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Catalytic Processes on Platinized Platinum Electrodes

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FOREWORD

This report covers a portion of the investigations
in progress at Baylor University, Waco, Texas, under
Contract No. AF 19(604)-8414. This research project was
administered under the direction of Dr. Kenneth Quinlan
of the Geophysics Research Directorate of the Air Force
Cambridge Research Laboratories of the Office of Aerospace
Research of the United States Air Force at Bedford,
Massachusetts.

ABSTRACT

Studies were made of the catalytic decomposition of formaldehyde and hydrogen peroxide and the catalytic hydrogenation of quinone on platinized platinum. The area available for catalysis was measured by the ability of the platinum to adsorb hydrogen as measured by a coulometric procedure.

It was found that in two normal sulfuric acid the rate of decomposition of hydrogen peroxide was first order with respect to hydrogen peroxide and first order with respect to the ability of the metal to adsorb hydrogen in the second surface form (the one oxidized at the more anodic potential). In both two normal sulfuric acid and two normal sodium hydroxide the rate of decomposition of formaldehyde was first order with respect to formaldehyde and first order with respect to the ability of the metal to adsorb hydrogen in the second surface form.

In the two normal sulfuric acid the hydrogenation of quinone was found to be zero order with respect to the quinone and first order with respect to the total ability of the metal to adsorb hydrogen.

It was also indicated that in basic solutions there is a rapid equilibrium between the second form of surface hydrogen and the absorbed hydrogen.

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I. Objectives and Introduction

As part of the studies of hydrogen adsorption on platinum and of the electrolytic oxidation of organic compounds on platinum, a study was made of the ability of the platinum electrodes to act as a catalyst. The first portion of this report is on work done by Mr. Donald H. McClelland on the catalytic decomposition of hydrogen peroxide and the catalytic hydrogenation of quinone. (We wish to thank Phillips Petroleum Company for the Fellowship that Mr. McClelland had while working on the hydrogen peroxide problem.) The last portion is a study carried out by Nellie Friel Franklin on the catalytic decomposition of formaldehyde.

II. Hydrogen Peroxide Decomposition and Hydrogenation of p-Benzoquinone

A. Historical Introduction

In the year 1775, Priestly and Cavendish reported that nitric and nitrous acids were formed in moist air during an electrical discharge.[1] Since that time electrochemistry has developed into a tool which is used extensively in other fields of chemistry. The historical development of electrochemical methods in analytical chemistry is reviewed by Delahay[2] and Lingane.[3] The development of the general field of electrochemistry is discussed in some detail by Korthum[4] and Cooke.[5]

Polarization studies are contributing most of the information now being reported in the field of electrochemistry in the journals. Polarization, as it is used in this dissertation, is a potential exhibited by a

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[1] G. Kortum and J. O'M. Bockris, Textbook of Electrochemistry, Elseview, New York, 1951, p. I.

[2] P. Delahay and C. N. Reilley, New Instrumental Methods in Electrochemistry, Interscience Publishers, Inc., New York, 1954.

[3] J. J. Lingane, Electroanalytical Chemistry, 2nd ed., Interscience Publishers, Inc., New York, 1958.

[4] G. Kortum and J. O'M. Bockris, op. cit.

[5] S. L. Cooke, Jr., ''A Voltammetric Study of the Hydrogen Electrode'', (Ph.D. dissertation, Dept. of Chemistry, Baylor University, 1957).

half-cell, while a current is passing, other than the normal equilibrium half-cell potential.[6] Polarization methods involve the simultaneous determination of the potential, and the current passing through the half-cell. The experimental methods for obtaining these current-voltage relationships fall generally into four groups, and are listed as follows: constant current, constant potential, A. C. and voltammetric methods. There are a number of review articles and books dealing with instrumentation and the theory involved in these methods.[7-25]

CONSTANT CURRENT METHODS.

Polarization of an electrode can be effected by the application of a constant current, the resulting voltage of the half-cell is easily obtained by classical methods.

[6]S. Glasstone, An Introduction to Electrochemistry, D. Van Nostrand Co., Inc., Toronto, New York, London, p. 435.

[7]Faraday Soc. Discussions, 1, (1947).

[8]J. O'M. Bockris, ''Annual Review of Physical Chemistry'', Vol. 5, p. 477, Annual Reviews, Inc., Stanford, Calif., 1954.

[9]D. C. Grahame, Ibid, 6, p. 337, 1955.

[10]P. Delahay, Ibid, 9, p. 229, 1958.

[11]G. Kortum and J. O'M. Bockris, op. cit.

[12]J. J. Lingane, op. cit.

[13]J. A. V. Butler, Electrical Phenomena at Interfaces, The MacMillan Co., New York, 1951, p. 167.

However, because of the ohmic potential drop across the solution, it is sometimes better to interrupt the current and then determine the potential of the electrode. (26-28)

The polarization voltage decays quite rapidly so it is necessary to determine the polarization potential very rapidly. The rate of decay of the polarization potential has been investigated.[29]

[14]I. M. Kolthoff and J. J. Lingane, "Polarography" Vol. I & II, Interscience Publishers, Inc., New York, London, 1952.

[15]J. O'M Bockris and B. E. Conway, Modern Aspects of Electrochemistry, Chapt. 4, Academic Press Inc., Publishers, New York, 1954.

[16]H. Gericher and R. P. Tischer, A. Elektrochemi., 58, 8190827 (1954).

[17]P. Delahay, J. Chim. Phys., 54, 369-77 (1957).

[18]A. N. Frumkin, Izvest. Akad. Nauk., SSSR, Otdel. Khim. Nauk, 1429-38 (1957).

[19]P. Delahay, Record Chem. Prog., 19, 83-105 (1958).

[20]H. R. Thirsk, Ann. Repts. Prog. Chem., 14, 17-29 (1957).

[21]M. Breiter, M. Kleinermann, and P. Delahay, J. Am. Chem. Soc., 80, 5111-17 (1958).

[22]J. Llopis and F. Colon, Proc. Intern. Comm. Electrochem., Thermodynam. and Kinet., 8th Meeting, 1958, 414-27.

[23]M. Fleischmann and K. B. Oldham, Ann. Repts. on Prog. Chem. (Chem. Soc. London), 55, 67-79 (1958).

[24]A. N. Frumkin, J. Electrochem. Soc., 107, 461-472 (1960).

[25]M. T. Kelly, W. C. Jones, and D. J. Fisher, Anal. Chem., 31, 1475-85 (1959).

Small current densities passing through the half-cell result in a constant voltage being maintained. Information is usually obtained from so-called ''Tafel Plots'' which are voltage vs. log current density. Tafel equations have been theoretically derived for various possible rate determining reactions.[30-32] The apparent rate determining step in the electrode reaction can be determined by comparison of the experimentally obtained Tafel Plot with the derived equations.

Polarization of the electrode by a large constant current density usually leads to concentration polarization in the electrode system. A charging curve is obtained from a plot of potential vs. time (or total amount of charge passed). In analytical chemistry, this curve is the well known chronopotentiometric

[26] B. D. Cahan and P. Ruetschi, J. Electrochem. Soc., 106, 543-7 (1959).

[27] W. E. Richeson and M. Eisenberg, J. Electrochem. Soc., 107, 642-7 (1960).

[28] S. Schuldiner, Naval Research Laboratory Report, 5091, (34 pp. and figs.), (March 17, 1958).

[29] B. D. Cahan and P. Ruetschi, op. cit.

[30] G. Kortum and J. O'M. Bockris, op. cit.

[31] J. O'M. Bockris and B. E. Conway, op. cit.

[32] J. A. V. Butler, op. cit.

[33] J. J. Lingane, Chap. 22, op. cit.

[34] M. A. Devanathen, J. O'M. Bockris and W. Mehl, J. Electroanalytical Chemistry, 1, 143-60 (1959-60).

curve,[33] which arises from concentration polarization caused by diffusion limited conditions. This method has also been used to study surface coverage of various metals by oxides, and by gases adsorbed from solution.[34-38]

CONSTANT POTENTIAL METHODS.

Polarization may also be obtained by the application of a constant potential. This method is just the reverse of the constant current type of study. If the electrode reaction is sufficiently fast, and the potential not too far from the normal equilibrium potential of the half-cell, the same current-voltage relationship is obtained, as was obtained using small constant current densities. However, if the current through the half-cell does not remain constant after the polarizing potential is applied, then information is gained from plots of current vs. the square root of time. This type of plot, yields exchange currents of electrode reactions. (39-41)

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[35]M. Breiter, C. A. Knorr, and V. Volkl, Z. Electrochemistry, 59, 681 (1955).

[36]J. A. V. Butler, chap. 9, op. cit.

[37]A. Hickling and G. G. Vrjosek, Trans. Faraday Soc., 57, 123-29 (1961).

[38]F. S. Feates, Trans. Faraday Soc., 56, 1671-9 (1960).

[39]H. Gerischer and W. Vielstich, A. Physik. Chem. (Frankfurt), 3, 16 (1955).

[40]Ibid, 4, 10 (1955).

A. C. METHODS.

A. C. bridge methods can be used to measure the capacitance of the double layer of the electrode surface directly.[42] It has been shown that it is possible to obtain values for the exchange currents of electrode processes from A. C. methods.[43-44] Even more information (45-47) has been obtained from the application of an A. C. potential superimposed upon a D. C. polarizing potential.

Not all of the A. C. methods make use of a sinusoidal wave. Breiter et. al.[48] have used a square current wave. Hickling and others[49-51] have used a square current wave, with both anodic and cathodic constant current. Schuldiner[52]

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[41]P. Delahay and C. N. Reilley, Chap. 4 & 5, op. cit.

[42]J. A. V. Butler, p. 48, op. cit.

[43]G. Kortum and J. O'M. Bockris, p. 416, op. cit.

[44]K. B. Oldham, J. Electrochem. Soc., 107, 761-72 (1960).

[45]R. Parsons, Trans. Faraday, Soc., 55, 999 (1959).

[46]K. Frank, C. A. Knorr, and M. Breiter, A. Electrochem., 63, 226-38 (1959).

[47]J. Lopis and F. Colon. C. A., 51, 161381 (1957).

[48]M. Breiter, K. Hoffmann, and C. A. Knorr, Z. Electrochem., 61, 1168 (1957).

[49]H. A. Laitinen and C. G. Enke, J. Electrochem. Soc., 107, 773-81 (1960).

[50]J. Giner, J. Elektrochem., 63, 386-97 P1959).

[51]A. Hickling and G. G. Vrjosek, op. cit.

[52]C. H. Presbrey, Jr., and S. Schuldinier, J. Electrochem. Soc., 108, 985-995 (1961).

has developed a method which makes use of a constant current pulse, where the height of the pulse and the duration of the pulse are controllable. With these methods it is possible to produce charging curves similar to those obtained by normal constant current methods.

Square wave voltages[53] are also used, the information obtained being similar to that obtained from constant potential methods. A method using a triangular voltage function has been used with success.[54-55]

VOLTAMMETRIC METHODS.

Instead of keeping the polarizing potential applied to an electrode constant, one can also apply a voltage which changes linearly as a function of time. Usually the voltage is increased slowly, so that the system is able to maintain equilibrium at all times. The current flowing through the cell can be determined by means of an automatic recorder, which gives current vs. time, and if the voltage is a linear function of time it also gives current vs. voltage. This method is the one normally used in polarographic analysis. This plot results

[53]J. J. McMullen and N. Hackerman, J. Electrochem. Soc., 106, 341-6 (1959).

[54]F. G. Will and C. A. Knorr, Z. Electrochem. Soc., 64, 258-69 (1960).

[55]M. Breiter and B. Kennel, ibid, 64, 1180-7 (1960).

in qualitative and quantitative information about the reacting species at the electrode surface.[56] The polarographic method has produced a surprising variety of information about the mechanisms in electrode reactions.

In A. C. polarography a sinusoidal voltage is employed rather than the saw-tooth function because of the instrumentation involved with the latter. This method has been very helpful in investigation of irreversible processes.[57]

One modification of the polarographic method in analytical chemistry is one which extends the range of the analysis to the 10^{-6} to 10^{-9} gr/25ml. region. This method was developed originally by Zbinden[58] and Zakhar'ewskit,[59] and improved by Rogers et al.[60] The underlying theory has been further extended by Rogers,[61] Shain,[62] and Nicholson.[63-64] In order to determine the

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[56] I. M. Kolthoff and J. J. Lingane, op. cit.

[57] Ibid.

[58] C. Abinden, Bull. Soc. Chim. Biol., 13, 35 P1931).

[59] M. S. Zakhar'ewskit, Khim. Referat. Zhur., 2, 84 (1939).

[60] S. S. Lord, R. C. O'Neill, and L. B. Rogers, Anal., Chem., 24, 84 (1939).

[61] K. W. Gardiner and L. B. Rogers, Ibid, 25, 1393 (1953).

[62] I. Shain and R. D. DeMars, Anal. Chem., 29, 1825-7 (1957).

[63] M. M. Nicholson, J. Am. Chem. Soc., 79, 7 (1957).

[64] M. M. Nicholson, Anal. Chem., 32, 1058-62 (1960).

amount of a reducible metal in the solution, the ions are reduced to the metal at the surface of a mercury or mercury coated platinum electrode, the metals then being polarographically oxidized on the electrode. A graphical integration of the resulting plot gives the number of coulombs necessary for the oxidation process, hence the total amount of metal in the solution.

Franklin et al.[65-66] have shown that it is also possible to determine the amount of hydrogen associated with a platinized- platinum electrode in a solution saturated with hydrogen. Further investigation has shown that this method is applicable to the determination of hydrogen on other metal surfaces.[67-68]

Cooke[68a] in his study of the case of hydrogen association with platinized platinum, however, found it not necessary to prepolarize the electrode since the platinum surface is a very good catalyst for the reaction;

$$H_2(soln.) \rightleftharpoons 2H_{(ads.)}$$
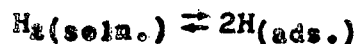
[65]S. L. Cooke, Jr., and T. C. Franklin, J. Electrochem. Soc., 107, 556-60 (1960).

[66]R. D. Sothern and T. C. Franklin, J. Phys. Chem., 58, 951 (1954).

[67]F. A. Matsuda and T. C. Franklin, Paper Presented at Electrochemistry Society Meeting, Fall, 1961.

[68]J. Goodwin, ''The Mechanism of the Action of Organic Brightening Agents in Electroplating Process,'' (Ph.D. dissertation, Dept. of Chemistry, Baylor University, 1956).

[68a]S. L. Cooke, Jr. and T. C. Franklin, op.cit.

where $H_{(ads.)}$ is hydrogen adsorbed on the platinum surface and $H_{2(soln)}$ is hydrogen in solution. In case of the platinized-platinum electrode the polarographic oxidation curve according to Cooke[68b] is shown in Figure 1.

The current-time (voltage) curve, exhibits three points of maximal current before the process of oxidation of the platinum starts thus indicating that hydrogen is bound to the platinum in three different manners. If the oxidation process had been continued, two other peaks would have occurred due to the formation of surface platinum oxides. To determine the amount of hydrogen being oxidized, the residual current (the current being used in processes other than the actual oxidation of the hydrogen itself) must be subtracted. Once the residual current has been determined in some manner, the amount of current necessary to oxidize the hydrogen can be determined by graphical integration if the recorder chart speed is known.

The exact reasons why there are three peaks in the current-voltage curves have not been entirely explained. The peaks correspond to different bonding energies between the hydrogen and the platinum. The first two peaks (I and II) have been shown to be due to surface related forms of hydrogen; the third (III) peak is caused by hydrogen absorbed in the bulk of the platinum.[69]

[68b] S. L. Cooke, Jr. and T. C. Franklin, op. cit.
[69] Ibid.

Figure 1   A Typical Current-Voltage Curve for the Oxidation of Hydrogen Sorbed on Platinized Platinum in 2 Normal Sulfuric Acid
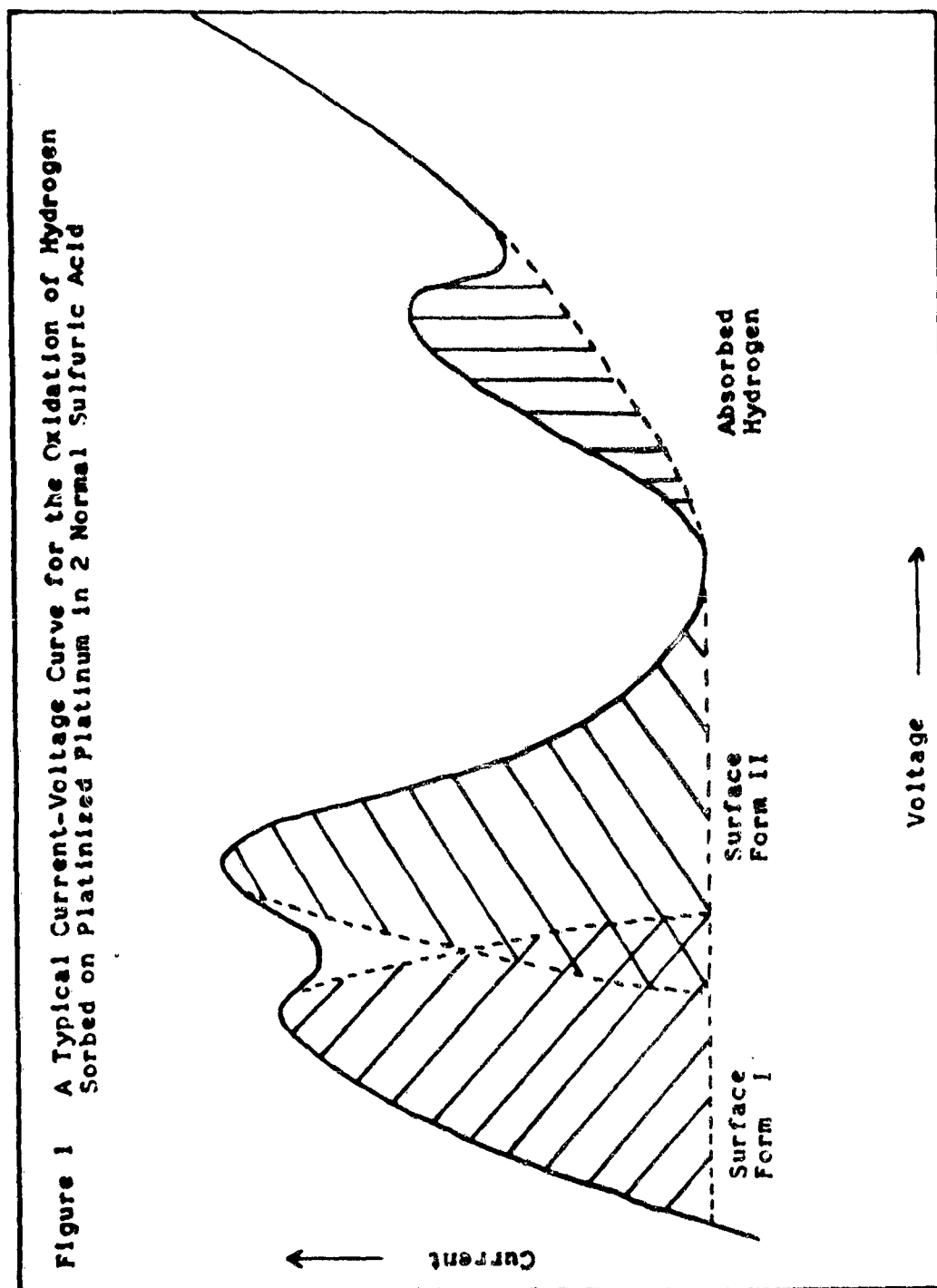
Other investigators have found that hydrogen is adsorbed on the surface of platinum in more than one form; Eucken and Weblus,[70] Wicke and Weblus,[71] and Breiter[72] found two forms using A. C. methods with a superimposed D. C. polarizing voltage. Breiter[73-74] and Knorr[75] also found two forms of hydrogen using a triangular voltage function applied to the electrode system. Schuldiner[76] has found it necessary to postulate two surface forms of hydrogen on platinum in his investigation of hydrogen overvoltage. By a method of very slow anodic polarization with constant current, Frumkin and

[70]A. Eucken and B. Weblus, Z. Elektrochem., 55, 114 1951.

