REPORT NO. 9

SEMI-ANNUAL PROGRESS REPORT

1 July 1966 to 3 December 1966

STUDIES IN FUNDAMENTAL CHEMISTRY OF FUEL CELL REACTIONS

NsG-325

Submitted to:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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Submitted by:

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Dr. Aleksander Damjanovic , Supervisor

Section III

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Dr. Ljerka Duic, Post-Doctoral Research Fellow

Dr. John O'M. Bockris, Supervisor

Section V

Dr. S. Srinivasan, Post Doctoral Research Fellow

Dr. John O'M. Bockris, Supervisor

Section VI

Mr. J. Diggle, Post-Doctoral Reserach Fellow

Dr. John O'M. Bockris, Supervisor

ABSTRACTS

SECTION I. THE MECHANISM OF POROUS ELECTRODES

The experimental work of this section has been completed, and the essential results of the study are summarized. Papers and a complete write-up are being prepared and will be submitted when complete.

SECTION II. THE MECHANISM OF ELECTROCATALYSIS

Work done in the field of Mechanism of Electrocatalysis for simple electrode reactions e.g. h.e.r. and Fe^{2+}/Fe^{3+} redox reactions were summarized together with some empirical generalizations based on the experimental data. The consequences of such data on the model for electrocatalysis is under evaluation. The thesis and Discussion Section (i.e., the end of the thesis) will terminate in March '67.

SECTION III. POTENTIAL OF ZERO CHARGE

In the present report period capacitance potential data are reported for platinum silver and nickel. Potential of zero charge for vacuum treated platinum is in the same range as earlier reported. Concentration variation in alkaline solutions for capacitance on platinum is studied. Potential of zero charge values are reported for silver and nickel. A new method for the measurement of this potential, - depending on the variation of friction with potential, - was invented.

SECTION IV. ADSORPTION IN THE DOUBLE LAYER WITH SPECIAL REFERENCE TO THERMAL EFFECTS

Measurements on benzene adsorption on platinized platinum were carried out by means of potential sweep (potentiodynamic) and galvanostatic method. Comparison between these two methods and radiotracer method was done. Apparatus for potentiostatic method was prepared, and measurements initiated. A paper which distinguishes the methods is in process. A new Project will be commenced in March '67.

SECTION V. ELECTRODE KINETIC ASPECTS OF ENERGY CONVERSION

The book with Dr. Srinivasan (MacGraw-Hill) continues to be written. It is between the 2nd and the 3rd draft. All chapters have now been sent to at least 2 referees per chapter and their comments taken into account in revisions made throughout the book. The time spent on the book at present is:

S. Srinivasan: 25 hours/week
J. O'M. Bockris*: 10 hours/week
Schedule: 3 chapters sent to publishers Feb. 1967; 7 further chapters (i.e., rest of book) May 1st, 1967

*Alternate: 2 day weekend stretches of about 20 hours in discussion with Dr. Srinivasan.

SECTION VI. THEORY OF CHARGE TRANSFER

Mr. J. Diggle, who is just completing the research degree of the Royal Institute of Chemistry, is delayed in arrival, due to thesis writing. He will work on the charge transfer problem in solution when he arrives.

SECTION VII. INTRODUCTION TO ELECTROCHEMISTRY

The third draft is arriving steadily from Dr. Reddy. 5 out of 10 chapters have been received and represent reworkings of the 2nd draft which was prepared in Bangalore by direct collaboration Bockris-Reddy in June and July, 1966.

Bockris then has to prepare the 4th draft, get it reviewed, take into account the criticism, and send to the publisher.

Time spent by Bockris: 10 hours/week.

Schedule: Reddy finishes sending 3rd draft by April 30, 1967. Bockris finishes other tasks August 1st, 1967.

SECTION I. THE MECHANISM OF POROUS ELECTRODES

The experimental section of this phase of the study of porous electrodes has been completed, and effort is being concentrated on the compilation and writing of a thesis and several papers which are to be presented in the near future (14 April - Miami meeting - ACS: May - Dallas meeting Elec. Soc.). When completed these papers will be attached to a future report.

The primary findings of this research have been:

1) It is not necessary to invoke a "thin-film" above the meniscus to explain the high currents obtainable in a "three-phase" electrode. While it is possible that some electrodes do operate with this configuration, the commonly employed wet-proofing and/or adsorbable organic impurities will tend to eliminate this mechanism in real fuel cells. Also, geometric considerations militate against the stability of 1μ thick films in pores of diameter any smaller than 2μ.

2) Total currents (per cm) obtainable from finite contact angle menisci (F.C.A.M.) may be slightly lower than those obtainable from a thin film meniscus (T.F.M.) but since the active area in a F.C.A.N. is much smaller (10^{-5} cm for F.C.A.M. vs 10^{-2} cm for T.F.M.) the effective current densities are much higher.

3) These high current densities (and thus high lost) power densities cause local heating, local evaporation in the meniscus, which can lead to flooding, and/or catalyst drying and deactivation.

4) Even in the T.F.M. local heating can cause evaporation of the thin film, forcing a transition to the F.C.A.M. (This situation was

produced and studied during the experimental section).

5) A computer solution of the postulated differential equation for the F.C.A.M. gives an excellent qualitative and quantitative agreement with the experimental data, and is thus probably a complete description of the situation, allowing its use for the calculation of curves under conditions other than those used experimentally. For example, using the constants for O_2 reduction in 10 NKOH, excellent agreement is found with data published by other workers (Hartner et al, Vol. 7 No. 4, Preprints of Papers Presented at N.Y. A.C.S. Sept. 8-13, 1963, p. 130-141) on the effect of pressure on O_2 reduction. Thus,

6) The equation can be used to <u>predict</u> the behavior of a porous electrode system operated under a wide variety of hypothetical conditions.

7) The computic solution showed in a "typical" porous electrode most (99%) of the randomly deposited catalyst is outside the actual working region.

8) On the basis of the extremely small dimensions involved in the actual current producing region as calculated from the equation, the thin film electrode was developed which gave extremely high current yields per gram of catalyst.

SECTION II. THE MECHANISM OF ELECTROCATALYSIS

In the previous NASA reports, the experimental work done to investigate the effect of electrode materials on simple electrochemical reactions have been described. The reactions chosen were the h.e.r. in acid and alkaline media and redox reaction. The following kinds of electrodes were studied:

a) Noble metals

b) Alloys of noble metals with noble or non-noble metals

c) Alloys of non-noble metals

d) Alloys of Pt with trace amount of redox catalysts (e.g. Mo and V)

e) Carbides of Ti, Ta and Boron

f) Tungsten Bronzes with general formula of the type, $Na_x \cdot WO_3$ (where $x<1$)

The results have been published in various reports. In the present report, we wish to present the phenomenological conclusions and generalisations that were derived from those experimental results.

It was agreed at the beginning of this project that the electrode treatment be kept as constant as possible. However, for reasons discussed in a previous report,[1] it was decided to change the procedure of electrode treatment.

However, with the data available in our work it was found as a general observation that the thermally treated electrodes were less active than the electrochemically treated ones.

Also it was observed in the hydrogen evolution reaction, that activities of the electrodes were greater in acid solution than in alkaline solution. However, the order of magnitude did not show any specific trend. Further data are necessary in order to make any quantitative generalisation.

The linear change in activity in Ni-Pd and Ni-Pt alloys for h.e.r. reported earlier may be linked with the linear change in lattice parameter in these alloys.[2]

The trend in the change in activity in Au-Pd and Au-Pt alloys have been linked with the number of 'd' electrons in the metal in a previous report.[1]

In the Fe^{3+}/Fe^{2+} redox reaction, the following generalisations could be made:

1) The log i_o values of the noble metals studied were found to vary linearly with work function, Φ. Since the work function values reported in literature vary tremendously, the most probable values were calculated and the uncertainties have been indicated in figure (1) showing the log i_o vs Φ plot.

Another important observation was that the heat of activation, calculated from the variation of log i_o vs 1/T on various noble metals did not show any dependence on the work function, Φ (cf. figure (2)).

The TiC, TiC and B_4C electrodes, as well as the tungsten bronze electrodes were found to behave as better catalysts in the redox reaction than in the hydrogen evolution reaction. Typical Tafel lines in both reactions are shown in figures (3) and (4).

REFERENCES

1. NASA Report, No. 5, 1 Oct., 1964 to June 30, 1965.
2. NASA Report, No. 6, 1 July, 1965 to 30 Sept. 1965.

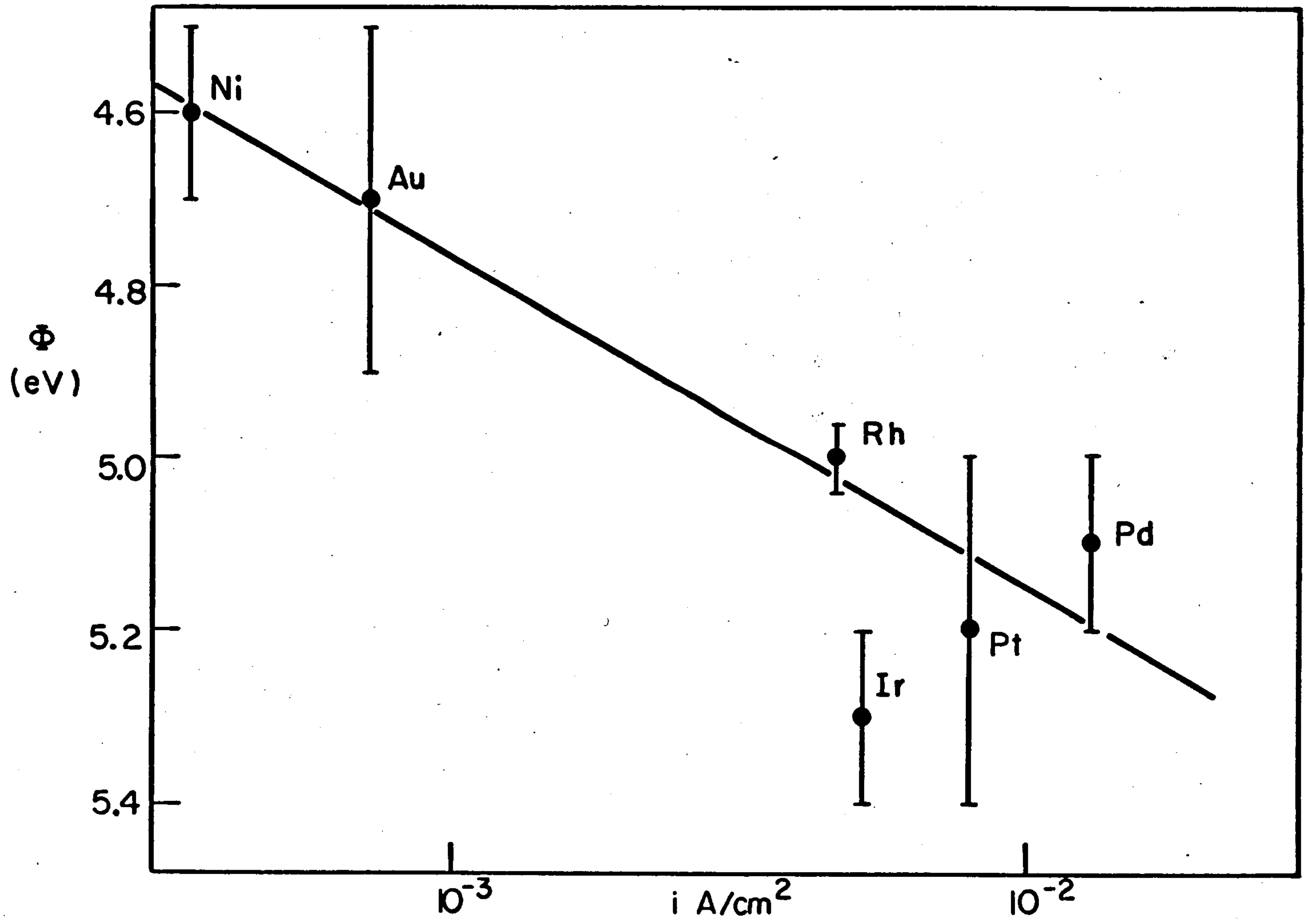


FIG. 1 The activity vs work function values in 0.1 M Fe^{2+}/Fe^{3+} solution.

