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An *In Situ* Method for Alteration of Catalytic Activity by Generation of a Reactant on the Surface of the Catalyst

Clyde Dunn Alley
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To the Graduate Council:

I am submitting herewith a dissertation written by Clyde Dunn Alley entitled "An *In Situ* Method for Alteration of Catalytic Activity by Generation of a Reactant on the Surface of the Catalyst." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Michael J. Joncich, Major Professor

We have read this dissertation and recommend its acceptance:

A Hamilton, W. Haines, Hilton A. Smith, D. A. Shirley

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

June 20, 1959

To the Graduate Council:

I am submitting herewith a dissertation written by Clyde Dunn Alley entitled "An In Situ Method for Alteration of Catalytic Activity by Generation of a Reactant on the Surface of the Catalyst." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

M. J. Gonsch
Major Professor

We have read this dissertation
and recommend its acceptance:

A. H. McLane

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Accepted for the Council:

Paul Henthorn
Dean of the Graduate School

AN IN SITU METHOD FOR ALTERATION OF CATALYTIC ACTIVITY BY
GENERATION OF A REACTANT ON THE SURFACE OF THE CATALYST

A DISSERTATION

Submitted to
The Graduate Council
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

by
Clyde Dunn Alley
August, 1959

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CHAPTER I

INTRODUCTION

A. Role of Surface Hydrogen in Catalysis

In many researches dealing with catalysis there are properties of the catalyst that are attributed to the effect of hydrogen on the surface of the catalyst. The interpretations of the effect of hydrogen on the catalyst surface range from statements^{1,2} which indicate that surface hydrogen is necessary for the reactions to proceed to statements³ that surface hydrogen is a poison in the reaction. A clearly interpreted picture of the role of hydrogen at the present time is not available.

Three investigations have explored the role of surface hydrogen in catalysis directly. McCabe and Halsey⁴ studied the hydrogenation of ethylene over copper. The initial activity of the catalyst is rapidly lost in a series of conventional experiments. The original activity could not be restored with reoxidation and rereduction. Other investigators⁵ have reported similar effects upon evaporated nickel films. However, McCabe and Halsey were able to restore the activity between each run by chemisorbing hydrogen on the copper surface by the following procedure. The catalyst was kept in a hydrogen atmosphere at 15 cm. Hg pressure and 0° for one-half hour to remove gross quantities of ethylene that might have affected further procedure. The catalyst was then heated with 15 cm. of fresh hydrogen for one hour at 200°, after which it was

allowed to cool slowly to room temperature. Finally it was cooled to 0° and pumped out. The control of the coverage of chemisorbed hydrogen allowed the catalytic activity to be reproduced to within 5 per cent over a series of 50 runs. This ability to return to reference activity shows that the copper surface is not irreversibly altered. Furthermore, their kinetic experiments show that the chemisorbed hydrogen does not serve as a reactant and can be considered to function as part of the catalyst.

Joncich and Hackerman⁶ studied the hydrogen-oxygen reaction in a stirred solution of dilute sulfuric acid on the surface of a submerged platinum catalyst. The rate of this reaction was studied as a function of the electrical potential applied to the catalyst. Cathodic polarization of the catalyst was ineffective in changing the reaction rate. Anodic polarization using a platinized platinum anode and a smooth platinum wire cathode caused a periodic change in the reaction rate as a function of time. The rate was increased by a. c. polarization at frequencies < 10 c.p.s.; the highest rate being observed at the lowest frequency used (0.01 c.p.s.) and at a current of 1 ma. Periodic behavior was observed for platinum and palladium but not for rhodium and iridium. A mechanism, consistent with the experimental data, was postulated in which the periodic change in the rate on anodic polarization was ascribed to periodic buildup and decomposition of oxide on the catalyst surface.

Joncich and Kowaka⁷ have studied the activity of a palladium catalyst with and without hydrogen diffusing onto the catalytic surface. The hydrogenations of ethylene and acetylene were studied on the inside of a

palladium thimble through which hydrogen could be caused to diffuse by making the outside of the thimble a cathode in an electrolysis bath. For the reaction with ethylene, hydrogen diffusion did not alter the rate at 25° but an acceleration was observed at 50°. In the case of acetylene hydrogenation, diffusing hydrogen was believed to increase the rate between 0° and 141°, being greater at the higher temperatures. Gas chromatography was used to analyze the products. However, the effect of these hydrocarbons on the rate of hydrogen diffusion was not determined. It was assumed that the diffusion rate was the same with and without their presence in the catalytic system.

B. Proposal of Problem

In view of the above results,^{4,6,7} it was thought profitable to continue the study of alteration of catalytic activity caused by generation of hydrogen on the surface of the catalyst. It was believed that a continuation of the study of the effect of electrolytic polarization of a platinum catalyst on the activity for the hydrogen-oxygen reaction as well as for other reactions such as the hydrogenation of organic compounds would be of value. Also, since the results of Joncich and Kowaka⁷ are dependent on the hitherto unmeasured effect of the presence of ethylene and acetylene on the hydrogen diffusion rate, a continuation of this work was thought profitable.

The compounds to be hydrogenated were somewhat arbitrarily chosen. It was desired that the reactions be previously well studied, the kinetics be relatively simple and the reactants be easily obtainable in a pure

state. In the case of the liquid phase studies on a submerged platinum catalyst, the hydrogenations of oxygen and allyl alcohol were chosen. The hydrogen-oxygen reaction yields water which also is to be used as the solvent, thus avoiding the accumulation of other substances in the system. Also, pure hydrogen and oxygen can be easily produced by the electrolysis of water. The hydrogenation of allyl alcohol was chosen for two reasons. First, the reaction is zero order with respect to the alcohol.⁸ Hence, its concentration could decrease as the reaction proceeded without affecting the rate. Secondly, allyl alcohol and the hydrogenated product, n-propanol, are highly soluble in water.⁹

In the case of the gas phase work, three reactions were chosen to be studied: the hydrogenation of ethylene, acetylene and oxygen. The kinetics of the first two of these are well understood and the third has been studied extensively.

C. Historical

1. Hydrogenation of Allyl Alcohol

The rate of absorption of hydrogen by unsaturated compounds in the presence of platinum or palladium black was first studied by Fokin¹⁰ who concluded that the action was unimolecular and dependent on the diminishing concentration of the unsaturated substance. In many of his experiments, however, the logarithmic nature of the change is evident in the final stages only, and a careful examination shows that the critical part of his curves forms a straight line.⁸

In the meantime, other observers¹¹⁻¹³ have pointed out that hydrogen is absorbed at a constant rate by unsaturated liquids in the presence of a metal catalyst. Lebedev, Kobiansky and Yabubchik⁸ carried out the hydrogenation of allyl alcohol on a platinum black catalyst in absolute ethanol at atmospheric pressure and 25°. Hydrogen was taken up by the solution at the rate of 22 cc./min. on 0.1 gm. of platinum to form n-propanol. The rate was found to be first order with respect to hydrogen pressure and zero order with respect to the alcohol.

Watt and Walling¹⁴ recently studied the reaction over Adams platinum in ethanol. The rate of hydrogenation of allyl alcohol was measured as a function of the temperature, hydrogen pressure, agitation frequency, concentration of acceptor and product, and the ratio of catalyst to acceptor. The reaction shows a very low activation energy and no inhibition by the product, n-propanol, until very high concentrations are reached. The data indicate that the most probable rate-controlling process is diffusion of hydrogen to the catalytic surface. On the assumption of a diffusion controlled process, the following equation relating the mode of variation of rate with weight of the catalyst, W, was presented:

$$-\frac{dP}{dt} = \frac{AWP_{H_2}}{1 + BW}$$

where A and B are constants.

2. Hydrogen-Oxygen Reaction

In 1818, Humphrey Davey¹⁵ reported that hydrogen and oxygen could be combined to form water over a metal catalyst. The reaction was explored further by Dobereiner¹⁶ a few years later. Many workers have since studied

this combination by one of three principal methods: 1. as a homogeneous, single phase gaseous system, in which photochemical, thermal and electrical initiators have been employed,¹⁷⁻²⁰ 2. as a heterogeneous, two phase system of the gases and a metal catalyst, and 3. as a heterogeneous, three phase system in which the dissolved gases are combined on a submerged metal catalyst in solution. The homogeneous, single phase gaseous system will not be discussed since it does not concern this research.

a. The heterogeneous, two phase gas reaction. A considerable amount of study has been performed concerning reacting hydrogen and oxygen gas on a metal catalyst. A variety of metal or metal oxide catalysts such as platinum, palladium, silver, nickel, nickel oxide, iron, gold, and cupric oxide have been used. Usually the reaction is carried out at over 100° to restrict the system to two phases. This is performed easiest with a flow system, in which a continuous stream of the two gases are passed over the catalyst.

Langmuir²¹⁻²³ used a platinum catalyst and found the rates to be irreproducible. He was unable to obtain quantitative data. He did find that platinum was inactive at room temperature unless it was previously heated in a mixture of hydrogen and oxygen. Hydrogen was observed to act as a catalytic poison for the reaction at high temperatures.

Bodenstein²⁴ found the reaction to be first order with respect to both hydrogen and oxygen on porcelain between 450° and 650° . His results indicate sparse coverage by both reactants on the surface.

Bone and Wheeler²⁵ using a variety of different catalysts determined the rate to be first order with respect to hydrogen and zero order with

oxygen. This is consistent with reaction between gaseous hydrogen and a layer of adsorbed oxygen which fully covers the surface.²⁶ Pease and Taylor^{27,28} and Benten and Emmett²⁹⁻³¹ confirmed the conclusion of Bone and Wheeler that, in the case of copper, the metal surface is always oxidized during this catalytic reaction. The oxide which forms simultaneously with water was found to be rapidly reduced by hydrogen. It was concluded that oxidation and reduction occur simultaneously, i.e., the metal is oxidized continually at the same rate that the oxide is continually reduced.

Chapman and Gregory³² found that adsorbed hydrogen inhibited the reaction on palladium whereas adsorbed oxygen acted as an accelerator. A layer of adsorbed hydrogen was presumed to prevent oxygen from reaching the surface. It was proposed that catalysis occurs by alternate oxidation and reduction of the oxide layer.

Donnelly and Hinshelwood³³ observed that the reaction rate on platinum was independent of hydrogen pressure but varied in a complex manner with oxygen pressure; at low pressures the increase was linear with a falling off from linearity at higher pressures but the rate continued to rise and never reached a limiting value. This was interpreted as a superposition of two Langmuir isotherms, one corresponding to saturation at low pressures, the other at higher pressures, indicating two types of centers for oxygen adsorption. The kinetics suggested that hydrogen formed a saturated layer on a third type of center.

The data of Benton and Elgin^{34,35} on silver indicated that the reaction rate was proportional to hydrogen pressure, independent of oxygen

pressure and inversely proportional to the water formed. Since there was no mutual displacement of hydrogen and oxygen, they were assumed to be adsorbed on different types of centers with the oxygen being strongly adsorbed and intermediate coverage by hydrogen.

Leidheiser and Gwathmey,³⁶ studying the reaction on different crystal faces of copper, found the rate varied appreciably from one face to another. Also a roughening of the surface was observed due to the reaction and the extent of roughening was dependent upon the face.

In summary, it is evident from the above that the reaction is still not understood completely in spite of the extensive work that has been done. The pressure of the reactants, temperature, catalyst, initial surface condition, water vapor, crystal face and trace poisons all have a marked influence on the reaction, lending to its complexity.

b. Combination of hydrogen and oxygen on a submerged catalyst.

Even more variables (such as pH and ionic strength) are introduced if the reaction is carried out in solution on a submerged catalyst.

Paal and Hartmann³⁷ are among the first investigators to study this catalytic reaction in solution. A sol consisting of colloidal palladium was the catalyst; water was used as the solvent. However, their results were not very reproducible or quantitative. Since the palladium, hydrogen and oxygen were not purified, this is easily understandable. They observed that the rate generally increased as the quantity of palladium sol was increased. Also, an excess of hydrogen in the gas mixture accelerated the reaction while an excess of oxygen inhibited it.

In a series of six articles, Hofmann^{3,38-42} and his co-workers described their work on this reaction. Various metal catalysts in aqueous solutions were used. Metals of the platinum group were found most effective in the reaction, which was postulated to be electrochemical in nature. In Hofmann's first article³⁸ a mechanism was proposed whereby hydrogen and oxygen were adsorbed on different portions of the catalyst surface and local cell action resulted. Reaction was said to occur between the adjacent hydrogen and oxygen electrodes. If the surface of the catalyst was pre-saturated with hydrogen, its activity decreased. The activity, however, was enhanced upon pre-exposure to oxygen, which was thought to hasten the attainment of equilibrium of the oxygen electrode (which is normally slow). It was found that the amount of oxygen held by the surface was insufficient to account for the increased catalytic activity, assuming that the surface oxygen acted as a supply of oxygen for the reaction.

Hofmann revised his mechanism somewhat in his second paper.³ Rather than pre-exposure of oxygen increasing the rate of establishment of the equilibrium potential, he postulated two types of hydrogen-charged platinum metals which he called "fresh" and "aged". A "fresh" catalyst which had been saturated with oxygen and exposed to a hydrogen-oxygen mixture would, under certain conditions, become a hydrogen electrode with increased activity, reducing the oxygen to water and developing a high hydrogen potential. An "aged" catalyst results from a "fresh" one being exposed to hydrogen during the reaction, becoming less effective as a reducing agent.

Hofmann was able to measure the potential of the catalysts during the course of the reaction by placing a hydrogen electrode in the system. From these measurements he concluded that the rate of the reaction is fastest when as great as possible a hydrogen or oxygen potential is developed and not when hydrogen and oxygen are adsorbed as they are used up on an electrically neutral pole.

