.7
4	19.0	14	70.3
5	24.8	15	73.0
6	31.2	16	75.0
7	38.4	17	76.6
8	45.8	18	77.2
9	51.6	19	77.8
10	56.4	20	78.0

(74)

Collie, Hasted and Ritson have shown that the macroscopic dielectric constant depends on the ionic strength. No such dependence is taken into consideration in the present work since no data for the dependence of the microscopic dielectric constant on ionic strength is yet available. For the dielectric constant near an ion,

$$\psi' = \frac{d\psi}{dx} = -\frac{e_o}{D x^2}, \qquad (22)$$

where x is the distance and e_o is the electronic charge. It should be noted that although equation (22) was originally derived for ions, it is valid for plane surfaces. From (22),

$$D = f_1(\psi'). \qquad (23)$$

For a dielectric medium, the dielectric displacement is related to the field strength S and the dielectric constant D by,

$$\mathcal{D} = DS. \qquad (24)$$

But, for one-dimensional change,

$$S = -\frac{d\psi}{dx} = -\psi'. \qquad (25)$$

Also, from Maxwell's theorem,

$$\operatorname{div} \mathcal{D} = \frac{d}{dx}\mathcal{D} = 4\pi\rho \qquad (26)$$

Therefore, from (23), (24), (25) and (26),

$$\frac{d}{dx}\left[f_1(\psi')\cdot\psi'\right] = -4\pi\rho. \qquad (27)$$

Taking the value of ρ for a 1:1 electrolyte as given by (9) and substituting it in (27), one gets,

$$\frac{d}{dx}\left[f_1(\psi')\cdot\psi'\right] = 8\pi n_0 e_0 z \sinh\frac{z e_0 \psi}{kT}$$
$$= k' \sinh k''\psi. \qquad (28)$$

$$\therefore \left(\frac{df_1(\psi')}{d\psi'} \times \frac{d\psi'}{dx}\right)\psi' + f_1(\psi')\frac{d\psi'}{dx}$$
$$= f_1'(\psi')\frac{d\psi'}{dx}\cdot\psi' + f_1(\psi')\frac{d\psi'}{dx}$$
$$= k' \sinh k''\psi \quad , \qquad (29)$$

where $f_1'(\psi')$ is the differential of $f_1(\psi')$ with respect to ψ'. Since $\psi' dx = d\psi$ (cf. equation 22), therefore multiplying both sides of (29) by $d\psi$ one gets,

$$\left(f_1'(\psi')\cdot(\psi')^2\right)d\psi' + \left(f_1(\psi')\cdot\psi'\right)d\psi'$$
$$= \left(k' \sinh k''\psi\right)d\psi. \qquad (30)$$

On integrating (30) between $\psi = 0$ $(\psi' = 0)$ and ψ one gets

$$\left((\psi')^2 f_1(\psi') - \int f_1(\psi')\cdot(\psi')\cdot d\psi'\right)_0^{\psi'} = \frac{k'}{k''}\cosh k''\psi - \frac{k'}{k''}. \qquad (31)$$

Putting the left hand side of equation (31) as $F_1(\psi')$ one gets,

$$F_1(\psi') + \frac{k'}{k''} = \frac{k'}{k''} \cosh k''\psi . \qquad (32)$$

From (32),

$$\psi = \frac{1}{k''} \cosh^{-1} \left(\frac{k''}{k'} F_1(\psi') + 1 \right) . \qquad (33)$$

Also from (32),

$$\psi' = f_2 \left(\frac{k'}{k''} \cosh k''\psi - \frac{k'}{k''} \right) . \qquad (34)$$

Since, $\psi' dx = d\psi$, therefore

$$x = \int dx = \int \frac{d\psi}{\psi'}$$

$$= \int \frac{d\psi}{f_2\left(\frac{k'}{k''} \cosh k''\psi - \frac{k'}{k''} \right)} = F_2(\psi) + m , \qquad (35)$$

where m is the integration constant.

From (35),

$$\psi = f_3(x) . \qquad (36)$$

Since ψ is a function of ψ' (cf. equation 33),

$$\psi' = f_4(x) . \qquad (37)$$

From (23) and (37),

$$D = f_5(x) . \qquad (38)$$

The solution of the previous equations is done graphically.

c. Graphical Method of Solution.

From Table II and equation (22) values of D are calculated for the corresponding values of ψ' These values are tabulated in Table III.

