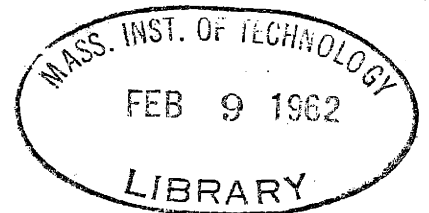


STEADY STATE RATES OF CATALYTIC DECOMPOSITION
OF LIQUID HYDROGEN PEROXIDE ON METAL SURFACES

by

RICHARD V.B. ROSSMAN

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Submitted in Partial Fulfillment
of the Requirements for the
Degree of Bachelor of Science

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

January, 1962

Signature of Author:

Department of Chemical Engineering,
January 15, 1962

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Massachusetts Institute of Technology
Cambridge 39, Massachusetts
January 15, 1962

Professor Philip Franklin
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Dear Sir:

I hereby submit my thesis, "Steady State Rates of Catalytic Decomposition of Liquid Hydrogen Peroxide on Metal Surfaces", in partial fulfillment of the requirements for the degree of Bachelor of Science at the Massachusetts Institute of Technology.

Respectfully yours,

Richard V.B. Rossman

ACKNOWLEDGEMENTS

The author expresses thanks to Professor C.N. Satterfield for his valuable guidance in these experiments. Also the author is grateful to Evan Buck for his helpful suggestions concerning this work and the legacy left to him in the majority of his equipment.

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I SUMMARY

The "steady-state" catalytic activities of gold, platinum, and palladium in the decomposition of liquid hydrogen peroxide were determined under conditions which controlled the effects of various pretreatments of the metal surfaces. The pretreatment of a metal surface with nitric acid was found to have varying initial effects on the catalytic activity of each metal studied. In gold the catalytic activity of the metal surface was initially low. Subsequently its catalytic activity would rise to a maximum value and then approach a slightly lower value as a limit. In platinum and palladium the pretreatment of the metal surface with nitric acid resulted in initially high values of catalytic activity which subsequently decreased to a limiting value.

In these experiments the effects of prolonged experimentation in hydrogen peroxide on the metal surface were simulated by continuous immersion of the metal foil in hydrogen peroxide for periods of over a week. This method of pretreatment produced steady-state catalytic activities in all three of the metals studied. The values found were as follows: gold -- 0.45 ± 0.05 ml O_2 /min per sq.in. of surface; for platinum -- 1.6 ± 0.1 ml O_2 /min per sq.in. of surface; for palladium -- 3.55 ± 0.05 ml O_2 /min per sq.in. of surface. Although these values are at slight variance with the results of previous investigations, evidence has been found that those investigators had neglected to carry their experiments to their logical conclusions.

II INTRODUCTION

Rate data on the catalytic decomposition of liquid hydrogen are desired in many areas of interest to the chemical engineer. On some fuel cells hydrogen peroxide is the undesired by-product of electro-chemical reaction. On the other hand, it would be possible to build a fuel cell using hydrogen peroxide as one of the chemical reagents, if only enough information were available on its catalytic decomposition. Also since the decomposition of hydrogen peroxide was one of the first catalysis reactions ever to be observed, it has long been of interest in the field of catalysis as a basic reaction.

Recently J. Fahrenfort (1) completed a study on the catalytic decomposition of gaseous formic acid on metal surfaces. His findings show that the decomposition reaction proceeds via the formation of a metal formate intermediate. By studying the rate of decomposition as a function of temperature, Fahrenfort found discrete values for the entropy of activation in the reaction. These were directly related to the sum of the entropy of formation of the metal formate and the entropies of adsorption and desorption of formic acid and its products respectively.

The catalytic decomposition of hydrogen peroxide is in several ways similar to the foregoing catalysis reaction. Both are heterogeneous reactions, although one is a liquid decomposition while the other was studied entirely in the gaseous state. However both exhibit the complexities of heterogeneous catalysis. Both reactions also take place readily on metal surfaces. Furthermore there is evidence for the presence of oxide layers on even the noblest of metals in the presence of hydrogen peroxide; and one suspects that hydrogen peroxide might decompose via an oxide or peroxide intermediate.

A. The Problem

In 1959, P.K. Sarda (2) was able to isolate the effects of various phenomena involved in the decomposition of aqueous hydrogen peroxide on metal surfaces. His study showed that the reaction is surface controlled and follows first order kinetics for fourteen heavy metal catalysts, excepting silver. In his experiments he exercised control over the purity of the materials used and the supersaturation effects of oxygen in hydrogen peroxide (3). The neglect of these latter two variables had in the past given rise to many misinterpretations of data.

Recently E. Buck (4) completed a study of the effects of various pretreatments of the metal surfaces in the catalytic decomposition of hydrogen peroxide. The object of his pursuit was the steady-state catalytic activity of gold and platinum surfaces. Pretreatment of the metal surface by short (1 to 5 minutes) dips in 5% nitric acid was found to be the most satisfactory method (5). The values he reported for the catalytic activities of the metals agreed with Sarda's values to within a factor of two.

The object of this study was then, 1) to reproduce Sarda's and Buck's data, and 2) to ascertain a procedure for obtaining accurate and reproducible values for the catalytic activities of platinum, gold, and palladium, expressed in ml. of oxygen evolved per minute per square inch of metal surface.