Hofmann measured the catalyst potential and the reaction rate simultaneously in his third paper.³⁹ It was found that the faster the initial potential of the catalyst changed, the more rapid the reaction became. He postulated that only active forms of oxygen and hydrogen reacted to form water.

In his fourth and sixth papers^{40,42} he discussed the formation of hydrogen peroxide. He concluded that diffusion of oxygen to the surface of an active catalyst was slow compared to the diffusion of hydrogen. Hence, there would be an excess of hydrogen at the surface and the product would be mostly water. If, however, the catalyst was coated with a hydride, its efficiency would be reduced. There would, therefore, be an excess of oxygen at the surface leading to the formation of a considerable amount of hydrogen peroxide.

Iridium was found to be a more ideal catalyst for the reaction than platinum or palladium in Hofmann's fifth paper.⁴¹ Pre-treatment of its surface with hydrogen or oxygen activated the reaction to the same degree. It was equally effective in an acid or alkaline solution and did not seem to adsorb either gas selectively (as shown by its potential).

A description of alternating current polarization of the catalyst was given in Hofmann's final paper. With frequencies up to 50 c.p.s., the catalytic activity was enhanced, but higher frequencies up to 1000 c.p.s. had no effect. About one minute elapsed before the effect of alternating current became evident. These results were explained by the fact that a surface free of hydride and oxide formation would lend itself to a more active state and that alternating polarization prevented their formation.

Shul'ts and his co-workers⁴³⁻⁴⁵ reported results of experiments on platinum catalysts that were generally in accord with those of Hofmann. They postulated that passivation of the catalyst is brought about by the covering of a large number of active sites by a pseudoxide film. Also it was found that the more active catalysts are most susceptible to poisoning.

More recently Levine and Rosentreter⁴⁶ studied this reaction on activated carbon containing 0.5 per cent platinum and using much improved experimental techniques such as ground-glass joints, magnetic stirrers, evacuated systems and constant temperature control. By using solutions of different pH values, a linear relation was found between the rate of the reaction and the pH in the range of 2 to 12, the rate increasing with decreasing pH. In all cases, the rate remained constant for the duration of the experiment. The rate fell off markedly at pH values less than 2, however. These authors concluded that the kinetics of the reaction are dependent upon the electrochemical potential of the carbon in a given solution, which in turn is dependent upon the pH of the solution.

3. Electrolytic Hydrogen Diffusion Through Palladium

In 1864 Gailletet⁴⁷ observed that some of the hydrogen evolved when iron was immersed in dilute sulfuric acid was absorbed in the iron. Shortly after this observation Graham⁴⁸⁻⁵⁰ began researches on hydrogen-palladium systems. Many investigations have since followed those of these pioneers on the diffusion of hydrogen in metals.

Hydrogen can be made to diffuse through palladium and iron by two principal methods. The first involves heating the metal above 150-200° with an atmosphere of hydrogen gas on one side. The hydrogen will diffuse into and through the metal due to the differential in hydrogen pressure. It has also been found^{47,51-57} that hydrogen gas in nascent form can penetrate metals such as palladium, iron and nickel at room temperature if the metal is made the cathode during electrolysis or if hydrogen is generated by chemical reaction at the surface. Only electrolytic hydrogen diffusion will be discussed since it alone was employed in this work.

Bodenstein⁵² was one of the first investigators to measure diffusion rates of cathodic hydrogen in a quantitative manner. Working with iron, he found the permeation rate through the metal to be directly proportional to the square root of the current density of the iron cathode. He believed that hydrogen diffused into the metal in an atomic form but left in the molecular state.

Since Bodenstein, many investigators have confirmed the relationship that the diffusion rate is proportional to the square root of the current density. However, the equation did not fit the data accurately in the low current density region. To explain this, Borelius and Lindblom⁵⁴

assumed that diffusion was not possible until the current density, I , exceeded what they called a temperature dependent threshold value of the electrolyzing current density, I_t . They presented the following equation for the diffusion rate, D , which incorporates the correction for low currents.

$$D = k (\sqrt{I} - \sqrt{I_t})$$

where k is a constant.

The diffusion through iron and palladium was further studied by Barrer⁵⁵ between 0° and 100°. His cathodes were very susceptible to poisoning and, hence, the data obtained were not very reproducible. He observed that palladium will absorb 800 times its volume in hydrogen. Also, the Bodenstein relation was found to hold except below 0.05 amperes/cm.². An activation energy of 8.5 kcals. was calculated for palladium diffusion.

More recently the validity of Borelius and Lindblom's threshold value of the current density has been challenged by Heath⁵⁷ who observed measurable diffusion through iron and palladium at current densities as low as 0.001 amperes/cm.². Below 0.03 amperes/cm.² the permeation rate was found to be directly proportional to the current density itself, while above this region the Bodenstein relation holds. Heath derived a theoretical equation which indicates that the same law does not hold at all current densities. It is interesting to note that the same conflict occurred with workers who diffused hydrogen through metals which were heated to high temperatures. Here a similar square root law was assumed to hold with the pressure of hydrogen being substituted for the current

density. Various investigators^{58,59} noted that the agreement with the square root law did not hold exactly at low pressures but attributed the divergence to experimental error. Smithells and Ransley⁶⁰ later showed that the departure from the square root law at low pressures was similar to that observed by Health with electrolytic hydrogen.

Experimental evidence indicates that hydrogen up to a H/Pd atomic ratio of 0.6 is dissolved as protons and above the form of the hydrogen is different.^{56,61,62} There are about 0.6 holes per atom in the d band of palladium. It was deduced^{61,62} by magnetic susceptibility measurements that up to an atomic ratio of H/Pd ~ 0.6 the dissolved hydrogen was completely ionized by giving up its electrons to the d bands. Additional evidence has been given by nuclear magnetic resonance measurements.⁶³ These measurements have also indicated that when H/Pd exceeds 0.6, the additional hydrogen is dissolved by a different mechanism. Schuldiner and Hoare⁶⁴ proposed that the initial hydrogen (up to a H/Pd of 0.6) is strongly bound in the interior of the palladium. Moreover, these workers proposed that the additional hydrogen is dissolved in the atomic form in the octahedral holes of the face-centered cubic lattice of beta palladium. Assuming a lattice constant, a , of 4.06 \AA the effective radius of an octahedral hole was calculated to be 0.595 \AA while that of a hydrogen atom is 0.37 \AA . The protons could be accommodated in either tetrahedral (effective radius 0.322 \AA) or octahedral holes because of their very small size. Recently, Worsham, Wilkinson and Shull⁶⁵ have determined by neutron diffraction experiments that both hydrogen and deuterium atoms in beta phase Pd-H and Pd-D are located in the octahedral

positions. Schuldiner and Hoare⁶⁴ further propose that this less firmly bound atomic hydrogen is the hydrogen that diffuses through palladium and, because of the concentration gradient across the palladium, these hydrogen atoms will diffuse through the octahedral holes.

Wahlin and Naumann⁶⁶ found that the hydrogen emerging from the exit surface of the palladium is quite active. Oxygen of the air was found to react on this surface to form water. Also the complete reduction of cyclohexene to cyclohexane and partial reduction of cyclohexanone to cyclohexanol was obtained. However, the authors did not observe the effect of these substances on the diffusion rate. Salmon, Randall and Wilk,⁶⁷ using the gas phase method of diffusion, studied the effect certain substances have on the diffusion rate if the downstream surface is exposed to the particular gas of interest for a fixed time and then is thoroughly pumped out. Hydrocarbons such as ethylene, ethane, acetylene, methane, and butane poisoned the exit surface thus slowing down the rate of diffusion. Hydrogen sulfide also poisoned the surface such that reactivation was not possible by heating in oxygen and then hydrogen as had been possible in the case of the hydrocarbons.

4. Hydrogenation of Ethylene

The hydrogenation of ethylene on a metal surface has been studied extensively since its discovery by Sabatier and Sanderens.⁶⁸ Recently, several excellent reviews⁶⁹⁻⁷¹ have been devoted to the reaction. In view of these articles and the large volume of work which has been reported for the reaction, the following discussion will be limited to that information which is most pertinent to this problem.

Most of the data for the reaction have been obtained with nickel catalysts.^{1,5,72-78} Reduction goes smoothly at 20° and 1:1 hydrogen-ethylene mixtures. If an excess of ethylene is avoided, the initial velocity is proportional to the hydrogen pressure and independent of the ethylene pressure for temperatures up to 156°. ^{1,72,76} An excess of ethylene and particularly pre-treatment of the catalyst with ethylene may give a decreased velocity. Schwab⁷⁹ pointed out that the effect of excess ethylene is partly irreversible and associated with the formation of poisoning polymers. Eley⁷⁰ considers the most accurate value for the activation energy to be 10.7 kcal. which was obtained by Beeck⁷² on evaporated nickel films from -80° to 100°. The value falls off at higher temperatures with the rate passing through a maximum around 150°-200°.

Beeck¹ has also reported the results of a lengthy study of other metal catalysts used in the form of evaporated films. The rate for these other catalysts is first order with respect to hydrogen pressure and zero order with ethylene as found in the case of nickel. A decrease in activity by a factor of 10^4 was observed over the series Rh > Pd > Pt > Ni (110) > Ni (random) > Fe > Cr. Preadsorbed ethylene lowered the initial rate by only a few per cent on platinum and rhodium, 60 per cent on nickel, 500 per cent on tungsten and 1000 per cent on tantalum. In general, the higher the initial heat of chemisorption of ethylene on the metal, the greater the degree of dissociation into acetylenic residues and polymers, the greater the inhibition, and the longer time required to clean the surface with hydrogen. Beeck found the reduction of ethylene with pre-

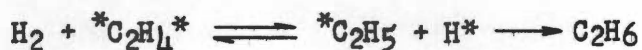
adsorbed hydrogen to be very rapid on nickel. It was postulated that this latter mechanism involved chemisorbed hydrogen reacting with ethylene from a van der Waals layer or the gas phase.

Stephens⁸⁰ has recently studied the hydrogenation of preadsorbed ethylene on evaporated palladium films. In agreement with Beeck's work on nickel,¹ it was found that ethylene is adsorbed on four palladium sites. This is explained by assuming dissociation into an acetylenic residue which occupies two sites and two hydrogen atoms, each occupying one site. Self-hydrogenation of ethylene occurs if an excess pressure of the gas is admitted to a film of preadsorbed ethylene. The excess gas removes the hydrogen atoms to give ethane. If hydrogen is introduced to the film, it is initially removed rapidly from the gas phase. Part is held by the film and the remainder reacts with the adsorbed layer to form hydrocarbons (98 per cent ethane). It was concluded that the reactivity of adsorbed ethylene toward hydrogen depends on the ability of the metal to catalyze the addition of hydrogen to dissociatively adsorbed hydrocarbon residues.

Joncich and Kowaka⁷ observed the reaction on palladium to follow the same rate expression as the above authors. Both hydrogen and ethylene pretreatment were found to poison the catalyst with hydrogen being a stronger inhibitor than ethylene. They report an activation energy of 3.7 kcal. which is lower by a factor of three than previously reported values.^{1,81}

Mechanistically, with regard to hydrogenation on nickel which is the most investigated, the balance of results⁷⁰ seems to favor Twigg's

development of the half-hydrogenated state mechanism.⁸²

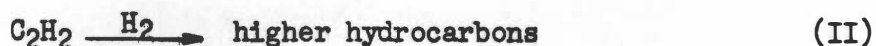


This reaction is assumed to occur on that part of the surface not already poisoned by chemisorbed acetylenic complexes. Beeck,^{1,72} on the other hand, proposes that the metal surface is largely covered by adsorbed acetylenic complexes which are only slowly removed by chemisorbed hydrogen due to their strong bonding. Rapid hydrogenation occurs by collision between ethylene from the gas phase and chemisorbed hydrogen. The high activation energy of 10.7 kcals. is attributed to the former clean-up reaction.

5. Hydrogenation of Acetylene

Sabatier and Senderens⁸³ first observed that the passage of hydrogen and acetylene over reduced nickel powder at room temperature caused the catalyst to heat up. Ethylene and ethane were formed as well as a considerable quantity of higher hydrocarbons whose yield was increased by raising the acetylene concentration.

Although this reaction has been one of the most widely studied in the field of hydrogenation catalysis, Eley⁸⁴ points out that the study of the hydrogenation of acetylene bonds has been greatly neglected in comparison with the large volume of work concerning the problems of olefin hydrogenation. G. C. Bond⁸⁵ and T. I. Taylor⁸⁶ have recently presented extensive reviews of the reaction. The metals most used for hydrogenation purposes are nickel, platinum and palladium. The reactions on each of these catalysts may be classified as follows:⁸⁵



By the above reactions it is evident that kinetic data obtained without simultaneous analysis of the reaction products are of little value.