To integrate equation (31), values of ψ' in Table III are multiplied by the corresponding values of D. The product is then plotted against ψ' and the resulting curve is graphically integrated between $\psi' = 0$ and any other value of ψ'. This gives the term $\int \psi' \cdot f_1(\psi') \cdot d\psi'$. The other term namely, $\left((\psi')^2 \cdot f_1(\psi')\right)$ is obtained by squaring (ψ') and multiplying that by the corresponding value of D. The integral thus obtained is equal to $F_1(\psi')$ in equation (32). Values of k' and k'' for a 1:1 electrolyte are calculated with the aid of (28)

To obtain $F_2(\psi)$ as given by (35) values of (ψ) are calculated from the corresponding values of (ψ') using equation (33). Values of ψ are then plotted against the reciprocal of ψ' (ψ' is given by equation 34) and the resulting curve is integrated between $\psi = 0$ i.e., the bulk of the solution where $x = \infty$ and $\psi = \psi^0$ referring to the outer plane of the Helmholyz double layer where x is taken as zero, thus eliminating the integration constant m. The integration of (35) leads to values of x corresponding to values of ψ and ψ'. The result of such integration is shown in tables IV, V and VI for 0.1, 0.01

and 0.001 gram ion (of a 1:1 electrolyte) per litre respectively. In tables IV, V and VI the dielectric constant corresponding to ψ' values is also included, and the relation between D and χ is therefore clear.

TABLE III

Evaluation of $F_1(\psi')$

$\psi' \cdot 10^{-2}$ e.s.u. cm^{-1}	$D = f_1(\psi')$	$f_1(\psi') \cdot \psi' \cdot 10^{-2}$	$\int \psi' \cdot f_1(\psi') \cdot d\psi' \times 10^{-4}$	$(\psi')^2 \cdot f_1(\psi') \times 10^{-4}$
0	78.0	0.0	0	0
1	78.0	78.0	-	-
2	77.5	155.0	156.0	309
3	72.0	216.0	-	-
4	68.0	272.0	586.0	1086
5	64.6	323.0	-	-
6	62.0	372.0	1231.0	2230
7	59.2	414.4	-	-
8	57.0	456.0	2059.9	3649
9	55.5	499.5	-	-
10	54.0	540.0	3058.0	5400
11	52.0	572.0	-	-
12	50.7	608.4	4203.5	7280
13	49.3	642.0	-	-
14	48.2	675.0	5487.0	9450
15	47.0	706.0	-	-
16	46.0	737.0	6899.0	11770
17	45.0	766.0	-	-
18	44.0	792.0	8430.0	14280
19	43.2	820.0	-	-

TABLE III

(cont.)

$\psi' \cdot 10^{-2}$ e.s.u.cm^{-1}	$D = f_1(\psi')$	$f_1(\psi') \cdot \psi' \cdot 10^{-2}$	$\int \psi' \cdot f_1(\psi') \cdot d\psi' \times 10^{-5}$	$(\psi')^2 \cdot f_1(\psi') \times 10^{-5}$
20	42.3	846	981	1696
30	36.0	1080	-	-
40	32.0	1280	2149	5120
50	29.5	1475	-	-
60	27.6	1656	5094	9920
70	26.2	1834	-	-
80	24.8	1984	8753	15940
90	23.7	2133	-	-
100	22.7	2270	13015	22700
200	17.0	3400	-	-
300	14.0	4200	66900	126100
400	11.8	4720	-	-
500	9.7	4850	160000	242000
600	9.3	5580	-	-
700	8.9	6230	271330	436000
800	8.6	6880	-	-
900	8.35	7515	408880	676000
1000	8.15	8150	487210	815000

TABLE III

(cont.)

$\psi' \cdot 10^{-2}$ e.s.u cm^{-1}.	$D = f_1(\psi')$	$\psi' f_1(\psi') \cdot 10^{-2}$	$\int \psi' f_1(\psi') \cdot d\psi \times 10^{-7}$	$(\psi')^2 f_1(\psi') \times 10^{-7}$
2000	6.50	13000	-	-
3000	5.65	16950	25700	50900
4000	5.22	20880	-	-
5000	5.10	25500	67690	127800
6000	5.05	30300	-	-
7000	5.00	35000	128257	245100
8000	5.00	40000	-	-
9000	5.00	45000	208253	405100

TABLE IV

Values of ψ, ψ', x and D

conc. = 0.1 g. ion/l.

ψ (V.)	x (Å) $\psi^0 = 0.2$ V	x (Å) $\psi^0 = 0.1$ V	$\psi' \cdot 10^{-2}$ e.s.u.cm^{-1}	D
0.20	0.0	-	1000	8.15
0.19	0.0	-	1000	8.15
0.18	0.0	-	980	8.22
0.17	0.10	-	920	8.35
0.16	0.14	-	715	8.9
0.15	0.19	-	556	9.5
0.14	0.26	-	417	11.7
0.13	0.34	-	333	13.2
0.12	0.46	-	250	15.5
0.11	0.61	-	185.2	17.6
0.10	0.81	0.0	142.5	19.8
0.09	1.08	0.27	117.5	22.1
0.08	1.41	0.60	84.8	24.0
0.07	1.86	1.05	65.9	26.5
0.06	2.45	1.64	49.1	30.0
0.05	3.27	2.46	33.4	34.0
0.04	4.46	3.65	22.7	38.0
0.03	6.24	5.43	15.4	46.5
0.02	9.04	8.23	8.77	56.0
0.01	14.40	13.61	4.77	65.5