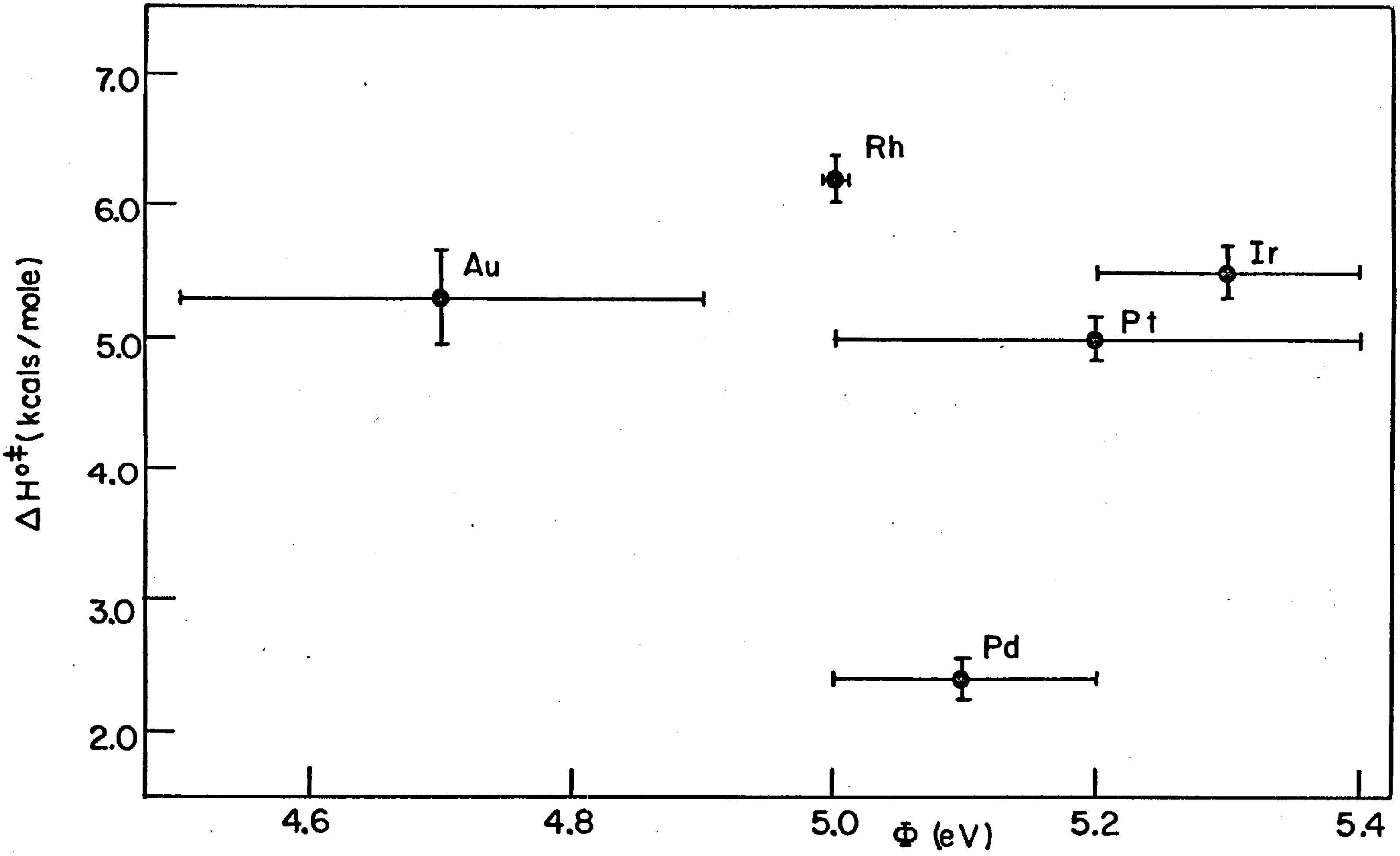


FIG. 2 The heat of activation values on metals vs the most probable work function values in 0.1 M Fe^{2+}/Fe^{3+} solution.

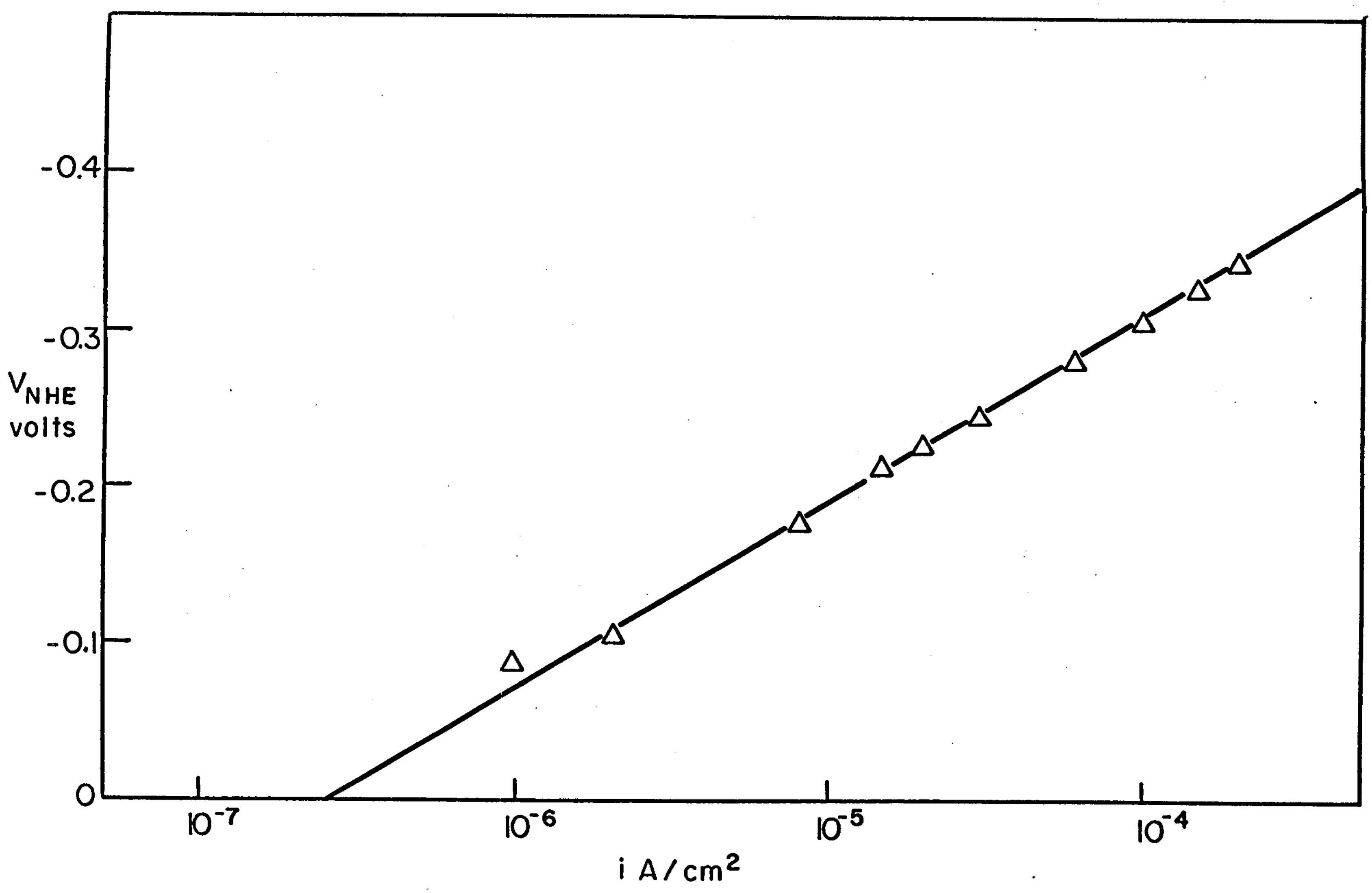


FIG. 3 Cathodic Tafel line on TiC electrode in 1 N H_2SO_4.

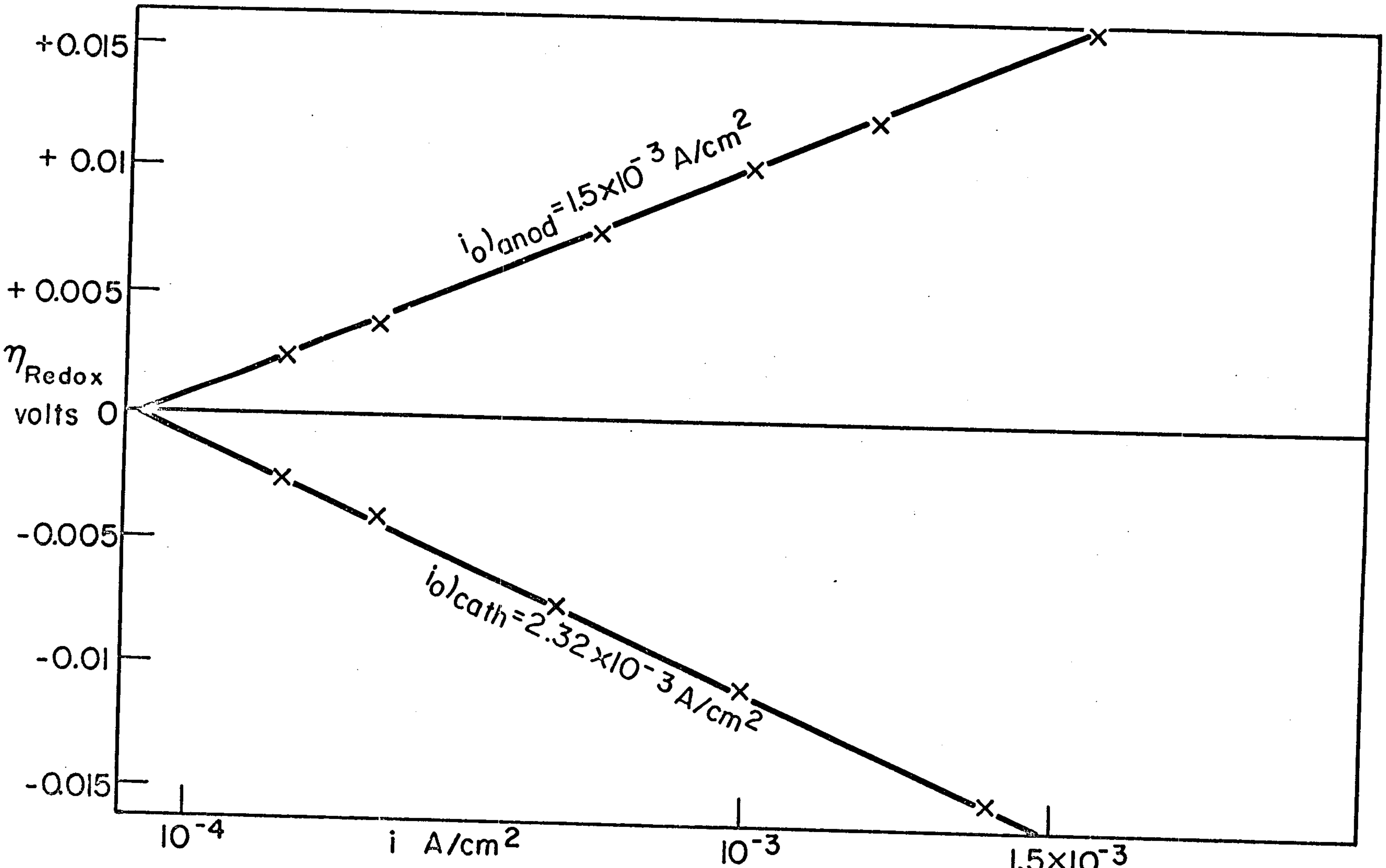


FIG. 4 The cathodic and anodic current-potential relation on TiC in 0.1 M Fe^{2+}/Fe^{3+} solution.

SECTION III. POTENTIALS OF ZERO CHARGE

Introduction

In the present report period measurements of potentials of zero charge on platinum were further continued to determine whether the platinum electrodes were free of hydrogen. Also, the effect of variation of electrolyte concentration on capacitance of platinum electrodes in alkaline solutions was studied. The capacitance method was extended to determine potentials of zero charge on silver and nickel. An apparatus for a third method has been designed and constructed.

Experimental and Results

Apparatus and experimentation used are described in a previous report.[1]

1. Platinum

a. To test the absence of H in Pt

It has been shown[2] that the effect of hydrogen occluded in platinum is to shift the p.z.c. in a negative direction. In this work, hydrogen-free platinum electrodes were obtained by heating in argon over a period of 3 hours. To test the validity of this treatment for removing H from platinum, following experiment was devised.

Pt wire was sealed in quartz which inturn was sealed to pyrex 'trubore' tubing. Platinum wire was melted into a bead in hydrogen-oxygen flame. The electrode prepared in this manner was put in a vacuum chamber (evaporation unit). The platinum bead was heated in a furnace (platinum wire wound on a quartz tube) to 800°C, in a vacuum of 10^{-6} mm or better for about 100 hours. This treatment freed platinum from any absorbed hydrogen. The electrode treated in this manner gave similar results to those previously obtained. See Fig. 1.

b. Electrolyte concentration variation of capacitance in alkaline solutions.

Fig. 2 shows the results of these experiments which were carried out in a similar manner to the experiments presented in the last report.[3] The concentration effect is well borne out to point out again that the minimum in capacitance is potential of zero charge in alkaline solutions as well.

2. Determination of potential of zero charge of silver.

The silver bead electrode was prepared necessarily in a controlled atmosphere of purified argon. Because at the melting point, silver absorbs large quantities of oxygen. A vycor furnace was built in which the trubore electrode could be moved to a desired position. Purified argon was passed to remove air completely. The vycor furnace was heated by a gas flame to red heat. Small amount of hydrogen was passed to reduce the oxide on silver wire. The furnace was heated strongly to melt the silver wire into a bead in argon atmosphere.

The electrode was again heated in argon, hydrogen and argon successively to remove any airborne oxide. The electrode was slipped into solution to carry out the measurements. Fig. 3 and Fig. 4 show the results obtained by giving different treatments to the silver electrode. When an electrode after dipping in the solution was given anodic-cathodic pulsing ending with a cathodic pulse results as shown in Fig. 3 were obtained. Whereas without giving any pulsing and making measurements from the cathodic side gave results like in Fig. 4. The potential of zero charge values of silver are: (i) P.Z.C. = -450 ± 25 mv (N.H.E.) at pH = 3. (ii) for anodic-cathodically pulsed silver, the potential of zero charge is closer to 0.0 (N.H.E.), at pH = 3 perchloric acid solution. The latter value is in fair agreement with that of the first method.