The results obtained on nickel catalysts will be discussed briefly since the larger portion of data has been obtained with this metal. By the method of initial rates of pressure fall, the reaction has been found to be first order with hydrogen pressure and zero or slightly negative order with respect to acetylene at 70°-80° on pumice supported nickel.⁸⁷ If hydrogen is initially in excess ($P_{\text{H}_2} > 2P_{\text{C}_2\text{H}_2}$), the hydrogenation rate is constant until about 70 per cent of the acetylene is removed, at which point the hydrogenation of ethylene begins to predominate. The rate, appearing to be solely determined by the initial pressure of the reactants, suggests that acetylene is strongly chemisorbed on the surface, and that hydrogenation is initiated when a gaseous hydrogen molecule strikes the adsorbed acetylene with sufficient kinetic energy.⁸⁵ Over reduced nickel powder at 30°, dePauw and Jungers⁸⁸ observed that the rate of pressure fall was constant until an amount of hydrogen had been consumed equivalent to the initial pressure of acetylene after which a marked acceleration occurred. This was attributed to a faster hydrogenation of ethylene formed previously. The experiments were carried out with hydrogen always in excess. The following initial rate law was deduced:

$$-\frac{dP}{dt} = kP_{\text{H}_2}P_{\text{C}_2\text{H}_2}^{-0.5}$$

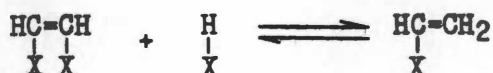
Acetylene and hydrogen combine over palladium to yield ethylene and ethane with 10 to 30 per cent of the unrecoverable acetylene being converted into less volatile hydrocarbons.⁸⁹⁻⁹³ Specific hydrogenation to ethylene has been determined to be more favored over palladium than nickel and platinum.⁹³ Cremer, Knorr and Fliening⁹⁴ regarded ethylene as the only product up to the point at which the rate of hydrogenation passed through a maximum. The kinetics indicated reaction between strongly adsorbed acetylene and weakly adsorbed hydrogen with acetylene suppressing ethane production due to its stronger adsorption. Sheridan⁹³ concluded that the large amount of hydrogen occluded in palladium did not change the mechanism from that on nickel and platinum. Using a palladium alumina catalyst, Tamaru⁹⁵ observed the reaction to occur in two distinct steps. In the first step acetylene is converted into ethylene and polymers whereas the second step involves hydrogenation of ethylene to ethane. The second step does not begin until all the acetylene is reduced to ethylene and is indicated by a sudden increase in the rate. This is similar to the results obtained for nickel. When the pressure of acetylene was small compared to that of hydrogen, polymerization was found to be decreased sharply giving high yield of ethylene and ethane. Tamaru expressed the kinetic equation in the form:

$$-\frac{dP}{dt} = \frac{kP_{H_2}}{1 + b P_{C_2H_2}}$$

Similar results were observed by him using a palladium-kieselguhr catalyst.⁹⁶

Since the results obtained using evaporated metal films differ markedly from those using conventional catalysts, they are omitted except to add that the heat of adsorption of acetylene as found by Wilson⁸⁵ is 67 kcals. on nickel compared to 58-25 kcals. for ethylene¹ on nickel. The value for ethylene decreases sharply with increased surface coverage whereas the heat of chemisorption for acetylene is unaffected.

The mechanisms proposed by Sheridan⁹⁷ for the polymerization of ethylene on nickel are based on surface chain reactions initiated through a half-hydrogenated state of the associatively chemisorbed acetylene.



He supports a mechanism for formation of ethylene through simultaneous addition of two atoms of the same weakly adsorbed hydrogen molecule to strongly adsorbed acetylene. This is similar to the mechanism suggested by Farkas and Farkas⁹⁸ in that it involves simultaneous addition of atoms from the same hydrogen molecule but it is nearer that of Twigg and Rideal^{76,99} in which weakly adsorbed hydrogen is involved.

CHAPTER II

EXPERIMENTAL

A. Liquid Phase Hydrogenations

1. Materials

a. Allyl alcohol. Eastman "white-label" allyl alcohol was fractionally distilled before use.

b. Sulfuric acid solutions. DuPont C. P. reagent grade sulfuric acid and conductance water were used in the preparation of all solutions containing sulfuric acid. The solutions were pre-electrolyzed overnight with platinum electrodes for purification.

c. Sodium sulfate solutions. All solutions containing sodium sulfate were prepared from anhydrous Baker and Adamson reagent grade sodium sulfate and conductance water. The solutions were purified by pre-electrolysis with platinum electrodes.

d. Sodium hydroxide solutions. Baker and Adamson reagent grade sodium hydroxide and conductance water were used to prepare all sodium hydroxide solutions. The solutions were pre-electrolyzed overnight using platinum electrodes.

e. Chloroplatinic acid solution. Engelhard reagent grade platinum chloride was dissolved in a 1.0 N hydrochloric acid solution made from duPont C. P. reagent grade hydrochloric acid and conductance water. The solution also contained Engelhard C. P. reagent grade lead acetate.

2. Preparation of Electrode Catalysts

Smooth and platinized-platinum catalysts were prepared from platinum wire 0.0138 cm. in diameter. These wires were sealed in soft glass tubing such that 1.5 cm. of the wire extended out from the seal. The wire was cleaned in hot aqua regia and washed in conductance water. The platinized-platinum electrode was prepared by platinizing one of the wires in a 2 per cent chloroplatinic acid solution containing 0.03 per cent lead acetate. A coil of platinum wire placed around the wire to be platinized was made the anode, and a current of 12.3 ma was passed through the solution for one hour. The platinized-platinum was cleaned by washing in conductance water.

3. The Hydrogenation System

a. Electrolysis cell. The drawing in Figure 1 shows the system used to study the hydrogenation of allyl alcohol. Hydrogen and oxygen were generated in flask A by the electrolysis of an aqueous 0.1 N sulfuric acid solution on electrodes E and E'. Since only the hydrogen was to be used in this reaction, it was necessary to evolve it within the reaction system and to force the oxygen to escape outside the system. To accomplish this, a porous vycor thimble¹⁰⁰ was connected to the reaction system with a ground glass joint. Electrode, E', was sealed in the pyrex glass above so it would hang down in the center of the thimble which was filled with the same solution as was present in A. Current in the form of ions can pass through this porous glass, and hence hydrogen could be generated on E' within the system. However, water is able to diffuse through the glass at only 0.00065 ml. per sq. cm. of area per atmosphere of pressure

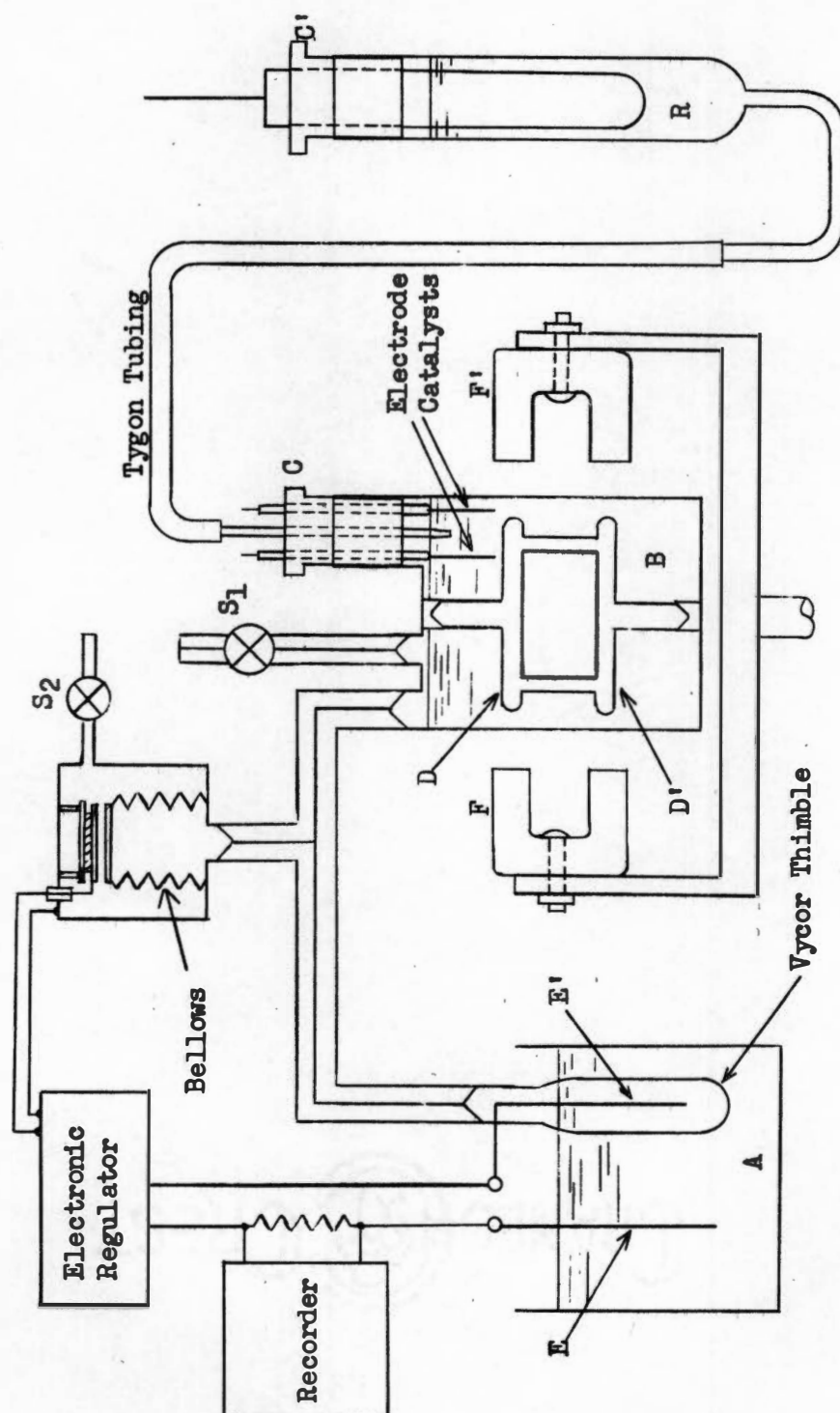


Figure 1. Reaction System for Hydrogenation of Allyl Alcohol.

per hour. Since the pressure difference of the atmosphere and that of the system never exceeded 2 or 3 cm. Hg, the reaction system was considered independent of changes in atmospheric pressure. The cathode, E', was tungsten since platinum was observed to act as a catalyst for the hydrogenation reaction at this point. Oxygen which was generated on the platinum anode, E, escaped into the atmosphere. The porous portion of the thimble was completely beneath the level of the electrolytic solution. Although there was no evidence of hydrogen diffusion through the glass, a stream of hydrogen was bubbled around the outside of the thimble as a precautionary measure.

The reaction system used for the study of the hydrogen-oxygen reaction was identical to the one shown in Figure 1 with the exception of the vycor thimble. Since both gases generated by electrolysis were to be reactants in this reaction, both the anode and cathode, E and E', were enclosed in a 50-ml. Erlenmeyer flask containing the sulfuric acid solution and sealed to the system.

b. Reaction cell. The electrolysis cell was connected by capillary glass tubing to flask B within which the reactions were carried out. The reactor contained 100 ml. of a 25 per cent allyl alcohol solution in 0.1 N sulfuric acid in the case of allyl alcohol reduction. For the hydrogen-oxygen reaction 0.1 N sulfuric acid was normally used as the solvent. The solution was stirred by two glass-covered bar magnets, D and D', which were held in place by solution-lubricated, glass bearings. These internal magnets were rotated by external horse-shoe magnets, F and F', which were connected to a variable speed motor by means of a flexible cable.

The electrode catalysts which were sealed to soft glass tubing were introduced into the reaction cell through a teflon plug, C, which in turn was fitted in a ground glass joint attached to the cell. A solution-filled glass probe connecting the reactor and a reference electrode cell, R, was also introduced through the teflon plug. The saturated calomel electrode which was employed as a reference electrode was fitted into the chamber, R, by another teflon plug, C'. These teflon plugs were machined to the exact taper of the ground glass joints and were found not to leak under a water aspirator vacuum.

Another neck of the reaction cell was joined to a teflon stopcock, S₁, which in turn could be connected to a water aspirator for evacuating the system.

c. Electronic regulator and bellows. It was desirable to construct a completely automatic system such that the reacting gas or gases would be evolved in the electrolysis cell at the same rate they were being depleted due to reaction. To accomplish this, an electronic regulating system similar to that described by Hannah, Joncich and Hackerman¹⁰¹ was used.

The current passing through the electrolysis cell was regulated by a pressure sensitive bellows device and an electronic current regulator. A Fulton Sylphon bellows, No. 1034, having a spring rate of 1160 lbs./in. corrugation was employed. The effective area of this bellows is 0.69 in.² and since there are ten corrugations, the spring rate is 116 lbs./in. Converting these values to pressure, it is seen that there is a pressure change of 4.65×10^3 mm. of water for every millimeter change in the

length of the bellows. The bellows connected to the system as shown in Figure 1 expanded or contracted as the gas pressure increased or decreased. An airtight housing surrounded the bellows and the pressure within the housing was adjusted to approximately 740 mm. Hg through stopcock, S₂, which was the pressure at which the reactions were to be carried out. The airtight housing around the bellows was necessary to maintain the position of the bellows independent of atmospheric pressure fluctuations. A condenser plate was attached to the end of the bellows and another mounted parallel to it. By using these two plates as an air condenser, it is seen that the capacitance of this condenser is regulated by the position of the plate at the end of the bellows. As the length of the bellows increases, the capacitance of this condenser increases, and as the length decreases the capacitance decreases. This capacitance was used as part of the frequency determining network of an oscillator, the frequency of the oscillator being dependent upon the position of the end of the bellows. The frequency of the oscillator is inversely proportional to the square root of the length of the bellows.

By amplifying the output of the oscillator and applying this output to a frequency discriminator and rectifier, a d. c. voltage was obtained which was a function of the frequency applied. Since the frequency is dependent upon the position of the bellows, it is seen that the d. c. voltage obtained was a function of the pressure of the system.

The output voltage of the frequency discriminator and rectifier was used to control the electrolyzing current by applying a voltage to the grid of a cathode follower. A 6J6 twin triode with both sections

connected in parallel was used to supply the current across the electrodes of the electrolysis cell. By these means, it was possible to control automatically the current so that the pressure within the system remained constant.

The current which is directly proportional to the reaction rate and, hence, to the catalytic activity was continuously passed through a Brown recorder to obtain a permanent record of the reaction rate.

d. Complete apparatus. Figure 2 depicts the arrangement of the complete apparatus used for the reaction studies with the exception of the glass work shown in Figure 1.