B. Apparatus

The apparatus used in these experiments consisted of a sealed reaction chamber immersed in a thermostatic bath and an oxygen recorder with which to measure the decomposition rate of the hydrogen peroxide. On the following page is a diagram of the apparatus, except for the oxygen

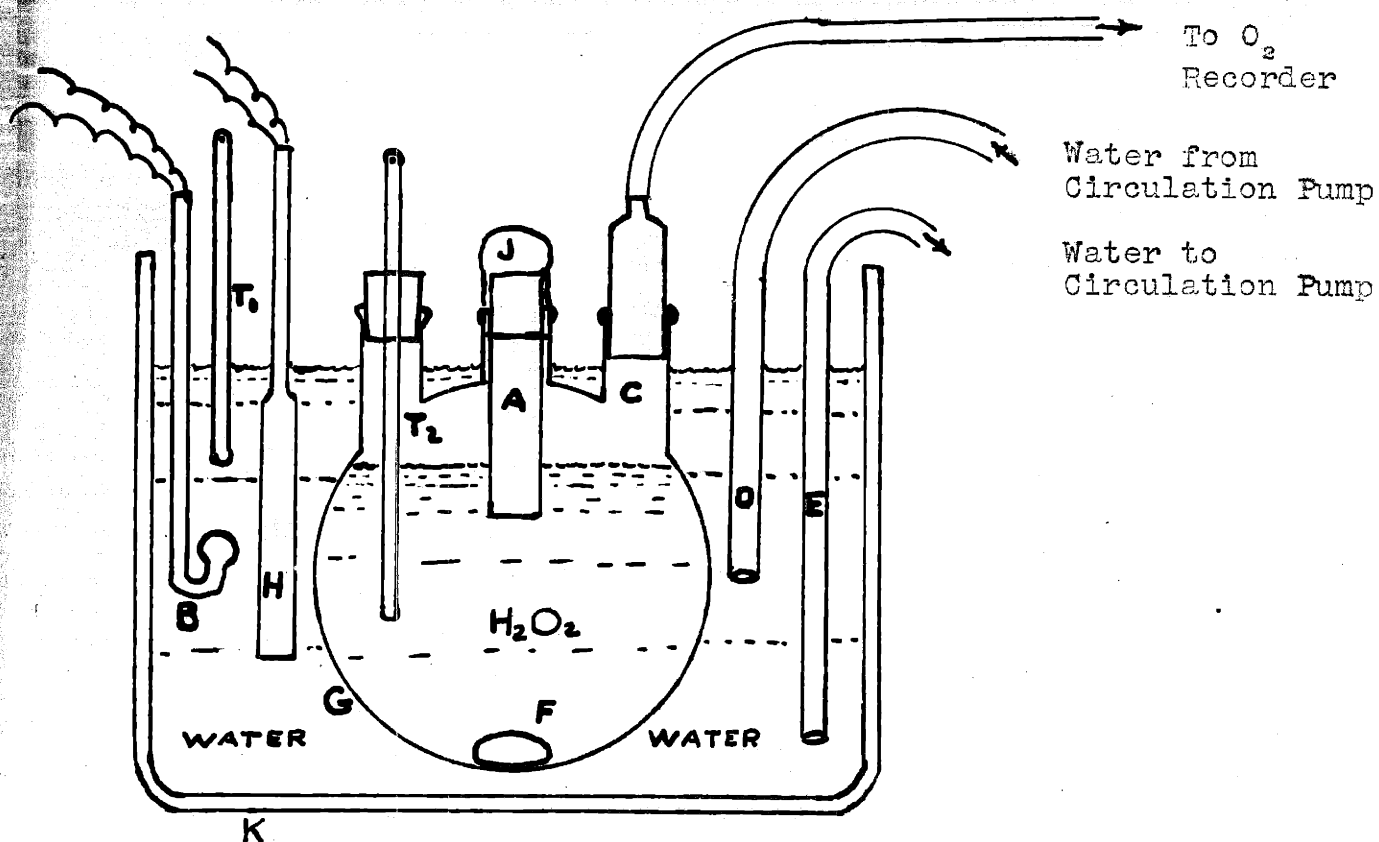


FIGURE 1

APPARATUS FOR MEASUREMENT OF CATALYSIS OF LIQUID HYDROGEN
PEROXIDE BY SLIT-SUSPENSION TECHNIQUE

LEGEND:

- A Teflon cylinder with slit for foil suspension.
- B Thermoregulator for thermostatic bath.
- C Oxygen outlet. Glass conector fitted to tygon tubing.
- D Rubber tubing inlet for circulating water.
- E Rubber tubing outlet for circulating water.
- F Teflon-coated magnetic stirrer.
- G Three-necked, one liter pyrex flask (reactor).
- H Heater.
- J Glass stopper, with hole fitting teflon cylinder.
- K Glass jar, 16 inch diameter.
- T₁ Thermostatic bath thermometer.
- T₂ Reactor thermometer.

recorder. The oxygen recorder was simply a 50 ml. tube, calibrated to the nearest 0.1 ml., in which oxygen displaced an aqueous $MgCl_2$ solution at a pressure regulated by the height of a pressure bulb. All readings were made at atmospheric pressure. The $MgCl_2$ solution was saturated before each run with oxygen from an outside source. The metal foils used were suspended inside the reactor from a slit in a teflon cylinder. All reactions were slow enough for accurate rate measurements. Also a circulation pump was used in a two-fold purpose: first to maintain agitation in the thermostatic bath while also circulating water at the reaction temperature around the oxygen recorder tube. Agitation inside the reactor flask was maintained by a teflon coated magnet operated by a magnetic stirrer. Lastly all materials in contact with the hydrogen peroxide were either glass, teflon, or the metal foil to be studied.

C. Materials Used

1. Gold and Platinum foils were obtained from the Laboratory Supplies at M.I.T.
2. The Palladium foils were those used by Sarda in his thesis work. Their numbers in this experiment correspond also to Sarda's numbers. Sarda's foils were originally "pure" palladium from A.D. Mackay Co., New York.
3. The Hydrogen Peroxide used in all tests was unstabilized SP-90 obtained from Becco Chemicals, Buffalo, New York. This is the purest form of hydrogen peroxide available commercially, and it contains not more than a few p.p.m. of impurities or stabilizer.
4. The water used in dilution of hydrogen peroxide and in the final cleansing of all materials to come

6

into contact with the hydrogen peroxide was distilled water, which had been percolated through a mixed ion exchange column. In this report it is henceforth referred to as "deionized water".