3. Potential of zero charge of nickel

In case of nickel also, a special procedure was necessary to make oxide free nickel electrodes. No transparent material can stand temperatures 200°C above m.p. of nickel. It presented considerable difficulties to achieve melting of nickel wire into a bead. It was carried out in an evaporation unit bell-jar having facilities to move the electrode up and down. The electrode with nickel wire was mounted in the unit. A heavy tungsten filament was placed just below the nickel wire. The chamber was evacuated to 5×10^{-7} mm of Hg. About 80 amp. current was passed through the conical tungsten wire basket to melt the 0.2 mm Ni wire into a spherical bead. The vapor pressure of tungsten at 2500°C is about 10^{-7} mm and that of nickel at 1550°C is 40 mm. Thus no contamination of Ni is to be expected from tungsten. The nickel electrode was heated in hydrogen and argon above the cell to remove the oxide on Ni, if any. The electrode was dipped in a sodium perchlorate solution of pH = 10 and capacitance measurements were carried out.

It can be seen that capacitance minimum occurs at -200 mv (N.H.E.) (cf. Fig. 5). This value is in fair agreement with the first method.

Future Work

The design and construction of the apparatus for measuring coefficient of friction as a function of potential will be presented in the next report. Preliminary measurements are being carried out at this time. The potentials of zero charge by this method will be reported later.

References

1. Report No. 7 for the period 1 Oct., 1965 to 31 Dec., 1965, NsG-325.
2. E. Gileadi, S. D. Argade and J. O'M. Bockris, J. Phys. Chem., 70, 2544 (1966).
3. Report No. 8 for the period 1 Jan., 1966 to 30 June, 1966.

CAPTIONS TO FIGURES

Fig. 1: Capacity in μF vs. potential in mv (RHE) for a platinum bead electrode which was treated in vacuum to remove traces of hydrogen.

Fig. 2: Capacity in μF cm^{-2} vs. potential in mv (RHE) for platinum as a function of $KClO_4$ concentration variation at a constant pH = 10. - o - NaOH only; - Δ - 6×10^{-4} M $KClO_4$; - x - 5×10^{-3} M $KClO_4$.

Fig. 3: Capacity in μF cm^{-2} vs. potential in mv (NHE) on silver which was anodically and cathodically pulsed. $HClO_4$ solution of pH = 3.

Fig. 4: Capacity in μF cm^{-2} vs. potential in mv (NHE) for silver which was not treated by pulsing. $HClO_4$ solution of pH = 3.

Fig. 5: Capacity in μF cm^{-2} vs. potential in mv (RHE) for nickel in $KClO_4$ solution at pH = 10. - o - 5×10^{-4} M $KClO_4$; - x - 7×10^{-3} M $KClO_4$.