The source of the polarization voltage was a 32 volt battery pack (lead storage cells). This voltage supply was placed in series with variable resistors, R_1 and R_2 , to produce small constant polarizing currents (0.025 to 1.0 ma) which were measured with ammeter A. A Wilson and Co. Model 1 repeat cycle timer was connected in parallel to the voltage source. Alternating currents from 0.05 to 2.0 c.p.s. could be produced by the timer as well as uneven cycles. When turned off, the timer allowed direct current to pass through it.

A Beckman Model H2 pH meter was employed to measure the potentials of the platinum catalysts with respect to the reference saturated calomel electrode. Also it was possible to measure the difference in the potentials of the two catalyst electrodes and record them continuously on the Brown Recorder by measuring the voltage drop across R_3 .

The electrolysis current was measured by feeding the potential drop across a 10 ohm. resistor, R_5 , to the Brown Recorder.

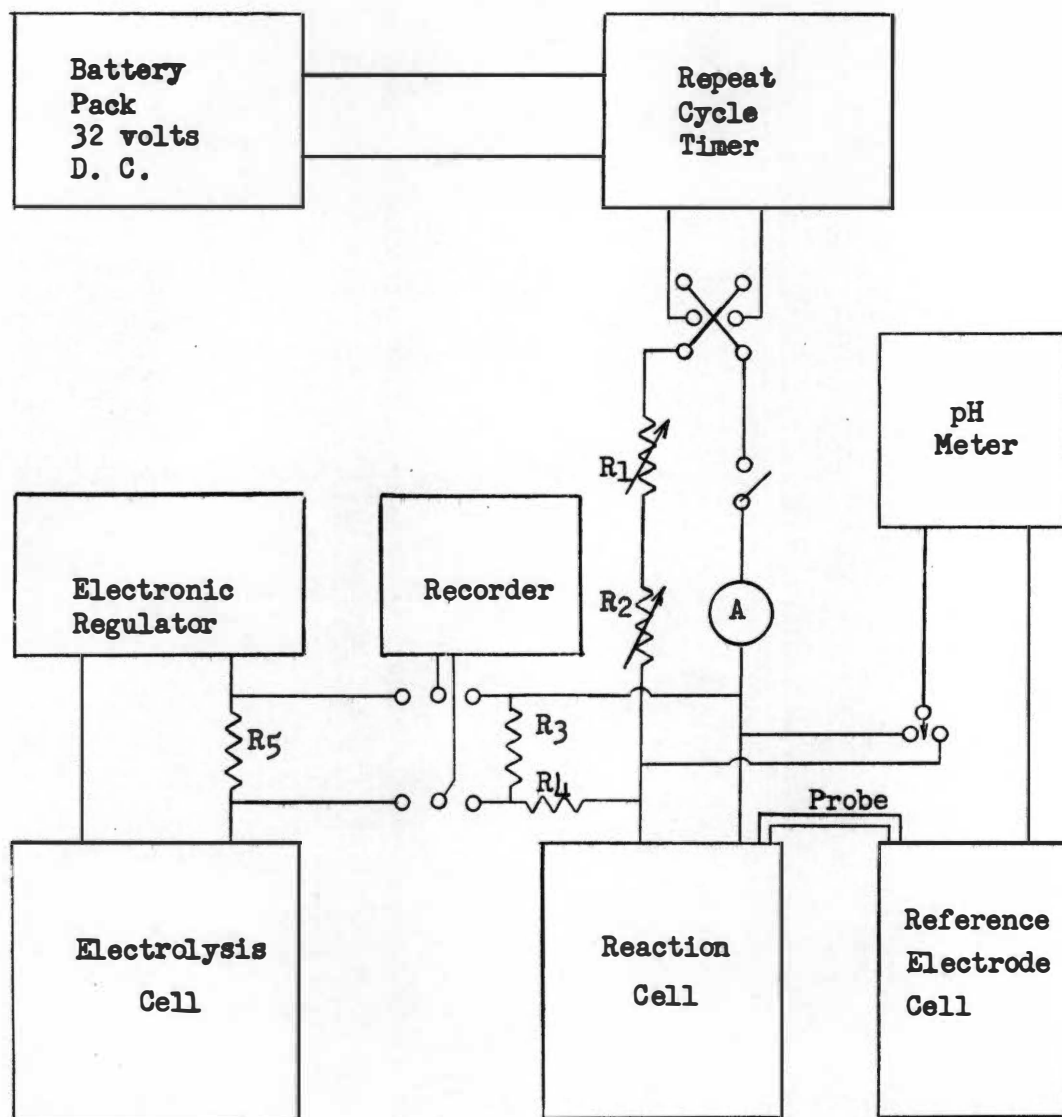


Figure 2. Block Diagram of Electrical Circuits.

e. Procedure. The solution was introduced into the reactor through the ground glass joint illustrated in Figure 1, after which the teflon plug, C, containing the catalyst was fitted into the joint. The system was then evacuated through stopcock, S_1 , until boiling occurred. The stopcock was then closed and hydrogen and oxygen were generated in the electrolysis cell until the desired pressure of gas was obtained as indicated by the balancing of the control system. This procedure was repeated a number of times to rid the system of other gases. The system was simultaneously brought to thermal equilibrium. The current recorder and stirrer were then turned on, and the reaction rate as a function of time read directly off the Brown recorder sheet.

4. Constant Temperature Air Bath

It was essential that the temperature of the system be held constant. The volume of the air-tight housing surrounding the bellows was different than the gas volume within the system. Hence, temperature fluctuations would give unequal pressure changes on either side of the bellows and affect its position, and, in turn, the measurement of the catalytic activity. For this reason, an air bath was constructed from an insulated cabinet whose outside dimensions were 22" x 18" x 24" to house the reaction system. The cabinet was insulated with 3.5" of rockwool. Two doors were in front of the cabinet, the outside one containing an inch of insulation and the other being made of glass. Horizontal iron rods were passed through the cabinet from the sides for the purpose of clamping the catalytic reaction system in place. Air was circulated in the cabinet by means of a 6", 3-blade fan which was driven by a 1725 r.p.m. motor, placed out-

side the cabinet. The motor was connected to the fan blade inside by means of a shaft introduced through the rear of the enclosure. In front of the fan were placed two heaters, one of which was a constant heater made with nichrome wire and the other an intermittent heater, a 60-watt light bulb, which was activated by a large mercury thermo-regulator. The current passing through the nichrome wire was adjusted with a variac to bring the temperature of the bath to within 3 or 4 degrees of the desired operating temperature. A Beckman differential thermometer was employed to determine the constancy of the air bath. No change in temperature could be detected using a magnifying glass attachment on the thermometer. This indicates that the bath temperature was constant to $\pm 0.01^\circ$. The operating temperature of the bath was 40° .

B. Gas-Phase Hydrogenations

1. Materials

a. Hydrogen and oxygen. These gases were generated by the electrolysis of a 1.0 N sulfuric acid solution. Each was passed through a Dry-Ice acetone trap and calcium chloride tube to remove the water vapor.

b. Ethylene. Matheson C. P. grade ethylene was purified by condensation with liquid nitrogen followed by alternate melting, freezing and pumping. Ethylene from the middle fraction of the distillate was finally passed through an activated charcoal trap at -79° .

c. Acetylene. Cylinder acetylene was purified by passage through the following solutions:⁸⁷ chromic acid, 10 per cent mercuric chloride in dilute hydrochloric acid, sodium hydrosulphite, sodium bisulphite and

pyrogallol in 50 per cent sodium hydroxide. The gas was passed through a Dry-Ice acetone trap and calcium chloride tube to remove the water vapor. It was then frozen with liquid nitrogen followed by pumping and sublimation.

d. Nitrogen. Cylinder nitrogen was passed through pyrogallol in 50 per cent sodium hydroxide and dried by passing it through a Dry-Ice acetone trap and calcium chloride trap.

2. Diffusion and Reaction System

a. Palladium. Palladium was used in the form of a tube closed at one end and welded at the other either to a platinum or kovar collar. The kovar collars were sealed directly to pyrex whereas the platinum collars were sealed to soft glass which was joined to the pyrex system by means of a graded seal. The thimbles used were 0.635 cm. outer diameter, 4.13 cm. long and 0.025 cm. wall thickness.

b. Electrolytic hydrogen diffusion. A thimble of one of the two types described above was connected to the vacuum system which was then evacuated to 10^{-5} mm. Hg. The thimble was surrounded by an electrolytic bath of 1.0 N sulfuric acid as shown in Figure 3. Only the palladium end of the tube (not the platinum or kovar) was immersed in the bath. The outside wall of the thimble was then made the cathode and a cylindrical piece of platinum foil surrounding the palladium was made the anode. Hydrogen produced electrochemically on the outside surface of the tube diffused into the metal. After the metal became saturated with hydrogen, the gas emerged from the inside surface into the evacuated system.

More reproducible results were obtained by oxidizing the thimble anodically for a few minutes initially. The oxide film formed was reduced

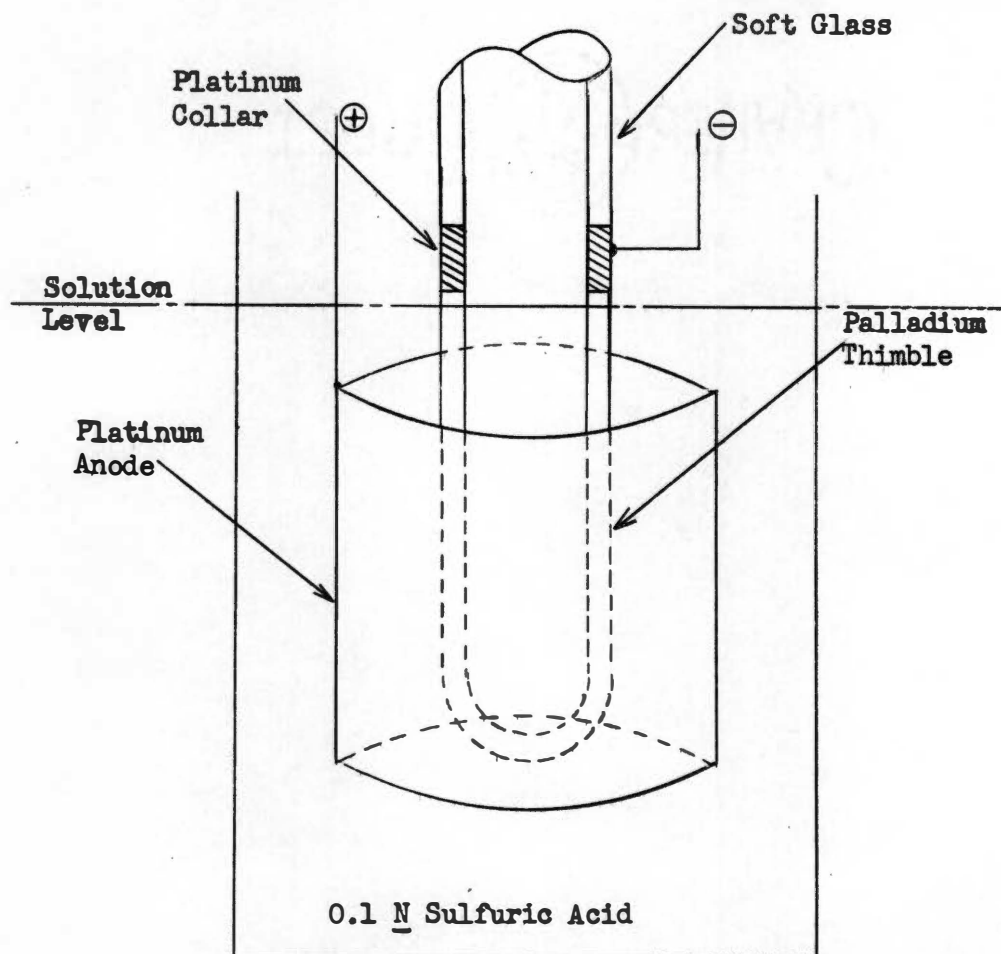


Figure 3. Section View of Palladium Thimble and Electrolysis Bath.

by hydrogen after the polarity was reversed. This probably roughened the outside surface of the palladium thus giving hydrogen a larger area into which to diffuse.

A Dewar flask through which water circulated from a constant temperature bath ($\pm 0.01^\circ$) was placed around the outside of the tube containing the electrolyzing bath.