TABLE V

Values of ψ, ψ', x and D

conc. = 0.01 g. ion/l

ψ (V.)	$\int(d\psi/\psi') = x$ (Å)		$\psi' \cdot 10^{-2}$ e.s.u cm.$^{-1}$	D
	$\psi^0 = 0.2$ V	$\psi^0 = 0.1$ V		
0.20	0.0	-	714.0	8.85
0.19	0.065	-	401.0	11.8
0.18	0.17	-	264.0	15.3
0.17	0.32	-	185.2	17.5
0.16	0.52	-	143.0	19.7
0.15	0.79	-	111.1	22.0
0.14	1.13	-	87.0	24.0
0.13	1.56	-	68.1	26.3
0.12	2.10	-	53.8	29.0
0.11	2.81	-	41.0	32.1
0.10	3.73	0.0	31.3	35.5
0.09	4.93	1.20	24.4	38.5
0.08	6.46	2.73	19.6	42.2
0.07	8.42	4.69	14.5	47.5
0.06	11.10	7.37	10.4	53.0
0.05	14.8	11.10	7.94	57.0
0.04	19.7	16.0	5.69	63.0
0.03	26.8	23.1	3.85	68.8
0.02	37.5	33.8	2.62	74.0
0.01	52.6	48.9	1.87	77.3

TABLE VI

Values of ψ, ψ', x and D

conc. = 0.001 g. ion/l.

ψ (V.)	$\int(d\psi/\psi') = x$ (Å)		$\psi' \cdot 10^{-2}$ e.s.u. cm^{-1}	D
	$\psi^o = 0.2$ V	$\psi^o = 0.1$ V		
0.20	0.0	-	90.9	23.5
0.19	0.42	-	69.5	26.0
0.18	0.97	-	53.8	29.0
0.17	1.66	-	42.6	32.0
0.16	2.54	-	32.7	34.0
0.15	3.72	-	25.0	38.0
0.14	5.23	-	19.7	42.5
0.13	7.12	-	15.6	46.5
0.12	9.53	-	12.3	50.5
0.11	12.6	-	9.62	54.5
0.10	16.5	0.0	7.57	58.0
0.09	21.5	5.0	5.88	62.5
0.08	27.9	11.4	4.54	66.0
0.07	36.3	19.8	3.5	70.5
0.06	47.2	30.7	2.68	75.0
0.05	61.4	44.9	2.04	77.0
0.04	79.8	63.3	1.56	77.8

3. DISCUSSION

From experiments on the double layer, Grahame found that the surface charge density (η^d) of the diffuse double layer has a limiting value (independent of the concentration) of 26 μ coulombs $cm.^{-2}$ He concluded, therefore, that the negative field strength S^o at the outer plane of the Helmholtz double layer (cf. equation 5) reaches a limiting value independent of concentration. This value of S^o (when $m = 0.5$ which is the value arbitrarily chosen by Grahame) is 6×10^6 volt $cm.^{-1}$ (cf. table I) and the corresponding value of D is 27. If Grahame's argument is correct one would expect that the dielectric constant, at the outer plane of the Helmholtz layer, will have a value independent of the concentration. However, from the work described above, this is proved to be incorrect. Table VII gives the values of $(\psi')^o = S^o$ together with the corresponding values of D and the concentration (cf. tables IV, V and VI), it being assumed that the potential (ψ^o) is 0.1 V for the three concentrations quoted. It is evident from table VII that $(\psi')^o$ changes with concentration.

TABLE VII

Variation of $(\psi')^0$ with Concentrations

conc. g. ion/l.	$(\psi')^0 \cdot 10^{-2}$ e.s.u.cm.$^{-1}$	ψ^0(V)	D
0.1	142.5	0.1	19.8
0.01	31.3	0.1	35.5
0.001	7.57	0.1	58.0

The cause of the uncertainty about Grahame's values of S^o and the corresponding values of D is most probably due to the uncertainty in ascertaining any value for the parameter m, and to the assumption of a limiting value of η^d independent of the concentration. The choice of one value of m for all concentrations will certainly result in one value of S^o (and the corresponding D) for all concentrations at constant η^d. However, there is no evidence that m will have the same value for all concentrations and that its value is 0.5. It is possible, therefore, to conclude that the use of Malsch's equation (11) is inadequate for the purpose of computing S^o and related parameters.