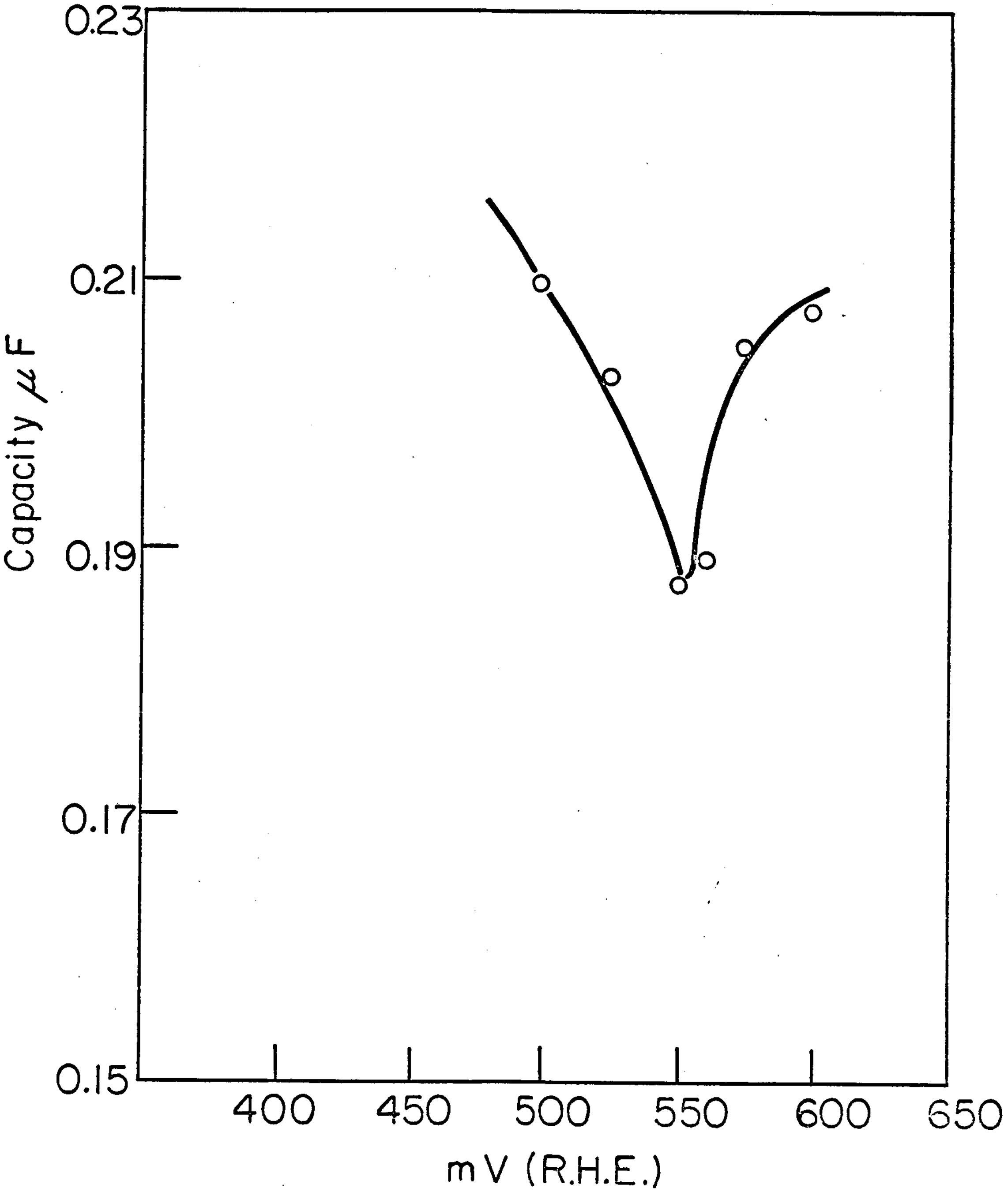


FIG. 1

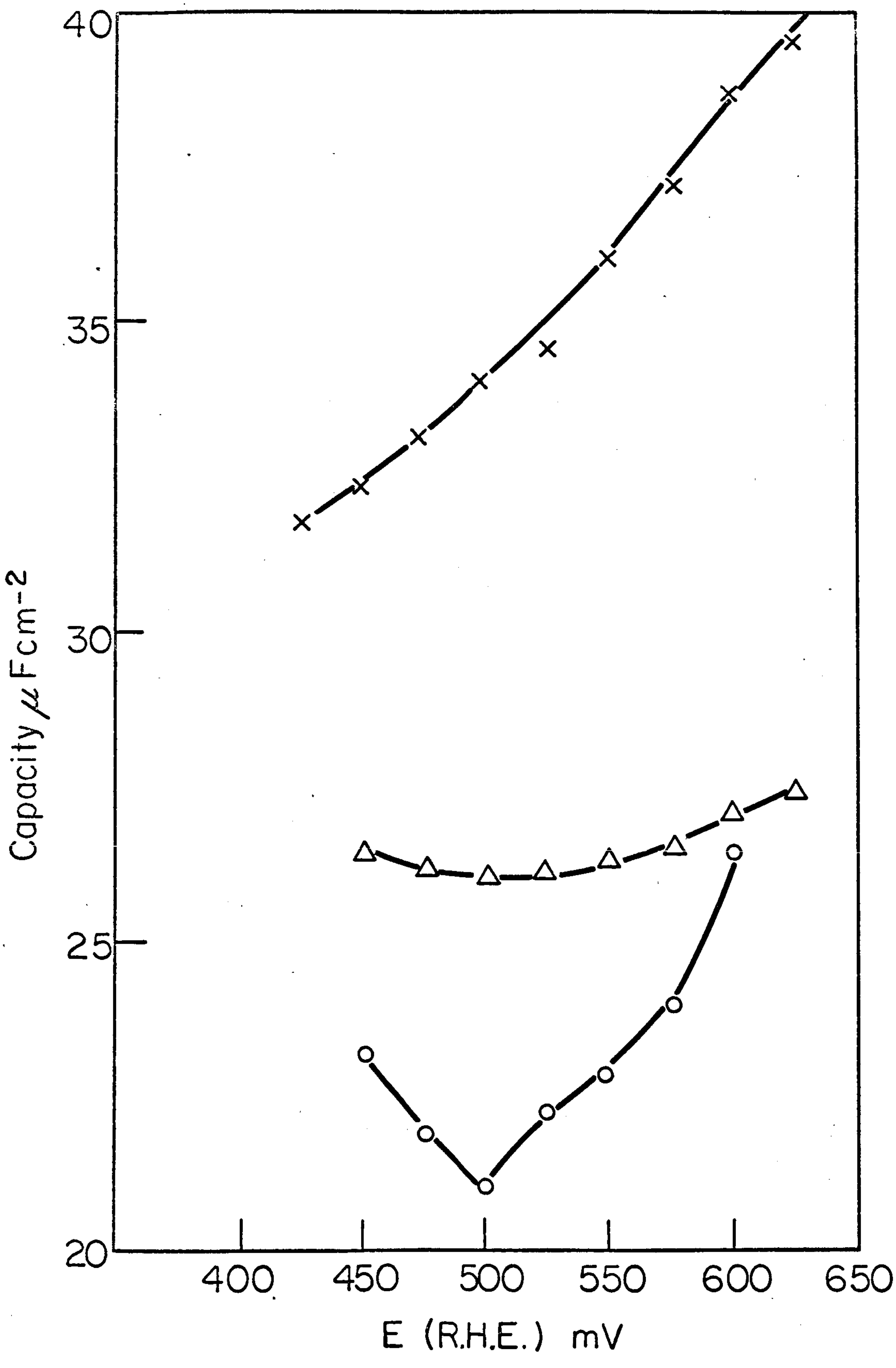


FIG. 2

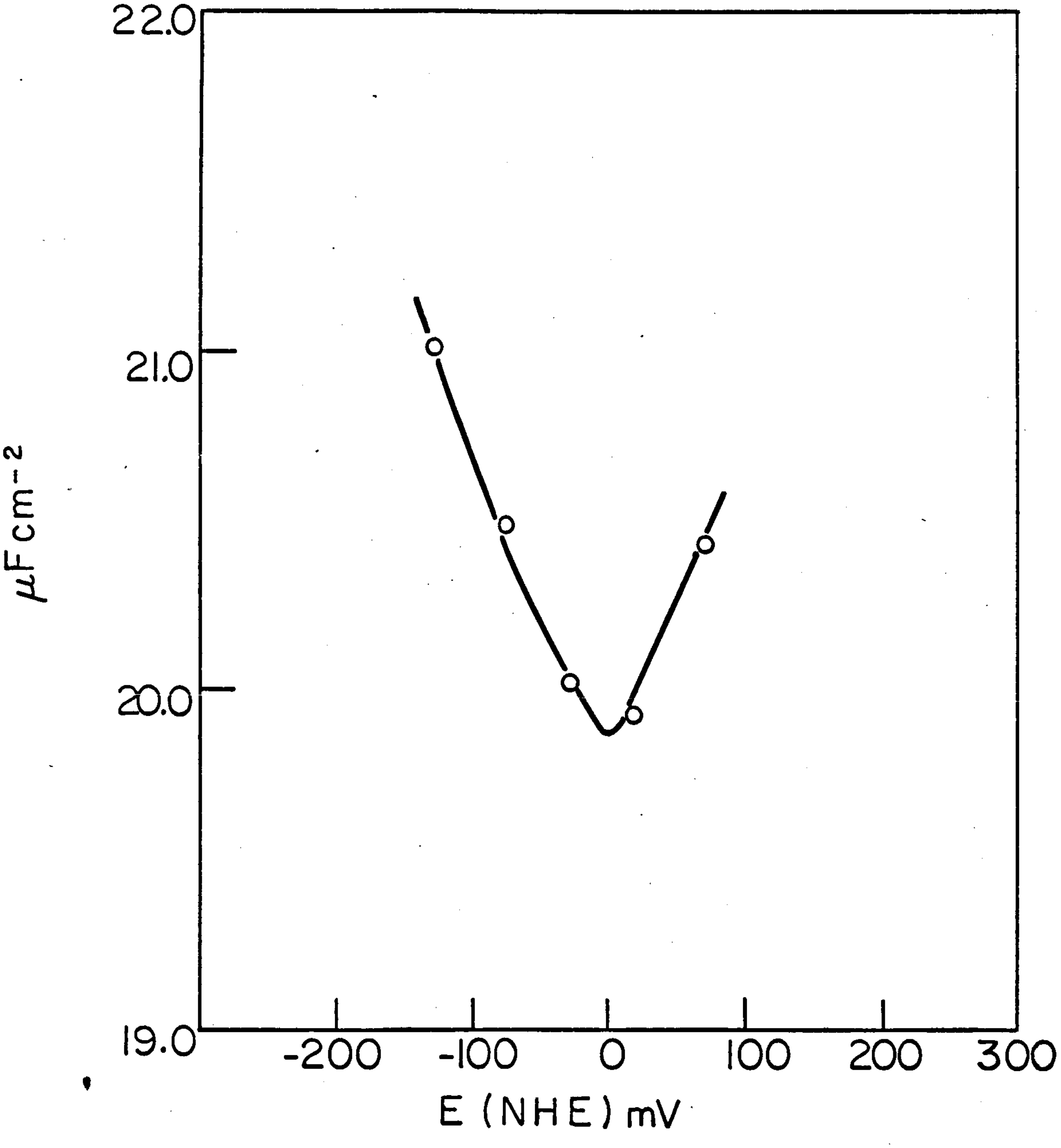


FIG. 3

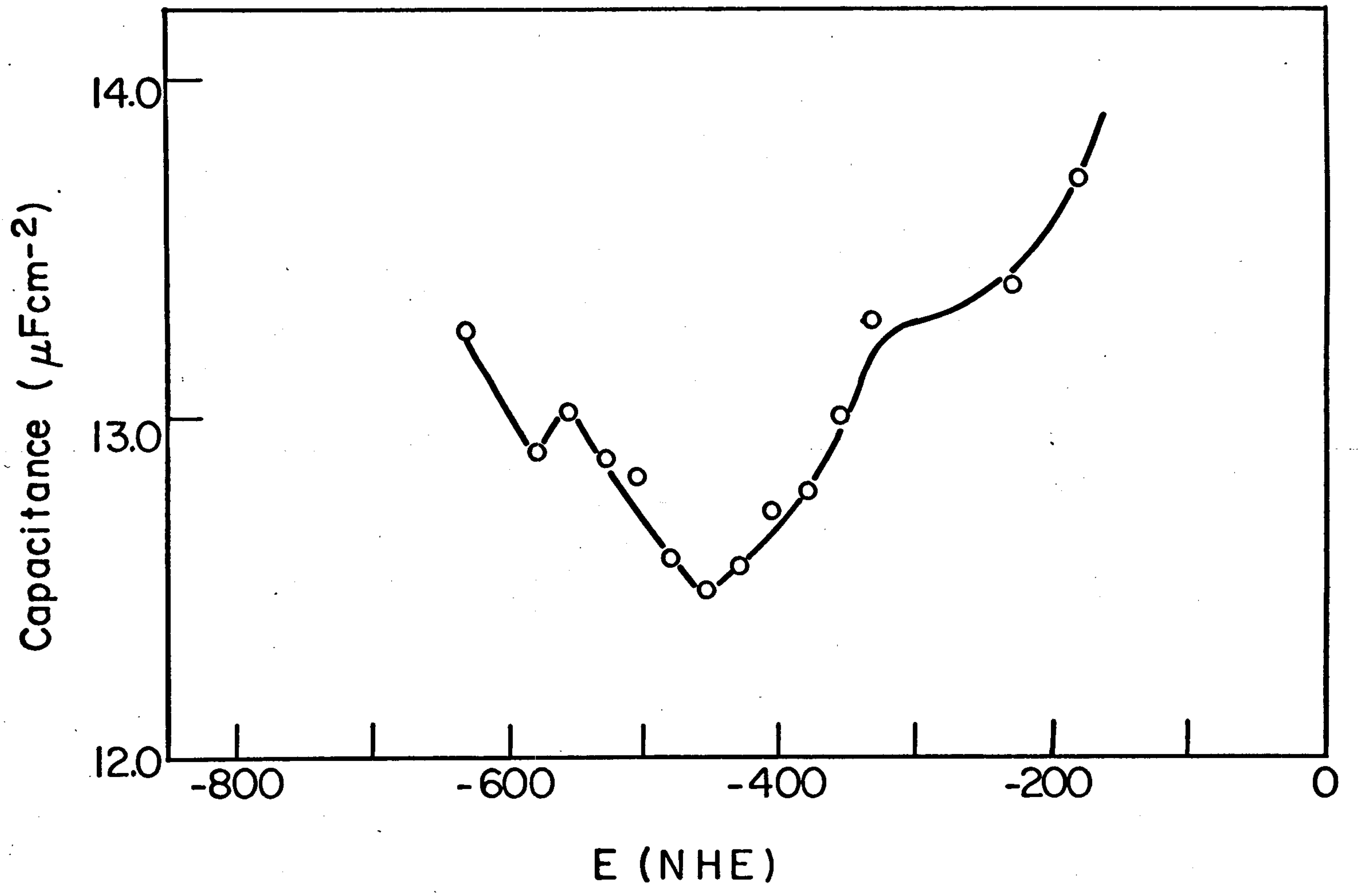


FIG. 4

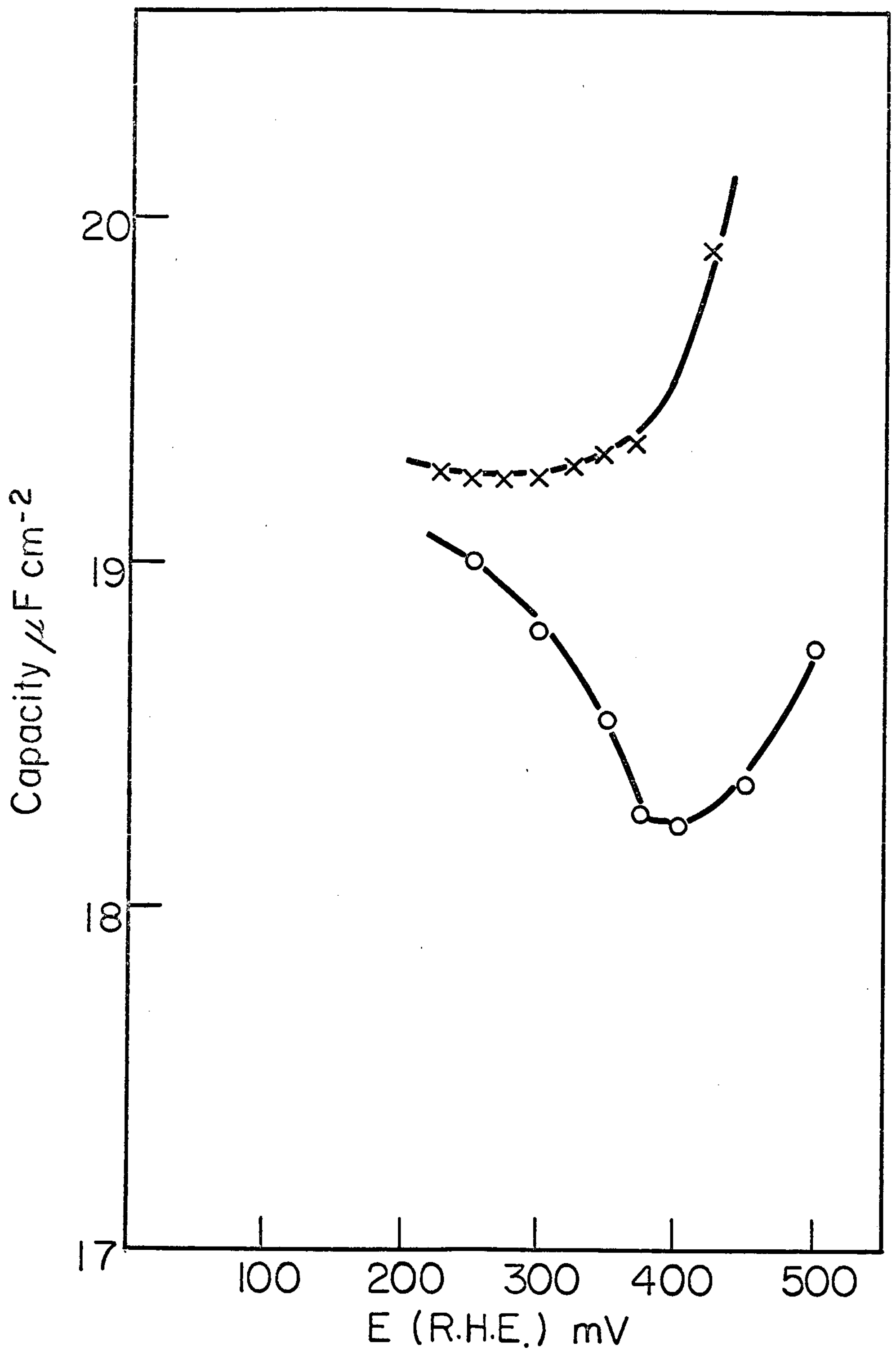


FIG. 5

SECTION IV. Adsorption in the Double Layer with Special Reference to Thermal Effects.

In the report period final measurements on systems with benzene were carried out in order to evaluate two methods on investigation of absorption. Measurements by potential sweep method and galvanostatic method came to the final stage in present frame work considering adsorption of benzene, and measurements by potentiostatic step method were initiated.

Experimental

Cell. To carry out the experimental work the same cell, for all three methods, has been used. The two compartments cell has been made from Pyrex glass [Fig. 1], and provides temperature control. As a heater served heating tape, and temperature controller was model 71 Yellow Spring Instruments.

Electrodes. As test electrode served platinized Pt bead, mounted in the centrum of the cell, close to the top of Luggin cappilary, and surrounded by platinum basket as counter electrode.

The real area of the test electrode was determined by capacity measurements (by galvanostatic charging method), as described earlier.[1]

Solution. All measurements were done in 1 N sulphuric acid, using bidistilled water and Baker grade Sulphuric acid, treated with H_2O_2 to oxidize eventually present organics. Before injecting benzene, through the solution prepurified nitrogen was bubbled for about two hours.

Labeled benzene was used, and the bulk concentration was always easily checked using liquid scintillation counter. This becomes important at higher temperatures (50° and 70°) due to evaporation of benzene from the solution.

Results

Potential sweep method. Measurements by P.S.M. were carefully reexamined at three different temperatures (30, 50 and 70°).

Time dependence of adsorption for different concentrations and at different temperatures is given in Fig. 2-4. As it is shown at lower temperature kinetics of adsorption is very slow even at high concentrations of benzene, and it gets faster with higher temperature (compare Figs. 2-4).

Isotherms are taken also at three mentioned temperatures and results are given in Fig. 5-7, along with results obtained by radiotracer method.

Potential dependence for different concentrations at 50°C is given in Fig. 8-10. Potential at which maximum of adsoprtion is achieved is 400 mV vs. N.H.E. The maximum is very well pronounced but with higher concentrations of benzene the maximum is somewhat shifted to a little bit more anodic region (between 400-500 mV). The way of calculation for P.S.N. was described previously.[2]

Galvanostatic method. At one temperature (50°C) measurements were carried out.

Time dependence for several concentrations was checked (Figs. 11 and 12).

Isotherm at 50° is given along with potential sweep measurements and radiotracer results in Fig. 6.

Potential dependence at two concentrations was examined and results are presented in Fig. 7 and 9 in comparison with radiotracer results and results obtained by potential sweep method.

The results given in these report for galvanostatic method are calculated in the same way as reported earlier.[2]

Potentiostatic method. Measurements in which potentiostatic method is applied are initiated. The potentiostatic switch is designed[3] which gives a possibility to potentiostate the test electrode at certain potential (V_{ad}) during the time τ_{ad}, and then to apply the potential step in the range from 0 to 1 V.

The preliminary measurements showed that to oxidize the adsorbed species it would be necessary to reach +1.5 V (vs. N.H.E.). In these measurements the test electrode was potentiostated at +500 mV, and then after time τ_{ad} the step of 1 V was applied. The same picture is taken in presence and in absence of benzene. Fig. 12 shows the area taken into account to get the number of coulombs used in oxidation of adsorbed benzene.

The integral under the I-t curve gives the number of coulombs. Curve A gives the amount of coulombs due to oxidation of the electrode and the area under the curve B gives the amount of electricity due to oxidation of adsorbed species and due to oxidation of electrode surface.

Thus,

$$Q_A = \int i(t)_A dt \qquad (1)$$

$$Q_B = \int i(t)_B dt \qquad (2)$$

The difference between these two integrals gives the amount of electricity consumed in oxidation of adsorbed species.

$$Q_B - Q_A = \int[i(t)_B - i(t)_A]dt \qquad (3)$$

DISCUSSION

The reported measurements by potential sweep method and galvanostatic method, show that results obtained by these two electrochemical methods are fairly close. Agreement is satisfactory good, and was expected. As it was shown previously[2] these two methods are equivalent, and one should expect the agreement as obtained.

The lack of experimental results does not allow to make analysis and conclusions about potentiostatic method in adsorption studies.

Isotherms. As it is shown in Fig. 6, isotherms obtained by different methods give very close results, and discrepancies obtained are within experimental errors of each of these methods.

One should have in mind that in case of galvanostatic results calculation should be carried out in a little different way. Namely, as with potential sweep measurements calculations took into account that amount of coulombs due to oxidation of the electrode would not be the same in absence as in presence of organics - the same estimation should be brought up in case of galvanostatic measurements. The difference is not expected to be significant (what is easy to check with potential sweep measurements).

Isotherms taken at 30° and 70°C show somewhat greater discrepancies but still within experimental errors expected for these methods.