[71]E. Wicke and B. Weblus, Ibid, 56, 169 (1952).

[72]M. Breiter, H. Kammermaier, and C. A. Knorr, Z. Elektrochem., 60, 37-47 (1956).

[73]W. Bold and M. Breiter, Ibid, 64, 897 (1960).

[74]B. Kennel and M. Breiter, Ibid, 64, 1180 (1960).

[75]F. G. Will and C. A. Knorr, Ibid., 64, 270 (1960).

[76]C. H. Presbrey and S. Schuldiner, op. cit.

[77]B. V. Erschler and A. N. Frumkin, Trans. Faraday Soc., 35, 464 (1939).

[78]P. Dohn, B. V. Erschler and A. N. Frumkin, Acta Physiocochem., U. R. SS, 13, 793, (1940).

[79]A. Frumkin and E. E. Aikasyan, Doklady Akad. Nauk., 100, 35 (1955).

[80]S. E. S. El, Wakked and S. H. Ermara, J. Chem. Soc., 461 (1952).

coworkers,[77-79] and Emara et al.[80] found that there are

at least two forms of hydrogen. Infra red investigations

in the vapor phase of the system hydrogen-platinum[81] have

also indicated two surface forms of adsorbed hydrogen.

As yet, there is no clear cut explanation pertaining

to the actual differences between the two forms of hydrogen.

It is generally accepted that both peaks (I and II) are

actually adsorbed forms on the surface, however, this is

not fully accepted by all investigators. It is possible

that one form is adsorbed on bare platinum, and the other

form is hydrogen in solution adjacent to the electrode

surface.[82]

If both kinds of hydrogen are surface adsorbed forms

it is possible to conceive of several explanations.

Breiter[83] suggests that one form is adsorbed on bare

platinum, and the other form is hydrogen adsorbed on

some oxide of platinum. Kavtorodze[84] and Shurman[85]

suggests the possibility, that the forms are adsorbed

atomic and molecular hydrogen.[86]

[81] W. A. Pliskin and R. P. Eischens, Z. Phys. Chem., 24, 11-23 (1960).

[82] S. L. Cooke, Jr., op. cit.

[83] M. Breiter, H. Kammermaier, and C. A. Knorr, op. cit.

[84] N. N. Kavtorooze, Zhur. Fiz. Khim., 32, 909-12 (1958).

[85] R. Shurman, G Wedler, and H. Gentsch, Z. Phys. Chem., 17, 350-360 (1958).

[86] R. Shurman and G. Wedler, Z. Electrochem., 63, 748-756 (1959).

Adsorption sites on the surface of the platinum with
two different electron affinities[87-88] (sites of different
catalytic activity), are also possible explanations.
Investigators have certainly proved that there are two
oxidation potentials for hydrogen at the platinum
surface.

The amount of hydrogen measured by the method of
anodic oxidation should be related to two primary factors;
the pressure, or the concentration of hydrogen in the
solution, and the activity, or the effective surface area
for the adsorption of hydrogen of the electrode. If the
hydrogen pressure is kept constant, the only remaining
variable is the activity of the electrode being studied.

There is no direct method for the determination of
surface areas of materials in solutions. There are
methods for the determination of surface areas of metals
in gases. The most successful of these have been the
Brunaur-Emmett-Teller method and its modifications.[89-90]

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[87]A. I. Shlygin and M. E. Manzhelel, Uchenye Zapiski
Kishinev. Gosudarst. Univ., 7, 13-19 (1953); Referat.
Zhur. Khim., 1954, No. 37490.

[88]Ibid., 332-34.

[89]P. H. Emmett, ''Advances in Catalysis,'' Vol. I,
Surface Area Measurements, p. 65, Academic Press Inc.,
Publishers, New York, 1948.

[90]T. L. Hill, Ibid., Vol. IV, Theory of Physical
Adsorption, p. 211, 1952.

The surface activity of a material can also be determined by its use in a catalytic reaction, such as a decomposition reaction or a hydrogenation of dehydrogenation reaction. A number of these reactions have been studied in detail. The decomposition reaction of hydrogen peroxide has been studied from both its connection with catalysis[91-97] and with electrochemistry.[98-111] The investigation of the

[91]V. A. Roiter, Ber. Ukrain. Wiss. Forsch.--Inst. Physik. Chem., 4, 49-53 (1934).

[92]D. A. MacInnes, J. Am. Chem. Soc., 36, 878 (1914).

[93]A. Sieverts and H. Bruning, Z. anorg. Allegem. Chem., 201, 391 (1932).

[94]J. Weiss, Trans. Faraday Soc., 31, 1547 (1935).

[95]M. Dole, D. Rudd, G. Muchow and C. Comte, J. Chem. Phys. 20, 961 (1952).

[96]A. A. Lopatkin and V. P. Lebedev, Zhur. Fiz. Khim., 30, 196 (1956).

[97]M. V. Tobin and K. F. Lyachow, Ukrain. Khim. Zhur., 25, 581 (1959).

[98]K. Bornmann, Z. Elektrochem., 15, 673 (1909).

[99]I. N. Bushmakin, I. I. Zhukov, and V. I. Strukova, J. Russ. Phys.-Chem. Soc., 61, 169 (1929).

[100]A. Rius, Z. Electrochem., 36, 149 (1930).

[101]R. Wolfe, Comp. Rend., 196, 1413 (1933).

[102]W. H. Wilson and A. Hickling, J. Electrochem. Soc., 98, 425 (1951).

[103]J. M. Kolthoff and J. Jordan, J. Am. Chem. Soc., 74, 570 (1952).

[104]G. Bianchi and B. Revolta, Chimica Industria, 36, 358 (1954).

hydrogen peroxide decomposition on platinum black was first reported by Bredig et al.[112-114] The reaction has been shown to be a free radical mechanism which is initiated by an oxidation and a reduction reaction of the surface of the platinum.[115] This reaction is very fast and has been determined to be first order with respect to the concentration of the hydrogen peroxide in the solution and to the amount of platinum used as the catalyst.[116-119]

[105]J. O'M. Bockris and L. F. Oldfield, Trans. Faraday Soc., 51, 249 (1955).

[106]R. Gerisher and H. Gerisher, Z. Physik. Chem., 6, 178 (1956).

[107]W. Forker, A. Physik. Chem., 205, 351 (1956).

[108]D. Winkelman, Z. Elektrochem., 60, 731 (1956).

[109]G. Bianchi and G. Caprioglio, Electrochem. Acta, 1, 18 (1959).

[110]J. Giner, Z. Elektrochem., 64, 491 (1960).

[111]G. Bianchi, G. Caprioglio, G. Davolio, F. Mazza, and Mussini, Chim. e ind., (Milan), 43, 146 (1961).

[112]G. Bredig and M. Von Berneck, A. Physik. Chem., 31, 258 (1899).

[113]G. Bredig and K. Ykeda, Ibid, 37, 1 (1901).

[114]G. Bredig, Z. Elektrochem., 12, 581 (1906).

[115]J. Weiss, Trans. Faraday Soc., 31, 1547-57 (1935).

[116]G. Bredig, op. cit.

[117]J. G. Telotov, J. Russ. Phys. Chem. Soc., 39, 1146 (1906).

[118]K. Barnmann, Z. Electrochem., 15, 673 (1909).

The activity of the catalyst was assumed, in these experiments, to be proportional to the amount of the platinum. The only way this condition can be attained experimentally is to prepare a large amount of the platinum catalyst at one time and then to subdivide it. So far, no method has been reported for reproducing a heterogenous catalyst with a constant activity per weight.

The decomposition reaction of hydrogen peroxide has been shown to be catalyzed by some oxidized form of the platinum surface rather than being catalyzed by the bare platinum.[120-122] The reaction is a purely electrochemical reaction, and takes place in two steps on the surface of the platinum; one anodic reaction and one cathodic reaction, with the platinum oxide acting as an electron acceptor and donor.[123-129] The anodic reactions are:

[119]D. A. MacInnis, J. Am. Chem. Soc., 36, 878 (1914).

[120]G. Bianchi, G. Caprioglio, G. Davolio, F. Mazza, and Mussini, op. cit.

[121]J. Giner, op. cit.

[122]M. V. Lobin and K. F. Lyashev, op. cit.

[123]Bangotzkie and Tablokova, Dokladi Akad. Nauk SSSR, 95, 1219 (1954).

[124]J. Giner, op. cit.

[125]R. Gerisher and H. Gerisher, op. cit.

[126]D. Winkelmen, op. cit.

[127]V. A. Roiter, op. cit.

18

(a) $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ (b) $H_2O_2 \rightarrow HO_2 + H^+ + 1\bar{e}$

$HO_2^- \rightarrow O_2 + H^+ + 2\bar{e}$ $HO_2^- \rightarrow HO_2 + 1\bar{e}$

and the cathodic reactions are:

(a) $H_2O_2 + 2H^+ + 2\bar{e} \rightarrow 2H_2O$

$H_2O_2 + H^+ + 1\bar{e} \rightarrow H_2O + OH$
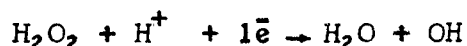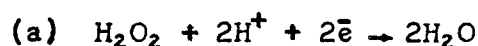
Another type of reaction, which can be used for the determination of the activity of a platinum surface, is hydrogenation. There are two types of mechanism postulated in hydrogenation reactions. Hydrogen or the compound to be reduced can be adsorbed on the surface of the platinum, and then this activated compound can react to produce the hydrogenated (reduced) compound. The reduction can also proceed by a purely electrochemical mechanism.[130-134]

The adsorption mechanism may be represented as follows:

$2M + H_2 \rightleftharpoons 2M\text{-}H$ $M + R \rightleftharpoons M\text{-}R$

$M\text{-}H + R \rightleftharpoons M\text{-}HR$ $2M\text{-}R + H_2 \rightleftharpoons 2M\text{-}RH$

$M\text{-}HR \rightleftharpoons M + HR$ $M\text{-}RH \rightleftharpoons M + RH$
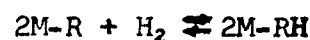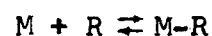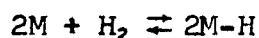
[128] J. Weiss, op. cit.

[129] J. Lopis and J. M. Guillen, Analyes real soc. espan. fis y quim. (Madrid), 53B, 5-16 (1957).

[130] M. V. Stackelberg and P. Wever, Z. Elektrochem., 56, 806-14 (1952).

[131] I. I. Telcs and F. Nagy, Magyar Kem. Folyoirat, 66, 150-3 (1960).

[132] M. V. Stackelberg and W. Stracke, Ibid., 53, 118 (1949).

[133] J. O'M Bockris, Ann. Reviews of Phys. Chem., 5, 487 (1954).

The electrochemical mechanism is represented as follows:

$$M + R \rightleftarrows M - R \qquad\qquad 2M + H_2 \rightleftarrows 2M - H$$

$$M - R + 1\bar{e} \rightleftarrows M - R^- \qquad\qquad M - H \rightleftarrows M + H^+ + 1\bar{e}$$

$$M - R^- + H^+ \rightleftarrows M - RH$$

$$M - RH \rightleftarrows M + RH$$
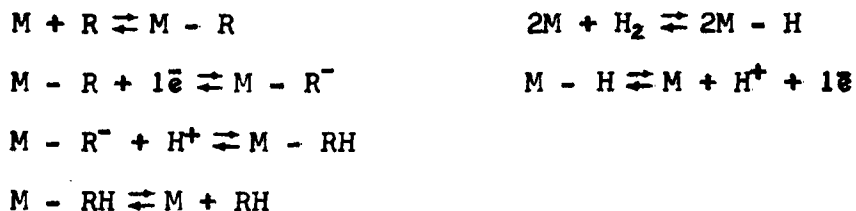
Oxidation and reduction reactions at the electrode surface have also been studied in detail. Not all of these experiments have met with success. However, in the case of these reactions, the general mechanisms are very similar to the catalytic hydrogenation reactions.[135-139] There are the reactions which proceed via the formation of oxidizing and reducing agents on the surface of the electrodes:

$$M + H_2O \rightleftarrows M - H_2O_{(ads)}$$

$$M + (H_2O)_{ads} \rightleftarrows M (OH)_{ads} + H^+ + 1\bar{e}$$

$$M - (OH)_{ads} + Re \rightleftarrows M + (Ox)_{ads}$$

$$M + H_2O \rightleftarrows M - H_2O_{ads}$$

$$M + (H_2O) + 1\bar{e} \rightleftarrows M(H)_{ads} + OH^-$$

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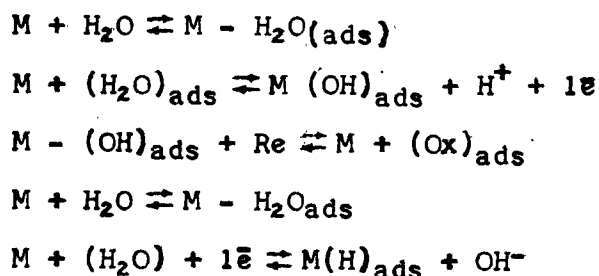
[134] N. I. Kobzev and N. A. Reshetovskaya, Zhur. Fiz. Khim., 23, 388 (1949).

[135] M. V. Stackelberg and P. Wever, op. cit.

[136] I. I. Telcs and F. Nagy, op. cit.

[137] M. V. Stackelberg and W. Stracke, op. cit.

[138] J. O'M. Bockris, op. cit.

[139] N. I. Kobzev and N. A. Reshetovskaya, op. cit.

$$M\text{--}(H)_{ads} + Ox \rightleftharpoons M - (Re)_{ads}$$

$$M\,(Re)_{ads} \rightleftharpoons M + Re$$

and the reactions which are electron transfer reactions:[140]

$$M + Re \rightleftharpoons M - (Re)_{ads}$$

$$M - (Re)_{ads} \rightleftharpoons M - (Ox)_{ads} + 1\bar{e}$$

$$M - (Ox)_{ads} \rightleftharpoons M + Ox$$

$$M + Ox \rightleftharpoons M\,(Ox)_{ads}$$

$$M - (Ox) + 1\bar{e} \rightleftharpoons M - (Re)_{ads}$$

$$M - (Re)_{ads} \rightleftharpoons M + Re$$

The reduction has been postulated to proceed by means of primary electron transfer when substances with reduction potentials more negative than -0.1 volts (normal hydrogen scale) and at a pH of O are used.[141-145]

The hydrogenation of p-benzoquinone proceeds very rapidly at the platinum surface.[146-147] The reaction requires very little activation energy and since the potential of the quinone on platinum is in the vicinity

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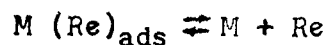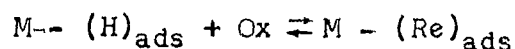[140] B. A. Bogdanovskii and A. I. Shylgin, Zhur, Fiz. Khim., 33, 1769-73 (1959).

[141] M. V. Stackelberg and P. Wever, op. cit.
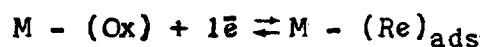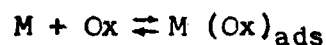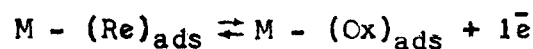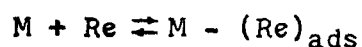
[142] I. I. Telcs and F. Nagy, op. cit.

[143] M. V. Stackelberg and W. Stracke, op. cit.

[144] J. O'M. Bockris, op. cit.

[145] N. I. Kobzev and N. A. Reshetovskaya, op. cit.

[146] E. F. Rosenblatt, J. Am. Chem. Soc., 62, 1092 (1940).

of -0.7 volts, the reaction can be assumed to be a purely electrochemical process.

The reaction is, as are many other catalytic reductions, zero order with respect to the concentration of the material to be reduced (p-benzoquinone); but no statement as to the dependence of the rate of the reaction of the amount of catalyst has been made.

The experimental material to be reported in this dissertation is the determination of the activities of platinized-platinum for: (1) the adsorption of hydrogen from solution (as measured by the method of Franklin), (2) the decomposition of hydrogen peroxide, and (3) the hydrogenation of quinone. The primary object of this investigation was to correlate the activities of the platinum for the various process. A secondary object was to gain information about the reason for the two forms of hydrogen on the platinized-platinum electrode.

B. Experimental

The electrodes used in these experiments were made from twenty gauge bright platinum wire. The platinum extended 1 to 4 cms. from the end of the glass in which it was imbedded. The electrodes were chemically cleaned in aqua regia, and then cleaned by charging the electrodes

[147]M. M. Popova and D. V. Sokol'skii, Trudy, Inst. Khim. Nauk, Akad. Nauk Kozakh, SSR, 2, 70-76, 84-93 (1958), Zhur, Fiz. Khim., 33, 2573 (1959).

cathodically and anodically several times in $2N$ H_2SO_4
(Baker and Adamson-C.P.). The electrodes were then
rinsed with redistilled water, placed in a plating
solution and plated with platinum black. The plating
solution contained a 3% solution of chloroplatinic acid
(Baker ''Analyzed'' Reagent) with various amounts of lead
acetate. The electrodes were plated at a current of
2-25ma. for 60-600 sec. depending on the amount of plati-
num desired. The plating procedure was varied over this
wide range in order to provide as much variation in the
catalytic activity of the electrodes as possible. After
plating, the electrodes were rinsed, and placed in $2N$ H_2SO_4.
The electrodes were again charged anodically and cathodi-
cally until the charging process took a constant length
of time (the time necessary for the potential of the
electrode to change from the oxygen evolution potential
to the hydrogen evolution potential). This charging
process was used since Cooke[148] had shown that the
surface activity for adsorption of hydrogen increases
slightly during the first several times that the plati-
num oxide is formed. It has also been stated that this
charging process is a good method for cleaning platinized
platinum electrodes of adsorbed materials. The constant
length of time necessary for the charging process indicates

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[148] S. L. Cooke, Jr., op. cit.

that changes are no longer taking place on the electrode surface.

All solutions were made from water which had been redistilled from basic-potassium permanganate, then slowly redistilled into pyrex. The water prepared in this manner had a maximum conductivity of $3X10^{-6}$ mhos/cm.

The (commercial tank) hydrogen used in this experiment was purified by passing the hydrogen over hot copper wire, hot platinized asbestos, sodium hydroxide pellets (Baker and Adamson-Reagent) and finally Selica get (Fisher, 6-16 mesh).