As has been pointed out before, Grahame suggests that the use of dielectric constant values, approaching the saturation value, for the diffuse double layer has no effect on the properties of the diffuse layer calculated on the assumption of a bulk value for D in this layer. However, this is not always true as shown below.

According to Chapman (75) the surface charge density of the diffuse layer is,

$$\eta^d = \sqrt{\frac{DRTn}{2\pi}} \left(e^{\frac{\psi^o F}{2RT}} - e^{-\frac{\psi^o F}{2RT}} \right) , \qquad (39)$$

where D is the dielectric constant in the diffuse layer (previously taken as equal to that of the bulk) and n is the concentration. However, if values of D taken from table VII are substituted in (39) the resulting value of η^d will be different from those based on the classical theory for the same concentration and will also vary with the concentration, a result which contradicts Grahame's argument. This conclusion, i.e., the dependence of η^d on the concentration, is also arrived at in the following way.

It is clear from tables IV, V and VI that ψ is a function of x and that the relation between ψ and x vary with concentration. Therefore, if values of ψ for different values of x (for a certain concentration) are substituted in the expression for ρ for a 1:1 electrolyte (cf. equation 9) and the resulting values of ρ are plotted against x and the curve obtained is then integrated between

x = corresponding to the outer plane of the Helmholtz layer and x = co, the integral will correspond to the surface charge density (η^d) of the diffuse layer (cf. equation 3). Since the relation between ψ and x is dependent on the concentration, the resulting value of η^d will, therefore, depend on the concentration.

A P P E N D I X I.

PREPARATION OF ALKALINE SOLUTIONS

1. INTRODUCTION.

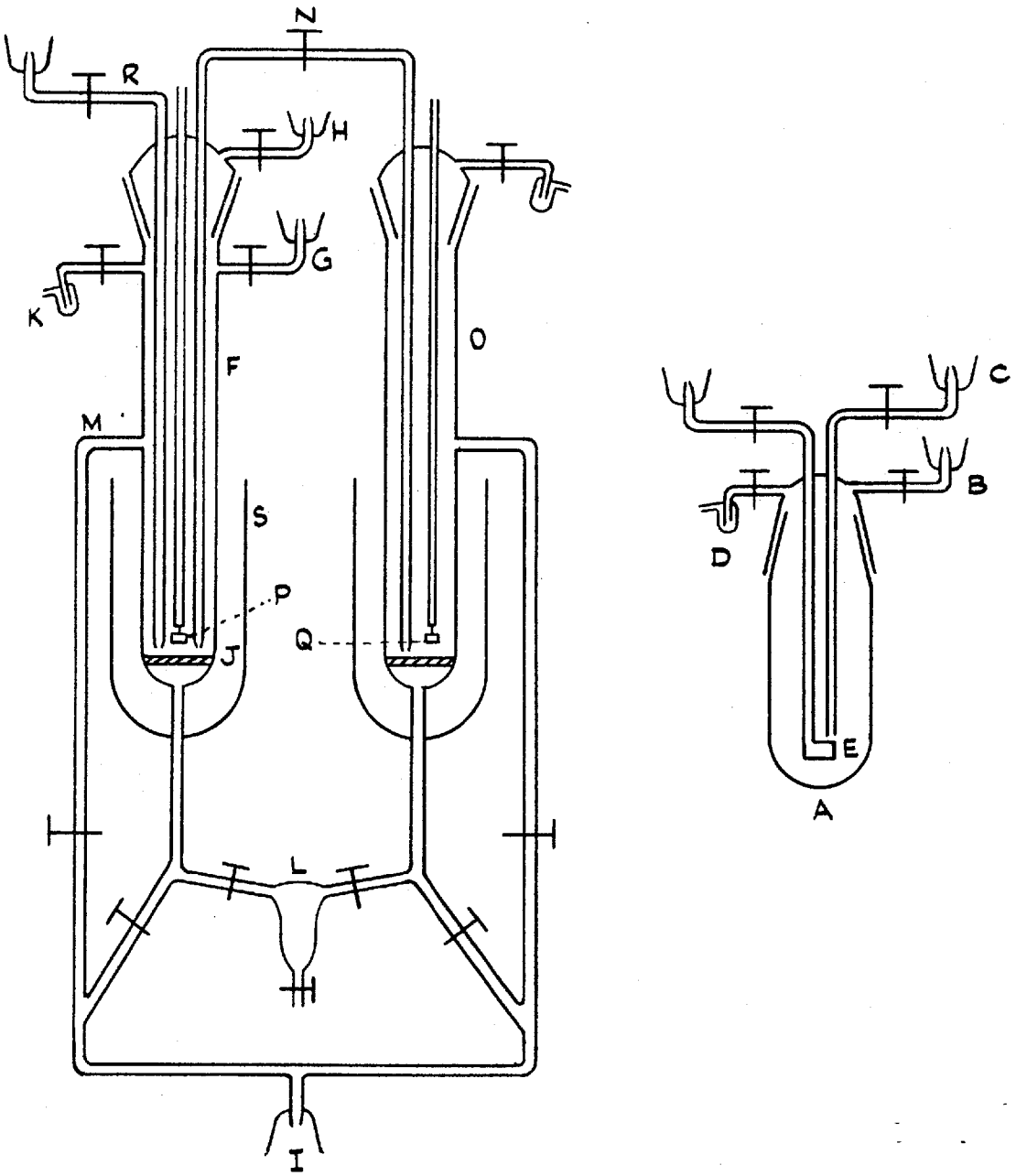
Some work was also carried out at an earlier stage on tungsten in alkaline solutions but no satisfactory results were obtained at low current densities. However, interesting aspects of the technique of preparing alkaline solutions are discussed here for future reference.