Potential dependence. As shown in Figs. 8-10 satisfactory good agreement is obtained, in some extent, between different methods. It is possible to see that "transient methods" results in θ-potential curve with some different shape then radiotracer method. Potential of maximum adsorption in case of transient methods is somewhat shifted to the cathodic region (≈ 100 mV) in reference to the radiotracer method. Also with these methods there is no sign of reaching the plateau in certain region of potential at higher concentrations of benzene, what is the case with radiotracer method.

Future work. Potentiostatic measurements should be finished, and quantitative analyses and comparison between electrochemical methods and radiotracer method should be done.

References:

1. E. Gileadi, B. T. Rubin, and J. O'M. Bockris, J. Phys. Chem., 69, 3355 (1965).
2. Semi-Annual Progress Report No. 8. (1 Jan- 30 June 1966) NsG-325.
3. B. D. Cahan, to be published.

Captions to Figures

1) The cell: 1 - test electrode, platinized platinum bead
2 - counter electrode, platinum basket
3 - magnetic stirrer
4 - reference electrode
5 - temperature controller

2) Time dependence of adsorption of benzene at 30°C. C = 190x10^{-7} moles/ℓ
Examined by potential sweep method.

3) Time dependence of adsorption of benzene: t = 50°C
Examined by potential sweep method. C = 140x10^{-7} moles/ℓ
V = 500 mV

4) Time dependence of adsorption of benzene: t = 70°C
Examined by potential sweep method. C = 72x10^{-7} moles/ℓ
V = 500 mV

5) Isotherms for benzene adsorption at 30°C, and 500 mV
squares - radiotracer method
0 circles - potential sweep method

6) Isotherm for adsorption of benzene at 50°C and 500 mV
squares - radiotracer method
0 circles - potential sweep method
X crosses - galvanostatic method

7) Isotherm for adsorption of benzene at 70°C, and 500 mV
squares - radiotracer method
0 circles - potential sweep method

8) Potential dependence of adsorption, t = 50°C
C = 12x10^{-7} moles/ℓ
squares - radiotracer method
0 circles - potential sweep method
X crosses - galvanostatic method

9) Potential dependence of adsorption, t = 50°C
squares - radiotracer method (70x10^{-7} moles/ℓ)
0 circles - potential sweep method (78x10^{-7} moles/ℓ)

10) Potential dependence of adsorption, t = 50°C
0 circles - potential sweep method (140x10^{-7} moles/ℓ)
X crosses - galvanostatic method (105x10^{-7} moles/ℓ)

11) Time dependence of adsorption of benzene at 50°C, examined by galvanostatic method.

12) Typical potentiostatic transient curve (A) in absence and (B) in presence of benzene for the potential step from 500 mV to 1500 mV.