The prepared electrode was rinsed and placed in the apparatus containing 2N H_2SO_4, using 2N $H_2SO_4/Hg_2SO_4/Hg$ as the nonpolarizable reference electrode. Hydrogen was bubbled through the solution until the potential of the platinized- platinum electrode became constant. The bubbling was stopped and the system was allowed to come to equilibrium for several minutes. The potential of the electrode was determined and the electrode was oxidized by means of a modified polarographic circuit.

The potentials were determined in the experiments with a Leeds and Northrup student potentiometer, using a galvanometer in the early experiments. The galvanometer was later replaced with a recorder (Sargent, SR, 125mv.). This replacement served two purposes; the recorder could plot potential vs. time automatically and the recorder allowed virtually no current.

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The polarographic circuit used in these experiments is shown in Figure 2. A slight modification of the normal polarographic circuit was made because of the large currents required to oxidize the large electrodes. If too large a current is drawn by the external circuit (electrode cell), then the finite value of the resistance of the slide wire causes a non-linearity in the voltage increment. The non-linear increase in the voltage function merges the current peaks, I and II, together so that the peaks are impossible to separate as well as making it impossible to accurately determine the residual current. The actual modification is merely a very simple current amplifier, the voltage amplification is somewhat smaller than unity.

The oxidation procedure was repeated until the current-voltage curves became reproducible. If the curves were not reproducible, but decreased after each oxidation, the apparatus was disassembled and recleaned. The areas were reproducible to within 2-3%.

A residual current line was drawn on the graph and the peaks were separated. The areas under each peak were integrated with a Keuffel and Esser model N4242 compensating polar planimeter, and tabulated. The average value for the last three oxidation current-voltage curves was used as the activity of the electrode for the adsorption and absorption of hydrogen. This procedure is essentially that reported by Cooke.[149]

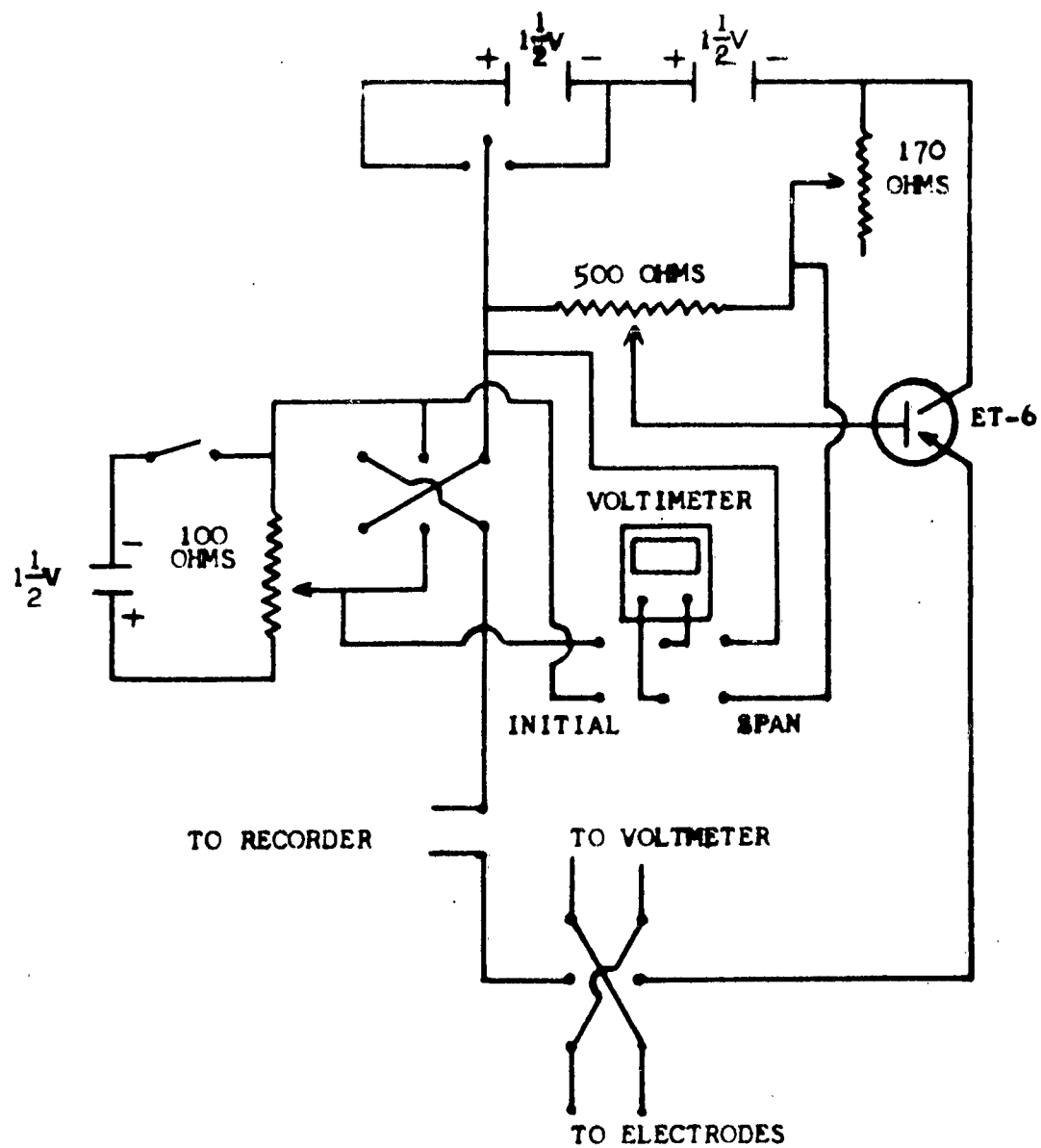[149]S. L. Cooke, Jr. and T. C. Franklin, op. cit.

Figure 2   Circuit Diagram for the Polarograph

The experimental arrangement for the hydrogen peroxide experiments is pictures in Figure 3. Hydrogen was bubbled through the solution until the potential of the platinized platinum electrode became constant. The bubbling was stopped and the system was allowed to come to equilibrium for several minutes. The potential of the electrode was determined and the amount of hydrogen was measured by the coulometric procedure. The oxidation procedure was repeated until reproducible results were obtained. In the hydrogen peroxide experiments the solution was then flushed with oxygen until the hydrogen was removed, leaving the solution saturated with oxygen. The concentration of the hydrogen peroxide was measured voltammetrically during the decomposition using a rotating microplatinum electrode.[150-151] The residual current was determined in the oxygen saturated solution then a known amount of hydrogen peroxide was added to the solution. Polarograms were obtained every 3 to 4 hours during the course of the decomposition.

The p-benzoquinone used was purified by recrystallization from petroleum ether (B. P. 80-110° C.). The bright yellow crystals were sublimed. The purity as

[150]D. Winkelmann, Z. Elektrochem., 60, 731 (1956).

[151]A. Hamamoto and T. Ansco, Oyo Denki Kenkyn-jo Iho, 9, 206 (1957).

Figure 3 Cell and Circuit Block Diagram for the Study of
the Decomposition of Hydrogen Peroxide

ROTATING PLATINUM MICRO ELECTRODE

Hg

H₂ INLET

REACTION
CELL

PLATINIZED
ELECTRODE

POLAROGRAPH   RECORDER

POTENTIOMETER

REFERENCE
CELL

Hg

TO OTHER CELLS

FINAL APPARATUS FOR CATALYTIC DECOMPOSITION
OF HYDROGEN PEROXIDE

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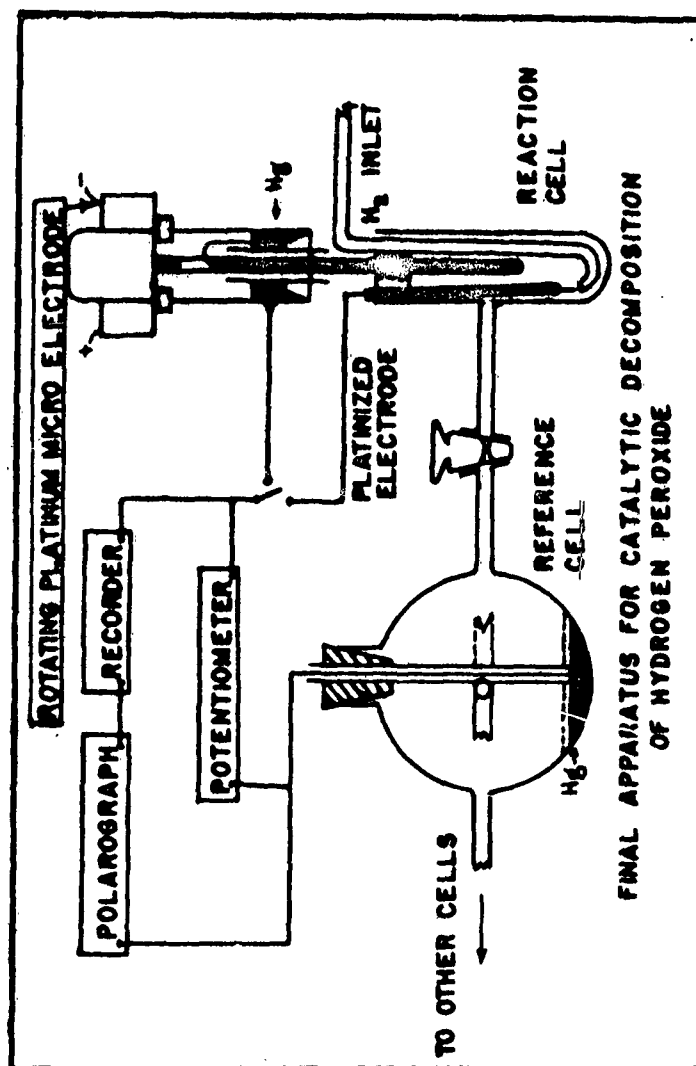
determined by titration with standard sodium thiosulfate using an amperometric end point was 99+%. Solutions of the p-benzoquinone were made by weighing directly and diluting in a volumetric flask with 2N sulfuric acid. The solutions of p-benzoquinone were made fresh for each run since the p-benzoquinone polymerized in the 2N sulfuric acid in a few hours. The fact that the polymerization was taking place was indicated by the formation of a very dark color (rate of formation depended on concentration, generally took 3-4 hours to appear), and the eventual formation of a black precipitate.

In the determination of the kinetics of the hydrogenation reaction, p-benzoquinone of a certain concentration was introduced into the reaction cell and hydrogen was bubbled at a constant and reproducible rate (150-160 bubbles/min.). The electrode was introduced into the solution and its potential was recorded as a function of time. The electrode retained the potential of the p-benzoquinone until almost all of the p-benzoquinone was gone, then returned to the potential of the hydrogen electrode. Using the length of time from the insertion of the electrode until the hydrogen potential returns as the time necessary for the sample to be hydrogenated, the kinetics of the reaction was determined. After rinsing the cell and the electrode with 2N sulfuric acid, the procedure was repeated for varying amounts of p-benzoquinone. Figure 4 shows the apparatus used in the

Figure 4 Cell and Circuit Block Diagram
for the Study of the Hydrogenation
of Quinone
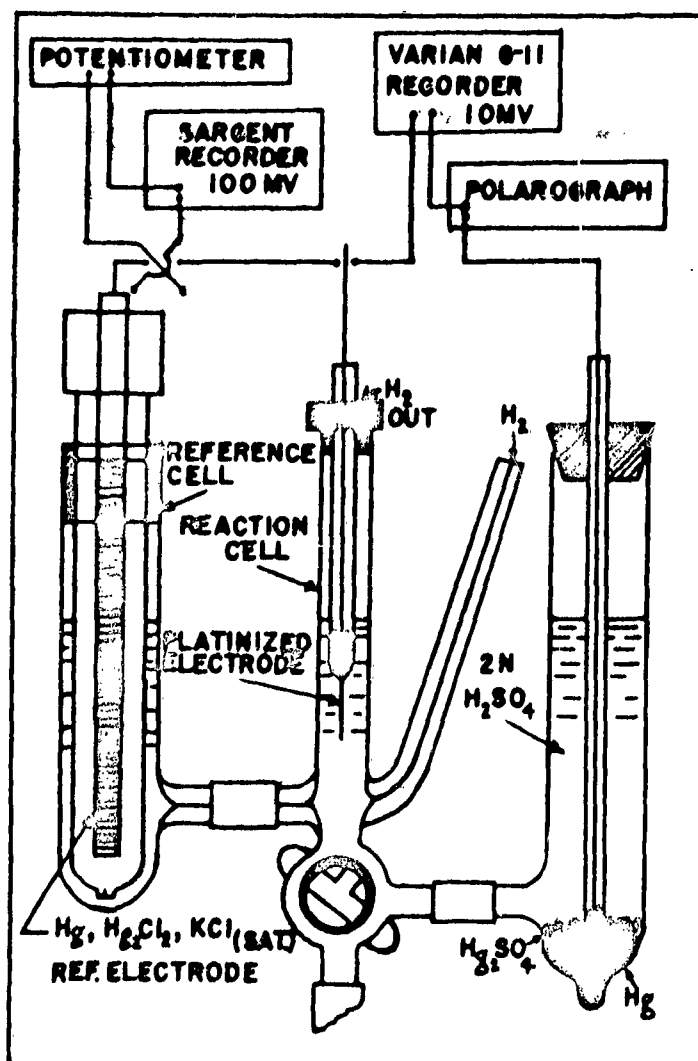
hydrogenation of p-benzoquinone. The activity of the
platinized-platinum electrode for the adsorption was
determined using the Hg_2SO_4/Hg electrode as the non-
polarizable reference electrode. The tubing connecting
the Beckman calomel electrode to the reaction cell was
used to prevent mixing of the solutions in the two cells.
The solutions were drained by opening the stopcock to a
flask mounted under the stopcock. The total volume of
the reaction cell was approximately 1.5 ml.

All glassware used in the apparatus was cleaned
with kerosene, washed with soap and water, then soaked
overnight in chromic acid solution. The kerosene was
required to remove any trace of the stopcock grease com-
pound (Dow Corning High Vacuum (Silicone) Grease) used.
The glassware was rinsed with distilled water then redis-
tilled water and finally soaked in redistilled water for
several hours. All connections in the glassware were
made with Tygon tubing which had been cleaned and soaked
in redistilled water. The stopcocks were ground with
grinding compound (Tripoli) to make them fit as closely
as possible. This was done to minimize the amount of
stopcock grease required. The stopcocks were kept closed
at a ll possible times.

The mercury used in the experiments was cleaned by
washing with dilute nitric acid and rinsing with redis-
tilled water. The mercury was then dried and distilled
twice in a vacuum system. The mercurous sulfate was

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reagent grade (Baker and Adamson)

All reactions were carried out at 25-0.2° C.

C. Results of Hydrogen Peroxide Decomposition Experiments

Figure 5 shows a plot of log concentration of hydro-
gen-peroxide vs. time for a typical run. The linear
relationship between these two functions is indicative
of a first order reaction. This relationship was dis-
cussed in Chapter IIA. The initial sec ion of the curve
has been left blank in Figure 5. The hydrogen in the
system must be removed before the catalytic decomposition
of the hydrogen peroxide takes place. If there is any
hydrogen in the system, it is catalytically oxidized by
the hydrogen peroxide. Moreover the decomposition of
the hydrogen peroxide has been postulated to be catalyzed
by some platinum oxide, so the bare platinum must be
oxidized by the hydrogen peroxide to the catalytically
active form. If the reaction solution is saturated with
oxygen before the hydrogen peroxide is introduced into
the reaction vessel, there is still an induction period for
the reaction. This is probably caused by the fact that
the platinum surface has been oxidized by the oxygen in
the solution, and the hydrogen peroxide must reduce this.
oxide to the lower platinum oxide which is catalytically
active. The maximum rate of decomposition was usually
reached in a few minutes to an hour depending on whether
or not oxygen had been bubbled through the solution and

Figure 5   The Log of the Hydrogen Peroxide Concentration Vs.
            Time for the Decomposition of Hydrogen Peroxide

33
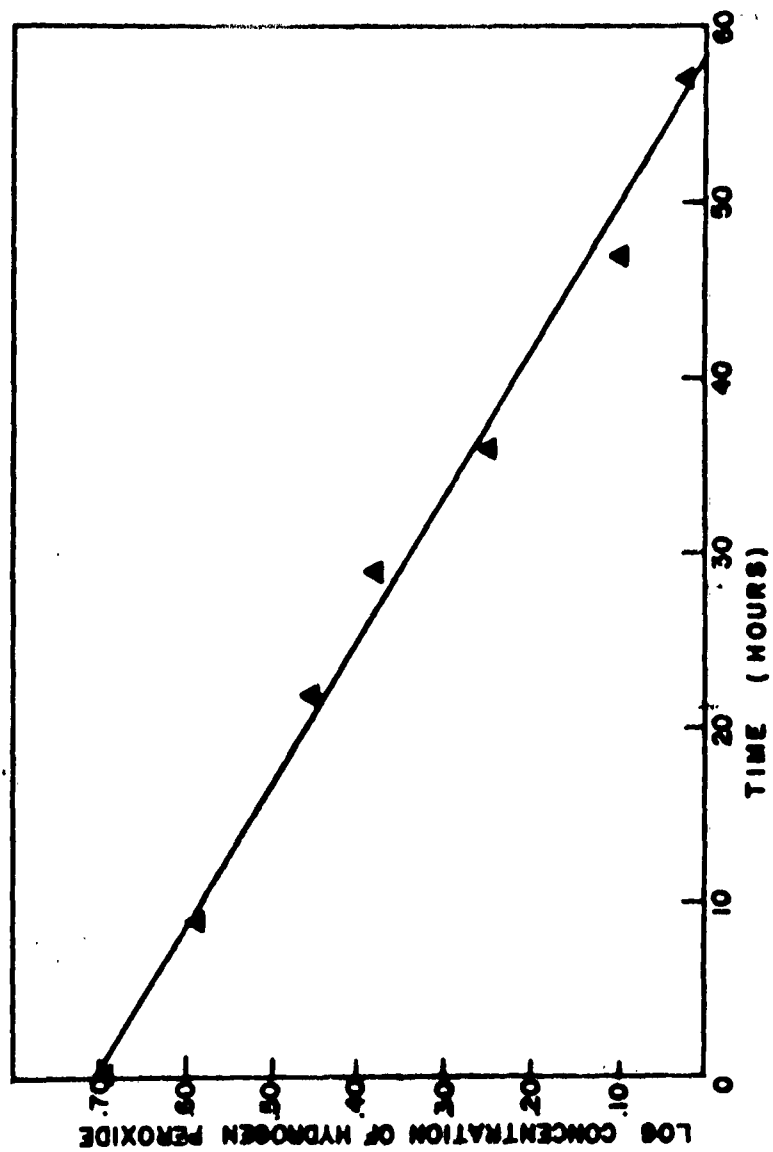
for how long.

In some cases the induction period was considerably longer than an hour. This occurred at higher concentrations of hydrogen peroxide. When this happened the rate of decomposition of the hydrogen peroxide was not first order with respect to its concentration, but somewhat lower. As more of the hydrogen peroxide decomposed, the rate became first order.