III PROCEDURE

A. Experimental

The following steps comprised an experimental run.

1. The concentration of the hydrogen peroxide was first determined by titration with a standardized KMnO_4 solution. The titration and standardization procedures are detailed on page of Schumb, Satterfield, and Wentworth (6).
2. The agitation of the hydrogen peroxide solution was then started to rid the solution of super-saturated oxygen.
3. Oxygen was next bubbled through the MgCl_2 solution in the oxygen recorder for 5 minutes to attain a state of oxygen saturation in the solution.
4. Fine adjustments in the temperature of the bath were made at this point to assure the proper temperature, usually 30.0°C .
5. The blank rate of catalytic decomposition was measured off and on during the next half hour, until an accurate measurement of a constant blank rate had been made.
6. The metal foil was then cleansed and pretreated in the manner described in the next section, usually ten minutes before beginning the run.
7. Just before the run was to begin the metal foil, which had been exposed to air in a clean and sealed flask, was inserted into the slit in the teflon foil holder. The foil was then plunged into the hydrogen peroxide reactor, and the run began.
8. At the end of a run the foil was washed in de-ionized water and stored in the same, awaiting later use.

The volume displacement of the $MgCl_2$ solution was measured continually throughout a run, recorded, and converted to rate data.

The nitric acid pretreatments were carried out with a thorough cleansing of the foil both before and after. When a foil was taken from the hydrogen peroxide storage solution, it was merely washed in deionized water. If the foil had been left in deionized water as a pretreatment, it was removed with no additional cleansing.

The procedural plan of the experiments was originally to compare the rate values obtained with the nitric acid pretreatments to those obtained from prolonged hydrogen peroxide pretreatments at or above 31% by weight of hydrogen peroxide. However as the experiments progressed, a slightly varied plan of action was developed to explore the indications of early results. This is discussed in the section containing the Discussion of the Results.

B. Cleaning

Initially the reactor flask and its parts were cleaned in laboratory glass cleanser, and then exposed to hot aqua regia, which was allowed to cool over a 20 hour period. Subsequent cleansings of the reactor, its parts, and all other materials which came into contact with the hydrogen peroxide were according to the following steps

1. Thorough washing in CCl_4 to remove grease.
2. Immediate washing in acetone to remove the rest of the CCl_4 and any organic impurities not removed by the CCl_4 .
3. Rinsing in deionized water to remove ionic impurities.

This latter step was usually repeated several times. Upon being cleansed, any part was then stored in a closed container away from dust.

IV PRESENTATION AND DISCUSSION OF THE RESULTS

The description of each run and its complete record of rate data are presented in the appendix, except for Run 5. This latter run ended in complete failure when the foil became dislodged from its teflon holder. Presented in this section is the summarized data of the non-redundant runs in the form of plots: catalytic activity versus time of contact with the hydrogen peroxide.

A. Palladium Foils (See Figure 2)

Run 1 was a preliminary attempt to reproduce Sarda's value for the catalytic activity of palladium, with no pretreatment. In this run a value much lower than the one Sarda found was indicated. Runs 2,3, and 4 following this one were also carried out with no pretreatment of the same foil. Their intent was to ascertain a value for the activation energy of this particular catalytic reaction by varying the temperature of the reaction. If such a value could be found it would be instructive to compare it to that of another palladium foil, which showed an activity close to that found by Sarda. If any difference between their activation energies could be found, different catalysis mechanisms would be suggested. However these attempts ended in failure, when the blank rate was found to increase exponentially with small increases in temperature to a value several times the actual foil rate. The inherent error in the blank rate determination increased to about 20% of the foil rate value.

Runs 6,7, and 8 all approached the same value for the catalytic activity of palladium, 3.55 ± 0.05 ml O₂/min-in³(Pd). The variation of the approach to this value by the different runs is very instructive. For example, Run 8 should have shown a rapid approach to a constant value-much more rapid than resulted, since the foil had been exposed to