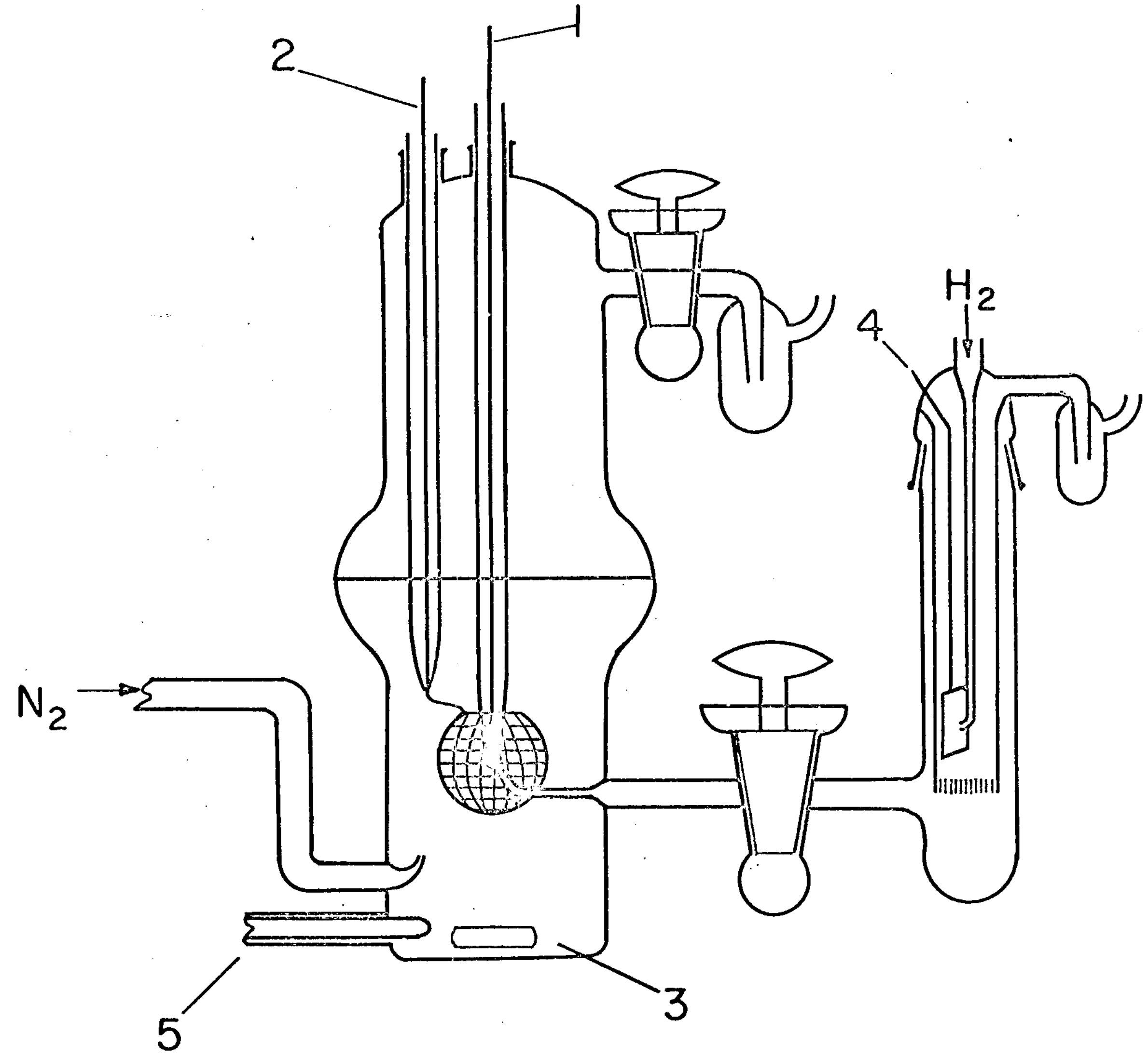


FIG. 1

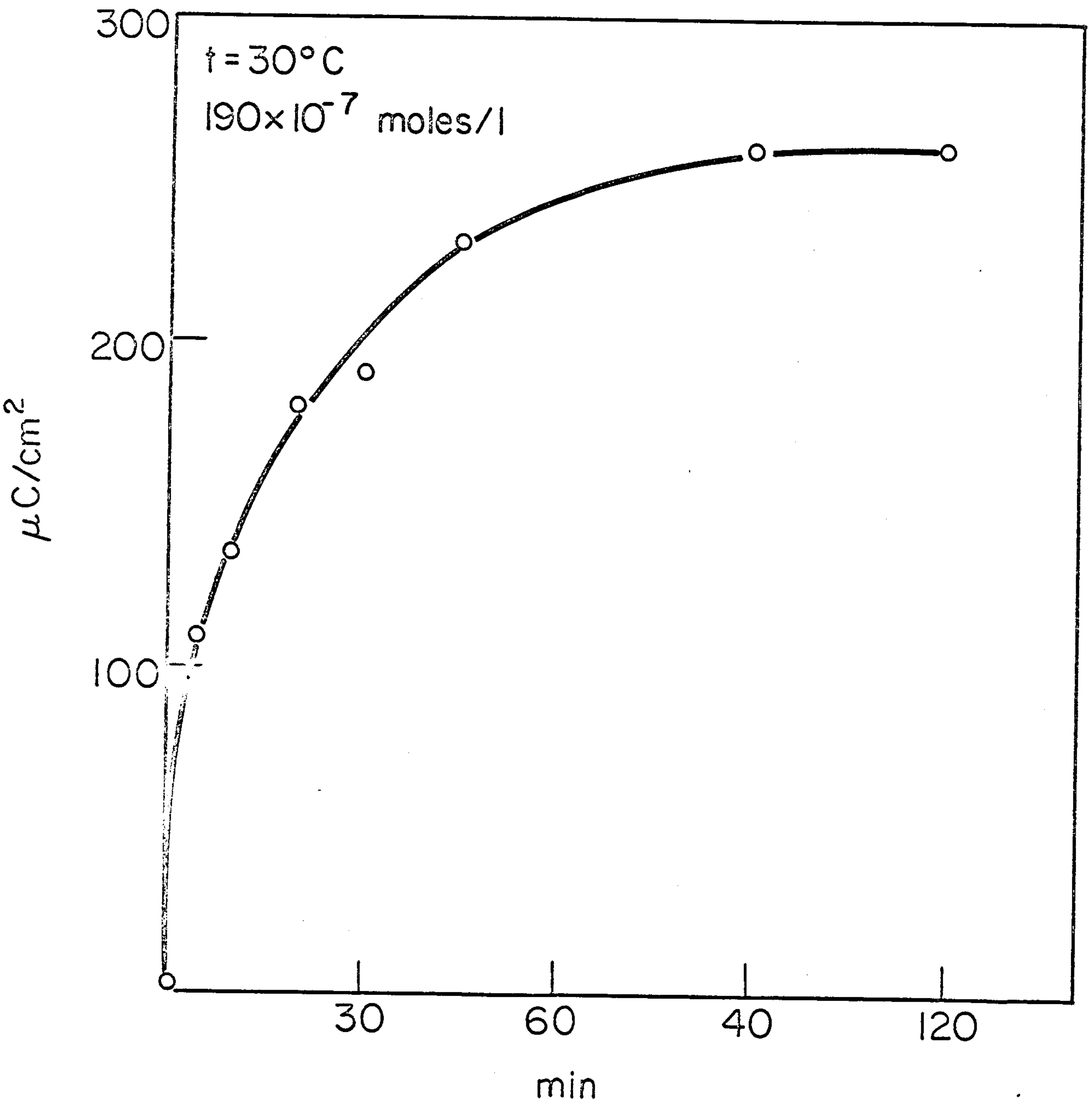


FIG. 2

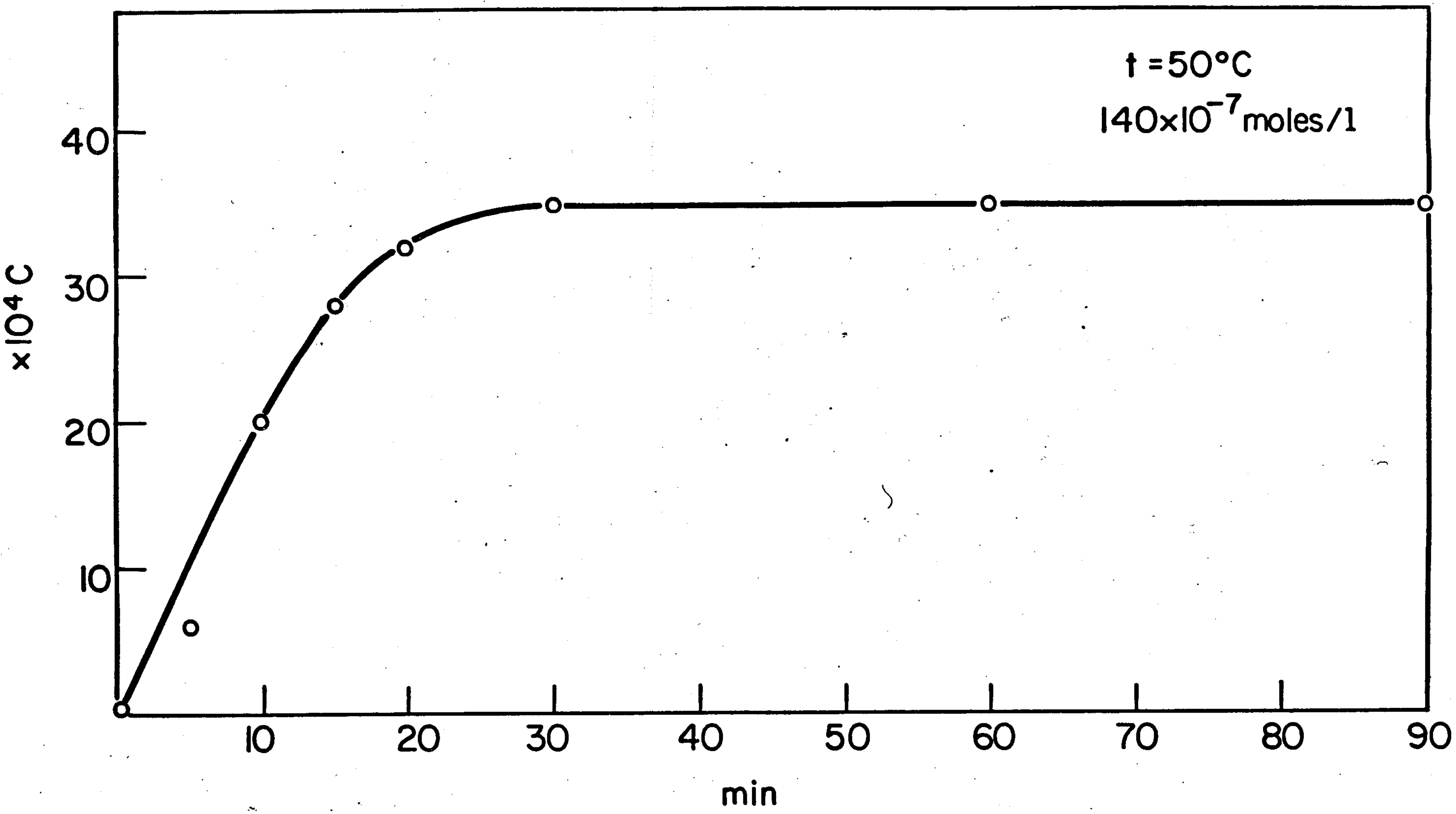


FIG. 3

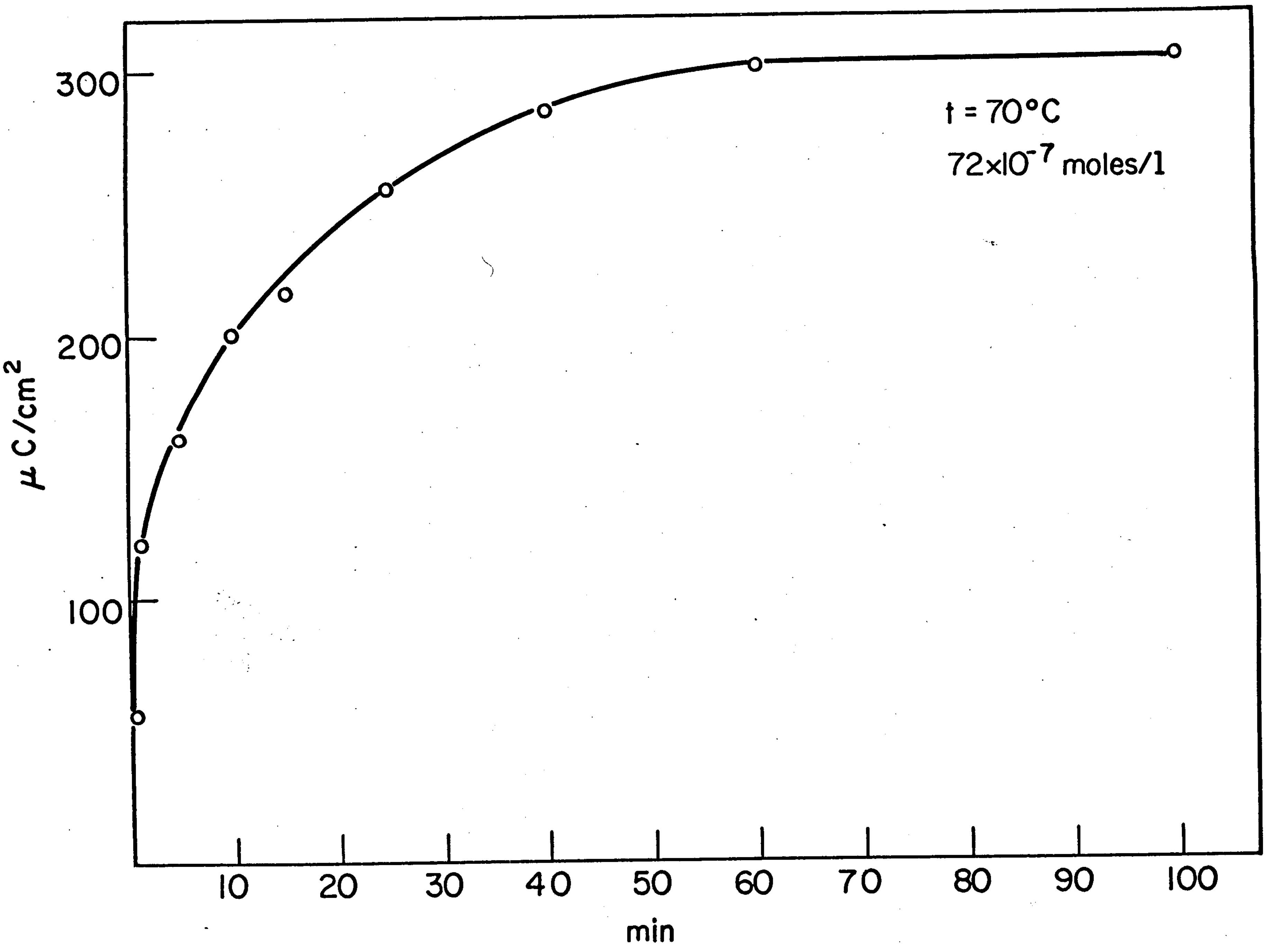
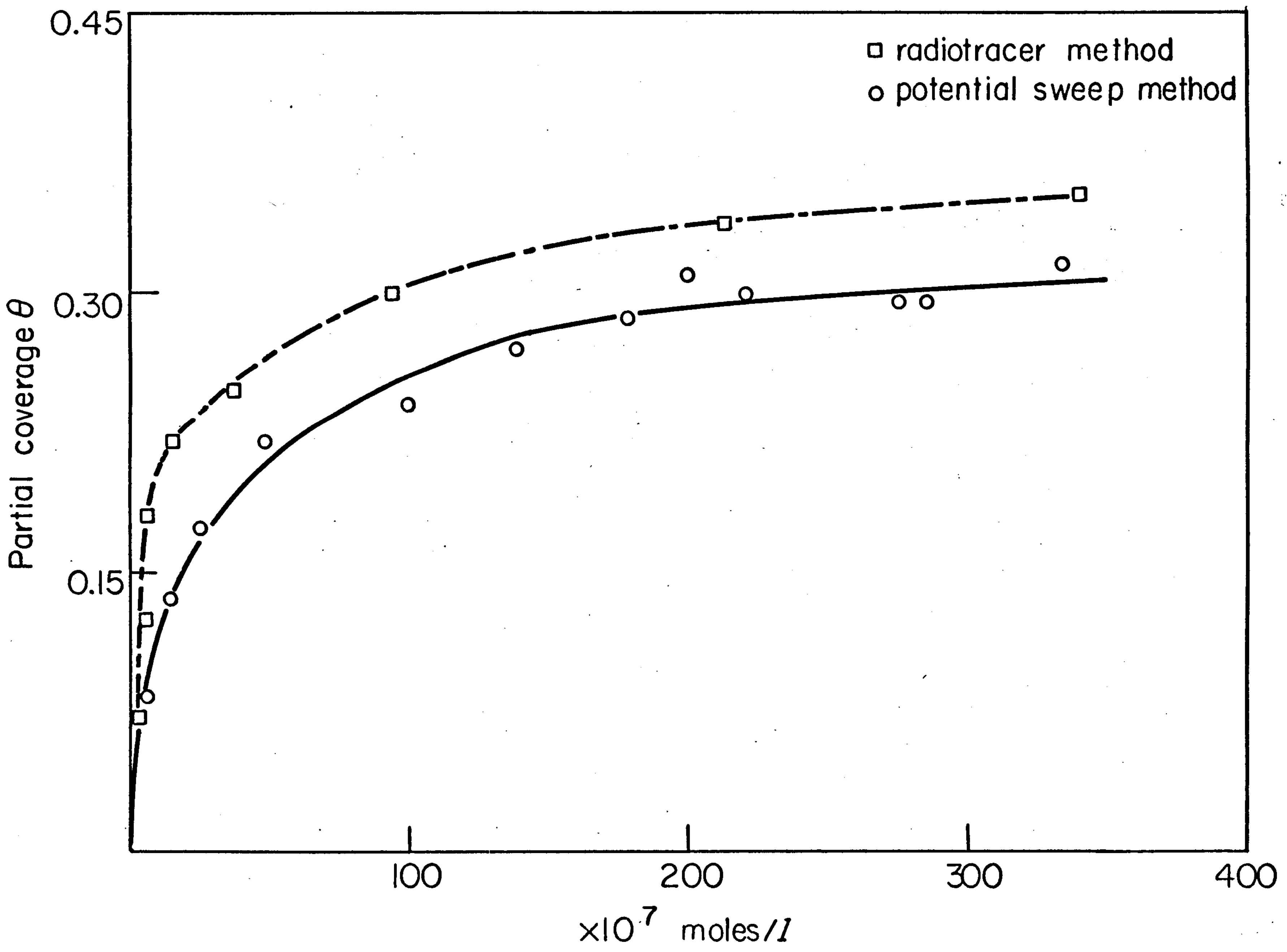

t = 70°C
72x10⁻⁷ moles/1
300
200
100
μC/cm²
10
20
30
40
50
60
70
80
90
100
min

FIG. 4



0.45
0.30
0.15
Partial coverage θ
□ radiotracer method
○ potential sweep method
100
200
300
400
×10⁻⁷ moles/l

FIG. 5

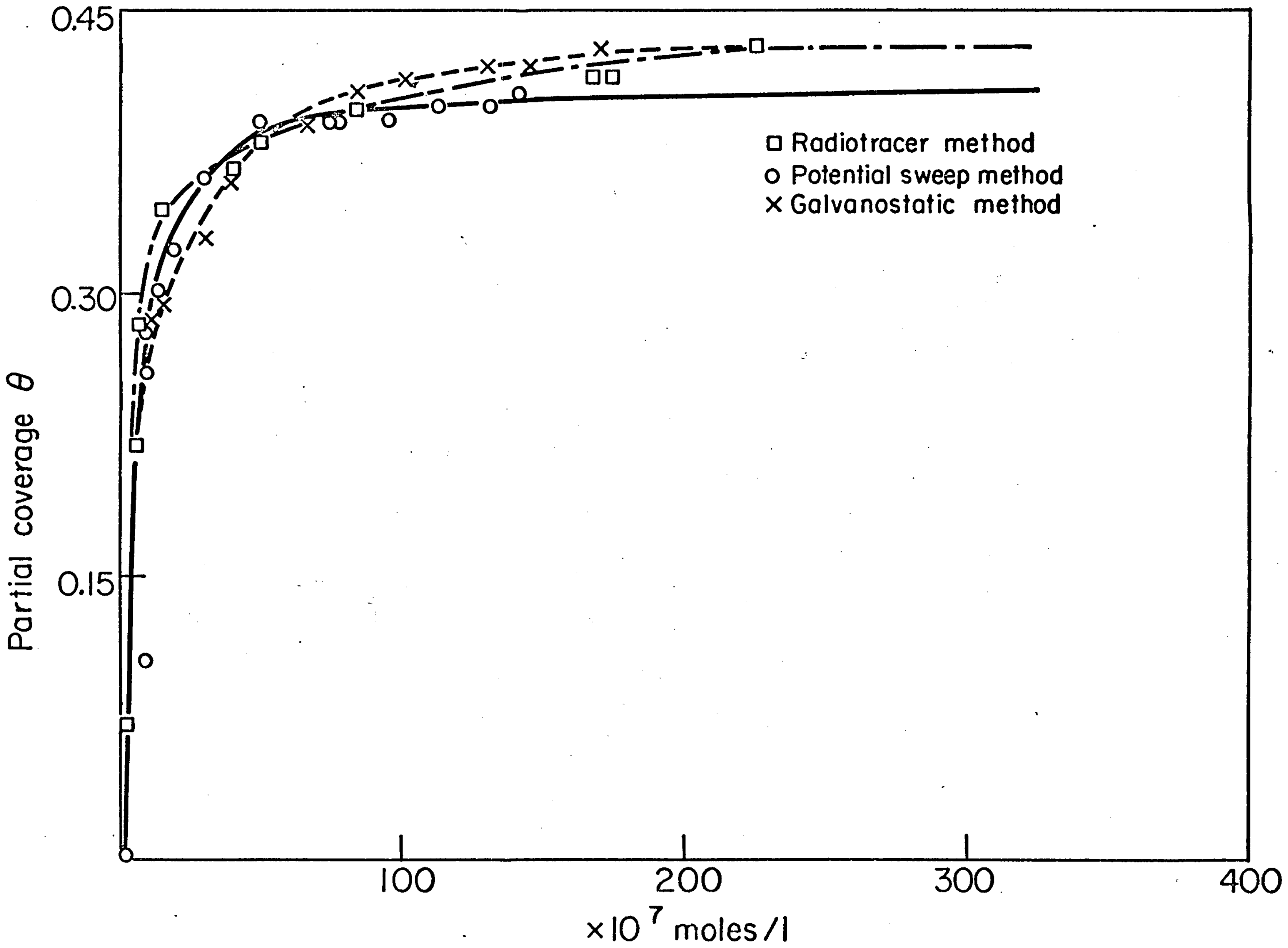

0.45
0.30
0.15
Partial coverage θ
100
200
300
400
×10 7 moles/l
□ Radiotracer method
○ Potential sweep method
× Galvanostatic method