The dependence of the rate of decomposition of hydrogen peroxide on the amount of catalyst used was discussed in Chapter IIA. The rate has been shown to be first order with respect to the amount of catalyst used. If this is true a plot of the rate constants vs. amount of catalyst should give a straight line. Figures 6 and 7 are plots of the activities of several electrodes for the decomposition of hydrogen peroxide (rate constants) vs. the activities of the same electrode for the adsorption of hydrogen as determined by polarographic anodic oxidation. Figure 6 is a plot of rate constants vs. total adsorbed hydrogen and vs. hydrogen adsorbed as form I. Figure 7 is a plot of rate constants vs. hydrogen adsorbed as form II. No plot of rate constants vs. amount of absorbed hydrogen (form III) has been reproduced since the amount of hydrogen in this form remained approximately constant for a given base electrode (bare unplatinized electrode).

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Figure 6 Rate Constants for the Heterogeneous Decomposition
of Hydrogen Peroxide on Platinized Platinum as a
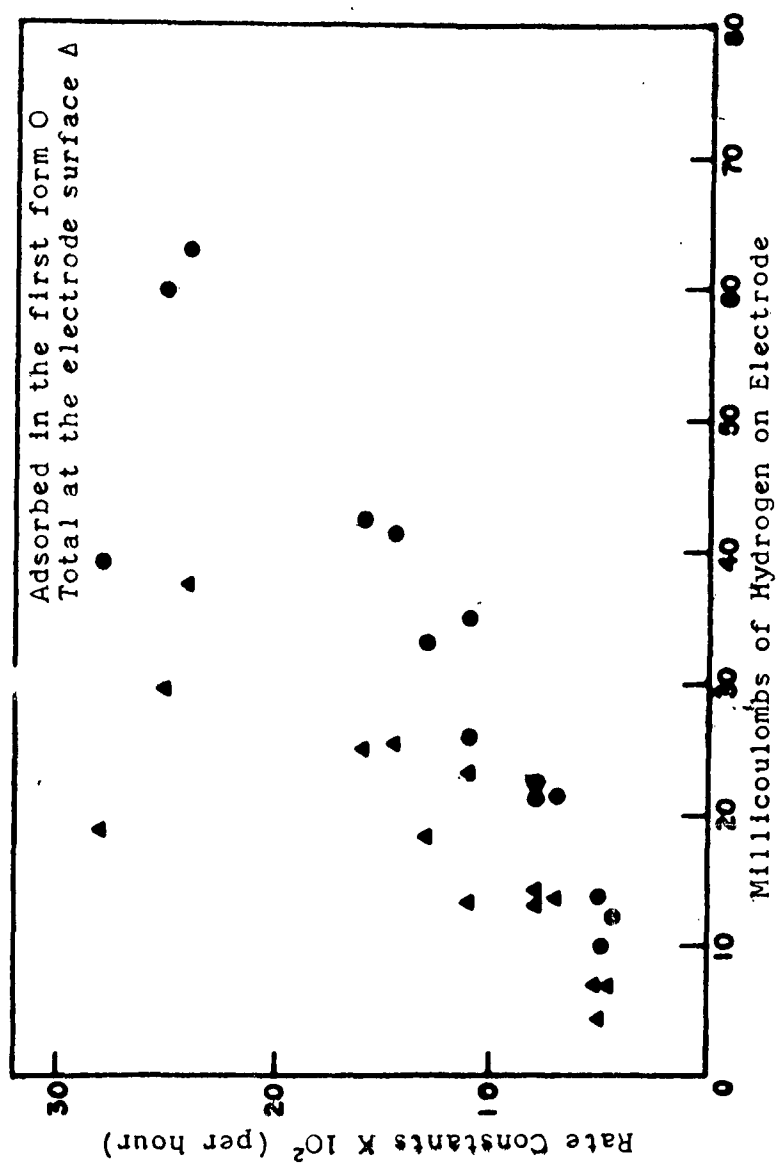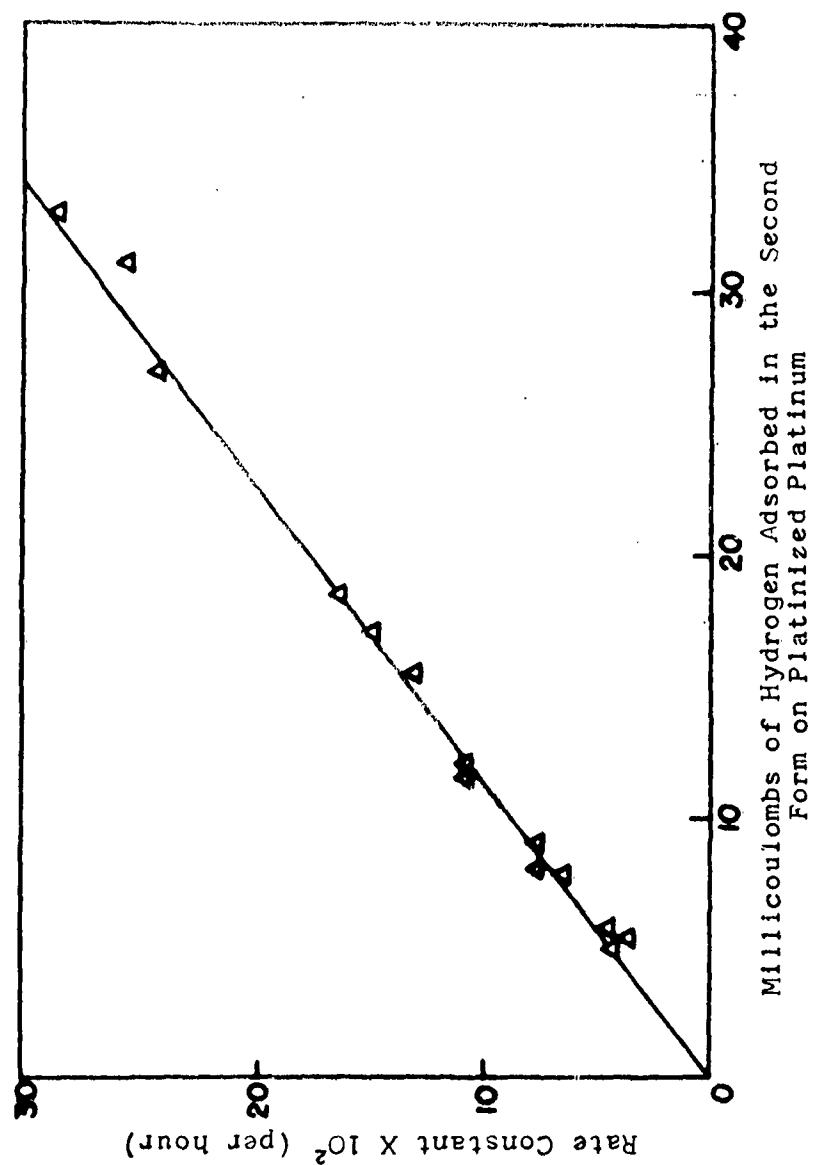Function of the Amount of the Hydrogen

35

Figure 7 Rate Constants for the Hetergeneous Decomposition of Hydrogen Peroxide on Platinized Platinum as a Function of the Amount of Hydrogen Adsorbed in the Second Form

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The expected linear relationship for rate vs. amount of catalyst is found only in Figure 7. There is no apparent relationship to be found in the other graph (Figure 6). It may be concluded from this, that the rate determining step in the decomposition of hydrogen peroxide is a reaction between the hydrogen peroxide and an oxide formed on the same platinum surface that is also able to adsorb hydrogen as form II.

Figure 8 shows a plot of log $\frac{K_0-K}{K_0}$ vs. log concentration of acetonitrile added to the reaction solution, where K_0 is the original rate constant and K is the rate constant at the particular concentration of acetonitrile. Acetonitrile was added to the solution to reduce the area of the electrode.

Figure 9 shows a plot of activity of platinized-platinum for the adsorption of hydrogen vs. the concentration of acetonitrile, which is again used as a poison. The plot is log $\frac{A_0-A}{A_0}$ vs. log concentration of acetonitrile where A_0 is the original amount of hydrogen adsorbed on the electrode and A is the amount of hydrogen adsorbed at the concentration of acetronitrile used. The two equations derived empirically from Figures 8 and 9 are:

$$\text{Log } \frac{K_0-K}{K_0} = 2/3 \text{ Log } \left[C_{CH_3CN}\right] + 1.7$$

and

$$\text{Log } \frac{A_0-A}{A_0} = 2/3 \text{ Log } \left[C_{CH_3CN}\right] + 2.4$$

37

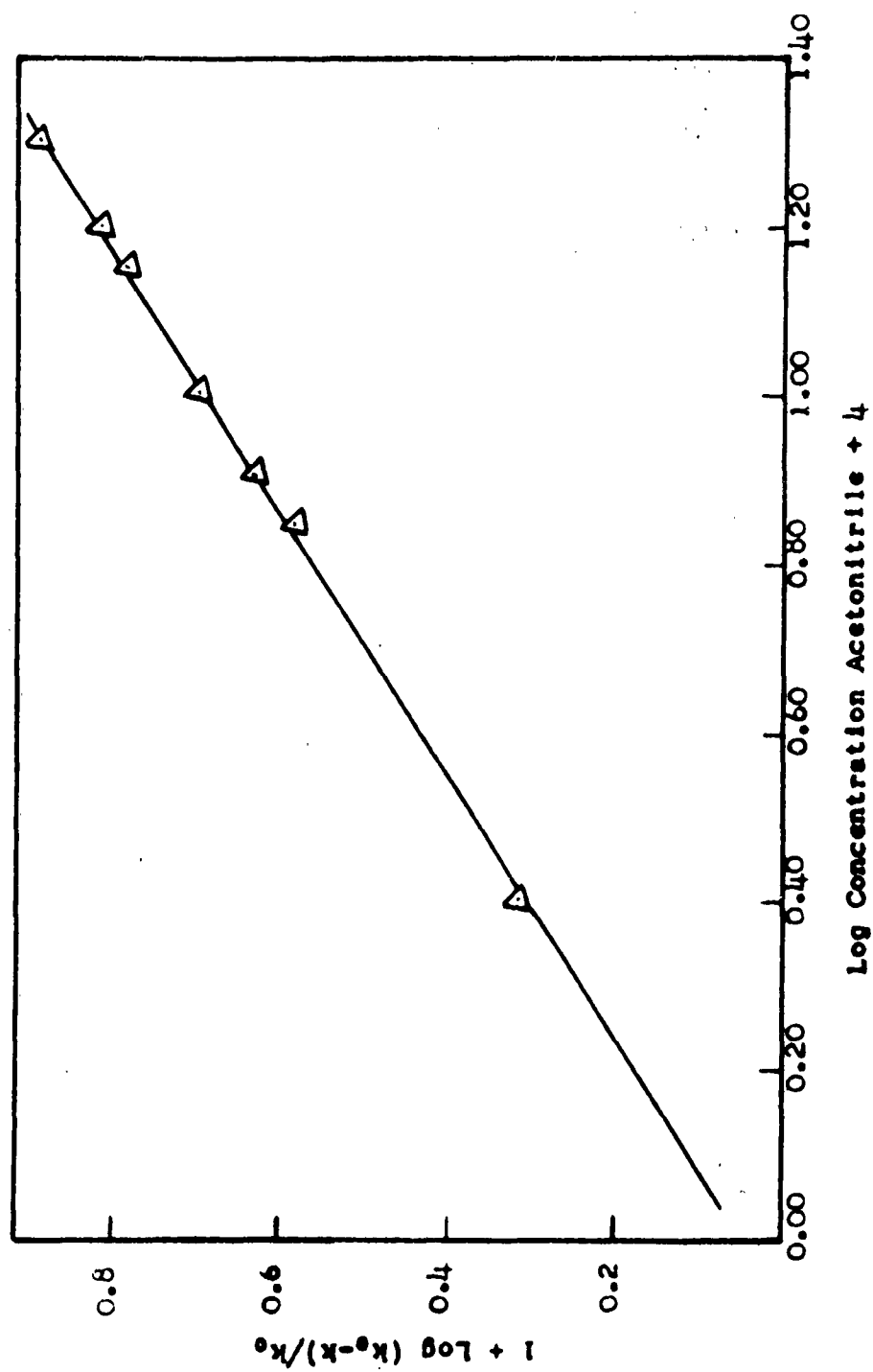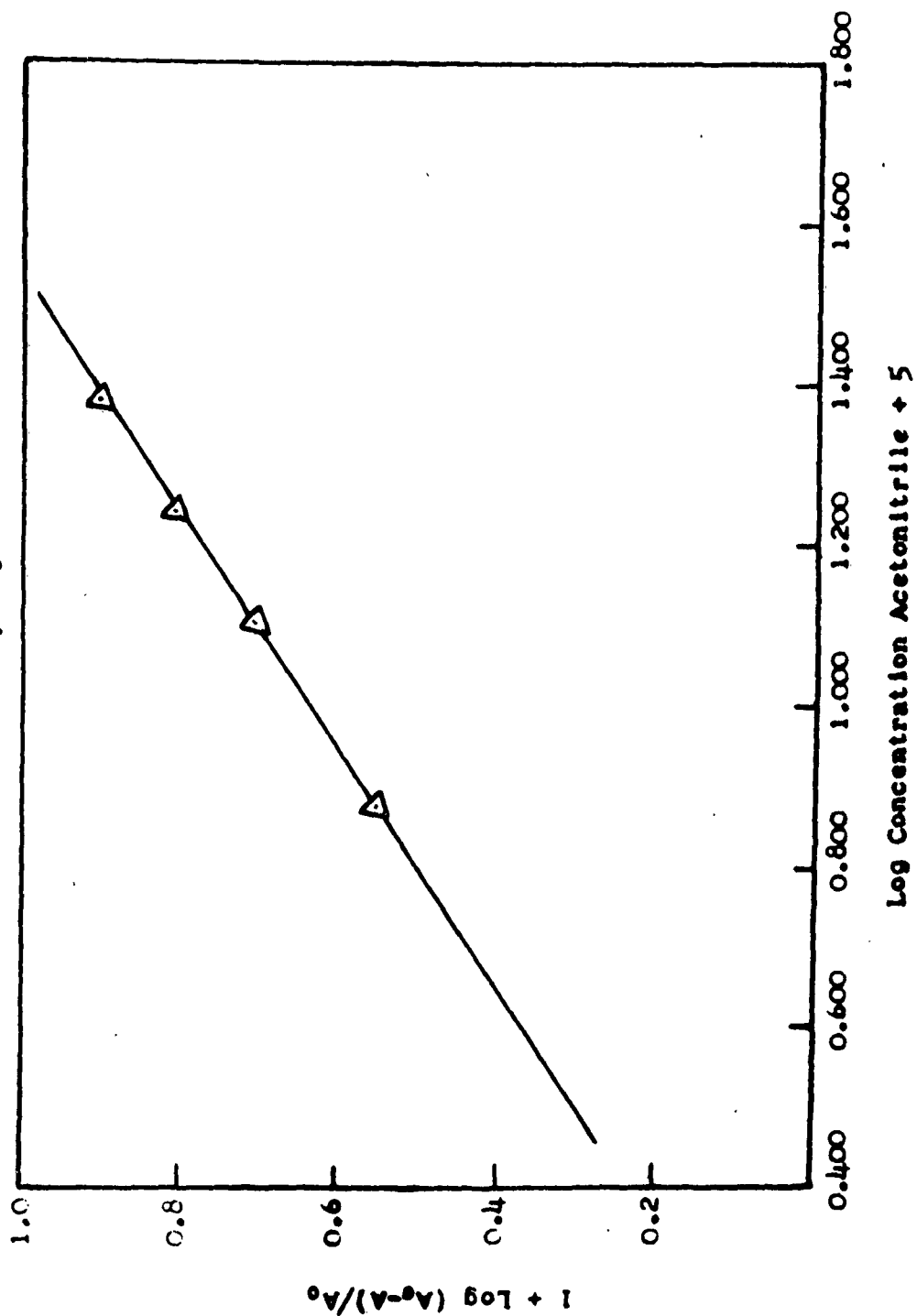Figure 8 The Effect of Acetonitrile on the Rate Constant for the Decomposition of Hydrogen Peroxide

Figure 9 The Effect of Acetonitrile on the Ability of the Electrode to Adsorb Hydrogen

Therefore:

$$\text{Log } \frac{K_0-K}{K_0} = \text{Log } \frac{A_0-A}{A_0} - \text{Log } 5$$

$$1 - \frac{K}{K_0} = 0.2 \quad 1 - \frac{A}{A_0}$$

$$\text{or} \quad K = \frac{0.2k_0}{A_0} A - 0.8K_0$$

Thus again a linear relationship is shown for the decomposition of hydrogen peroxide and the adsorption of hydrogen.

Figure 10 shows the dependence of the potential of the electrode on time during the course of the decomposition of the hydrogen peroxide. Little or no change in potential is shown during the reaction.

D. Results of p-Benzoquinone Hydrogenation Experiments

Figure 11 shows a plot of the ratio of the total amount of hydrogen adsorbed on an electrode at the particular concentration of benzoquinone to the initial amount of hydrogen at zero concentration, benzoquinone vs. the concentration of added benzoquinone. There is an initial rise in the plot meaning that if a very small amount of benzoquinone is added to the solution, it has the effect of actually increasing the amount of hydrogen on the electrode. However, upon increasing the concentration of the quinone the amount of adsorbed hydrogen decreases linearly.