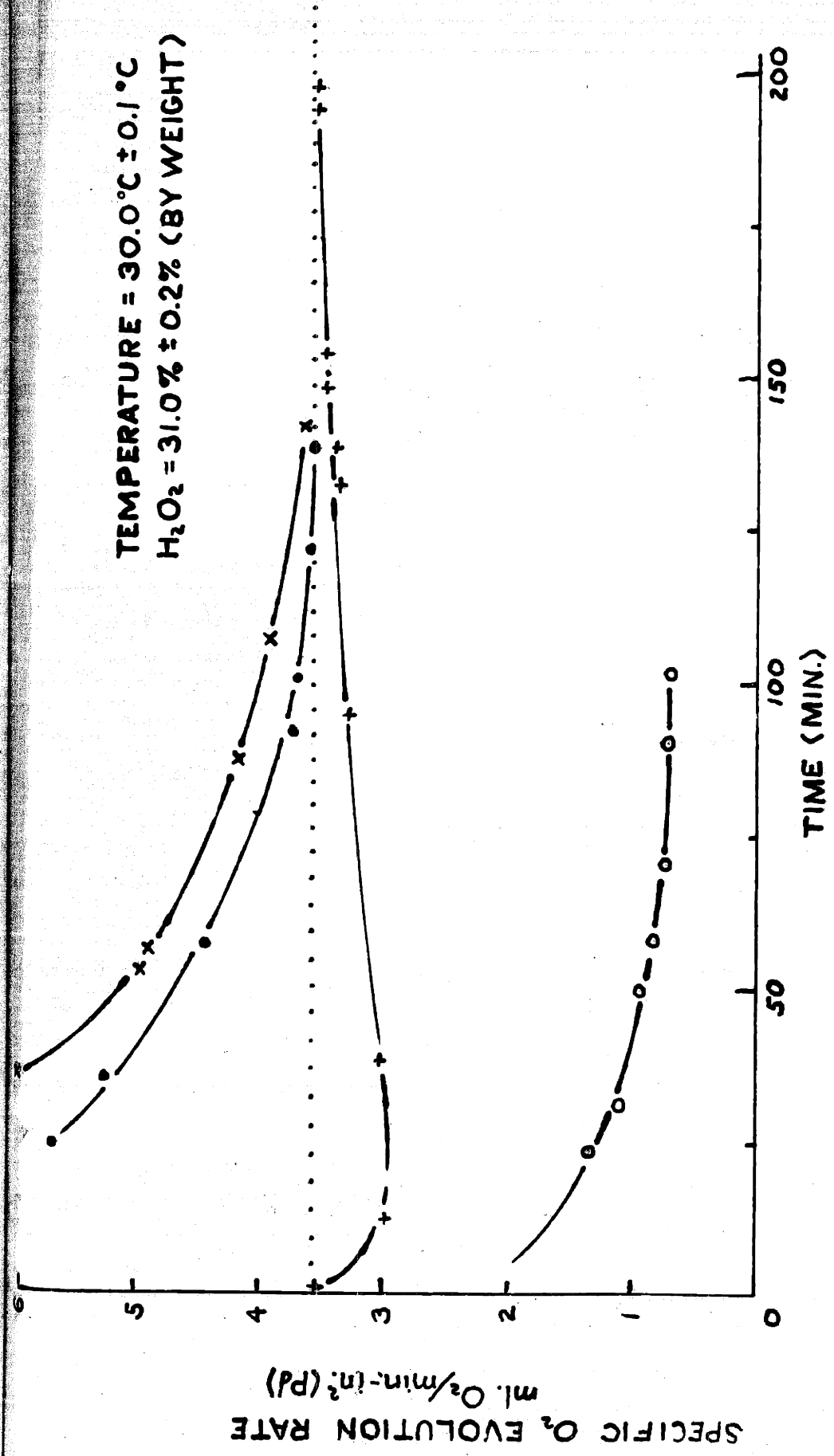


FIGURE 2. CATALYTIC DECOMPOSITION OF H₂O₂ BY PALLADIUM FOIL

- RUN 1 - NO PRETREATMENT - 3 DAYS STORAGE IN DEIONIZED WATER
- RUN 6 - PRETREATMENT IN 30% HNO₃ - 5 MIN. IN DEIONIZED WATER
- × RUN 7 - PRETREATMENT IN 30% HNO₃
- + RUN 8 - PRETREATMENT IN 31% H₂O₂ - 15 MIN. IN DEIONIZED WATER

31% hydrogen peroxide for many hours. The only possible explanation for its deactivation is the 15 minute storage in deionized water just previous to the run. A deactivating influence of deionized water would also explain the great departure of Run 1 from the others. The effect of a one minute dip in 30% HNO_3 also appears as a transitory increase in the catalytic activity of palladium. Conversely the effect of long contact with deionized water is a nearly permanent depression of the catalytic activity. However Runs 6 and 7 also show that the pretreatment of palladium with HNO_3 has an "erasing" effect on its previous history. In runs 6 and 7 it was also noticed and reported in the appendix that the Palladium foil surfaces were slightly etched by the HNO_3 . However this etching had no apparent effect on the results.

B. Platinum Foils (See Figure 3)

The two instructive runs of this section, 10, and 11, indicate that platinum is slow in approaching its steady state value of catalytic activity, as compared with palladium. It is assumed that if Run 11 had begun with pretreatment in 31% hydrogen peroxide, the catalytic activity of the Platinum foil would have rapidly approached and remained at the steady-state rate, which is only closely approached here. This fact would indicate also that a pretreatment in a hydrogen peroxide solution of strength greater than 31% increases the catalytic activity of the foil's surface. However no corroborative runs were made to establish this point. The steady state rate of decomposition of the hydrogen peroxide was indicated at about 1.6 ± 0.1 ml $\text{O}_2/\text{min-in}^2(\text{Pt})$. Run 10 closely approximates the experimental conditions of Buck's platinum

TEMPERATURE = 30.0°C ± 0.1°C
 H₂O₂ = 31.0% ± 0.2% (BY WEIGHT)