The electrolysis current was produced by a constant current source similar to that described by Wise, Gille and Reynolds.¹⁰² The current furnished by this instrument was found by Holmes¹⁰³ to have a maximum deviation of 0.004 per cent and an average deviation of 0.002 per cent. Currents from 5 to 40 ma were used.

e. Vacuum system. The system used for determining the rate of hydrogen diffusion through palladium is shown in Figure 4. The palladium thimble was connected in series to a Dry-Ice acetone trap, the purpose of which was to remove mercury and stopcock grease vapors, then to a mercury manometer which was opened at the other end to the atmosphere. The manometer was employed in the system to measure the change in pressure due to hydrogen diffusion at constant volume. A tungsten wire, W', was sealed in the upper part of the manometer arm connected to the system. Another wire, W, was sealed into the lower section of the manometer which was always in contact with the mercury. These wires were fed into an electronic relay, R, which in turn controlled a reversible motor. The motor turned a vertical threaded shaft onto which the leveling bulb of the manometer was mounted. The gas volume of the system into which hydrogen diffused was defined by stopcocks S₁, S₂ and S₃ and the mercury level

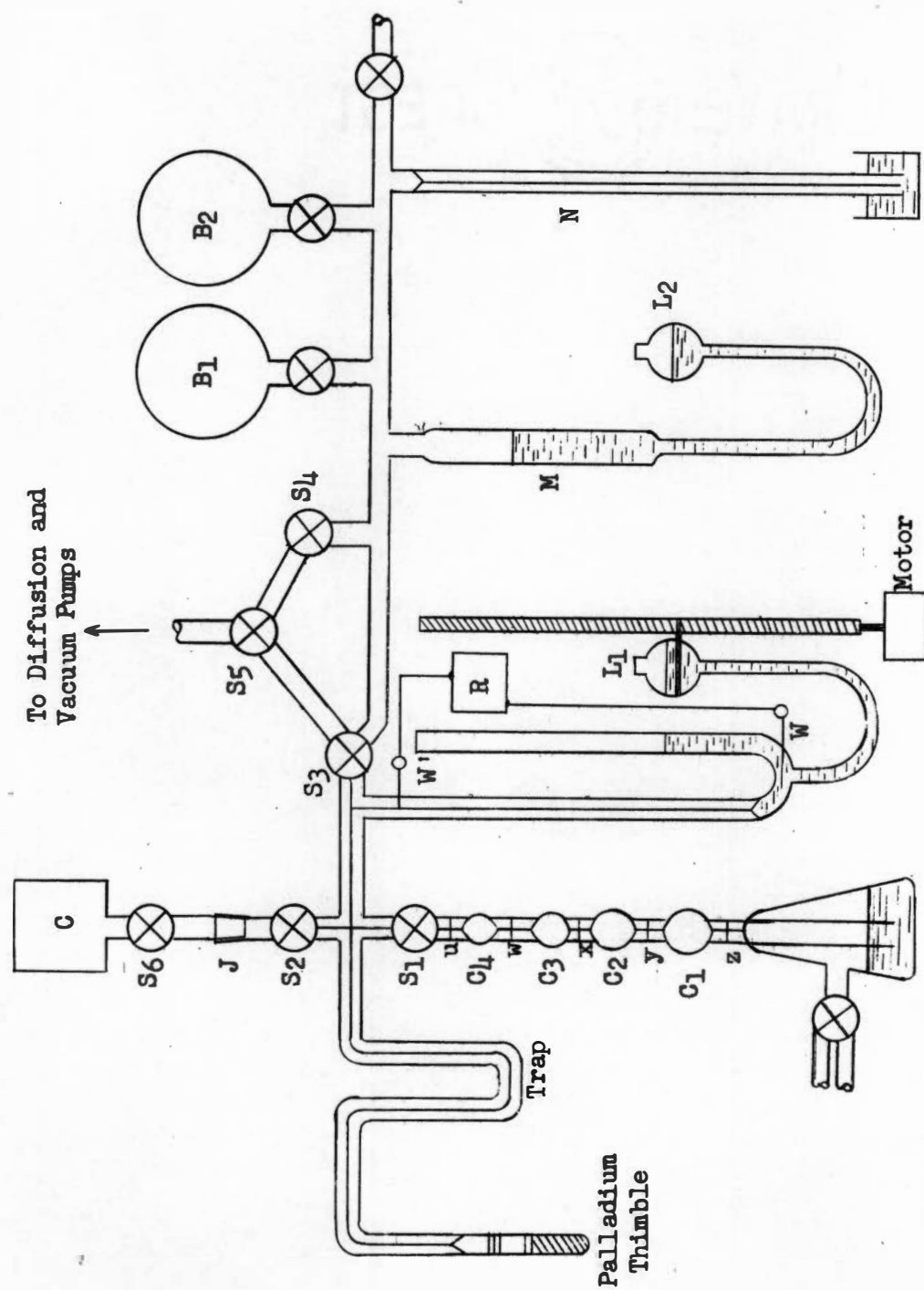


Figure 4. Gas Phase Hydrogenation System.

of the manometer which just touched the tungsten wire, W'. As the pressure within this volume increased due to hydrogen diffusion, the mercury level was forced down, thus breaking contact with W'. This activated the relay which turned the motor on. The motor, by turning the threaded shaft, moved the leveling bulb up until contact was again made between the mercury column and W'. As hydrogen diffused into the system the leveling bulb and the mercury in the outside arm of the manometer moved up in a series of small steps. From a meterstick placed between the two arms of the manometer, the pressure difference between the system and that of the atmosphere was measured at various time intervals. This difference was subtracted from atmospheric pressure to obtain the pressure of hydrogen within the system. The pressure increase as a function of time can be converted into the hydrogen diffusion rate by the ideal gas law if the volume of the system is known using

$$\Delta n/\Delta t = \Delta P/\Delta t \left(\frac{V}{RT} \right),$$

where $\Delta n/\Delta t$ is the number of moles of hydrogen introduced per unit time, $\Delta P/\Delta t$ the pressure change per unit time, V the volume, R the gas constant and T the absolute temperature.

3. Volume Determination

The volume of the system defined by stopcocks S₁, S₂, S₃ and the mercury thread at W' was determined using a multiple bulb buret consisting of four bulbs, C₁ to C₄, of decreasing sizes connected with short lengths of capillary tubing. Bulbs such as these were used by Joncich¹⁰⁴ to determine the dead space in a low volume krypton adsorption apparatus.

Each bulb has a reference point above and below it and the volume between the marks was accurately determined by calibration with mercury before attachment to the rest of the system. The volumes of the bulbs C_1 , C_2 , C_3 and C_4 were determined to be 6.730, 3.350, 1.896 and 1.024 ml., respectively. The volume, V_1 , between the top mark, u, and stopcock S_1 is 0.224 ml.

The method used here makes possible the determination of the volume from a plot of a series of pressure and volume readings, using the same increment of gas. Air was the gas used in this work. The method provides an automatic check on the validity of the measurements since an incorrect pressure value results in a non-linear plot, while a straight line indicates the volume value is correct.

Experimentally the procedure is to introduce a small amount of air into the system with the multibulb buret filled to mark u. The pressure is then measured and the mercury in the buret is lowered to the second mark and the pressure measured again. The mercury is then lowered to the third, fourth and fifth marks with the pressure measured at each of these points.

Let V_0 be the volume of the system, V_1 the volume between stopcock S_1 and mark u of the buret, V_b the volume of the buret, V the total volume, i.e., $V_0 + V_1 + V_b$, and P the pressure reading. A constant amount of air was used throughout and the temperature remained constant during the calibration. If it is assumed that air under these conditions (1 to 10 cm. Hg pressure and room temperature) is ideal, Boyle's law gives:

$$PV = PV_0 + PV_1 + PV_b = K$$

where K is a constant.

Rearrangement of the above equation yields:

$$PV_b = K - P(V_0 + V_1).$$

Differentiation of this equation gives:

$$\frac{d PV_b}{d P} = - (V_0 + V_1).$$

A plot of PV_b versus P should give a straight line, the slope of which is the negative of the volume $V_0 + V_1$. Since all quantities except V_0 are known, the volume of the system may be calculated. A treatment of data for the determination of the volume is given in the Appendix.

4. Catalytic Reaction System

a. Apparatus. The same system was used for the catalytic reaction studies as for the hydrogen diffusion experiments as illustrated in Figure 4. The reactants were stored after purification in 1-l. bulbs, B₁ and B₂. Manometers (not shown) were connected to these bulbs to measure the quantity of gas in each.

An ionization chamber, C, used to collect samples of hydrogen-tritium mixtures was connected to the reaction portion of the system through stopcock S₂. The volume of this chamber is 250 ml. while the volume of the system in which reactions are carried out and that between S₂ and the stopcock of C is about 5 ml. Hence, approximately 98 per cent of the gas mixture could be transferred into the ionization chamber.

b. Procedure. One of the gases to be hydrogenated and hydrogen were separately introduced into the mixing chamber, M, and the pressure of each was measured with manometer, N. The two gases were mixed by raising and lowering the leveling bulb, L₂, several times. The two mixed gases were then admitted into the evacuated reaction portion by means of stopcock S₃. In the hydrogenations of ethylene, acetylene and oxygen, the total gas pressure decreases during reaction. The mercury level of the manometer would therefore rise necessitating the lowering of L₁ to maintain a constant volume. The motor was manually turned on and off lowering the mercury thread during the reaction so it just touched the tungsten wire, W'. Changes in pressure were thus measured as a function of time.

In a portion of the work, hydrogen was allowed to diffuse through the palladium thimble during the hydrogenation reactions. Since there are two phenomena occurring in this case, the diffusion of hydrogen into the system raising the pressure and the reduction reaction on the inside of the thimble lowering the pressure, it was not possible to ascertain these two rates by merely measuring the total pressure change of the system. Hence, tritiated water was used in the electrolytic bath causing tritium as well as hydrogen to diffuse through the thimble. The tritium content of the diffused mixture being proportional to the total amount of gas, could be determined by making use of its radioactive property. Hence, the tritium content of a gas mixture which had diffused through the palladium during a time interval (usually ten minutes) was determined with and without the presence of another gas within the reaction volume.

By this procedure, the diffusion rate of hydrogen could be determined with other gases exposed to the inside thimble surface.

Experimentally, the reaction volume including the ionization chamber was evacuated, after which stopcocks S₂ and S₃ were closed allowing hydrogen and tritium, which diffused through the thimble for ten minutes, to be trapped. During this time pressure-time measurements were also taken. Stopcock S₂ was then momentarily opened permitting the gases to enter the ionization chamber. Stopcock S₆ was closed and the chamber removed from the system via the ground glass joint connection, J. The chamber was then filled to atmospheric pressure with cylinder hydrogen and the tritium content determined. By a like procedure the tritium contents were measured after various quantities of one of the reactant gases were admitted into the reactor. Knowing the diffusion rate of hydrogen in the presence of a reacting gas, the reaction rate of hydrogen with the gas could be determined by subtracting the pressure change due to hydrogen diffusion from the total pressure change.

c. Tritium analysis. Hydrogen-tritium mixtures at low pressures were introduced into a 250-ml. stainless steel Borkowski ionization chamber which was then filled to atmospheric pressure with non-radioactive hydrogen gas as described above. The chamber used for ion current measurements consists of a gas-tight conducting shell having an insulated electrode and a guard ring to shield the insulator. Tritium emits low energy beta particles in its disintegrations. These particles ionize the gas within the chamber. Electrons so formed by the radiation are collected on the positive electrode when a voltage negative with respect to ground is

applied to the shell.¹⁰⁵

A vibrating reed electrometer (Applied Physics Corporation, Model 31) was employed to measure the small ion currents thus produced. The ion current was fed to a capacitor in the vibrating-reed-electrometer. This capacitor is formed by the close proximity of a reed which is grounded and an "anvil" or static plate of a dynamic condenser. An electromagnet causes the reed to vibrate so that the capacity varies cyclically at this frequency. Any voltage appearing across the vibrating reed results in an a. c. voltage of the same frequency as the mechanical frequency of the reed. This a. c. voltage is amplified and synchronously rectified. The rectifier output, which is proportional to the input d. c. voltage, causes current to flow through the meter circuit. Thus a small current (usually less than 10^{-13} amperes) is measured by the rate of charge of a capacitance about 12×10^{-10} farads within the electrometer.¹⁰⁶

The shorting switch of the electrometer was opened when the tritium content was to be determined and the rate at which the charge on the capacitor increased was measured. This rate is directly proportional to the radiation or activity in the chamber. The actual readings were the number of seconds, t_1 , required for a microammeter needle to travel seven-tenths of the distance across the dial. Ten readings were taken for the measurement of each activity and the average value was used to calculate the tritium content of the sample. The activity, a_1 , is related to t_1 by the following equation:

$$a_1 = k/t_1$$

where k is a proportionality constant.

Background radiation activity which is due to extraneous radiation and insulator leakage is also included in a_1 . To correct for this, the rate at which current flows through the ionization chamber containing only non-radioactive hydrogen is also determined. The time required for the needle movement in this measurement is designated t_2 . Hence the true activity of the tritium sample, a , is

$$a = k \left(\frac{1}{t_1} - \frac{1}{t_2} \right).$$

Since k in the above equation is not known, only relative activities may be determined from it. However, it is customary to express activities in millicuries (mc.) or microcuries (μ c.). To do this a standard sample of tritium of 3.728×10^{-4} mc. activity was contained in another ionization chamber. Let t_s be the time required for the charge to be produced on the condenser. Since the proportionality constant is the same for any particular instrument, it may be cancelled out in the following equation:

$$\frac{a}{3.728 \times 10^{-4} \text{ mc.}} = \frac{k \left(\frac{1}{t_1} - \frac{1}{t_2} \right)}{k/t_s}$$

which gives

$$a = 3.728 \times 10^{-4} \text{ mc.} \cdot t_s \left(\frac{1}{t_1} - \frac{1}{t_2} \right).$$

CHAPTER III

RESULTS

A. Liquid Phase Hydrogenations

1. Hydrogenation of Allyl Alcohol

The hydrogenation of allyl alcohol was carried out in a 0.1 N sulfuric acid solution over numerous platinized and smooth platinum catalysts at 40° for long periods of time. The reaction was found to be independent of the concentration of the alcohol and constant at constant hydrogen pressure (740 mm. Hg) in the absence of polarization. The reaction absorbed 0.50 ml. of hydrogen per hour based on a 0.6 ma. electrolysis current to maintain the pressure constant.

A variable speed motor was employed to enable the study of the reaction rate as a function of the stirring rate. Data obtained for the hydrogen-oxygen reaction are shown graphically in Figure 5. Results for the allyl alcohol hydrogenation are similar to these. A maximum reaction rate was obtained at stirring rates exceeding 300 r.p.m. For the remainder of the experiments, a stirring rate of 450 r.p.m. was used to prevent the rate of solution of the gases from being the rate determining step.