Figure 10 The Potential of the Platinum Electrode during the Hydrogen Peroxide Decomposition

41

Figure 11   The Effect of Quinone on the
Amount of Total Adsorbed Hydrogen
on the Platinum Electrode
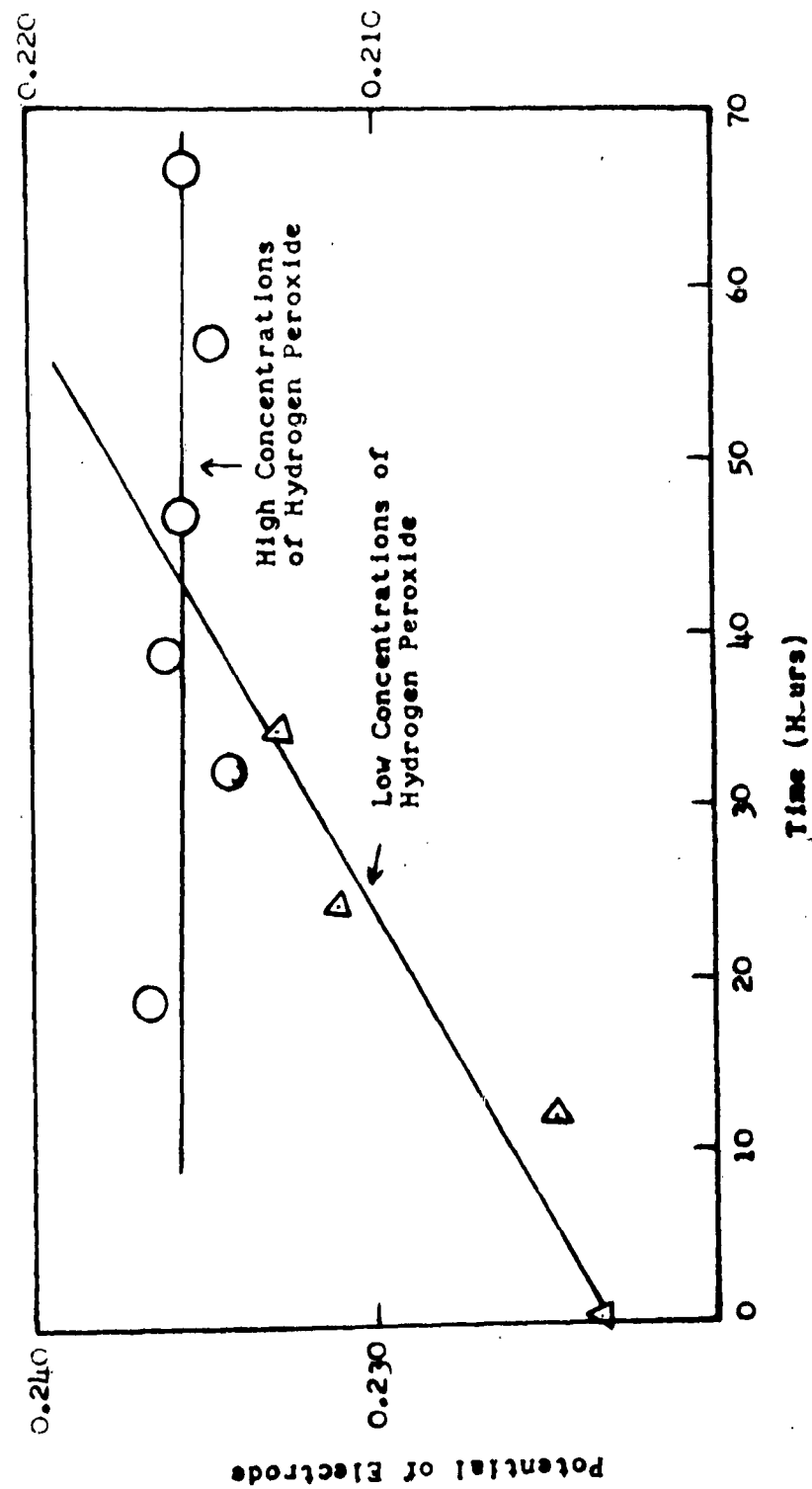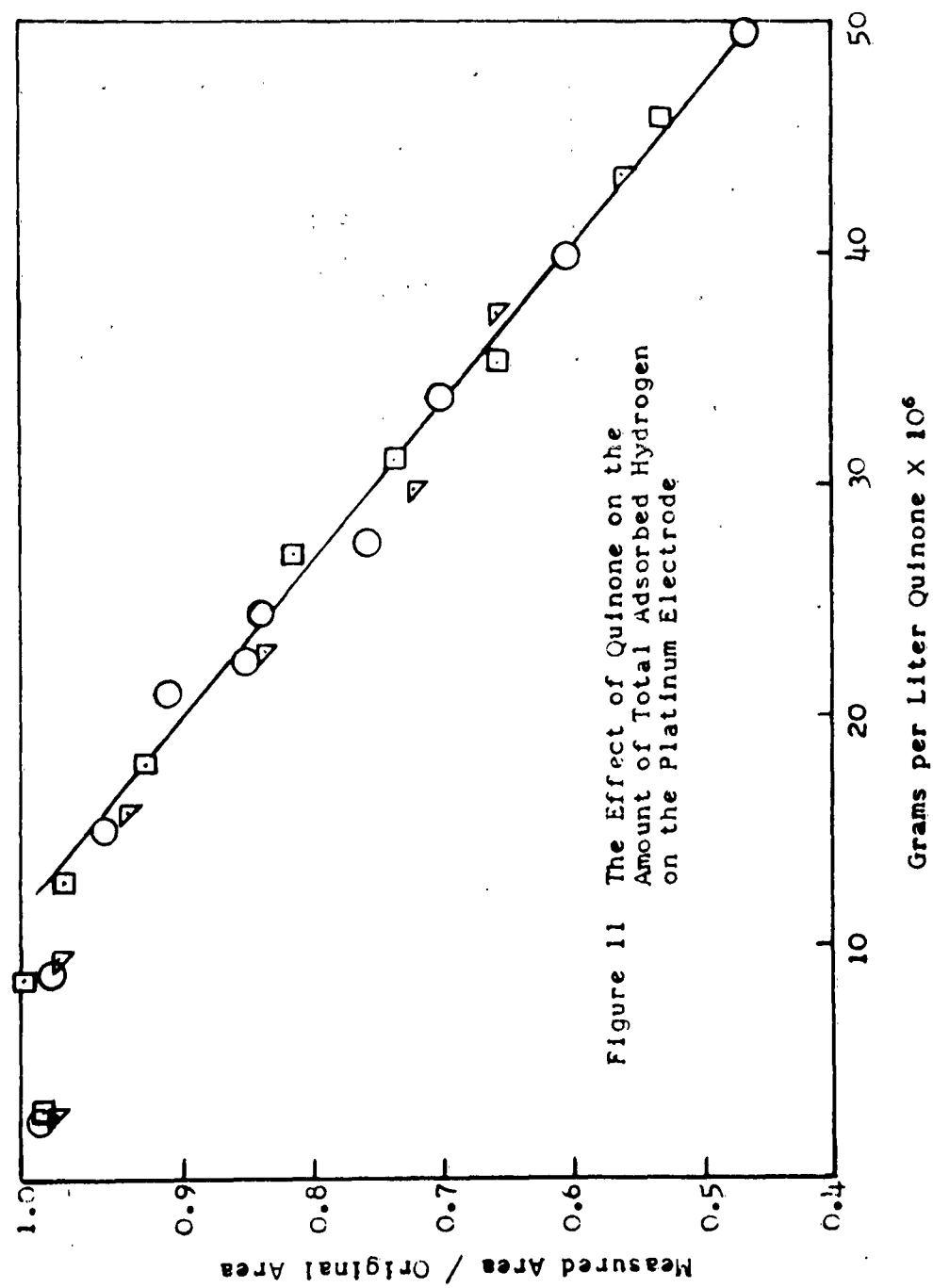
Upon further increases of concentration the area becomes so small that the determination of the amount of adsorbed hydrogen on the surface becomes very difficult and the results become very erratic; the slope changes to a smaller value of d $\frac{A}{A_0}$/dC$_{(quinone)}$. This continues until suddenly there is no hydrogen on the surface of the electrode.
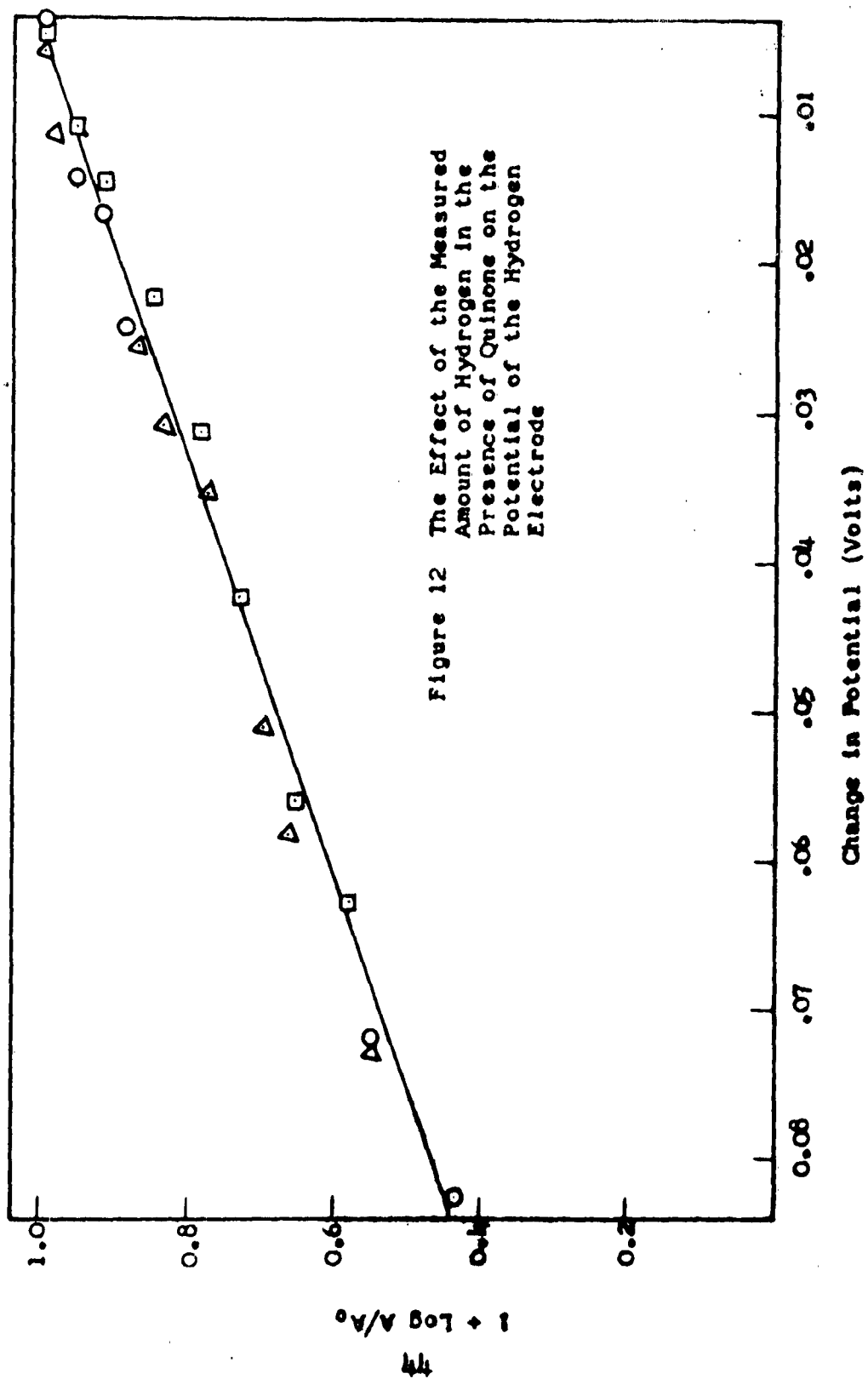
Stirring has very little effect on the curve shown. It increases the amount of hydrogen only slightly. During the later portion of the curve (after the change of slope)(not shown) the stirring has the effect of decreasing the amount of hydrogen on the surface of the electrode.

Figure 12 is a plot of the change in potential, exhibited by the electrode vs. the log of the ratio of the area. This shows a linear relationship with a slope of 2.5 x .059 indicating a z of .4.

The plot becomes erratic with further increases of concentration of quinone, and stirring has the effect of increasing the potential of the electrode in the range of potentials shown in the figure. However, further increases of concentration of quinone has the effect of reversing the effect of stirring.

Figure 13 is a plot of change in potential vs. the log of the concentration of quinone added.

The potential vs. time relationships for a particular electrode using various amounts of benzoquinone are shown in Figure 14. The electrode is initially at the potential

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Figure 12 The Effect of the Measured
Amount of Hydrogen in the
Presence of Quinone on the
Potential of the Hydrogen
Electrode

Change in Potential (Volts)

$1 + Log A/A_o$

44

Figure 13   The Effect of Quinone on the
              Potential of the Platinised
              Platinum Electrode

Change In Potential

Log Concentration + 5 (G/L)
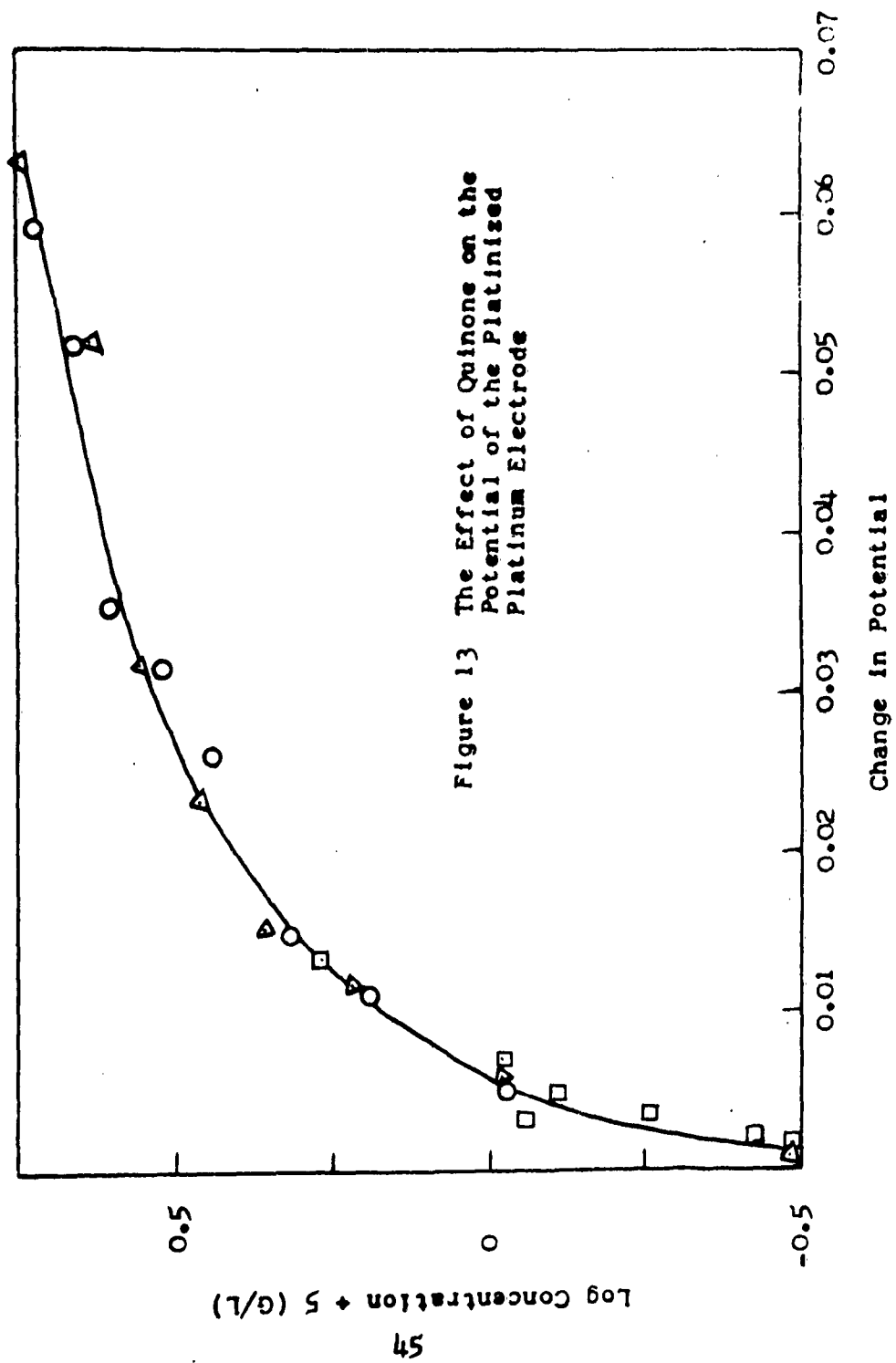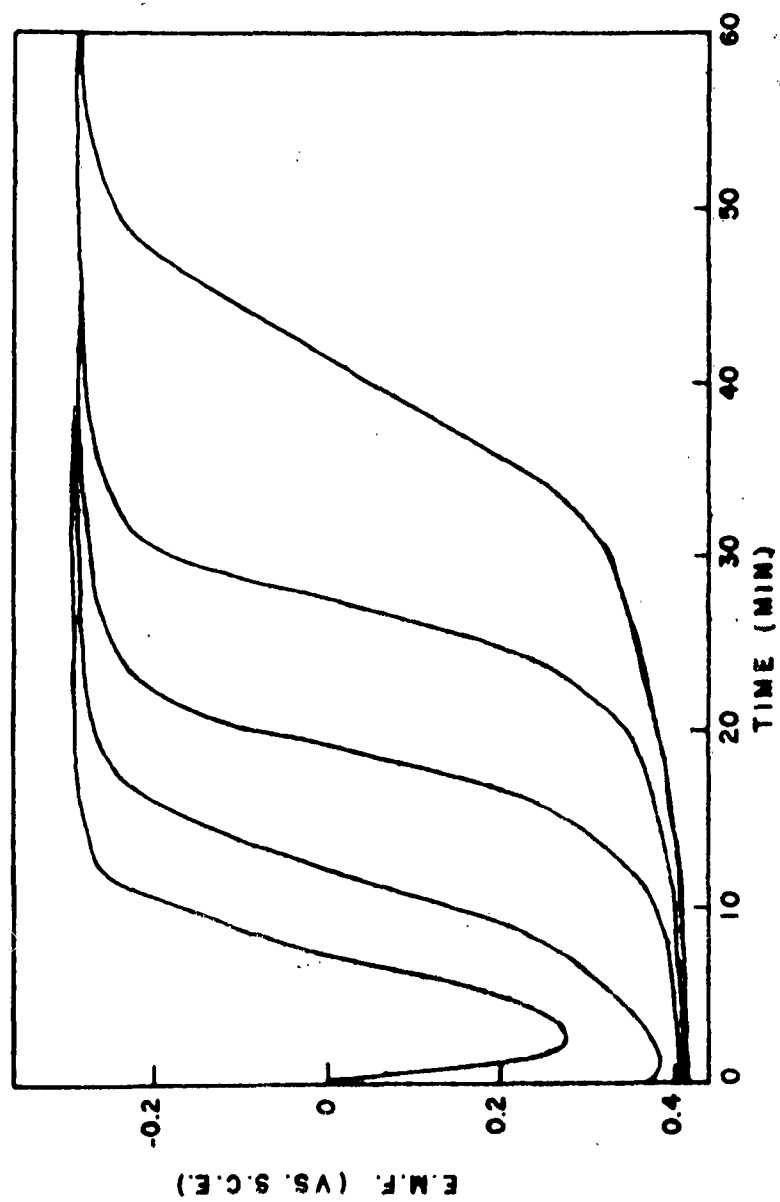
45

Figure 14   The Potential of the Electrode (Vs. Saturated
             Calomel Electrode) Vs. Time for Varying Amounts
             of Added Quinone

of the quinone electrode but as the quinone is hydro-
genated to hydroquinone the potential returns to the
potential of the hydrogen electrode.

In Figure 15 the time which is necessary to return
to zero potential vs. S.C.E. is plotted against the
amount of quinone added. This plot shows a linear rela-
tionship which indicates a reaction that is zero order
with respect to quinone.

The zero potential was chosen rather arbitrally.
Figure 14 shows that the potential is changing at a
maximum rate in this area and the error in the time is
at a minimum. Since this is a zero order reaction, only
the time necessary to react a definite amount of the
material need be known, even though a constant amount
of material is left unreacted.

Figure 15 does not give a zero time intercept. This
is to be expected from the previous discussion, indicating
that a constant amount is unreacted when the potential
goes through zero.

Figure 16 is a plot of the rate constants for the
hydrogenation reaction vs. the amount of hydrogen
adsorbed on the electrode without added quinone. There
is no apparent relationship. However, if the points
are separated according to the base electrode (the
electrode used for plating the platinized-platinum)
then four lines appear.