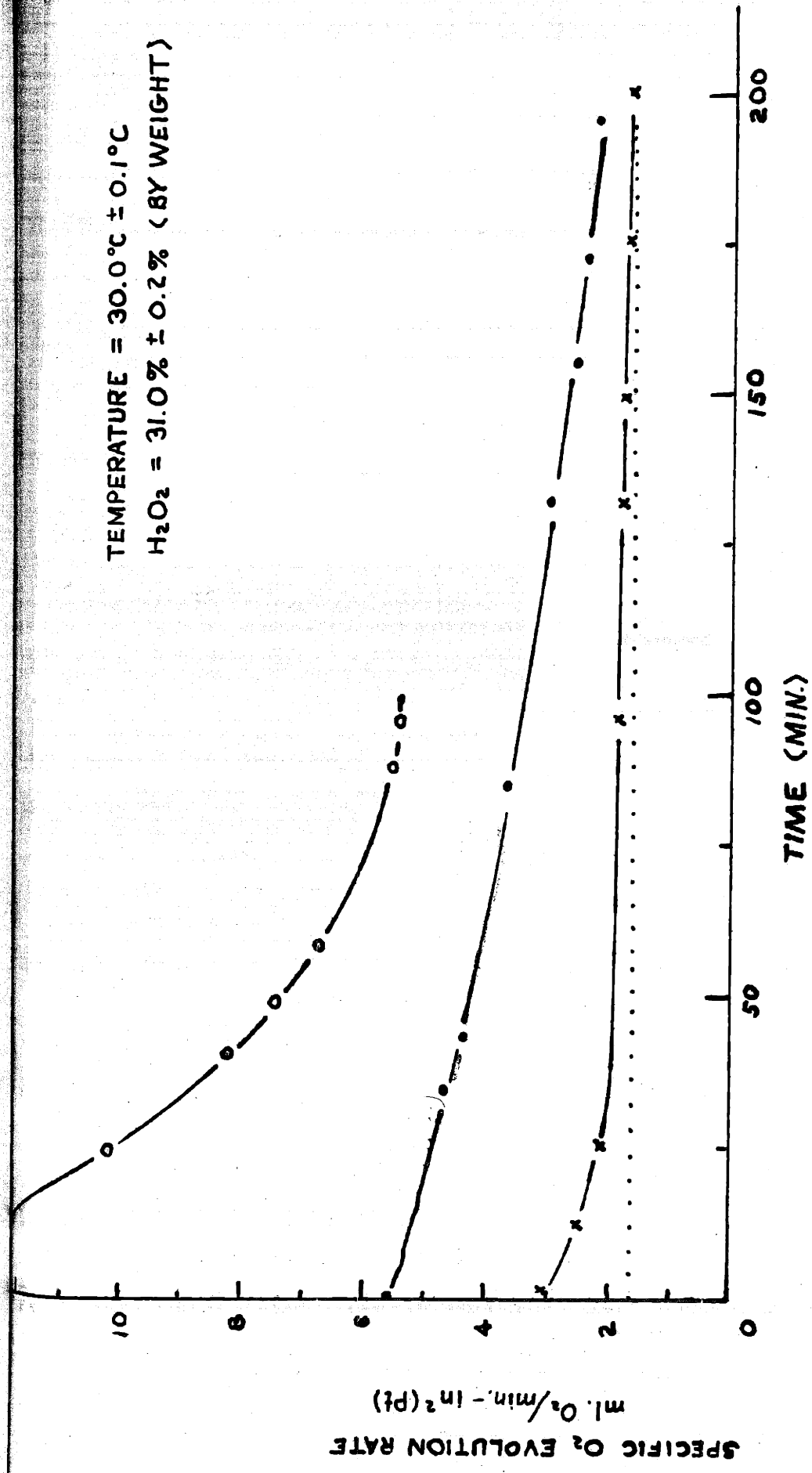


FIGURE 3. CATALYTIC DECOMPOSITION OF H₂O₂ BY PLATINUM FOIL

- RUN 10 - PRETREATMENT IN 30% HNO₃ - FIRST 100 MIN.
- RUN 10 - LAST 200 MIN.
- × RUN 11 - PRETREATMENT IN 46% H₂O₂

runs: none ran much over 200 minutes of time, and all important runs were made with HNO₃ pretreatments. Thus Run 10 indicates that Buck had not taken his experimentation time far enough - hence his value of 2.0 ml O₂/min-in²(Pt) for the steady state catalytic activity of platinum.

C. Gold Foils (See Figure 4)

Runs 12 and 13 indicate that gold is even slower than platinum, and much slower than palladium, in approaching its steady state catalytic activity. In Run 13 a pretreatment in HNO₃ results in a radical variation of catalytic activity of the gold foil. The catalytic activity rises right through the steady state value indicated by Run 14. However over time the catalytic activity of the gold surface comes back to the steady state value indicated, because Run 14 is actually a sixteen-hour extension of Run 13. This foil was never actually removed from the reactor and left in continuous contact with a quiescent 31% hydrogen peroxide solution.

Again in Run 12, as in Run 11 of the platinum series, there was demonstrated the fact that contact with a hydrogen peroxide solution of greater strength than the test solution results in the initial increase of the catalytic activity. If there exists any generalization such as-- a pretreatment in a hydrogen peroxide solution varies the initial catalytic activity of the metal surface in proportion to the difference in strengths between the pretreatment and test solutions - it remains to be demonstrated in future work.

D. In General

The catalytic activities of gold, platinum, and palladium all demonstrated a limiting value upon increasing contact with the 31.0% by wt. hydrogen peroxide at 30.0°C. The HNO₃ pretreatment of the foil surfaces studied produced initial changes in their catalytic activities such that they all approached their limiting values