FIG. 6

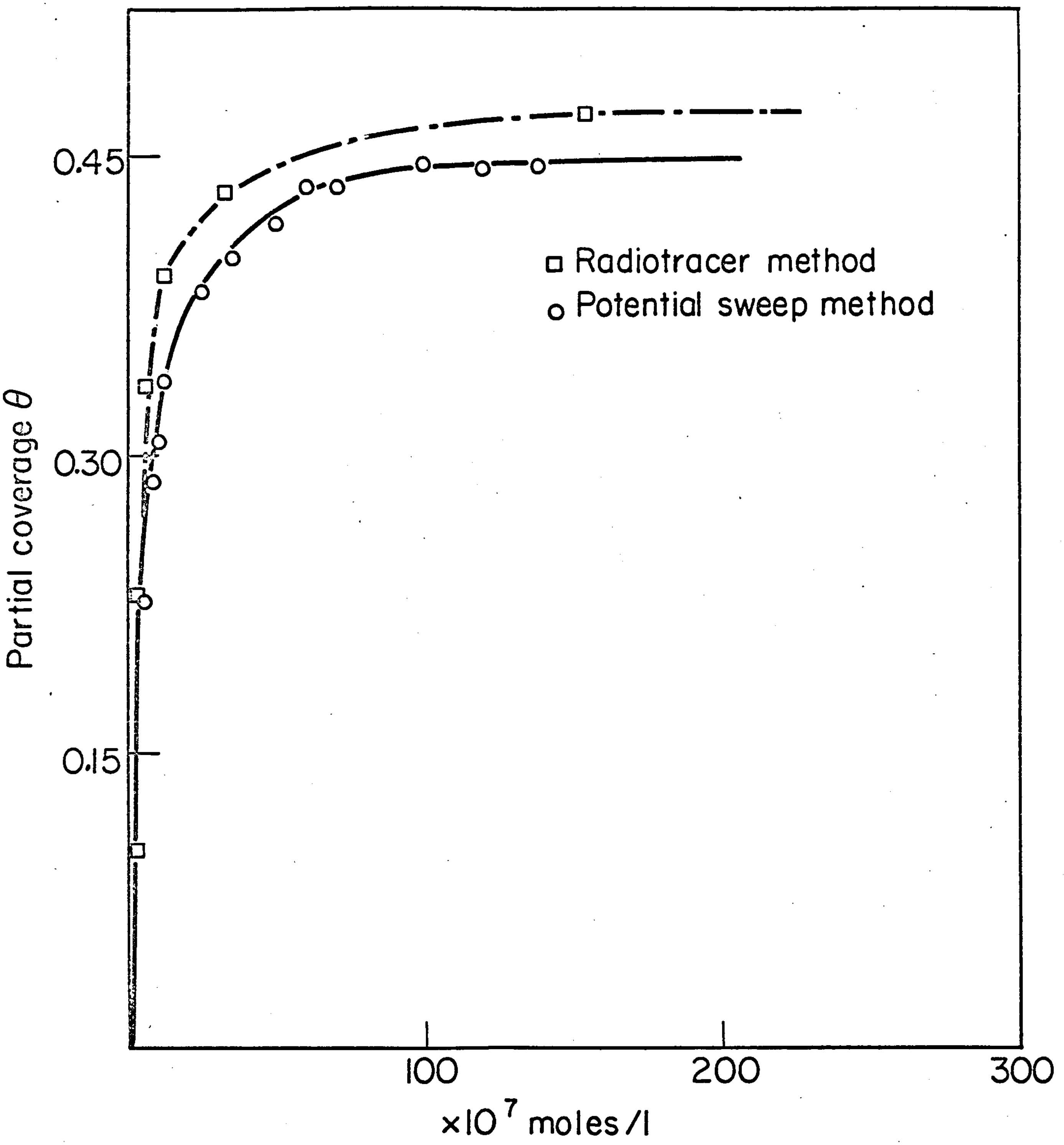

□ Radiotracer method
○ Potential sweep method
Partial coverage θ
0.45
0.30
0.15
100
200
300
×10⁷ moles/l

FIG.7

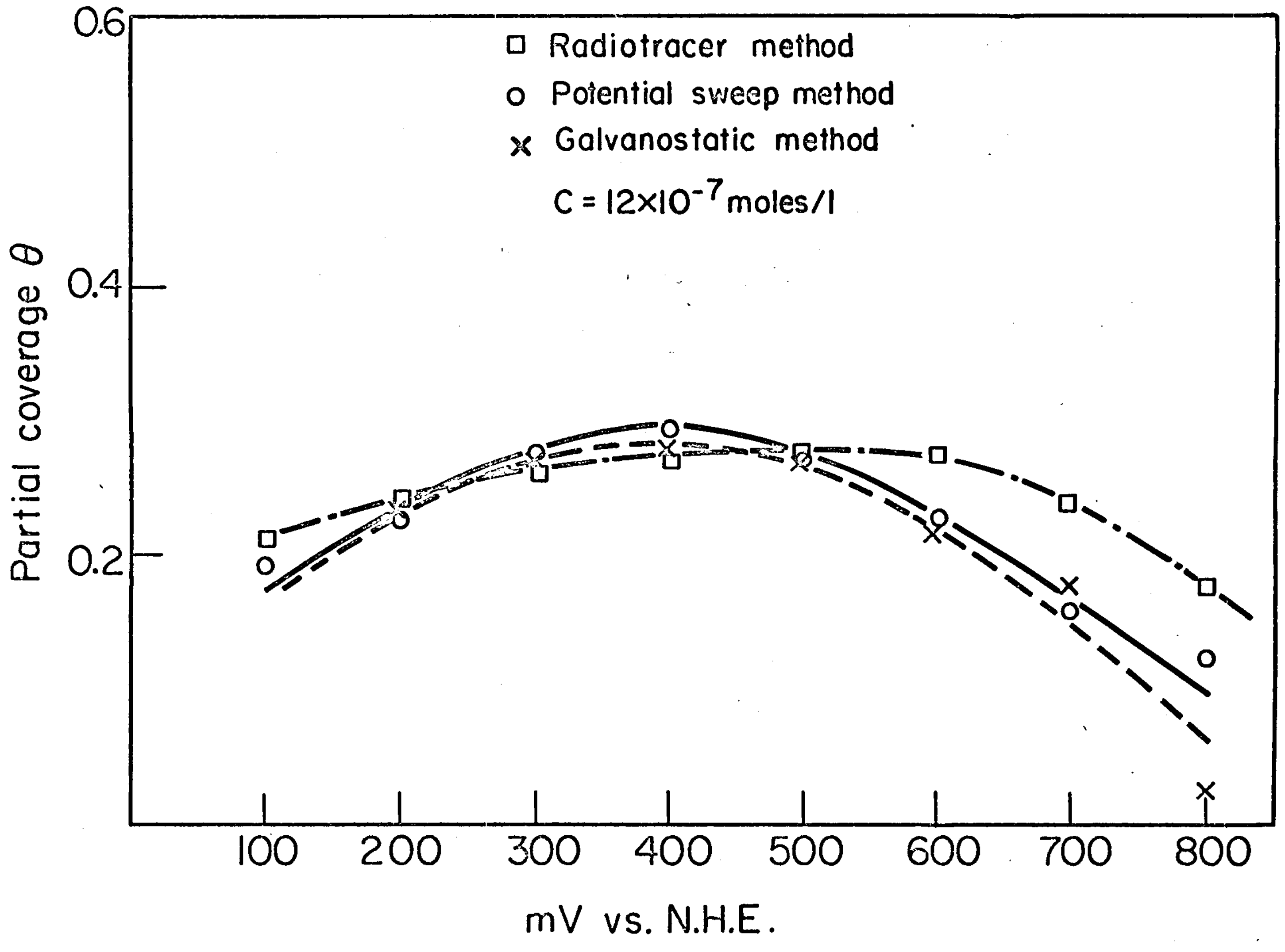
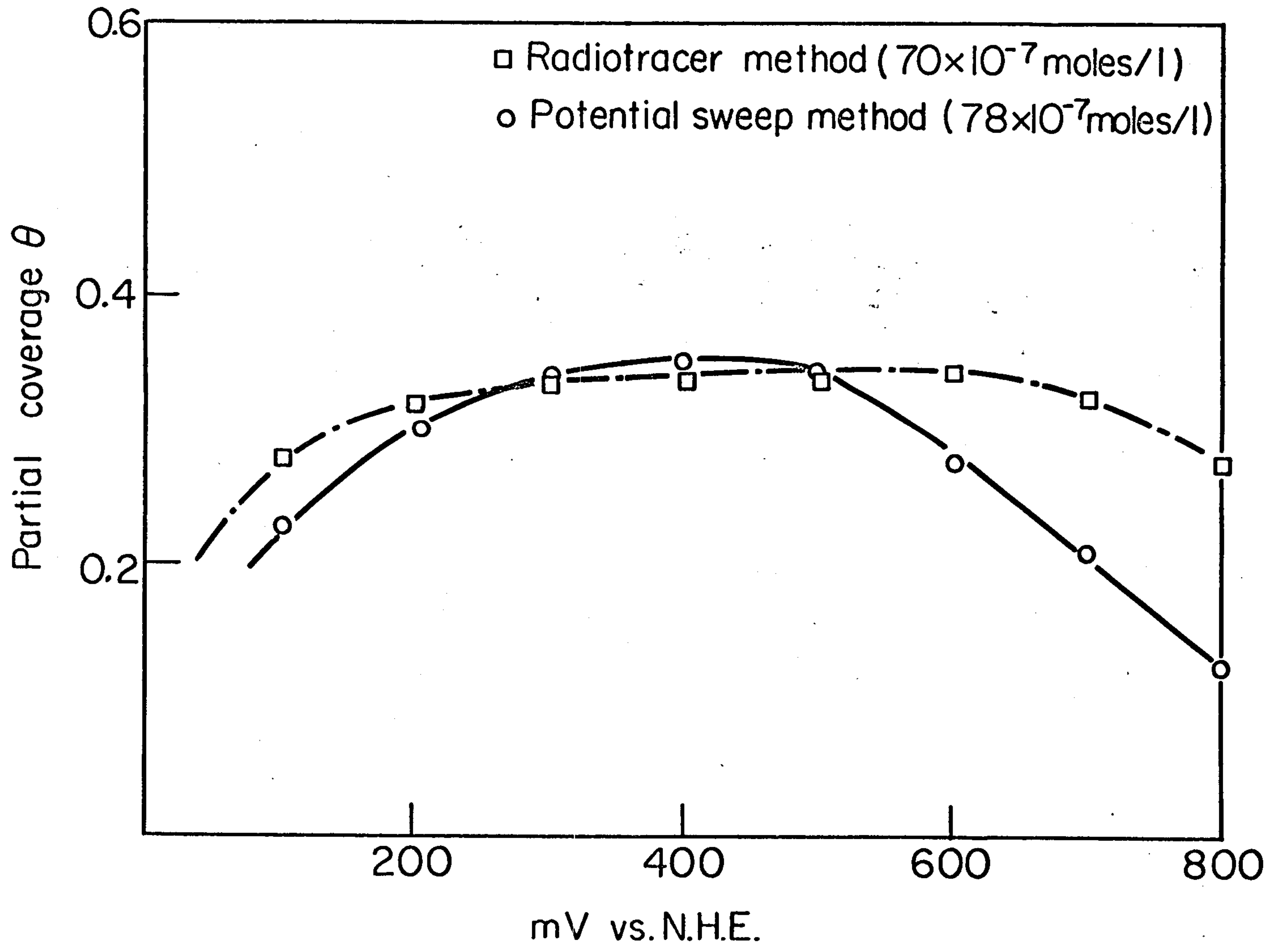

□ Radiotracer method
○ Potential sweep method
× Galvanostatic method
C = 12×10⁻⁷ moles/l
Partial coverage θ
0.6
0.4
0.2
100
200
300
400
500
600
700
800
mV vs. N.H.E.

FIG. 8



□ Radiotracer method (70×10^{-7} moles/l)
○ Potential sweep method (78×10^{-7} moles/l)
Partial coverage θ
0.6
0.4
0.2
200
400
600
800
mV vs. N.H.E.