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Figure 15 Grams of p-benzoquinone Vs. Time
Necessary for the Potential of the
Electrode to Return to 0.00 v.
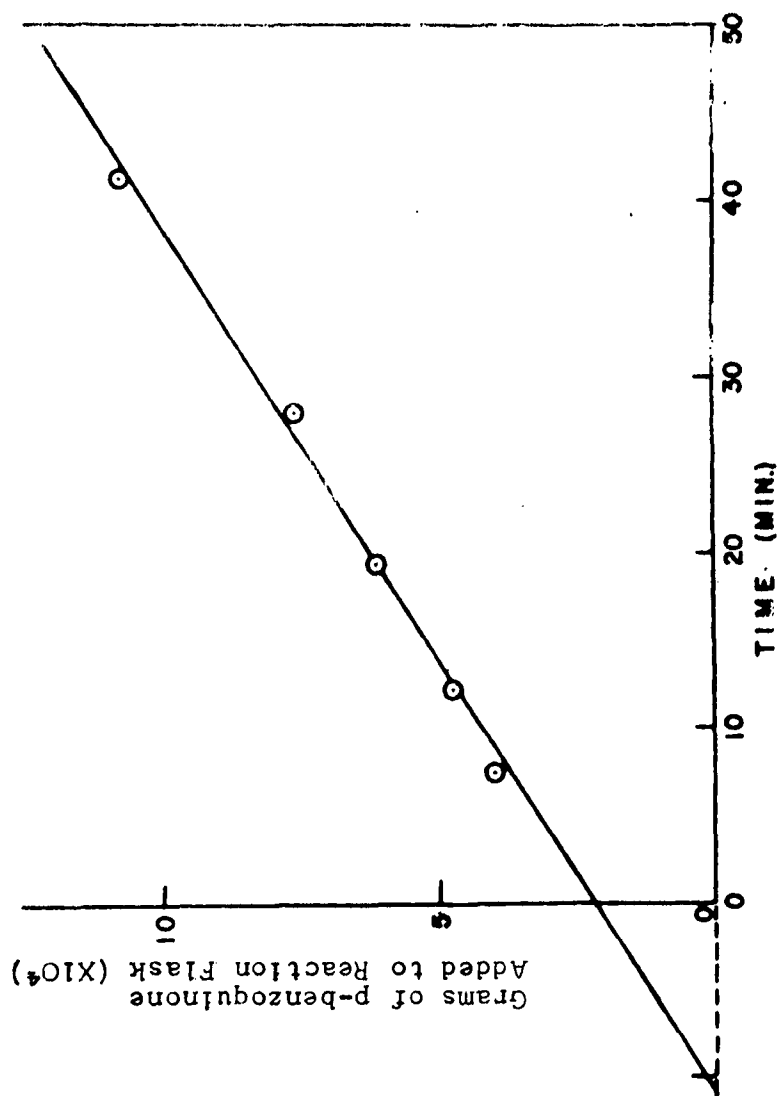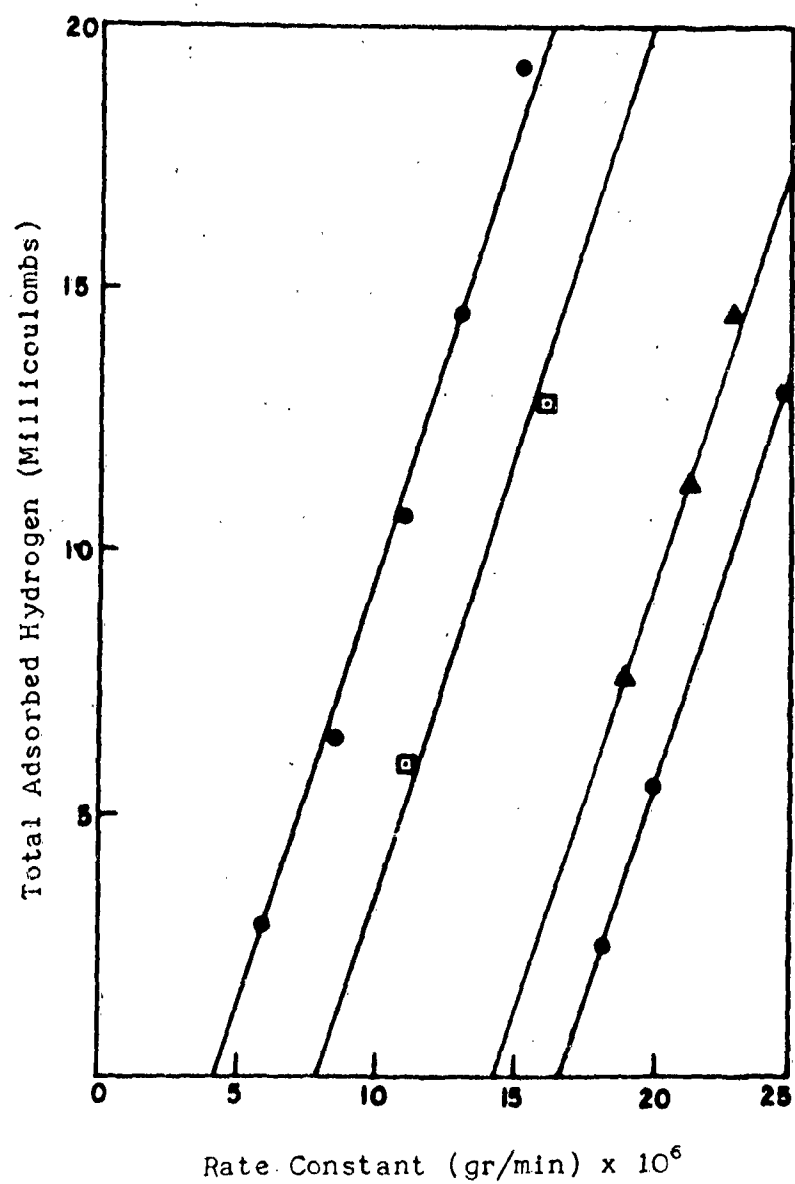(Vs. Saturated Calomel Electrode)

Figure 16   Rate Constants Vs. Amount of
Total Adsorbable Hydrogen on
Platinized Electrodes

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It was observed that the intercepts depended on the geometrical area of the base electrode (Figure 17). This indicated that in addition to the hydrogenation reaction governed by the surface area of the electrode there is another slower reaction governed by the geometric area. This could very easily be a diffusion controlled reaction.

Other functions might have been used here, since the electrodes were of approximately the same radius. This means that the areas and the volumes of the electrodes are both proportional to the lengths of the electrodes. In addition, the absorbed hydrogen as measured by anodic oxidation is also approximately proportional to the volume of the electrode.

The third form, or the absorbed form should be discussed somewhat further at this point. This form of hydrogen is only observed upon standing for long lengths of time. This slow process was observed by Cooke in a purified system. However, with the addition of an organic material to the system, the third form was seen to form much more rapidly than in t⋅ nine hours necessary in the pure system. This increase in the rate of absorption was observed in both the case of added quinone and added maleic acid. No quantitative measurements were made of this phenomenon since this was not of direct bearing on the problem at the time. However, the third form appeared almost as fast as the first two forms did in the system with the added

Figure 17   Zero Adsorbed Hydrogen Intercept Vs.
Geometric Area of Various Electrodes
Used
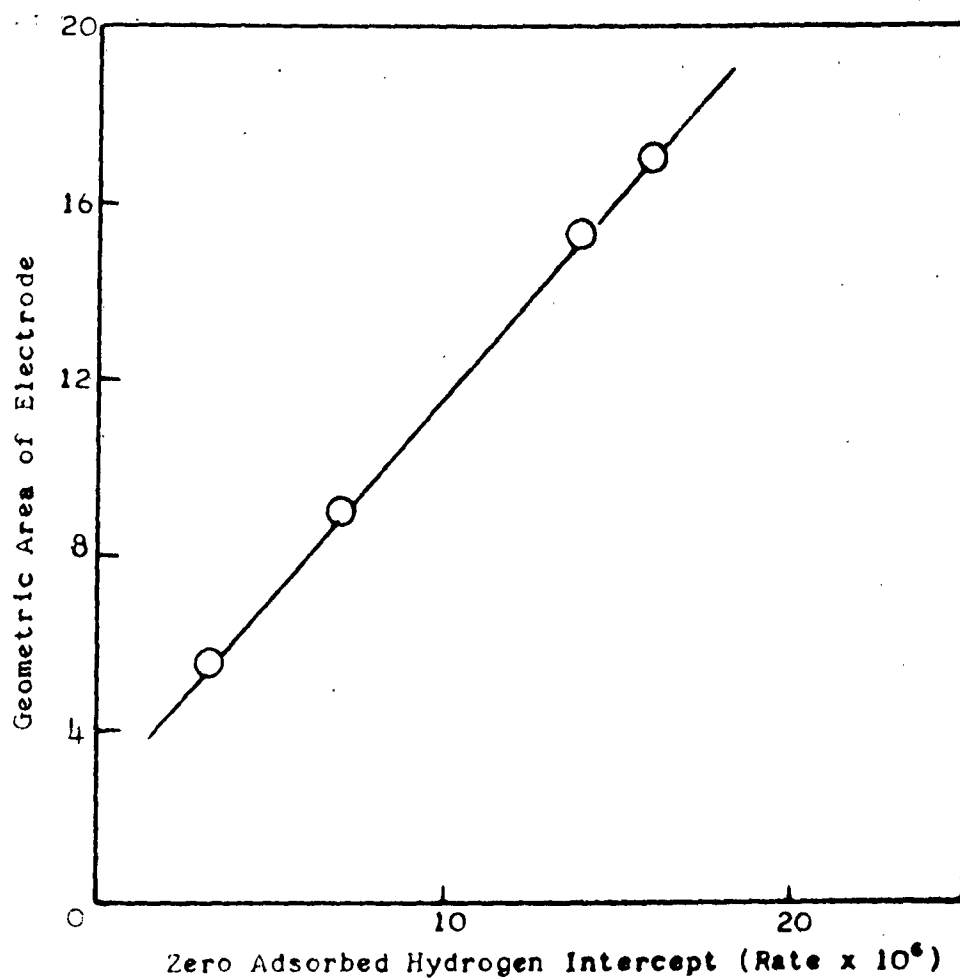
organic material.

The final figure, Figure 18, shows the plot of amount of adsorbed hydrogen vs. an adjusted rate constant for the reaction. This adjusted rate constant is the observed rate constant minus the intercept as observed from figure eight for the various base electrodes. This plot shows that the rate of hydrogenation is directly proportional to the amount of adsorbable hydrogen on platinum black.

E. Discussion of Results of Hydrogenation Experiments

The results as presented in the first part of the previous section show that the potential of the electrode, for very small concentrations of quinone, is a function only of the degree of coverage by hydrogen and follows an equation:

$$\Delta E_A = \frac{RT}{\alpha z F} \ln \frac{A}{A_0} = \frac{RT}{\alpha z F} \ln (k)(\Theta)$$

where Θ is the degree of coverage. Also:

$$\frac{dE}{d \text{ Log } \frac{A}{A_0}} = \frac{2.3RT}{0.4F}$$

This form of equation does not conform exactly to the Nernst equation but rather to a kinetic form of the Nernst equation, the Tafel equation. The Tafel equation generally requires a term αz. z is the number of electrons transferred in the rate determining electrochemical reaction and α is a term generally accepted to be approximately

52

Figure 18   The Effect of the Ability of the
Electrode to Adsorb Hydrogen on
the Hydrogenation Rate Constants
(Results Reduced to One Electrode)

Y-axis: Total Adsorbable Hydrogen (Millicoulombs)

X-axis: Rate Constant (g/min) X 10⁶

53
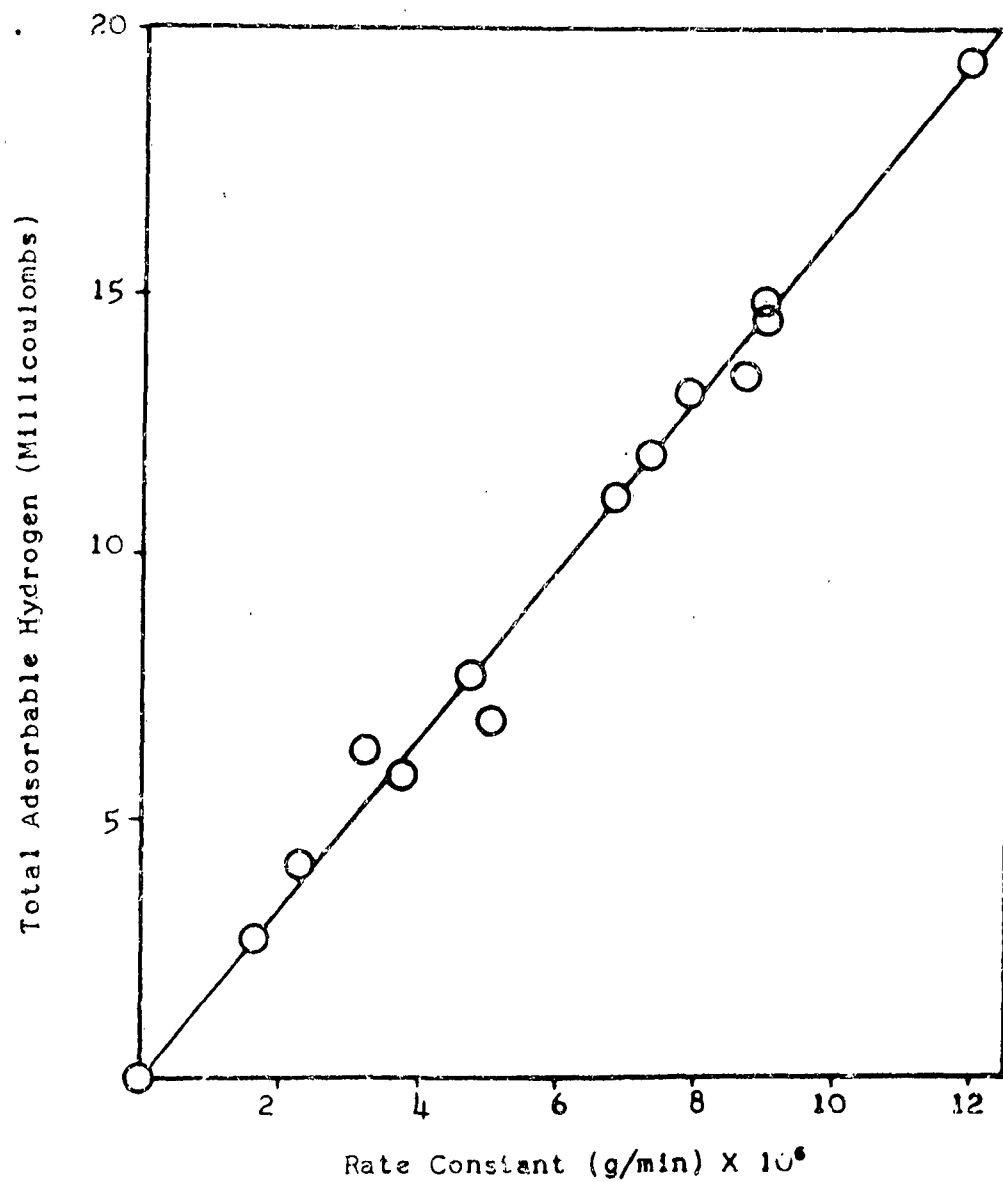
equal to .5. Thus the added quinone acts just as a constant
current applied to the platinum electrode and the potential
determining reaction becomes:

$$XH_2 + nPt \rightarrow 2Pt_{\frac{n}{2}} H_x \text{ (Ads)}$$

$$H_{(ads)} \rightarrow H^+ + e^-$$
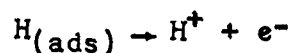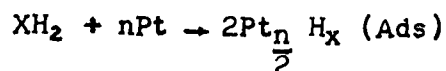
The results also show that the proportion of adsorbed
hydrogen on the surface is inversely proportional to the
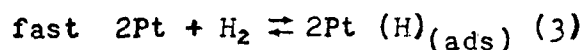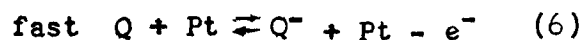concentration of quinone at very low concentrations of
quinone.

The study of the kinetics of the hydrogenation of the
p-benzoquinone showed that:

1. The rate has a zero order dependence on the
concentration of quinone at higher concentrations of quinone.

2. The rate is dependent on the amount of surface
available for hydrogen adsorption in the following manner:

$$\text{Rate} = k_1 (A) + k_2 (x)$$

where A is the amount of adsorbable hydrogen on the sur-
face as measured by polarographic anodic oxidation and X
is a linear function of the geometric area of the base
electrode.

A proposed mechanism for the reaction then becomes:

fast $Q + Pt \rightleftharpoons Q^- + Pt - e^-$ (6)

fast $2Pt + H_2 \rightleftharpoons 2Pt (H)_{(ads)}$ (3)

slow $2Pt\ (H)_{(ads)} \rightleftharpoons \alpha Pt + 2H^+ + 2e^-$ (4)

fast $Q^- + H^+ \rightleftharpoons HQ$ (7)

fast $HQ + Pt \rightleftharpoons HQ^- + Pt - e^-$ (8)

fast $HQ^- + H^+ \rightleftharpoons H_2Q$ (9)
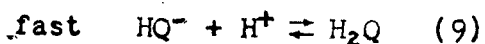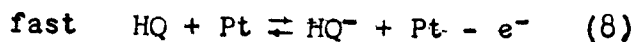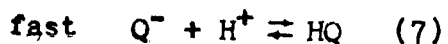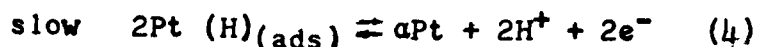
and the over all reaction is:

$$Q + H_2 \overset{Pt}{\rightleftharpoons} QH_2$$

The one electron transfer mechanism for the reduction of quinone is supported the investigation by Vetter.[152]

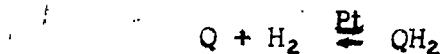These results show that two distinct forms of hydrogen occur on the surface of platinized platinum which are adsorbed independently of each other on different sites. Quinone is a sufficiently electrochemically positive material to oxidize both forms from the surface of platinum.

III.   The Catalytic Decomposition of Formaldehyde

A. Introduction

A continuation of the catalytic studies was made investigating the catalytic decomposition of formaldehyde on platinum black electrodes. This is important, just as the previous reactions were, as a method of studying the mechanism of interaction between hydrogen and the platinum black and the organic compound and platinum. It is also important in that many fuel cell studies are concerned

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[152]K. J. Vetter, Z. Elektrochem., 56, 797 (1952).

with the electrolytic oxidation of formaldehyde at low
potentials. It is entirely possible that this is merely
oxidation of hydrogen formed by the catalytic decomposition
of the formaldehyde.

B. Experimental

The electrodes used were made from platinum wires
varying in diameter from 0.8 to 1.1 mm. and in length
from 9 to 3 cm. These electrodes were cleaned with aqua
regia and rinsed with distilled water. They were platinized
with a variety of current densities and plating times in
an approximately 3% chloroplatinic acid solution containing
varying amounts of lead acetate (0.01, 0.03, 0.05 and 0.06%).
In this manner electrodes were obtained that had varying
abilities to adsorb hydrogen.