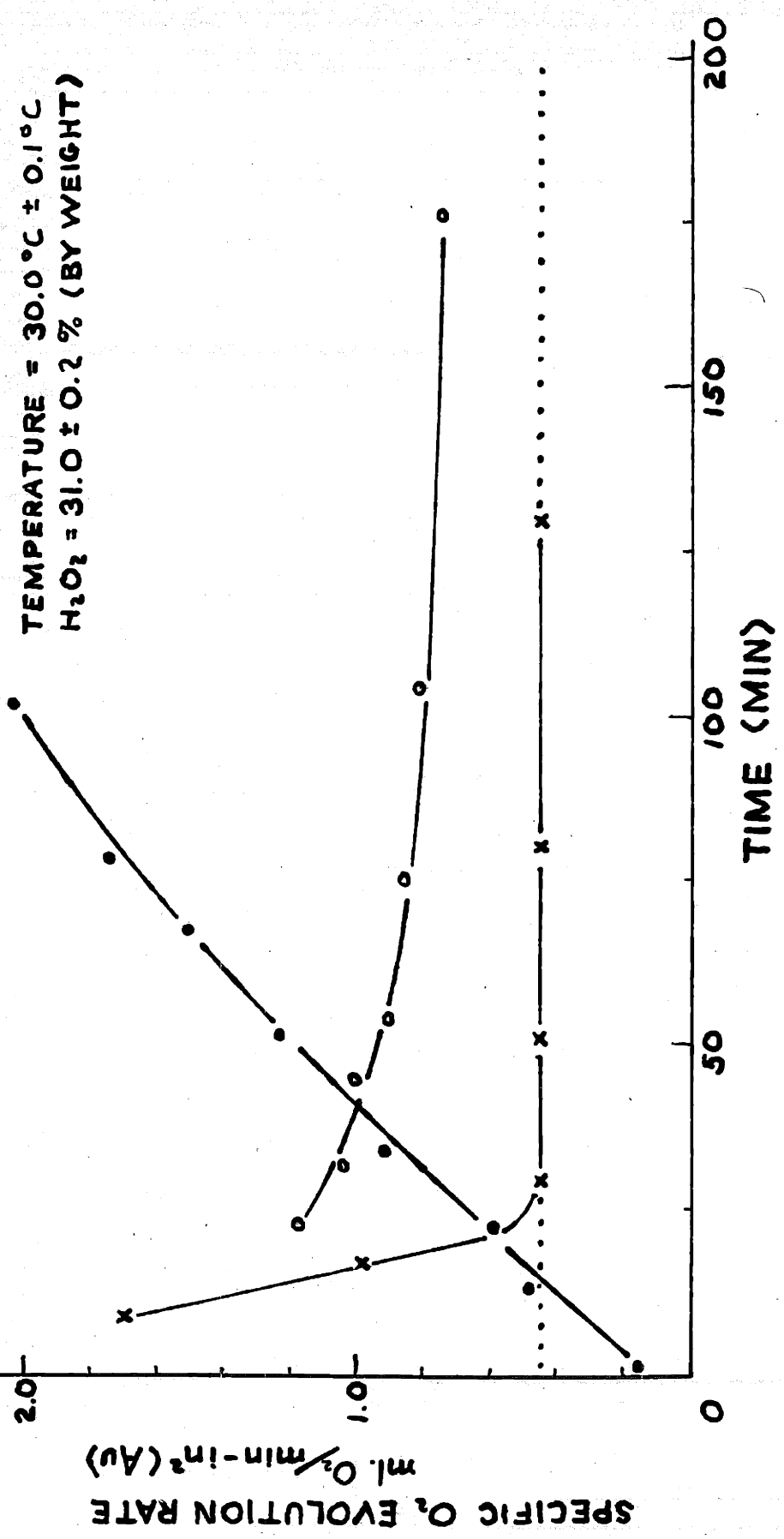


FIGURE 4. CATALYTIC DECOMPOSITION OF H₂O₂ BY GOLD FOIL

- RUN 12 PRETREATMENT IN 45% H₂O₂
- RUN 13 PRETREATMENT IN 10% HNO₃
- × RUN 14 PRETREATMENT IN 31% H₂O₂

from a state of increased catalytic activity. The only demonstrably reliable method of ascertaining the catalytic activities of the metal foils studied is that of simulating or carrying out prolonged experimental runs.

In runs 8 and 14 supersaturation effects entered the data in the form apparently of high initial catalytic activities. Other sources of error were confined to the intrinsic limitations of the apparatus. Between volume displacement readings, the pressure inside the system could not always be kept at atmospheric pressure. This resulted in the slight supersaturations or desupersaturations of oxygen in the reactor solution when the pressure was brought back to atmospheric pressure for the reading. Also the blank rates of catalytic decomposition of the liquid hydrogen peroxide apparently varied during the runs slightly. All blank rates reported were averages between the initial and final values. This latter error could be kept small by reducing the rate of agitation of the reactor solution. The + and - variations in the limiting rate values are merely estimates by the author. Finally about 1% to 2% of the foil surface was covered by inserting it into the slit of the holder. This factor was not considered in the area calculations.

CONCLUSIONS

1. The steady state rates of decomposition of hydrogen peroxide on Palladium, Platinum, and Gold at 30.0°C and 31.0% by wt. of hydrogen peroxide are: 3.55 ± 0.05 , 1.6 ± 0.1 , and 0.45 ± 0.05 ml O₂/min per sq. in. of foil surface respectively.
2. The rate of approach to the steady state value is roughly proportional to the steady state value itself.
3. The pretreatment of the foil surfaces in approximately 31% hydrogen peroxide has proven to be the most reliable method of obtaining the said steady state values.
4. Previous investigators in this area of catalysis have neglected to carry their experiments to their logical conclusions.
5. The pretreatment of the metal surfaces studied with nitric acid in general results in the approach to the steady state values of catalytic activity from a state of increased catalytic activity.

RECOMMENDATIONS

1. A detailed study of the effects of variation of catalytic activity with variations of the hydrogen peroxide pretreatment strength.
2. An attempt to find the activation energy of the catalysis reaction by variation of the reaction temperature.
3. The complete logging of the metal foil's history immediately before an experimental run in any subsequent studies of this type.

V APPENDIX

A. Tabulation of Data

Temp. = 30.0°C

Initial H₂O₂ = 31.1% by wt.

Foil Area = 2.248 in.²

Duration of Run = 105 min.

Previous One Hour History:

1 hr. - storage in deionized water.

Blank Rate = 1.16 ml/min.

Remarks:

Foil surface covered 50% by bubbles at end of 15 minutes. Rest of run showed decrease in % of bubbles to about 20% by end of run.