Aqueous solutions of sodium hydroxide were prepared by dissolving crystallised sodium hydroxide in conductivity water under an atmosphere of hydrogen. The solution thus prepared was then pre-electrolysed and a part of the catholyte was transferred with a stream of hydrogen into the compartment B of the electrolytic cell (Fig. II 8).

2. PURIFICATION OF SODIUM HYDROXIDE.

The apparatus was first constructed on the same principle as that used by Potter.[26] It is shown in Fig. (a). Solid analar sodium hydroxide was introduced into A and conductivity water was distilled over it (through B), with a stream of hydrogen. This compartment A was immersed in an ice bath to absorb the heat evolved during the dissolution of sodium

FIG (a)



hydroxide. Purified hydrogen was passed through the solution via C and was let out to the atmosphere through the bubbler D. The solution was then transferred to the compartment F through the sintered glass disc E (porosity 1), and the ground glass joint G. This transfer was accomplished by a glass bridge. The sintered glass disc E helped to keep the organic impurities present in the solid analar material, such as cork, etc. The solution in F was diluted with conductivity water introduced through H. Purified hydrogen was introduced through I and the sintered glass disc J (porosity 3) into F and was allowed to escape through the bubbler K.

A freezing mixture composed of solid carbon dioxide and methylated spirit was added into S, with hydrogen still passing through J. This mixture was sucked out as soon as crystals of hydrated sodium hydroxide started to form. The solution was left until the crystallisation was complete. The liquor was then sucked out with a water pump through L. The crystals were melted, and the melt was transferred with a stream of hydrogen from M into the other compartment O through the bridge N. The process of crystallisation was repeated in O, and the liquor was also sucked out through L. After melting the crystals, they were transferred back to F, where another process of crystallisation was carried out. The resulting solution of sodium hydroxide was divided between the two compartments F and O filling the bridge N. This

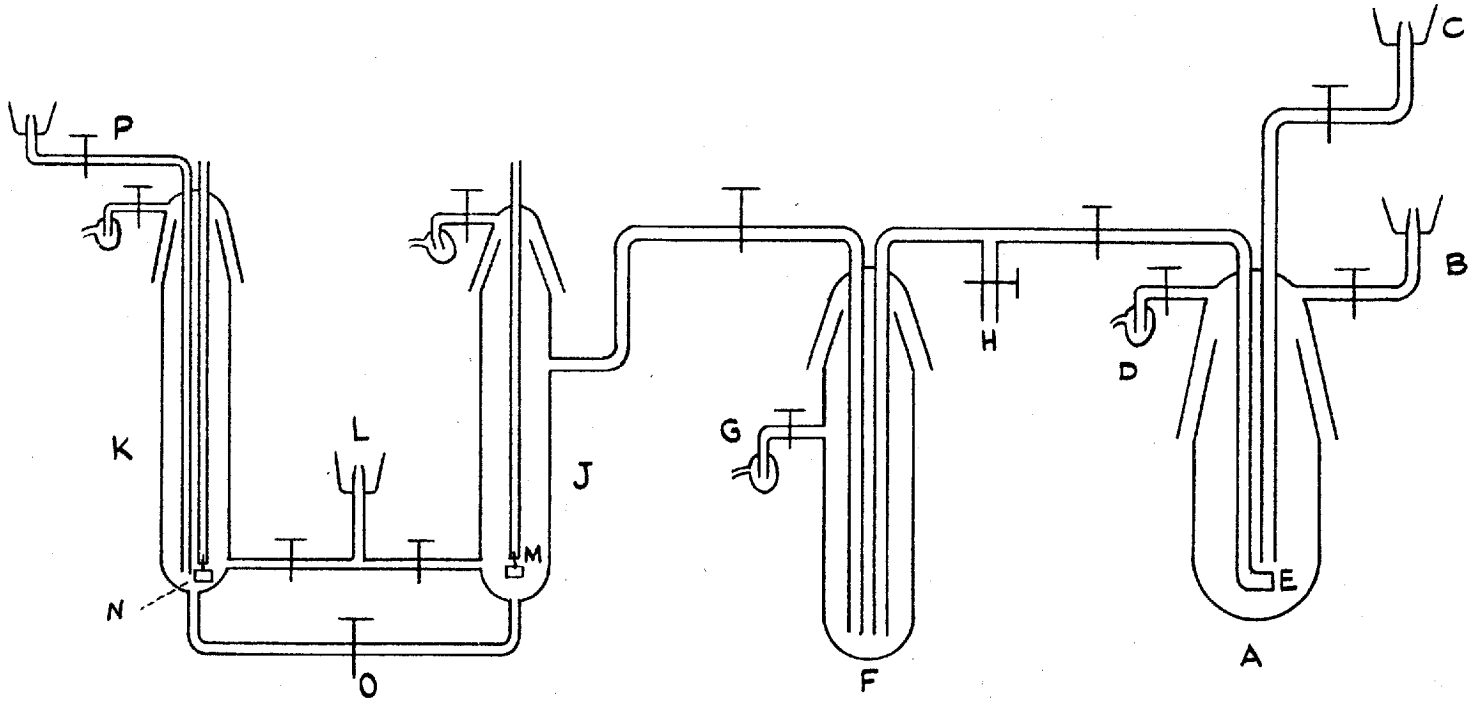
solution was purified by pre-electrolysis (c.d. 2 x 10^{-1} amp . cm.$^{-2}$) between the anode Q and the cathode P, with purified hydrogen passing into the two compartments, for about 40 hours. When pre-electrolysis was complete, part of the catholyte was pushed with a stream of hydrogen through the tube R into the compartment B of the electrolytic cell (Fig. II 8). This was diluted with conductivity water to the required concentration.