After platinizing, the electrode was rinsed with water
and placed in a cell containing a large platinized platinum
gauze electrode. Two series of experiments were run using,
on the one hand, 2N sodium hydroxide and, on the other, 2N
sulfuric acid as the solvent. Hydrogen was bubbled through
the solution until the voltage between the test electrode
and the gauze electrode reached a constant value. The ·
hydrogen flow was then turned off and a polarogram was run
oxidizing the hydrogen on the electrode. This was repeated
until two or three of the curves appeared to have the same
shape and area. It usually took about three runs before
reproducible curves were obtained. In agreement with the

56

previous work[153] for short bubbling times the polarograms in the basic solutions contained three maxima and those in acid solutions contained two maxima.

The electrode was then removed from the cell and placed in a test tube containing 15 mls of either 2N sodium hydroxide or 2N sulfuric acid and approximately 3×10^{-4} g. of formaldehyde. In one series of runs the solution contained approximately 6×10^{-5} g. of formaldehyde.

During the run 1.00 ml. of samples were withdrawn at different times. These samples were diluted with 2 ml. of distilled water and 5 mls. of a chromotropic acid solution (0.4 g. chromotropic acid in 4 ml. of distilled water and 96 ml. of concentrated sulfuric acid) were added. The resulting solution was placed in a water bath and boiled for 30 minutes, cooled, and diluted to 10 mls. with distilled water. The resulting samples were analyzed with a Klett-Summerson Colorimeter.

Blank runs were made without the platinum electrode. No other reaction appeared to go fast enough to interfere.

All reagents were the purest grades available commercially. All experiments were run in a water bath maintained at $25.0 \pm 0.2°$ C.

C. Results of Experiments in Sodium Hydroxide

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[153]S. L. Cooke, Jr. and T. C. Franklin, J. Electrochem. Soc., 107, 556-60 (1960).

The decomposition of formaldehyde on platinized platinum was found to be first order with respect to the formaldehyde as is seen from Figure 19. This plot is from data from a typical run.

The rates of the reaction, as obtained from the slopes of plots similar to those in Figure 19, are plotted against the areas of the electrodes as measured by their ability to adsorb and absorb hydrogen in the various forms. (Figures 20, 21, and 22) It is seen that the rate of the reaction is linearly proportional to the area of the electrode as measured by its ability to adsorb hydrogen in the second surface form (the third peak). It was observed that the rate was also proportional to the area under the second peak. This peak as shown by Cooke is due to the oxidation of hydrogen absorbed by the platinum. There does not seem to be any reason for the rate of decomposition to be dependent on the ability of the electrode to absorb hydrogen. It seems more likely that, as was observed by Matsuda on iron[154], there is an equilibrium between adsorbed hydrogen and absorbed hydrogen. As is shown in Table I, it was found that an equilibrium existed between the amount of hydrogen adsorbed in the second form and the amount absorbed in the metal. The ratio of the second to third peak areas remains approximately constant. There-

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[154]F. A. Matsuda and T. C. Franklin, Paper Presented at Electrochemistry Society Meeting, Fall, 1961.
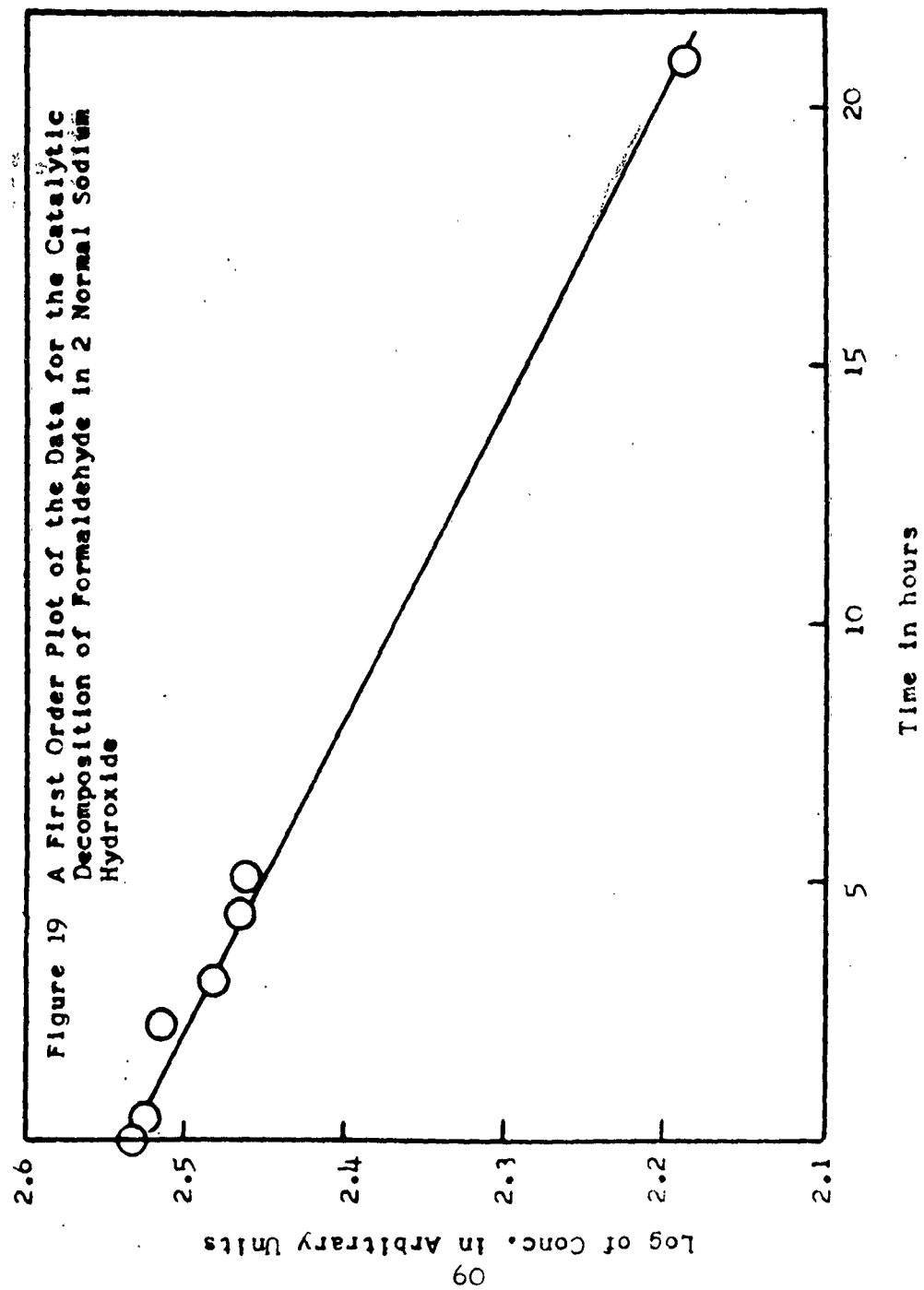
Table I

Effect of Poisoning on the Different Hydrogen Peaks

| Electrode Treatment | Area Under Different Peaks* | | | Area of the 2nd Pe: |
	1st	2nd	3rd	Area of the 3rd Pe:
Freshly Platinized Electrode	0.0189	0.0028	0.0160	0.701
After Standing for 2 hours	0.0087	0.0161	0.0123	0.763
After adding 0.03g. sulfonate°	0.0061	0.0132	0.0103	0.780
After adding 0.06g. sulfonate	0.0055	0.0114	0.0071	0.623
After adding 0.09g. sulfonate	0.0044	0.0117	0.0073	0.624
After adding 0.12g. sulfonate	0.0067	0.0116	0.0069	0.594

*These peak areas are recorded in planimeter readings.

°The sodium salt of naphthalene disulfonic acid.

Figure 19 A First Order Plot of the Data for the Catalytic Decomposition of Formaldehyde in 2 Normal Sodium Hydroxide

Time in hours

Log of Conc. in Arbitrary Units

Figure 20   The Rate Constant for the Decomposition of
Formaldehyde in 2 Normal Sodium Hydroxide
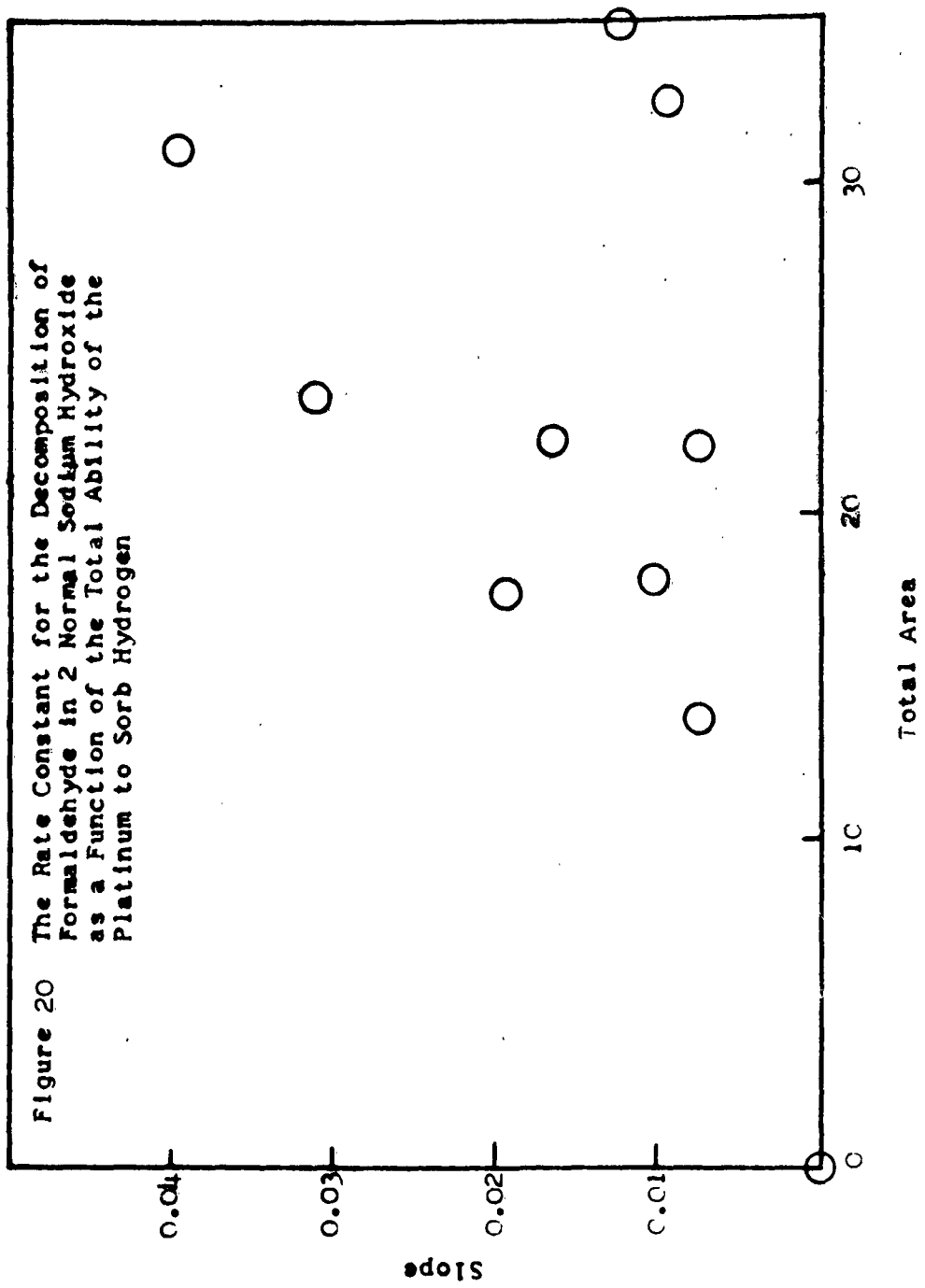as a Function of the Total Ability of the
Platinum to Sorb Hydrogen

Figure 21 The Rate Constant for the Decomposition of
Formaldehyde in 2 Normal Sodium Hydroxide
as a Function of the Ability of the Platinum
to Sorb Hydrogen in the First Form
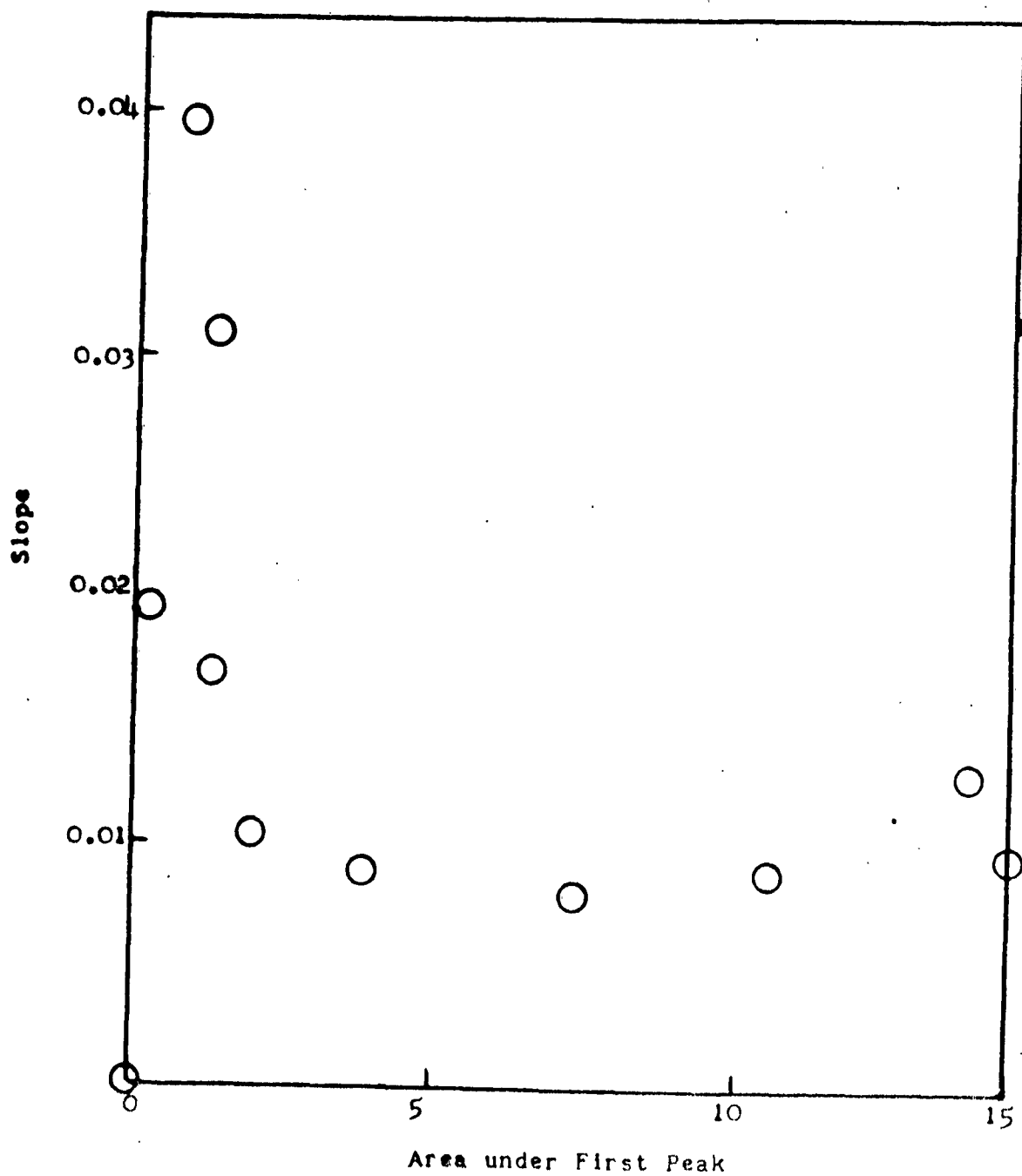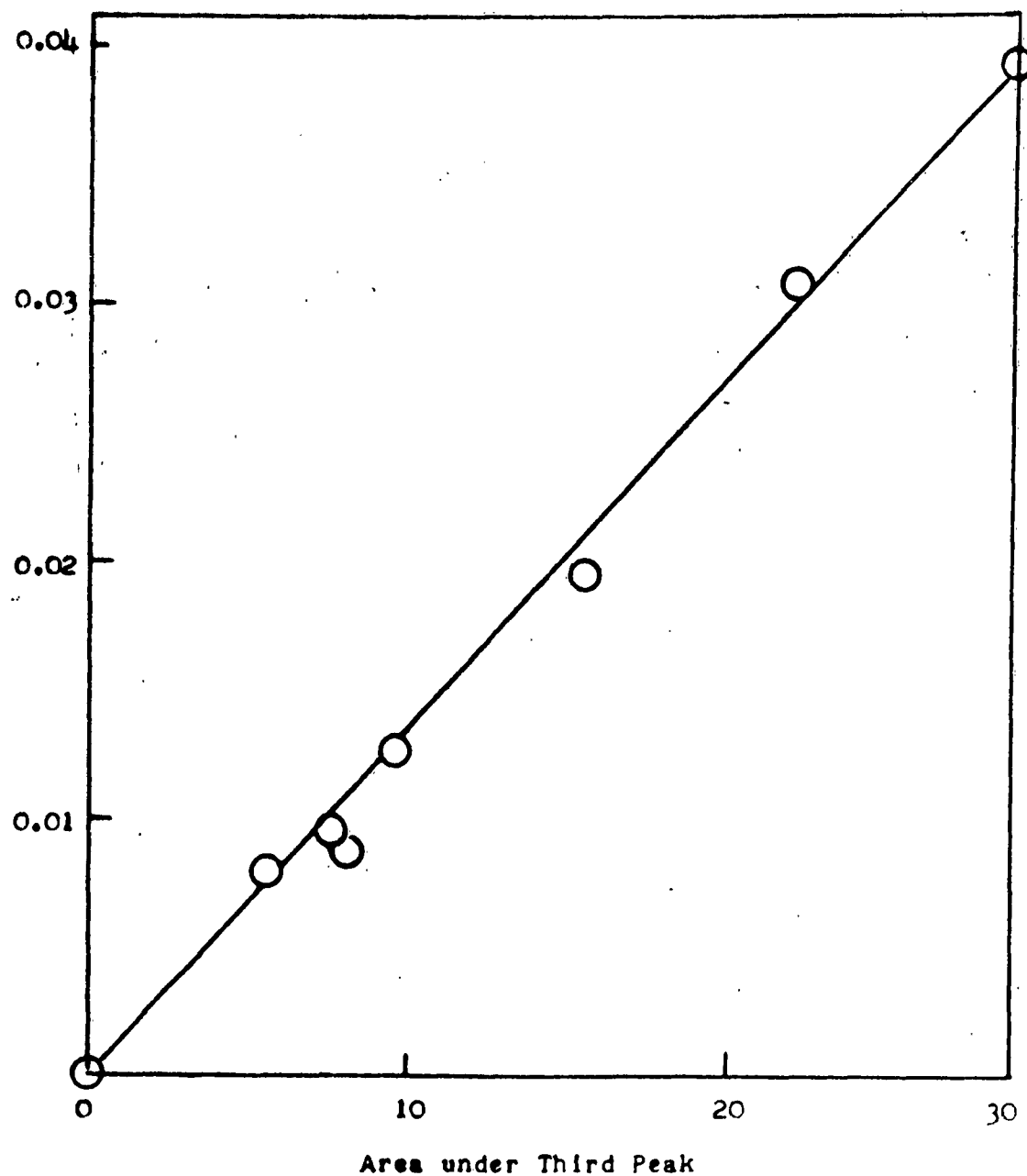

Area under First Peak

62

Figure 22 The Rate Constant for the Decomposition of
Formaldehyde in 2 Normal Sodium Hydroxide
as a Function of the Ability of the Platinum
to Sorb Hydrogen in the Third Form

Area under Third Peak

63

fore, it was concluded that the rate of decomposition varied only with the area of the electrode as measured by its ability to adsorb hydrogen in the second surface form.