For these experiments one electrode catalyst was smooth platinum and the other was platinized-platinum. These catalysts were subjected to three types of electrolytic polarization: 1. cathodic polarization of the platinized-platinum electrode; 2. anodic polarization of the

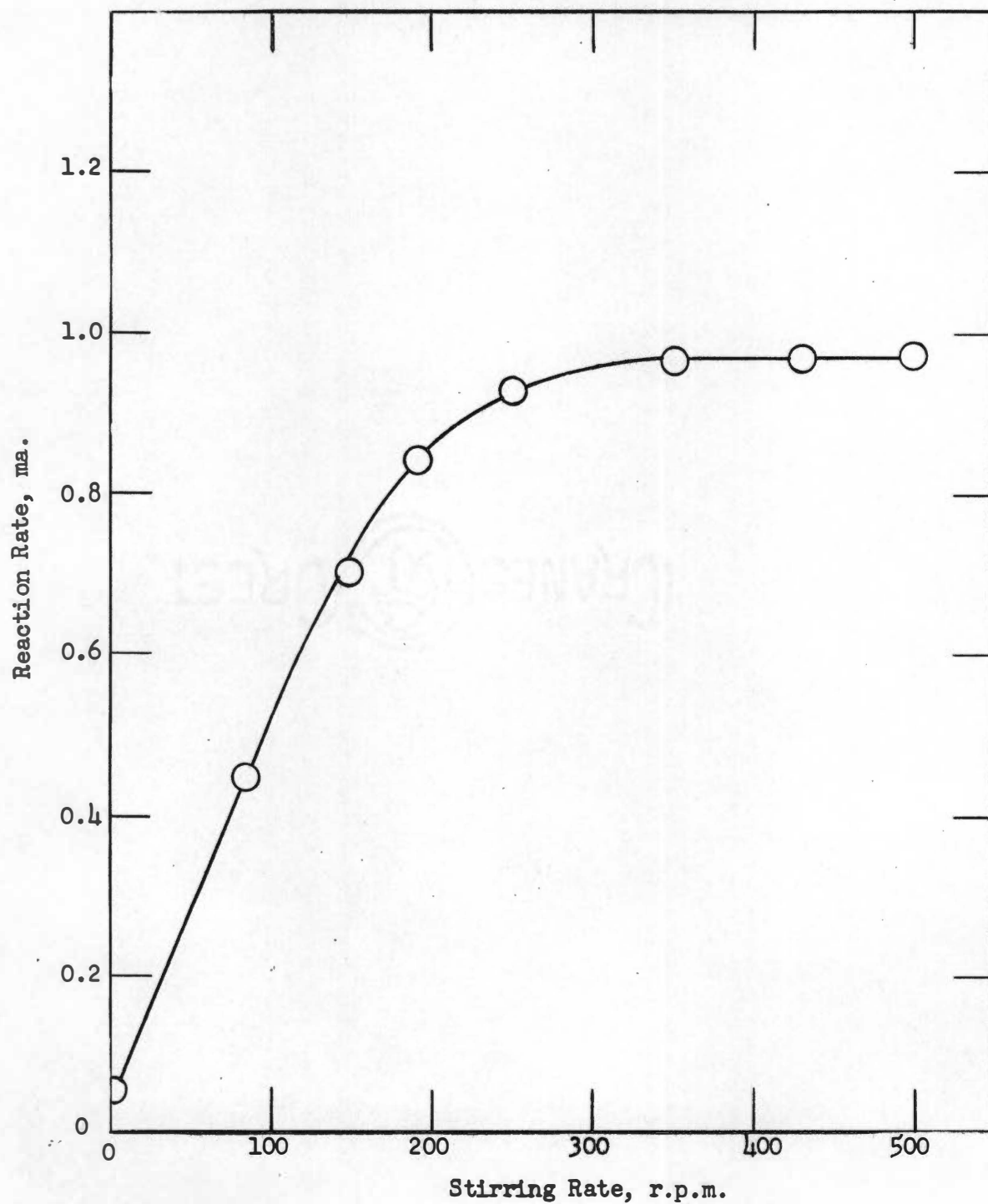


Figure 5. The Effect of Stirring Rate on the Catalytic Combination of Hydrogen and Oxygen

platinized-platinum electrode; and, 3. alternating polarization.

The application of low cathodic polarizing currents (0.05 to 0.5 ma.) had no effect on the reaction rate. At higher currents the decomposition potential of the solution was attained. The resulting evolution of hydrogen and oxygen gas prevented measurement of the reaction rate.

Upon application of anodic polarization, the reaction rate decreased slightly. The greater the polarization, the faster the rate of decline. At 1.0 ma. anodic polarization the rate dropped to practically zero within an hour. When the polarization was stopped, the rate immediately rose to the initial value, or more likely, to a slightly higher value. This higher activity was not permanent, however, but fell slowly within an hour to the normal rate without polarization.

The potential difference between the two platinum electrodes was also observed during anodic and cathodic polarization. At times it was found to vary periodically, rising slowly to 1.0-1.2 volts and suddenly falling to almost zero. The length of these cycles depended upon the magnitude of polarization. With a current of 1.0 ma. the cycles were about fifteen minutes in length. As the polarization current was lowered the cycles became longer, disappearing at currents below 0.5 ma. This periodicity was not reproducible. In fact, it was absent in most of the direct polarization experiments. Also, no periodic behavior in the catalytic activity was observed during those cases in which potential changed periodically.

The effect of alternating current polarization on the catalytic activity was also studied. It was previously observed that upon changing the polarity of the catalysts suddenly, the rate temporarily rose to a higher value which was approximately one and a half times the normal activity with a polarization current of 1 ma. Hence, it was not surprising to find that alternating polarization also enhanced the catalytic activity. Upon application of a. c. polarization, the rate rose slowly to a higher value, depending on the magnitude of the polarization and the frequency, and remained at this value as long as polarization was applied. Figures 6 and 7 show the effect of varying the time on one of the half-cycles while allowing the time on the other half-cycle to remain constant. The curve in Figure 6 was obtained by varying the time the platinized-platinum electrode remained the cathode. There exists an optimum time (two seconds) on cathodic polarization which gives a maximum rise in catalytic activity. Figure 7 shows the curve obtained by varying the time the platinized-platinum electrode is the anode. The maximum for this curve exists at thirty seconds. In Figure 8 the variation of the reaction rate at various magnitudes of a. c. current is plotted as a function of the logarithm of the frequency. In this case the times on each half-cycle were identical. Frequencies ranging from 0.05 to 2 cps. were employed. The maximum of each curve shifts toward the higher frequencies as the polarization current increases.

Similar results were observed using a neutral reaction solution of sodium sulfate as the electrolyte instead of sulfuric acid. However, no periodic voltage behavior between the two catalysts was found. In a basic

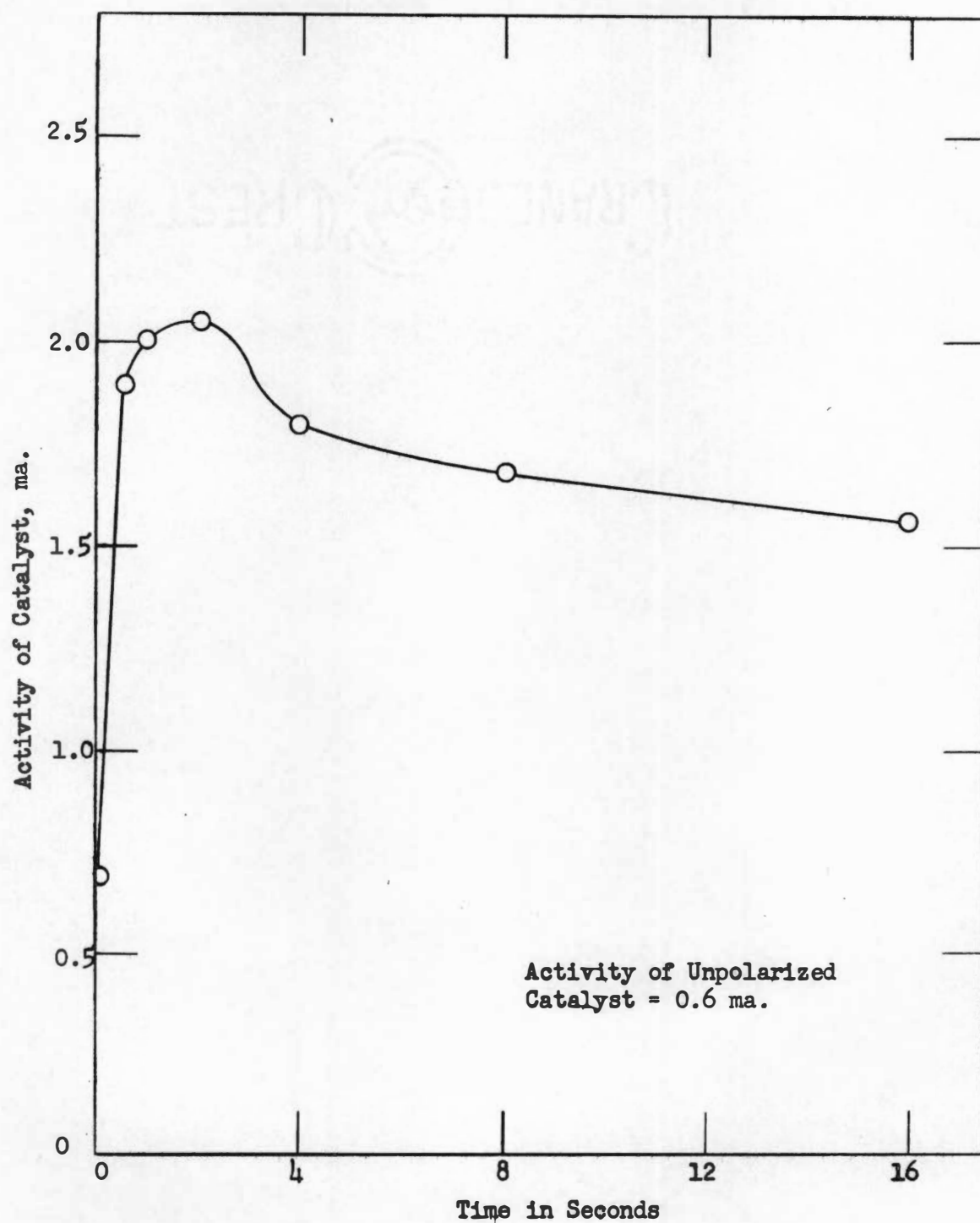


Figure 6. The Effect of Alternating Polarization on the Catalytic Hydrogenation of Allyl Alcohol. Seconds on Cathodic Polarization Per 30 Seconds on Anodic Polarization

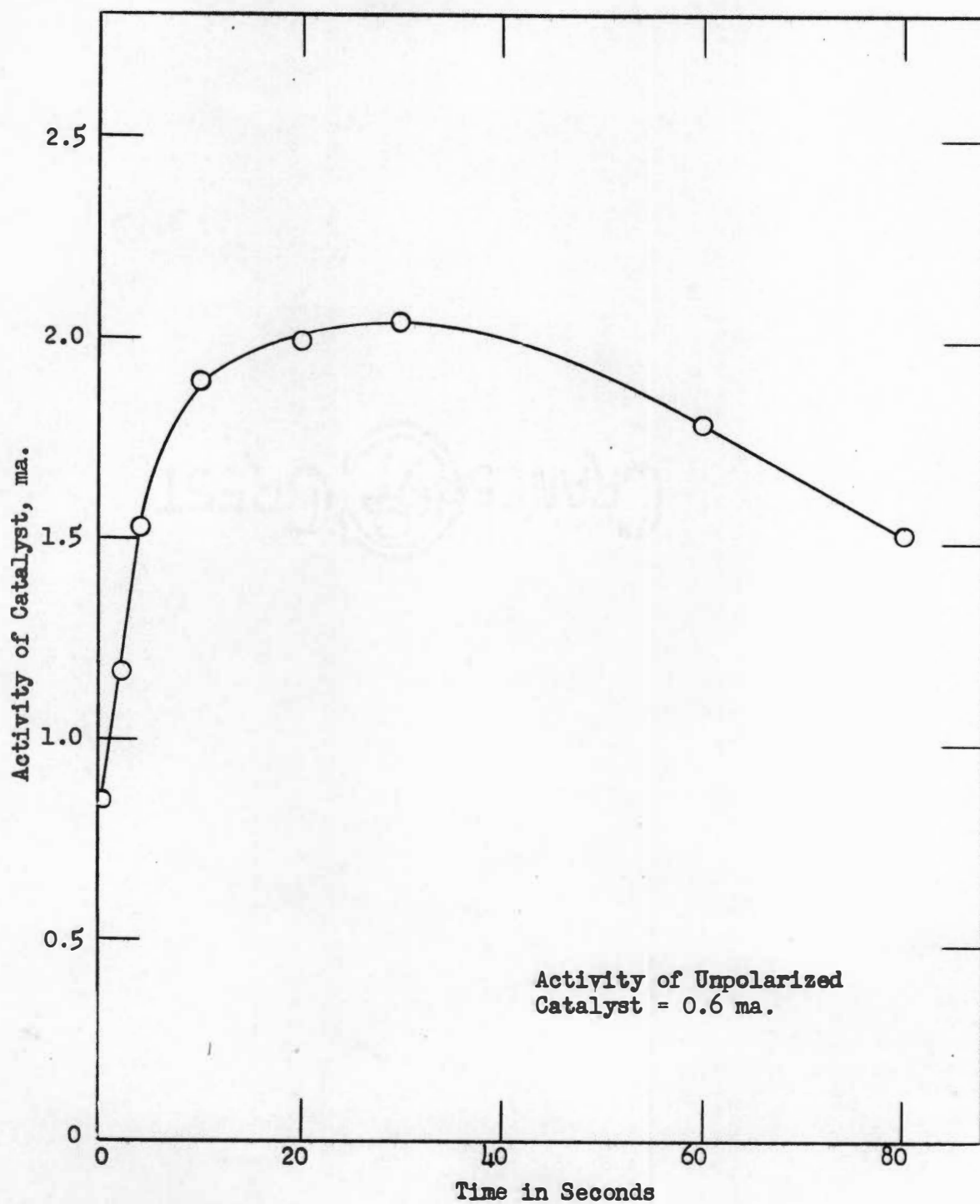


Figure 7. The Effect of Alternating Polarization on the Catalytic Hydrogenation of Allyl Alcohol. Seconds on Anodic Polarization Per 2 Seconds on Cathodic Polarization