FIG. 9

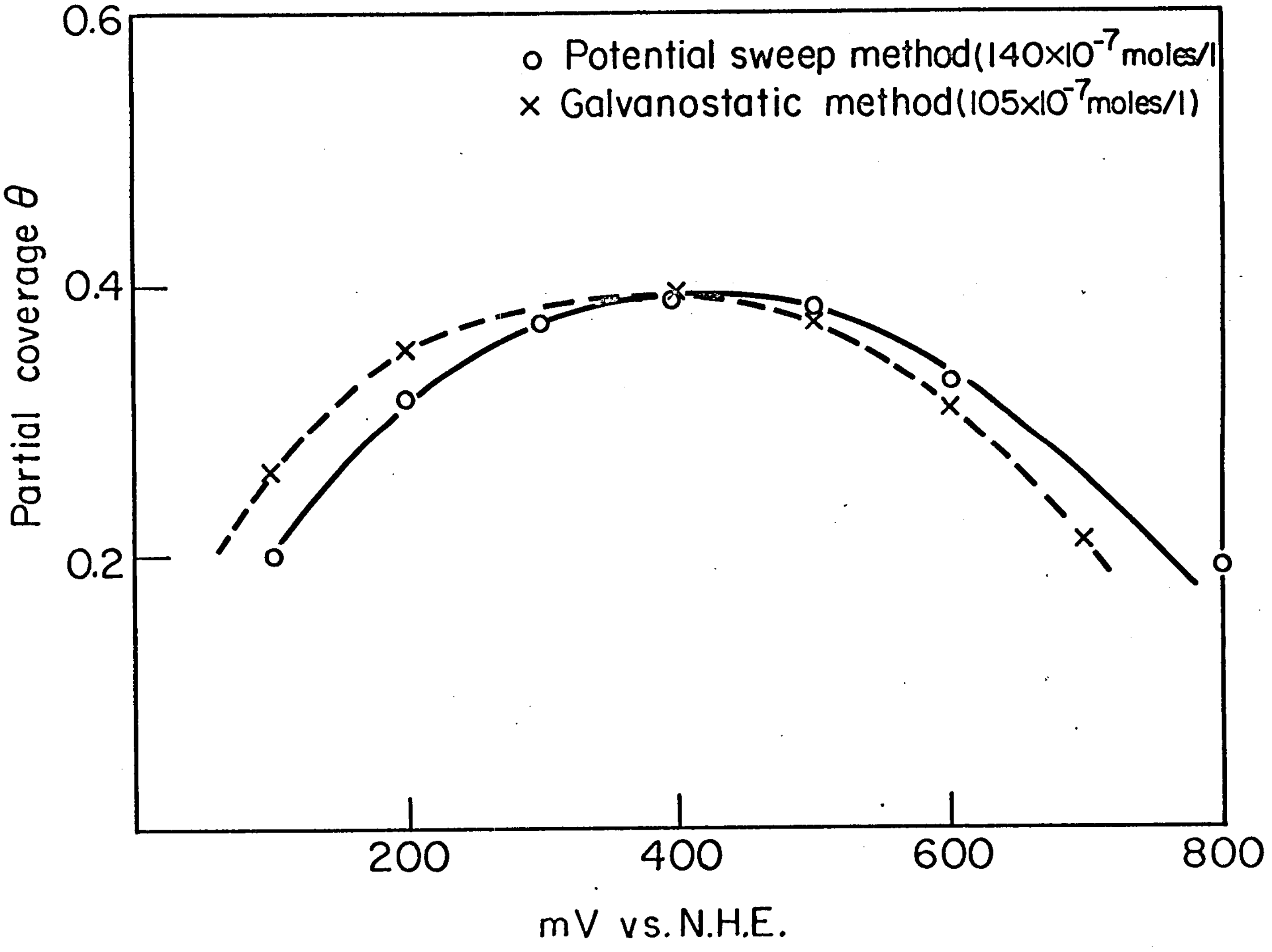

0.6
0.4
0.2
Partial coverage θ
○ Potential sweep method(140×10⁻⁷ moles/l
× Galvanostatic method(105×10⁻⁷ moles/l)
200
400
600
800
mV vs. N.H.E.

FIG. 10

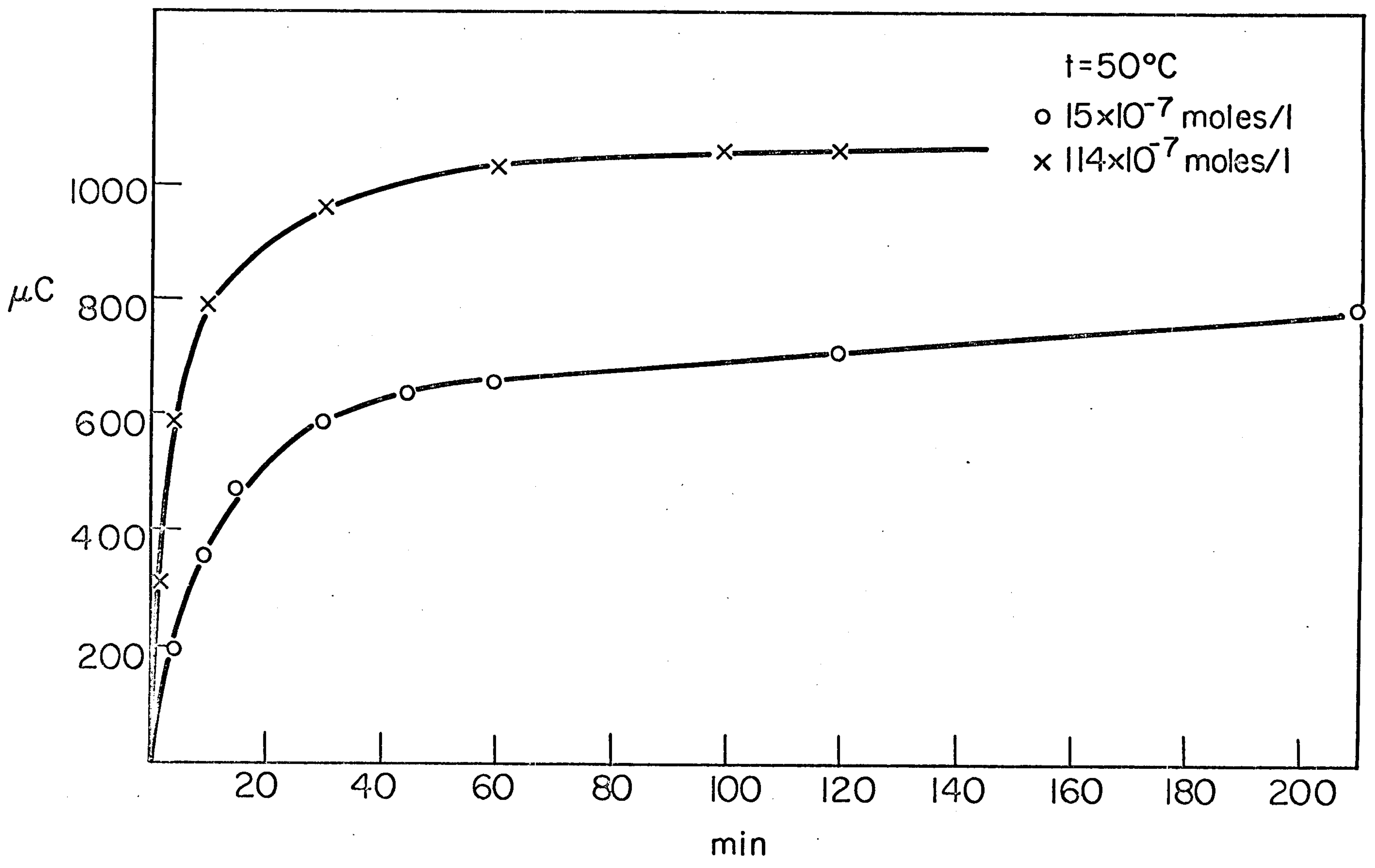

t=50°C
○ 15×10⁻⁷ moles/l
× 114×10⁻⁷ moles/l
μC
1000
800
600
400
200
20
40
60
80
100
120
140
160
180
200
min

FIG. 11

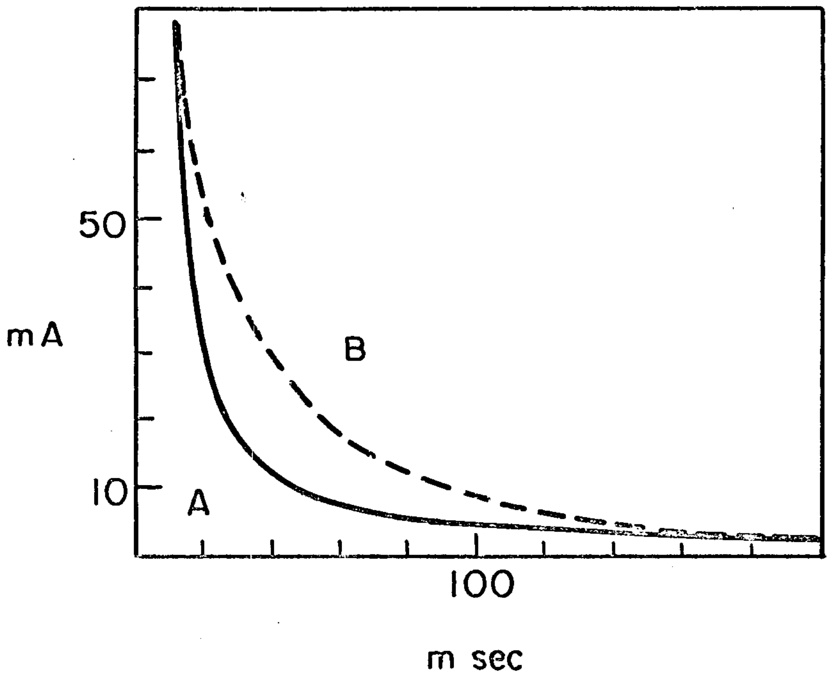


FIG.12

SECTION V. ELECTRODE KINETIC ASPECTS OF ENERGY CONVERSION

The book with Dr. Srinivasan (MacGraw-Hill) continues to be written. It is between the 2nd and the 3rd draft. All chapters have now been sent to at least 2 referees per chapter and their comments taken into account in revisions made throughout the book. The time spent on the book at present is:

S. Srinivasan: 25 hours/week
J. O'M. Bockris*: 10 hours/week
Schedule: 3 chapters sent to publishers Feb. 1967
7 further chapters (i.e., rest of book) May 1st, 1967

*Alternative: 2 day weekend stretches of about 20 hours in discussion with Dr. Srinivasan.

SECTION VI. THEORY OF CHARGE TRANSFER

Mr. J. Diggle, who is just completing the research degree of the Royal Institute of Chemistry, is delayed in arrival, due to thesis writing. He will work on the charge transfer problem in solution when he arrives.

SECTION VII. INTRODUCTION TO ELECTROCHEMISTRY

The third draft is arriving steadily from Dr. Reddy. 5 out of 10 chapters have been received and represent reworkings of the 2nd draft which was prepared in Bangalore by direct collaboration Bockris - Reddy in June and July, 1966.

Bockris then has to prepare the 4th darft, get it reviewed, take into account the criticism, and send to the publisher.

Time spent by Bockris: 10 hours/week.

Schedule: Reddy finishes sending 3rd draft by April 30, 1967.

Bockris finishes other tasks August 1st, 1967.

SECTION VIII. PUBLICATIONS UNDER GRANT NsG-325

1. Forces involved in the Specific Adsorption of Ions on metals from aqueous solution, J. O'M. Bockris and T. Anderson, Electrochimica Acta, 9, 347 (1964).

2. Electrochemical Kinetics of Parallel Reactions, E. Gileadi and S. Srinivasan, J. of Electroanal. Chem., 7 (1964) 452-457.

3. Electrocatalysis, J. O'M. Bockris and H. Wroblowa, J. Electroanal. Chem., 7 (1964) 428-451.

4. Basis of possible continuous self activation in an electrochemical energy converter, J. O'M. Bockris, B. J. Piersma, E. Gileadi and B. D. Cahan, J. Electroanal. Chem., 7 (1964) 487-490.

5. Ellipsometry in Electrochemical Studies, A. K. N. Reddy and J. O'M. Bockris, U. S. Dept. Comm. Natl. Bureau of Standards, Misc. Publication 256, Sept. 15, 1964, 229-244.

6. Ellipsometric Study of oxygen-containing films on Platinum electrodes. A. K. N. Reddy, M. Genshaw and J. O'M. Bockris, J. Electroanal. Chem., 8 (1964) 406-407.

7. Ellipsometric Determination of the Film Thickness and Conductivity during the Passivation Process on Nickel, A. K. N. Reddy, M. G. B. Rao and J. O'M. Bockris, J. Chem. Phys., 42, 6, 2246-2248, 15 March 1965.

8. A Brief Outline of Electrocatalysis, J. O'M. Bockris and S. Srinivasan, 19th Annual Proceedings Power Sources Conference, May 1965.

9. Proton Transfer across Double Layers, J. O'M. Bockris, S. Srinivasan, and D. B. Matthews, Disc. Faraday Soc., 1965, No. 39.

10. Fundamental studies of the mechanism of porous electrodes, J. O'M. Bockris, L. Nanis and B. D. Cahan, J. Electroanal. Chem., 9 (1965) 474-476.

11. The Potential of Zero Charge on Pt and its pH Dependence, E. Gileadi, S. D. Argade and J. O'M. Bockris, J. Phys. Chem., 1966, Vol. 70, 2044.

12. The Potential Sweep Method: A Theoretical Analysis, S. Srinivasan and E. Gileadi, Electrochim. Acta, 11, (1966) 321-335.

13. Electrode Kinetic Aspects of Electrochemical Energy Conversion, J. O'M. Bockris and S. Srinivasan, J. Electroanal. Chem., 11, (1966) 350-389.

14. An Ellipsometric Determination of the Mechanism of Passivity of Nickel, J. O'M. Bockris, A. K. N. Reddy and B. Rao, J. Electrochem. Soc., 113, 11, (1966) 1133-1144.

The following are in course of publication

15. An ellipsometric study of oxide films on platinum in acid solutions, J. O'M. Bockris, A. K. N. Reddy and M. Genshaw.

16. Electrocatalysis in Ethylene Oxidation, A. Kuhn, H. Wroblowa and J. O'M. Bockris.

17. Electrosorption, edited by E. Gileadi, Plenum Press.

18. Theory of Porous Gas Diffusion Electrodes Using the Thin Film Model, S. Srinivasan and H. D. Hurwitz, Electrochem. Acta.

19. Chapter on Electrochemical Techniques in Fuel Cell Research, to be published in Handbook on Fuel Cell Technology, edited by C. Berger, Prentice Hall.

20. Potential of Zero Charge, S. D. Argade and E. Gileadi, in Electrosorption. Ed. by E. Gileadi, Plenum Press (1967).

21. On a Comparison of Techniques for Measuring the Adsorption of Organic Materials on Electrodic Catalysts, L. Duic and J. O'M. Bockris.

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