The presence of the sintered glass disc J and the thin tube at the bottom of F and O caused a certain amount of trouble. Crystals of sodium hydroxide, having a volume bigger than that of the solution, caused the thin tubes as well as the tubes F and O to crack near the sintered glass discs. It was also difficult to keep the bridge N filled with the solution for 40 hours. Hydrogen passing through O and F caused a bubble to form in this bridge, thus stopping the pre-electrolysis current. Furthermore, it was not necessary to carry out any crystallisation in the compartment O. The three processes of crystallisation could be carried out in F.

It was, therefore, necessary to design another apparatus, for routine re-crystallisation of sodium hydroxide, thus eliminating the above mentioned difficulties. This is shown in Fig. (b).

Concentrated solution of sodium hydroxide prepared in A as mentioned above was introduced into F with a stream of hydrogen. This solution was crystallised in F with hydrogen

FIG (b)



still passing into it. The liquor was sucked out through H, and the crystals were allowed to melt. This crystallisation was repeated three times. After melting the crystals, the solution was introduced into J and K and was then pre-electrolysed between the anode M and the cathode N, with the tap O closed. The anode and the cathode were of platinum. During pre-electrolysis hydrogen was passed into J and K through L. After pre-electrolysis (c.d. 2×10^{-1} amps. $cm.^{-2}$) part of the solution in K was pushed with a stream of hydrogen into the electrolytic cell through P. This solution was diluted to the required concentration and was again pre-electrolysed before the measurements were taken.

All taps used in the purification apparatus were of the water-sealed type.