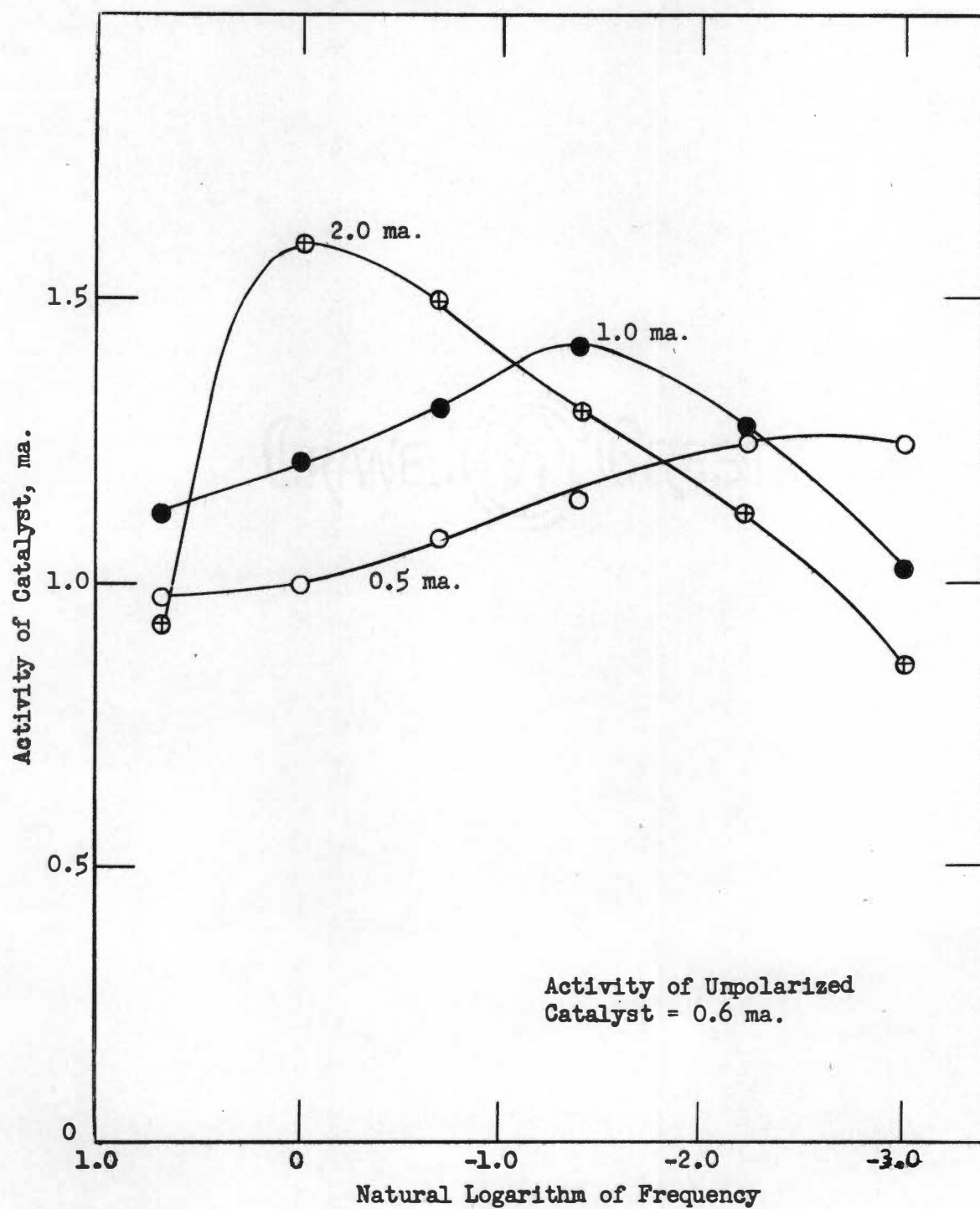


Figure 8. Activity of Catalyst as a Function of the Logarithm of the Frequency for the Hydrogenation of Allyl Alcohol

solution of sodium hydroxide ($\text{pH} = 11$), anodic, cathodic or alternating polarization did not effect the catalytic activity.

2. The Hydrogen-Oxygen Reaction

The hydrogen-oxygen reaction was carried out at 40° in acid, basic and neutral solutions over various platinum catalyst electrodes.

The results obtained in solutions of sulfuric acid ($\text{pH} = 0$ to $\text{pH} = 3$) were identical. On making the smooth platinum electrode the anode, a periodic reaction was observed as shown in Figure 9. In this case the cathode was platinized-platinum. This periodicity was observed with polarizing currents ranging from 0.025 to 0.8 ma. The length of the cycles increased slightly with time. Also, the average activity of the catalyst increased as the magnitude of the polarizing current was increased. The potentials of the anode and cathode were also measured with respect to a standard saturated calomel electrode. The potential of the cathode remained constant for any particular polarizing current, whereas the potential of the anode varied periodically. The periodic cycles of the anodic potential corresponded to those of the catalytic activity with regard to length of time. With a polarizing current of 0.1 ma., the anodic potential increased sharply from +0.3 v. with respect to the saturated calomel electrode to +0.75 v. upon application of the polarization. It remained at this value only momentarily and fell to -0.5 v., after which it rose slowly to about +0.15 v. At this point it began a sinusoidal fluctuation. The cycles increased in amplitude and length with time. When the maximum of the fluctuations reached about +0.35 v., the potential again rose

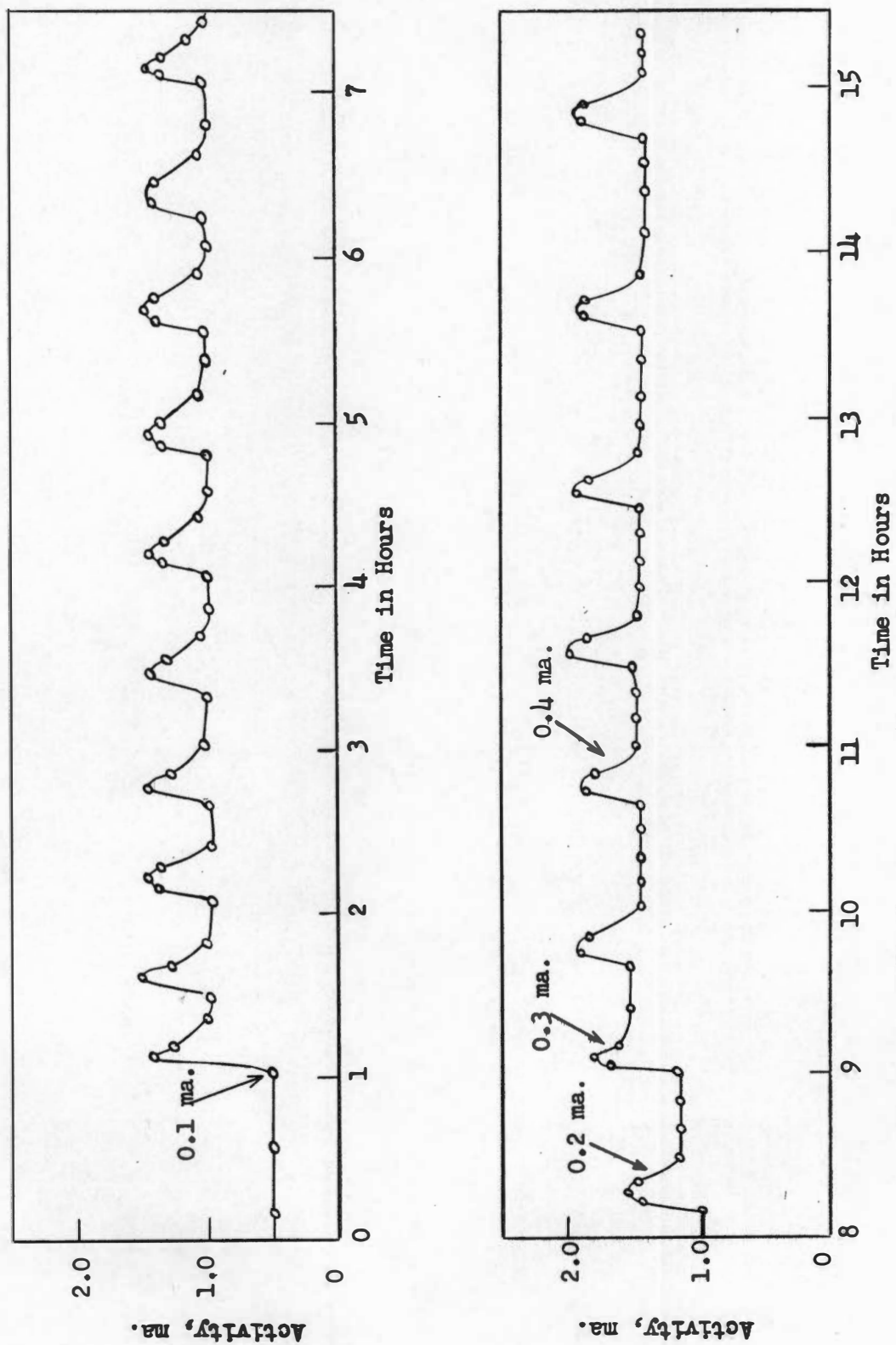


Figure 9. Reaction Rate as a Function of Time Showing Effect of Smooth Platinum Anode and Platinized-Platinum Cathode

swiftly to +0.75 v. after which the cycle was repeated. The catalytic activity increased immediately following the anodic potential's fall to -0.5 v. At times, particularly with higher polarization currents, the anodic potential remained at +0.75 to +0.80 v. for several minutes. In such cases the catalytic activity decreased until the potential fell. Periodicity was not observed with platinized-platinum anodes.

Figure 10 shows the simultaneous values of the catalytic activity and the anode potential. In this study both of the catalysts were smooth platinum electrodes. The lower curve in this graph represents the activity of the catalyst as a function of time, while the potentials of the anode and cathode with respect to the saturated calomel electrode are plotted on the upper portion of the graph. The cycles are shorter with a smooth platinum cathode than with a platinized-platinum cathode. Also, the increase in catalytic activity was less with a smooth platinum cathode.

The results of a prolonged study of the potentials of two smooth platinum catalysts, using various direct polarization currents are shown in Figure 11. The length of the cycles decrease as the current is increased. When the polarization is changed to a higher value, the initial period following the increase is observed to be shorter than the other periods, whereas when the polarization is decreased, the initial period following the decrease is longer than the other periods.

The periodic behavior of the catalytic activity and anodic potential described above was not observed in neutral solutions of sodium sulfate or basic solutions of sodium hydroxide. It did occur, however, in solutions of sulfuric acid which were 0.001 to 2.0 N in sodium sulfate.

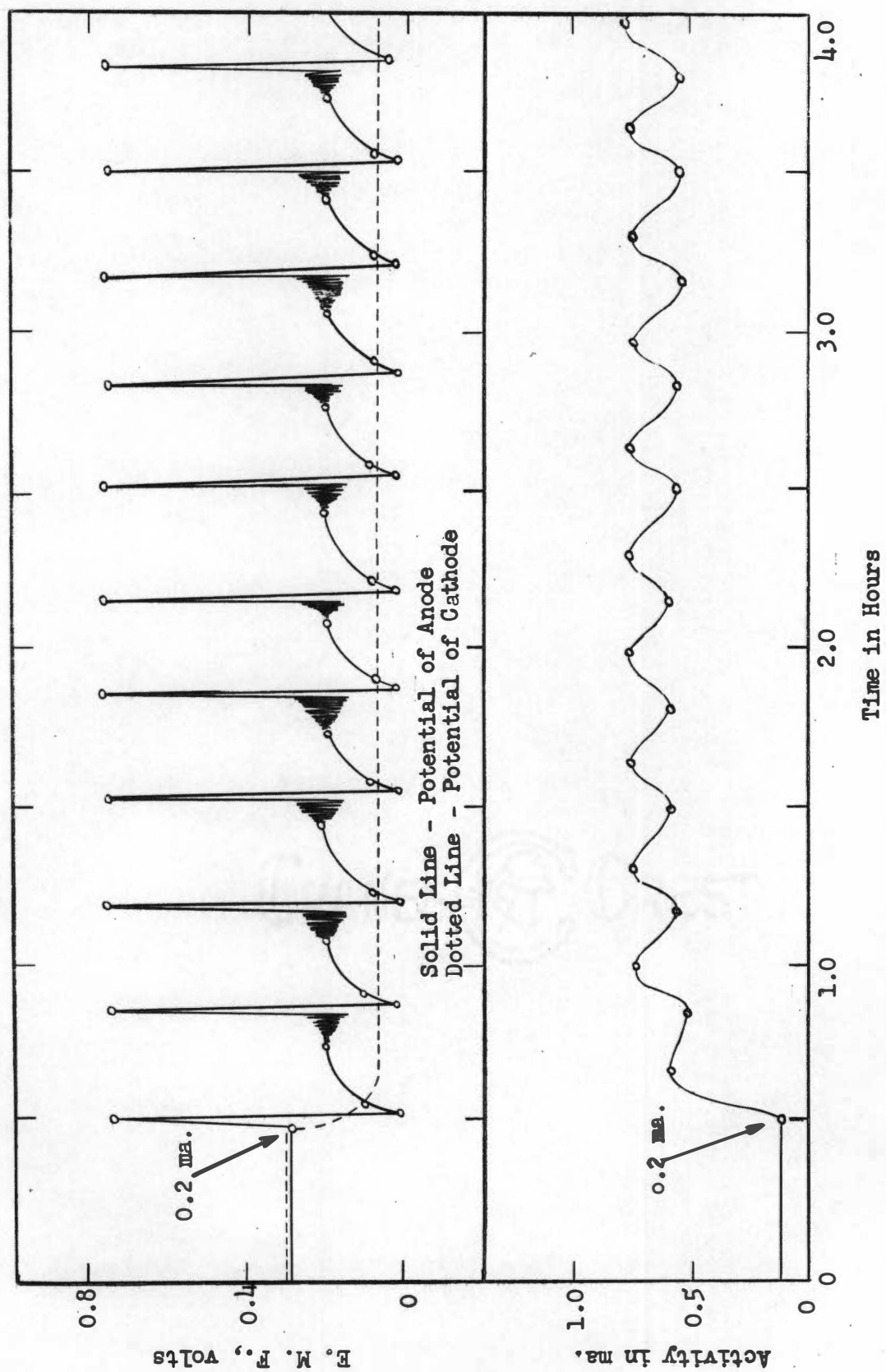


Figure 10. Correspondence of Catalytic Activity to Potentials of Smooth Platinum Anode and Cathode