D. Results of Experiments in Sulfuric Acid

Figure 23 shows that the rate of decomposition of formaldehyde in 2N sulfuric acid was first order with respect to the formaldehyde just as it was in sodium hydroxide. However, the reaction was much faster in basic than in acidic solutions.

In 2N sulfuric acid solutions the rate of absorption of hydrogen by platinum is much slower than in 2N sodium hydroxide. Therefore, it was necessary to study only the effects of the two surface forms of hydrogen. Figures 24, 25 and 26 show that in these solutions the rate of decomposition of formaldehyde is also proportional to the area of the electrode as measured by its ability to adsorb hydrogen in the second form.

From this it is possible to conclude that in both acidic and basic solutions the reaction is occurring on the same type of sites and that the two forms of hydrogen are hydrogen adsorbed on two kinds of sites on the electrode surface.

IV. Summary

Figure 23   A First Order Plot of the Data for the Catalytic
Decomposition of Formaldehyde in 2 Normal Sulfuric
Acid

Time in hours

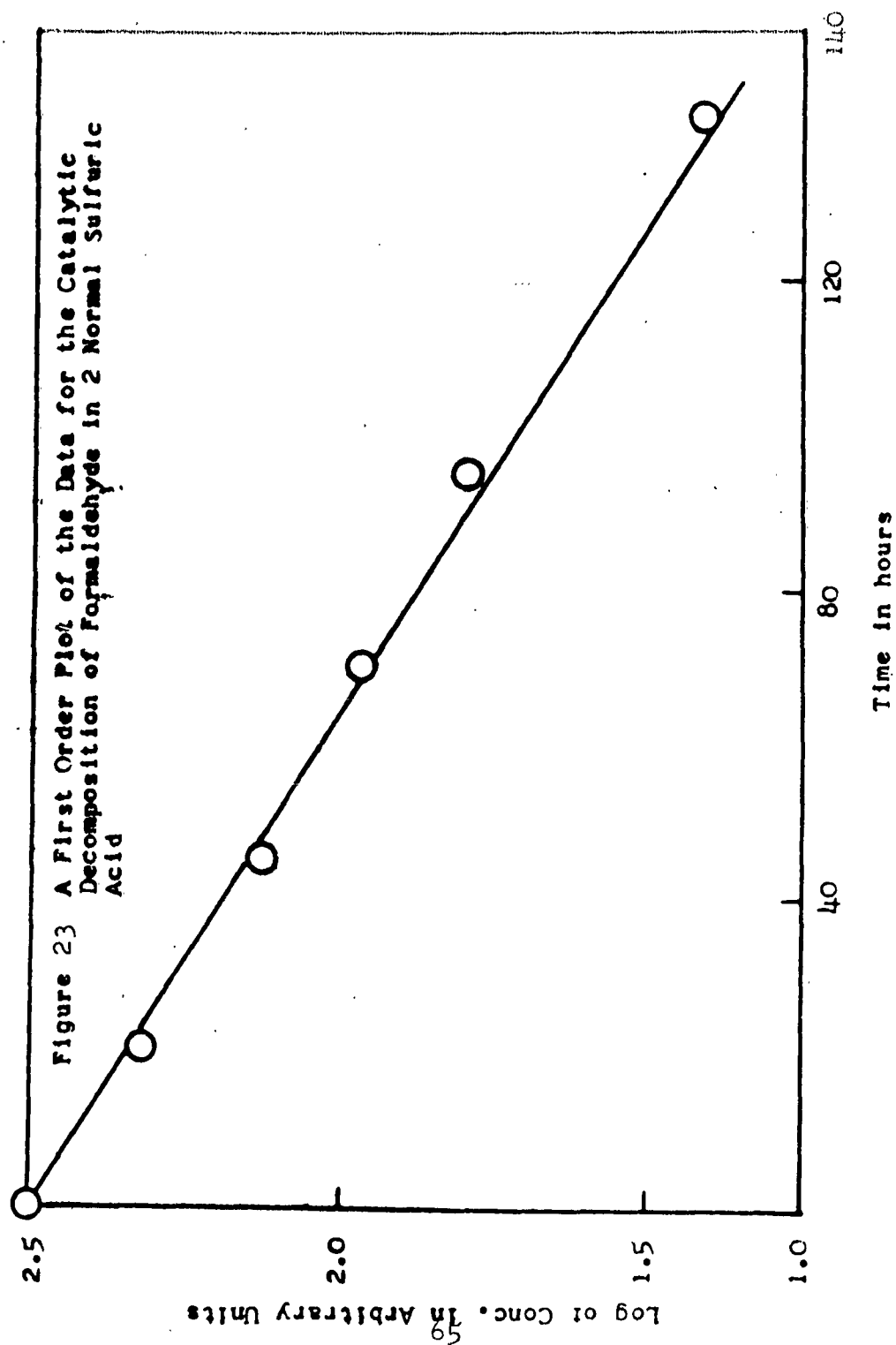Log of Conc. in Arbitrary Units

59

Figure 24. The Rate Constant for the Decomposition of
Formaldehyde in 2 Normal Sulfuric Acid as a
Function of the Ability of the Platinum to
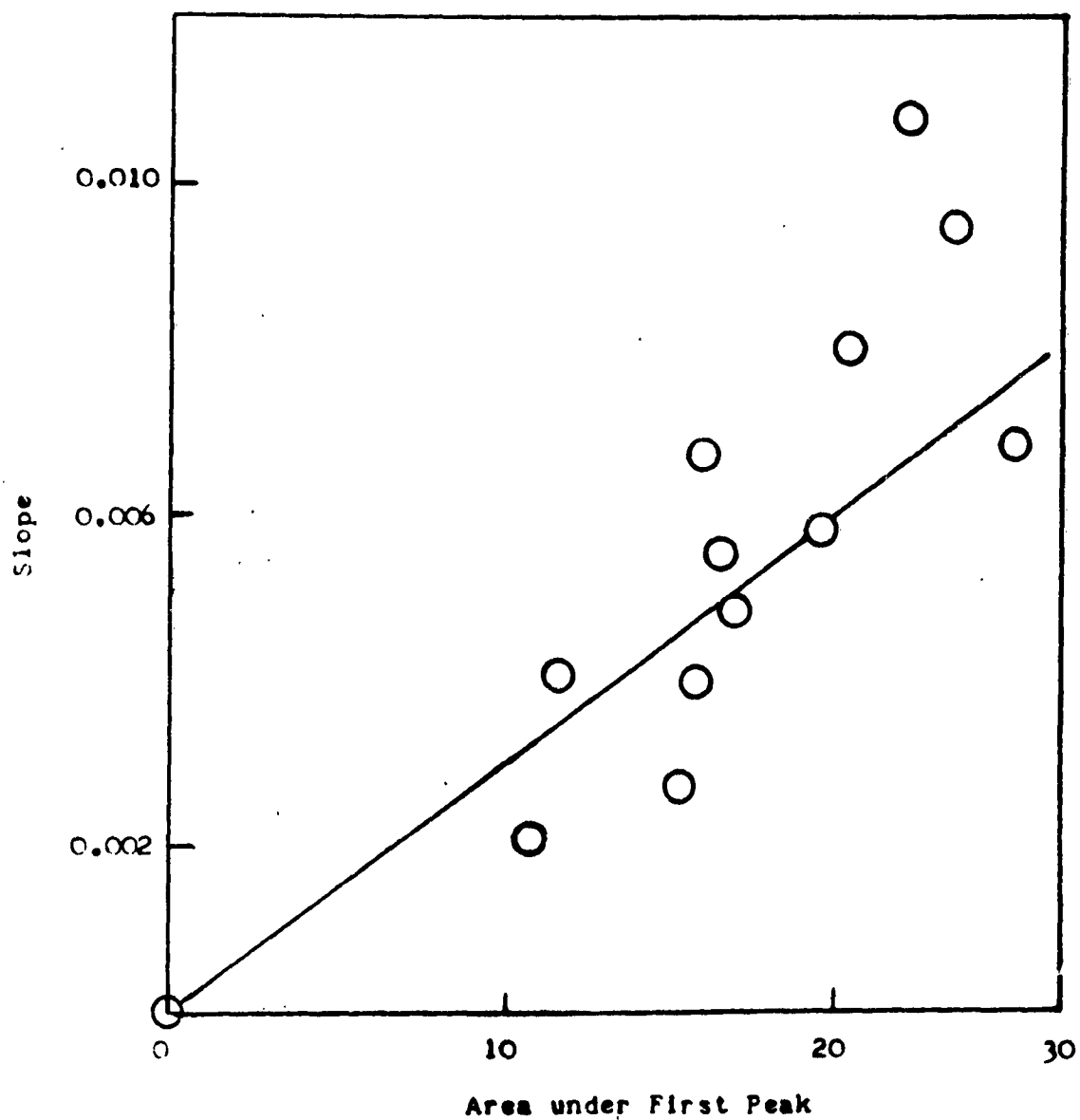Sorb Hydrogen in the First Form

Figure 25 The Rate Constant for the Decomposition of
Formaldehyde in 2 Normal Sulfuric Acid as a
Function of the Ability of the Platinum to
Sorb Hydrogen in the Second Form

Area under Second Peak
67

Figure 26 The Rate Constant for the Decomposition of
Formaldehyde in 2 Normal Sulfuric Acid as a
Function of the Total Ability of the Platinum
to Sorb Hydrogen

Total Area

Slope

0.010

0.008

0.002

89
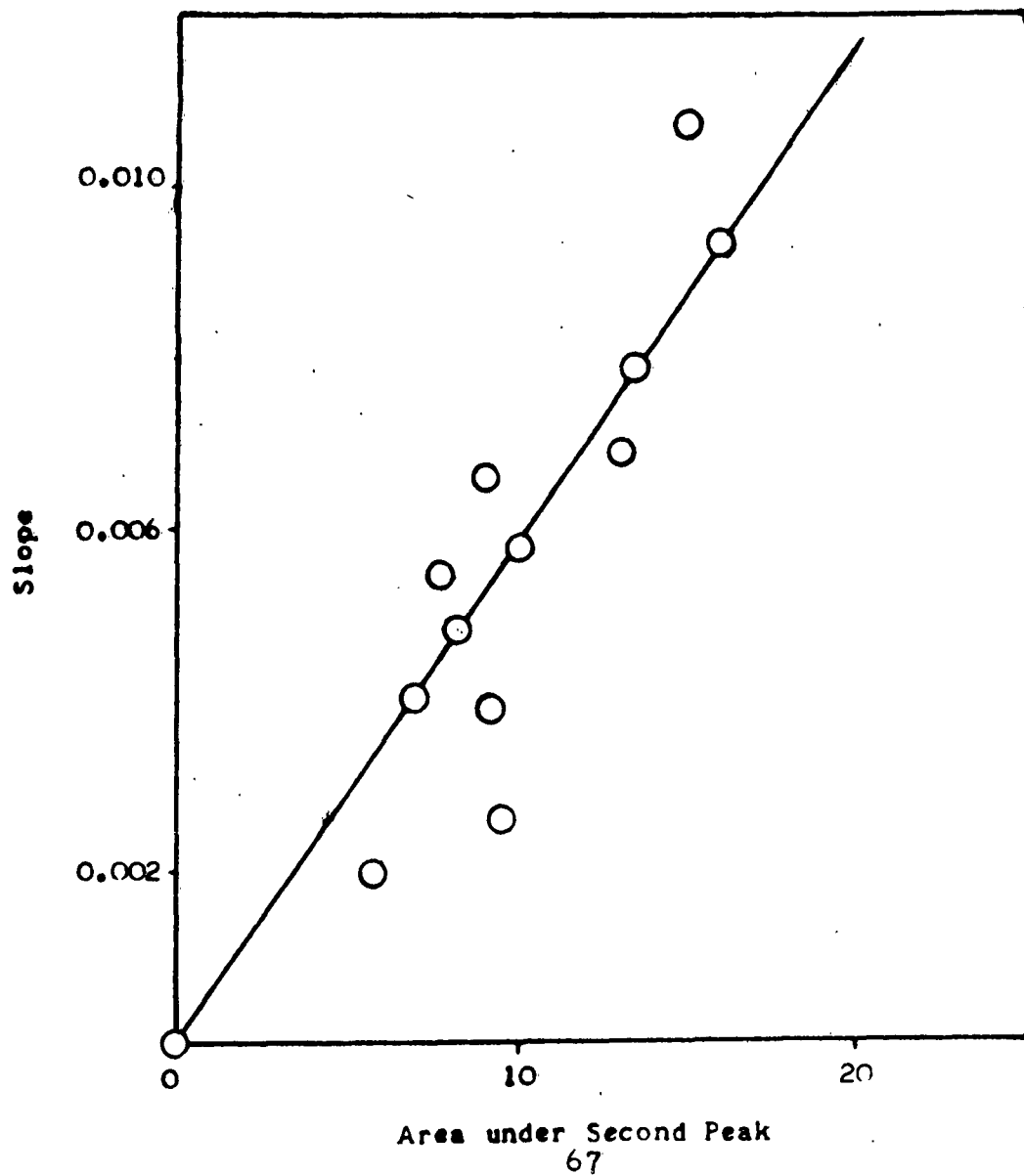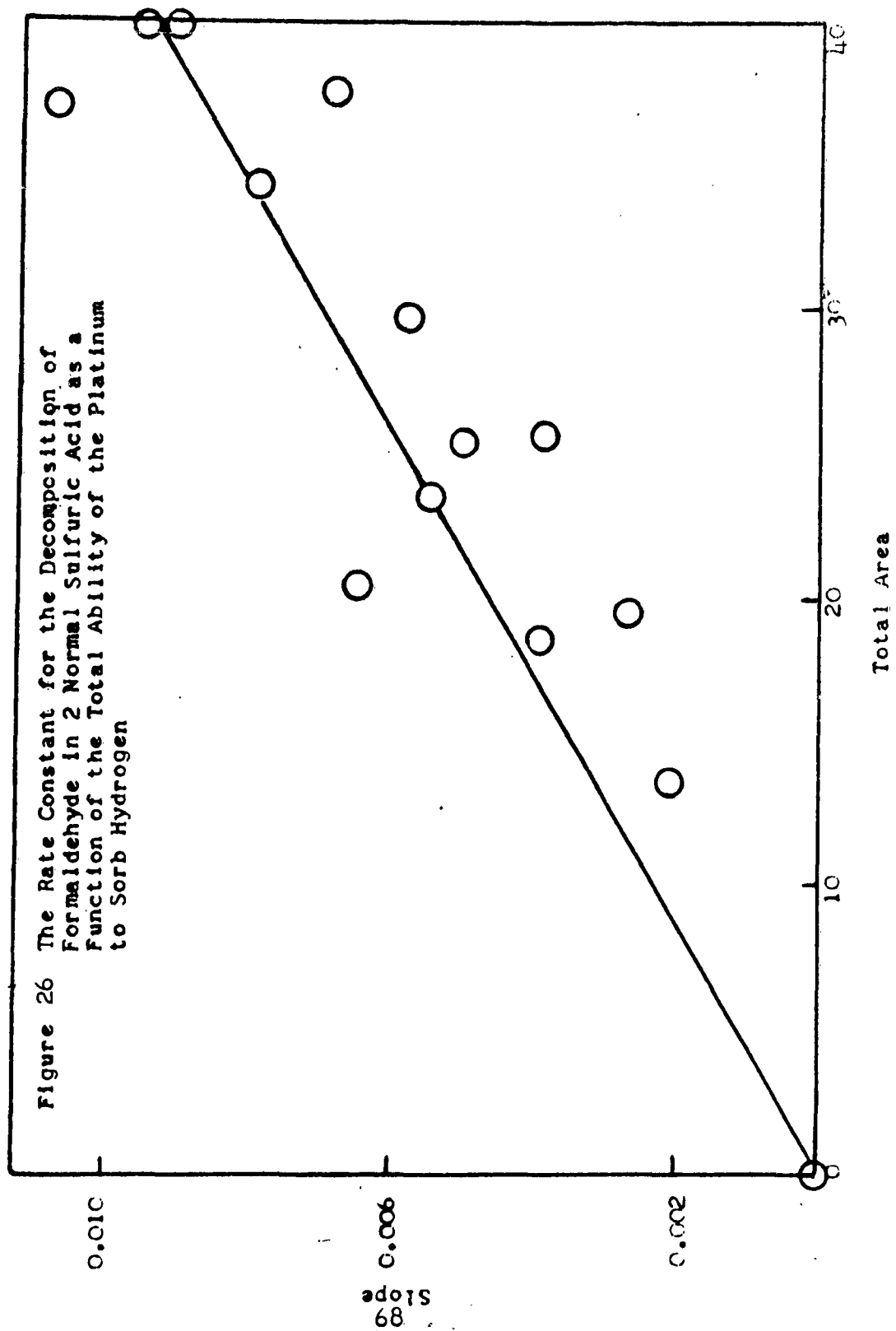
The decomposition of hydrogen peroxide, a reaction that occurs on the oxidized platinum surface apparently occurs on the same sites used for adsorption of the second form of surface hydrogen. The decomposition of formaldehyde, a reaction that might logically occur on bare platinum, since hydrogen is produced, also occurs on the sites used for adsorption of the second form of surface hydrogen. On the other hand, the hydrogenation of quinone occurs on the whole surface of the electrode. Changing the solution from 2N sodium hydroxide to 2N sulfuric acid changed the rate of decomposition, but did not alter the nature of the sites on which the reaction occurred.

From these experiments it is evident that there are two basically different types of adsorption sites on the surface of the platinum. These sites are still different when the surface is oxidized. They are also different in their ability to catalyze these decomposition reactions.

In addition, it was observed that a rapid equilibrium is reached in basic solutions between the absorbed hydrogen and the second form of surface hydrogen.

It also seems reasonable from the formaldehyde study that fuel cells operated at low potentials using formalde-hyde as a fuel are in actuallity merely hydrogen fuel cells operating on the hydrogen obtained from the catalytic de-composition reaction.

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Studies were made of the catalytic decom-
position of formaldehyde and hydrogen
peroxide and the hydrogenation of quinone
on platinized platinum using the ability
to adsorb hydrogen as a measure of the
area of the platinum. In aqueous solu-
tions the rate of decomposition of both
hydrogen peroxide and formaldehyde was
first order with respect to the compound
and first order with respect to the abi-
lity of the metal to adsorb hydrogen in
the second, more strongly bound, form.
The hydrogenation of quinone was zero
order with respect to the quinone and
first order with respect to the total
ability of the metal to adsorb hydrogen.

1. Catalysis
2. Platinum
3. Hydrogen
4. Hydrogen
   Peroxide
5. Quinone
6. Formaldehyde
7. Electrodes

I. T. C. Franklin,
   et. al.