Run 1 -- Pd Foil 1

<u>Minutes</u>	<u>mlO₂/min</u>	<u>mlO₂/min-in²</u>
23	4.05	1.29
26	3.85	1.20
31	3.65	1.11
50	3.25	0.93
60.5	2.97	0.82
70.2	2.73	0.70
90	2.70	0.69
102.5	2.62	0.65

Run 2 -- Pd Foil 1

Temp. = 35.0°C

No Pretreatment

Initial H₂O₂ = 31.1%

Previous One Hour History:

1 hr. storage in deionized water.

Blank Rate = 1.90 ml/min.

Remarks:

Foil surface covered about 20%

by bubbles throughout run.

Duration of Run = 73 min.

<u>Minutes</u>	<u>ml O₂/min</u>	<u>ml O₂/min-in²</u>
23.5	4.63	1.22
29.5	4.03	0.95
41	3.80	0.85
50.5	3.73	0.81
61	3.73	0.81
71	3.61	0.76

Run 3 -- Pd Foil 1

Temp. = 40.0°C

No Pretreatment

Initial H_2O_2 = 31.0%

Duration of Run = 92 min.

Previous One Hour History:

1 hr.-storage in deionized water.

Blank Rate = 4.20 ml/min.

Remarks:

Foil surface covered about 20%
by bubbles throughout run.

<u>Minutes</u>	<u>ml O_2/min</u>	<u>ml O_2/min-in²</u>
22	7.88	1.73
30	6.08	0.84
40	5.63	0.64
50	5.48	0.57
60	5.27	0.48
70	5.08	0.39
80	4.97	0.34
90	4.97	0.34

Run 4 -- Pd Foil 1

Temp. = 30.0°C
 Initial H₂O₂ = 31.0% by wt.
 Foil Area = 2.248 in².
 Duration of Run = 110 min.
 Previous One Hour History:
 1 hr. storage in deionized water.
 Blank Rate = 1.62 ml O₂/min.

Remarks:
 Foil surface covered 20% by
 bubbles throughout run.

<u>Minutes</u>	<u>ml O₂/min</u>	<u>ml O₂/min-in²</u>
21.5	2.37	.333
27	2.12	.222
34	1.98	.160
47	1.90	.124
68	1.88	.115
89	1.83	.093
105	1.76	.062

Run 6 -- Pd Foil 1

Temp. = 30.0°C

Initial H_2O_2 = 31.0% by wt.

Foil Area = 2.248 in².

Previous One Hour History:

50 min. in deionized water

1 min. in 30% HNO_3

9 min. dry

Blank Rate = 1.14 ml O_2 /min

Remarks:

Foil surface etched by HNO_3
showing streaks originating
presumably in foil rolling
process. No bubbles adhering
to foil surface.

<u>Minutes</u>	<u>ml O_2/min-in²</u>
5	7.70
15	6.72
20	6.01
25.5	5.71
35.5	5.26
57	4.43
92	3.83
101	3.74
121	3.58
136	3.53

Run 7 -- Pd Foil 1

Temp. = 30.0°C

Initial H_2O_2 = 31.0% by wt.

Foil Area = 2.248 in²

Previous One Hour History:

50 min. in deionized water

1 min. in 30% HNO_3

9 min. dry

Blank Rate = 1.10 ml O_2 /min.

Remarks:

Foil surface still etched by
 HNO_3 . No bubbles adhering to
foil surface during run.

<u>Minutes</u>	<u>ml O_2/min-in²</u>
0	12.50
14	8.50
26	6.98
36.5	6.13
53.5	4.98
57.5	4.86
87	4.17
109	3.88
138	3.57

Run 8 -- Pd Foil 2

Temp. = 30.0°C

Initial H₂O₂ = 31.2%

Foil Area = 2.404 in².

Duration of Run = 200 min.

Previous One Hour History:

45 min. in 31.2% H₂O₂.

15 min. in deionized water.

Blank Rate = 1.44 ml O₂/min.

Remarks:

Foil surface clean and shiny.

No bubbles adhering to surface.

<u>Minutes</u>	<u>ml O₂/min</u>	<u>ml O₂/min-in²</u>
0	9.8	3.49
12	8.55	2.96
38	8.73	3.03
94	9.38	3.32
133	9.65	3.41
138	9.75	3.45
148	9.775	3.47
154	9.800	3.49
192	10.050	3.57
197	10.025	3.56

Run 9 -- Pt Foil 1

Temp. = 30.0°C

Initial H₂O₂ = 31.1% by wt.

Duration of Run = 94 min.

Previous One Hour History:

50 min. in deionized water.

1 min. in 30% HNO₃.

9 min. dry

Blank Rate = 0.45 ml O₂/min.

Remarks:

No bubbles adhering to foil
surface.

<u>Minutes</u>	<u>ml O₂/min</u>	<u>ml O₂/min-in²</u>
0	24.2	21.2
10	18.5	16.1
20	14.2	12.3
24	12.3	10.6
38	12.17	9.45
44	8.10	6.83
53	7.24	6.02
69	6.10	5.04
71	6.0	4.96
73	5.7	4.68
77	5.8	4.77
79	5.4	4.42
81	6.2	5.13
87	5.28	4.26
90	5.22	4.22

Run 10 -- Pt 1

Temp. = 30.0°C

Initial H_2O_2 = 31.1% by wt.

Foil Area = 1.120 in².

Duration of Run = 290 min.

Previous One Hour History:

50 min. in deionized water.

1 min. in 30% HNO_3 .

9 min. dry

Blank Rate = 0.22 ml O_2 /min.

Remarks:

No bubbles adhering to foil surface.