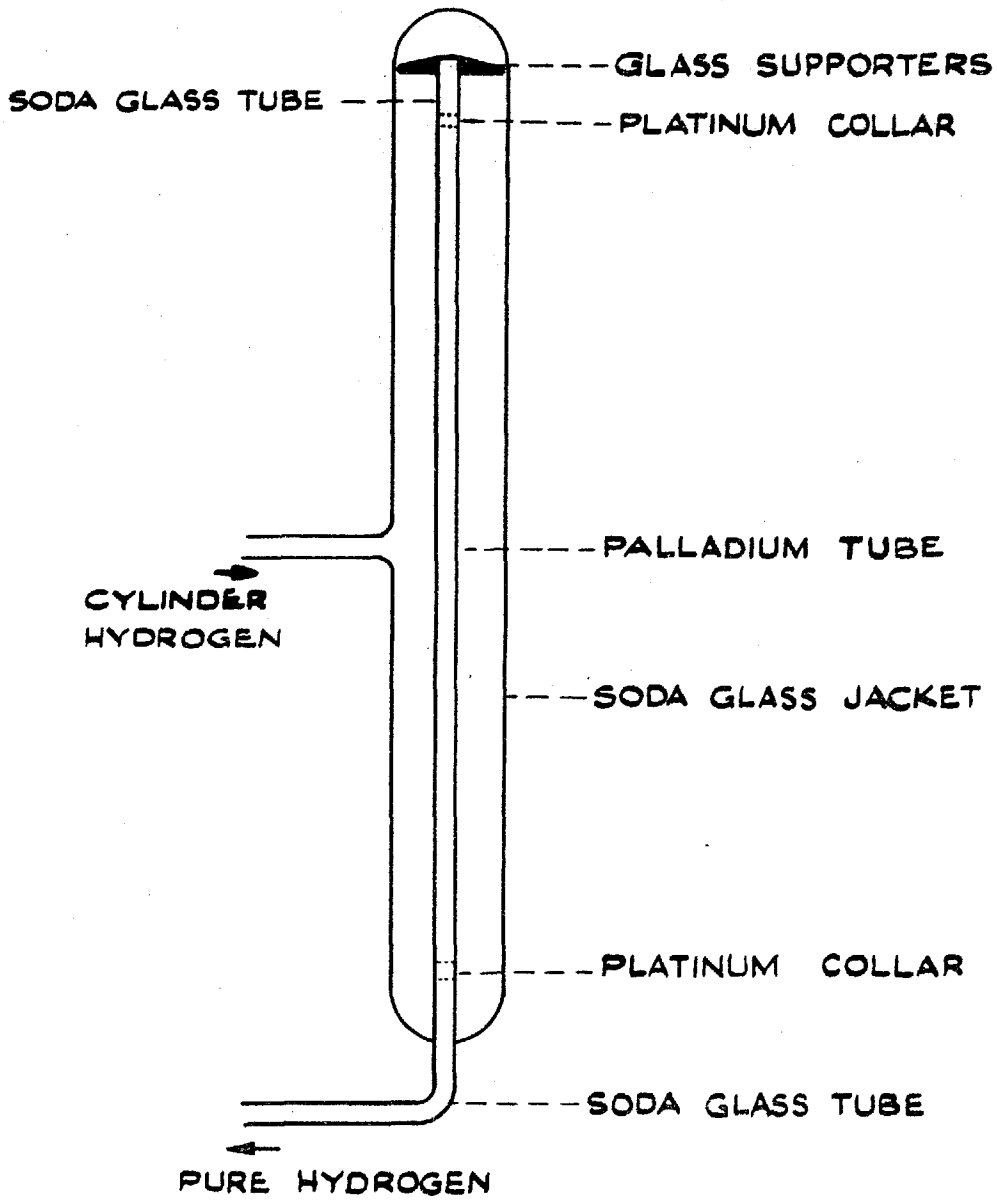
APPENDIX II

Work has recently been carried out to improve the technique of hydrogen overpotential studies and several points of interest are discussed below.

1. PURIFICATION OF HYDROGEN.

A more satisfactory method, than that given in Section II, is the purification of hydrogen by diffusion through palladium. A palladium tube, 1 cm. in diameter, 50 cm. long and having a wall thickness of 0.005 " will pass 10 litres of hydrogen per hour (at atmospheric pressure) under a differential pressure of one atmosphere and at a working temperature of 400°C. Such tubes are supplied with platinum collars which are easily sealed to soda glass. The best arrangement (cf. Fig. c) is to seal the palladium tube to a soda glass tube (about one cm. in diameter) by means of the platinum collars at both ends. The soda glass tube connected to one end of the palladium tube is sealed off while that at the other end is sealed to a jacket of soda glass (about 5 cm. in diameter). Owing to the difference between the coefficient of expansion for soda glass and that for palladium, it is advisable to fix the palladium tube by one end only. The free end must be supported (by glass supporters just touching the inside of the jacket), to prevent sagging of the palladium

FIG (c)


GLASS SUPPORTERS
SODA GLASS TUBE
PLATINUM COLLAR
PALLADIUM TUBE
CYLINDER
HYDROGEN
SODA GLASS JACKET
PLATINUM COLLAR
SODA GLASS TUBE
PURE HYDROGEN