<u>Minutes</u>	<u>ml O_2/min</u>	<u>ml O_2/min-in²</u>
0.5	23.5	20.8
13	15.1	13.3
24.5	11.7	10.3
29	11.0	9.64
34	10.125	8.86
49	8.575	7.45
59	7.700	6.58
87	6.417	5.63
94	6.383	5.50
121	5.550	4.76
128	5.183	4.42
129	5.117	4.36
171	4.400	3.73
180	4.300	3.65
220	3.610	3.03
232	3.380	2.82
244	3.2125	2.68
273	2.981	2.46
283.5	2.88	2.38

Run 11 -- Pt Foil 2

Temp. = 30.0°C

Initial H₂O₂ = 31.1% by wt.

Foil Area = 0.896 in².

Duration of Run = 210 min.

Previous One Hour History:

58 min. in 46% H₂O₂.

2 min. dry

Blank Rate = 0.365 ml O₂/min.

Remarks:

No bubbles adhering to foil surface.

<u>Minutes</u>	<u>ml O₂/min</u>	<u>ml O₂/min-in²</u>
1.5	3.13	3.09
4	2.80	2.86
9.5	2.67	2.58
12.5	2.63	2.53
21	2.47	2.35
25	2.45	2.09
94.5	2.077	1.93
115.5	2.071	1.91
132	1.990	1.82
149.5	1.962	1.79
167.5	1.920	1.76
176.5	1.874	1.69
200.5	1.800	1.62

Run 12 -- Au Foil 2

Temp. = 30.0°C

Initial H₂O₂ = 31.1%

Foil Area = 0.944 in².

Duration of Run = 190 min.

Previous One Hour History:

58 min. in 46% H₂O₂.

2 min. dry

Blank Rate = 0.331 ml O₂/min.

Remarks:

No bubbles adhering to foil
surface.

<u>Minutes</u>	<u>ml O₂/min</u>	<u>ml O₂/min-in²</u>
23	1.433	1.18
33	1.300	1.03
44	1.267	1.00
54	1.157	.883
67	1.147	.872
85.5	1.111	.835
105	1.070	.802
178	1.035	.765

Run 13 -- Au Foil 1

Temp. = 30.0°C
 Initial H₂O₂ = 31.2%
 Foil Area = 1.092 in².
 Duration of Run = 120 min.
 Previous One Hour History:
 20 min. in deionized water.
 30 min. in 10% HNO₃.
 10 min. dry.
 Blank Rate = .340

Remarks:
 No bubbles adhering to foil surface.

<u>Minutes</u>	<u>ml O₂/min</u>	<u>ml O₂/min-in²</u>
2.5	0.50	0.15
12.5	0.858	0.47
22.5	1.080	0.59
33	1.340	0.91
40	1.433	1.01
46	1.567	1.12
51	1.675	1.22
54	1.750	1.29
68	1.980	1.50
78	2.250	1.75
102	2.550	2.02

Run 14 -- Au Foil 1

Temp. = 30.0°C

Initial H_2O_2 = 31.1% by wt.

Foil Area = 1.092 in².

Duration of Run = 140 min.

Previous History:

Foil left in reactor's quiescent
31% H_2O_2 solution for previous
16 hours.

Blank Rate = 0.583 ml O_2 /min.

Remarks:

This run is merely the 18 hour
extension of Run 13 with a
16 hour quiescent interim.

<u>Minutes</u>	<u>ml O_2/min</u>	<u>ml O_2/min-in²</u>
1	2.1	1.3
2	6.6	5.5
3.5	16.5	14.6
4.5	9.3	8.0
6	6.4	5.3
8	3.2	2.5
10	2.5	1.7
15	1.64	0.97
30	1.05	0.43
40	1.09	0.47
51	1.07	0.45
82	1.06	0.44
130	1.07	0.45

B. Complete History of Foils

1. Pd 1

3 days in deionized water.

Run 1, 1 hr. in deionized water.

Run 2, 1 hr. in deionized water.

Run 3, 12 hrs. in deionized water.

Run 4, Run 5*, 12 hrs. in deionized water.

1 min. dip in 30% HNO₃, 10 min. dry.

Run 6, 1 hr. in deionized water, 1 min. dip

in 30 % HNO₃, 10 min. dry.

Run 7, final storage in deionized water.

2. Pt 1

8 days in deionized water, 1 min. dip in

30% HNO₃, 10 min. dry.

Run 9, 1 hr. in deionized water, 1 min. dip

in 30% HNO₃, 10 min. dry.

Run 10, final storage in deionized water.

3. Au 1

14 days in deionized water, 1 min. dip in

30% HNO₃, 10 min. dry.

Run 13, 16 hrs. in quiescent 31% H₂O₂,

Run 14, final storage in deionized water

All treatments in preceding three sections were begun with a cleansing of the foils according to the procedure, except in the interum between Runs 13 and 14.

*of 1 hr. duration in 31% H₂O₂

4. Series 2 Foils, Pd, Pt, Au.

<u>Day</u>	<u>Hour</u>	<u>Remarks</u>
0	0	3 foils put in fresh 50% H_2O_2 solution, after 3 day's storage in deionized water and a thorough cleansing
0	3	Reaction got hot; reaction flask continuously cooled in tap water.
1	0	Foils washed in deionized water, fresh solution of 50% H_2O_2
2	1.5	$H_2O_2 = 43.0\%$
2	5.5	$H_2O_2 = 39.5\%$
2	23	$H_2O_2 = 22.5\%$
3	6	Foils washed in deionized water, fresh solution of 44.1% H_2O_2
3	23	$H_2O_2 = 44.1\%$
4	0	Pd 2 removed, 15 min. in deionized water, Run 8, final storage.
6	5	$H_2O_2 = 23.8\%$
7	21	Foils washed, fresh H_2O_2
7	21.5	$H_2O_2 = 46.3\%$
7	22	Pt 2 removed, Run 11, final storage.
8	21	Au 2 removed, Run 12, final storage.

VI LITERATURE CITATIONS

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