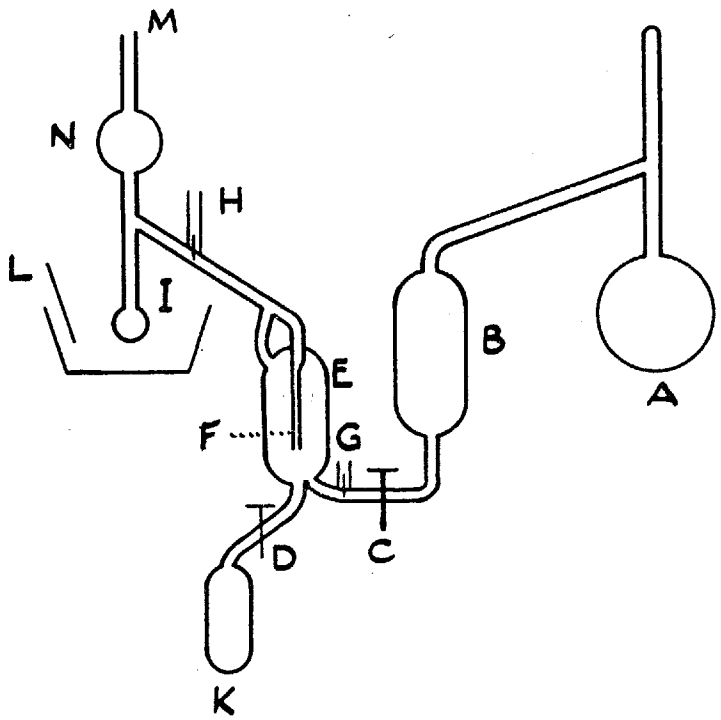
tube when it is heated. The jacket has a side seal through which cylinder hydrogen is passed and heat is supplied by a nichrome furnace around this jacket. The temperature to which the palladium tube could be heated is limited by the maximum practicable working temperature of soda glass. Pure hydrogen is drawn from the thin soda tube connected to the end of the palladium tube. The palladium tube is easily evacuated from the inside, to prevent the contamination of the pure hydrogen by air already present in it. It is also necessary to purge the impure hydrogen in the jacket from time to time.

2. THE ELECTROLYTIC CELL.

Although it has not been possible to develop an electrolytic cell, which can be evacuated to a very high vacuum, for hydrogen overpotential work on solid electrodes, a cell that can be evacuated to 10^{-5} - 10^{-6} mms Hg was developed by Grew[17] for the work on mercury. The main advantage of this cell was that it avoided the diffusion of anodically produced oxygen to the cathode by polarising through a bulb consisting of lead glass. A disadvantage of this cell was that it did not allow for the process of pre-electrolysis to be carried out. A cell which overcomes this difficulty is discussed below and is shown in Fig. (d).

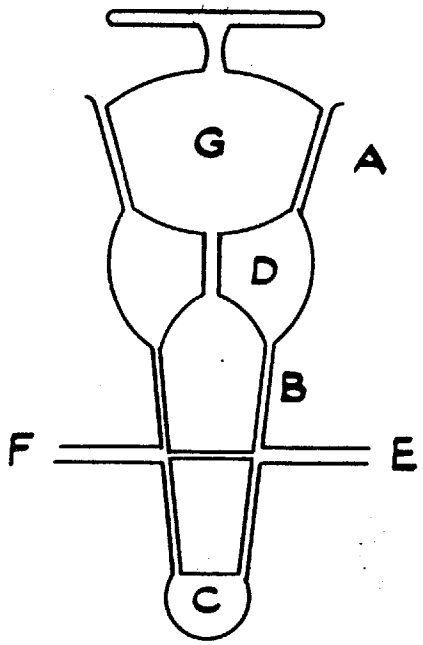
Mercury which has been electrolytically purified and distilled under reduced pressure, is introduced into A and the

FIG (d)



top of A is sealed off. The cell is then evacuated to 10^{-5} - 10^{-6} mms Hg through M, with taps C and D open (these taps are constructed in such a way to allow the evacuation of the cell and also to prevent the contamination of mercury with vacuum grease; details of such taps are given below). C and D are then closed and mercury is distilled under vacuum into the reservoir B. Part of the mercury in B is then introduced into the cathode compartment E. A p.d. is then applied between the cathode G and the anode L. The anode L is placed in a beaker containing a solution of the same concentration as that required for overpotential measurements. The solution is introduced with a stream of hydrogen through M to fill the conductivity glass bulb I, the cathode compartment E and the tube connecting I with E. M is then sealed off and care must be taken to avoid explosion. After pre-electrolysis the mercury in E is transferred to K by opening D, without switching off the pre-electrolysis current. A clean amount of mercury from B is then introduced into E, and is allowed to touch the tip of the Luggin capillary F. Measurements are then carried out, using a piece of bright platinum wire H as a reference electrode. The use of the bulb N is to provide a space into which hydrogen, evolved on mercury during pre-electrolysis, is allowed to escape, thus avoiding the formation of gas bubbles in the tube connecting I and E.

FIG(e)



4. TAP TO WITHSTAND HIGH VACUUM IN THE PRESENCE OF ELECTROLYTIC SOLUTIONS EASILY CONTAMINATED BY GREASE.

The taps used in the above cell are represented by Fig. (e), where A is a greased ground glass joint and the part B is loosely ground. In evacuating the cell, the spaces represented by C, D and G are evacuated too. It is to be noted that in introducing mercury from E to F, it is not contaminated by grease if the grinding of B is not too loose to allow mercury to come in contact with A.

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