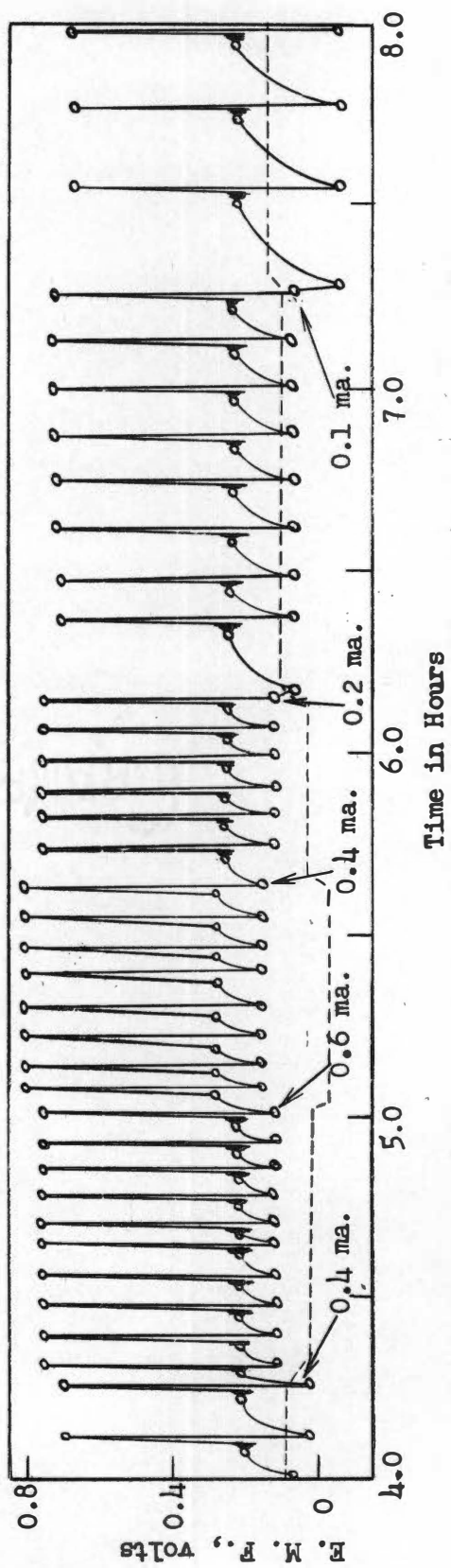
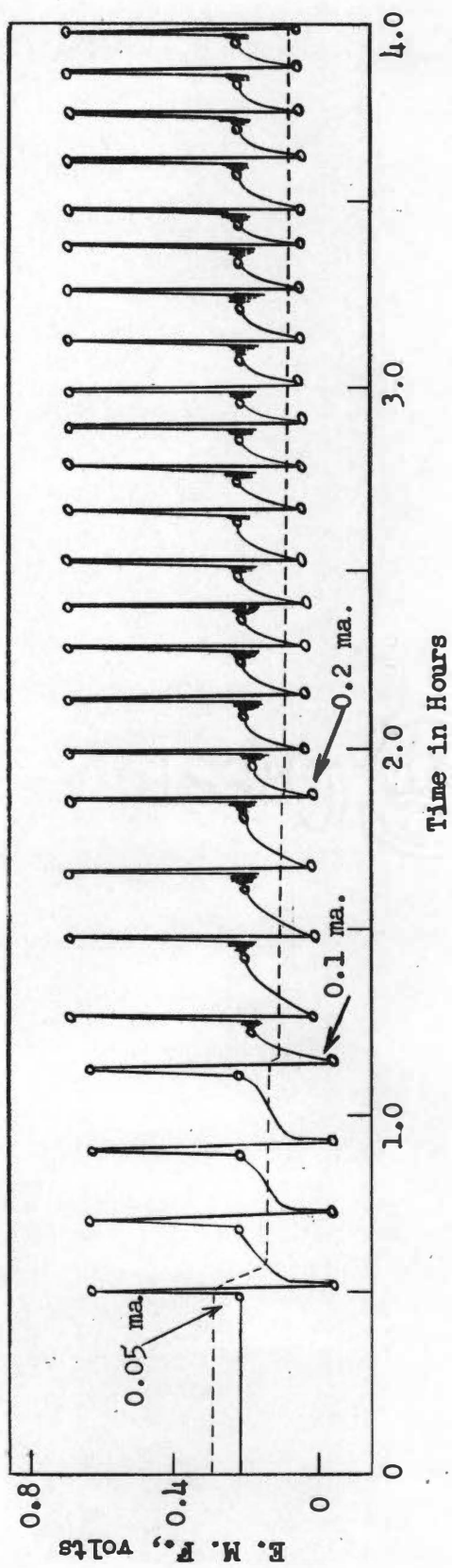


Figure 11. Variation in Potentials of Smooth Platinum Electrodes Upon Direct Polarization

Some experiments were performed in which air, rather than the stoichiometric hydrogen-oxygen mixture, was introduced above the solution. The periodic behavior of the anodic potential was not observed in these cases. Further, periodic behavior was not observed when low pressures (< 300 mm. Hg) of the hydrogen-oxygen mixture were above the solution.

In Figure 12 the variation in catalytic activity as a function of the logarithm of the frequency of the alternating current is shown. An enhanced activity was also obtained with alternating current polarization in neutral solutions but not in basic solutions.

B. Diffusion of Hydrogen Through Palladium

Electrolytic hydrogen was caused to diffuse through a palladium thimble into an evacuated system by making the outside of the thimble the cathode in an electrolytic solution of 0.1 N sulfuric acid. Current densities ranging from 0.50 to 4.41 ma./cm.^2 were employed at temperatures from 0° to 70° . Approximately $2,000$ coulombs of electricity were passed through the bath before hydrogen could be observed (by pressure measurements) to pass through the thimble. The wall thickness of the thimble was 0.025 cm. The rate of diffusion was very small when the gas initially came through the metal. After this slow initial rate, the rate gradually increased to a constant value which was dependent on the current density and temperature. Diffusion rates were observed to remain constant for as long as two weeks. When the electrolysis current was stopped, the rate slowly decreased to zero within several hours.

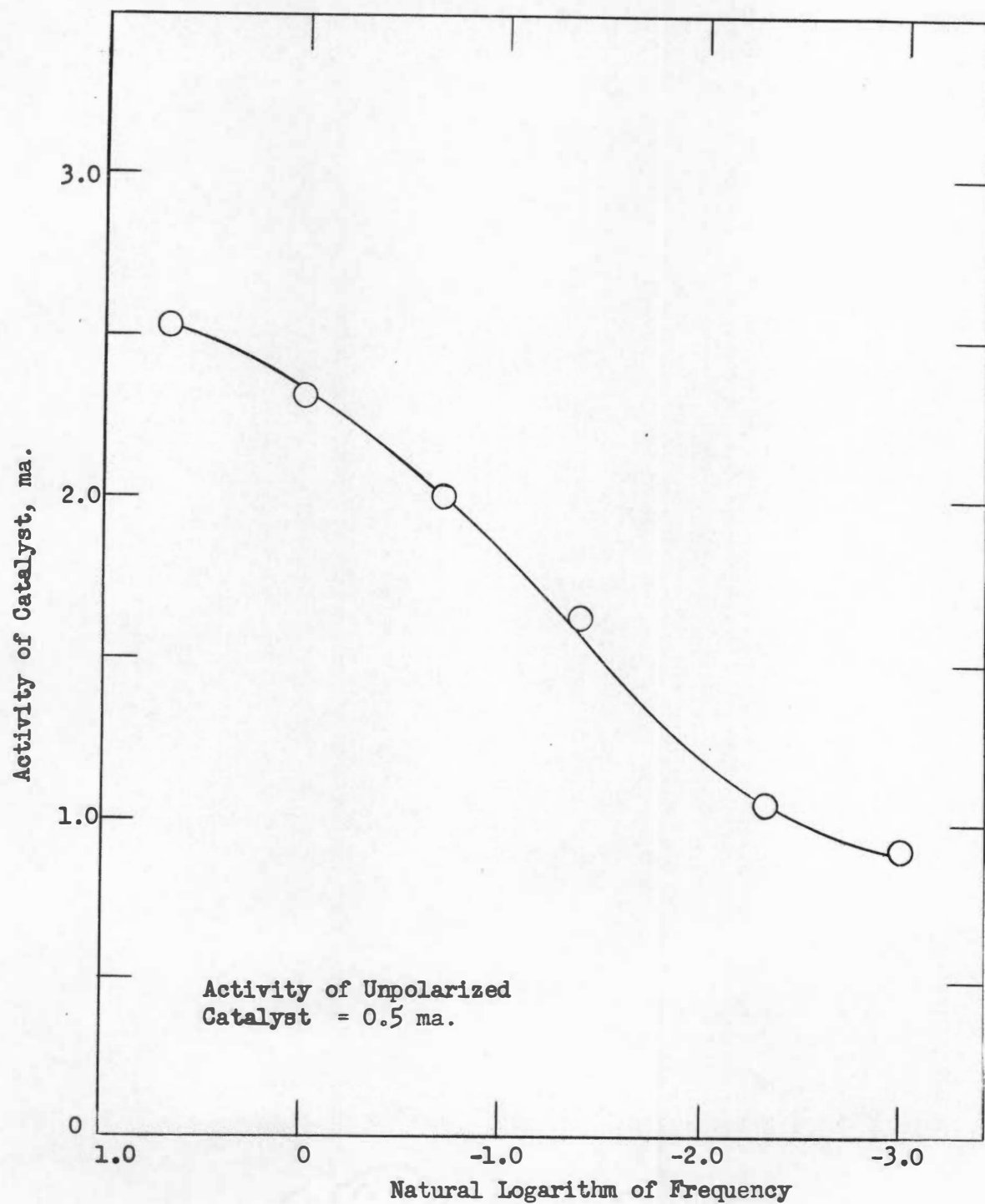


Figure 12. Effect of 1.5 ma. Alternating Polarization for the Hydrogen-Oxygen Reaction

Many unsuccessful attempts were made before reproducible diffusion rates were obtained. Impurities on either side of the palladium were found to alter greatly the diffusion rate. For this reason a very pure solution was required in the electrolysis bath. A Dry-Ice acetone trap was installed between the thimble and the rest of the system to prevent stopcock grease and mercury vapor from reaching the inside of the thimble. Attempts to remove impurities by etching the thimble with aqua regia or heating the outside to 400° while drawing a vacuum on the inside of the thimble were unsuccessful. Also, attempts to roughen the surface of a clean thimble with aqua regia resulted in much lower diffusion rates. The permeability of a palladium thimble could be restored by annealing it at 775° in a vacuum of 1×10^{-5} mm. Hg for forty-five minutes. The thimbles were usually anodically oxidized for a few minutes prior to the diffusion studies to improve the reproducibility of the hydrogen diffusion rates.

In Table I some results obtained from hydrogen diffusion studies at 30° are presented. The per cent transmission, i.e., the amount of hydrogen that diffused through the metal per unit time divided by the total amount produced on the outside of the thimble by electrolysis per unit time, is very nearly the same for the range of current densities studied (at constant temperature).

The volume of hydrogen that diffused through the palladium is plotted as a function of time for various current densities at 30° in Figure 13. This linear relationship indicates that hydrogen pressure within the system does not have a measurable effect on the diffusion rate in the pressure

TABLE I

HYDROGEN DIFFUSION THROUGH PALLADIUM AT 30°*

Current ma.	Current Density ma./cm. ²	Permeation Rate		Per Cent Transmission
		moles/min.	ml./cm. ² /sec.	
39.5	4.41	5.81×10^{-6}	2.41×10^{-4}	23.7
29.5	3.29	4.22×10^{-6}	1.76×10^{-4}	23.1
19.5	2.17	2.88×10^{-6}	1.20×10^{-4}	23.7
14.5	1.62	1.98×10^{-6}	0.825×10^{-4}	21.9
9.5	1.06	1.32×10^{-6}	0.55×10^{-4}	22.3
4.5	0.501	0.712×10^{-6}	0.30×10^{-4}	25.5

*The volume of the system was 4.98 ml.

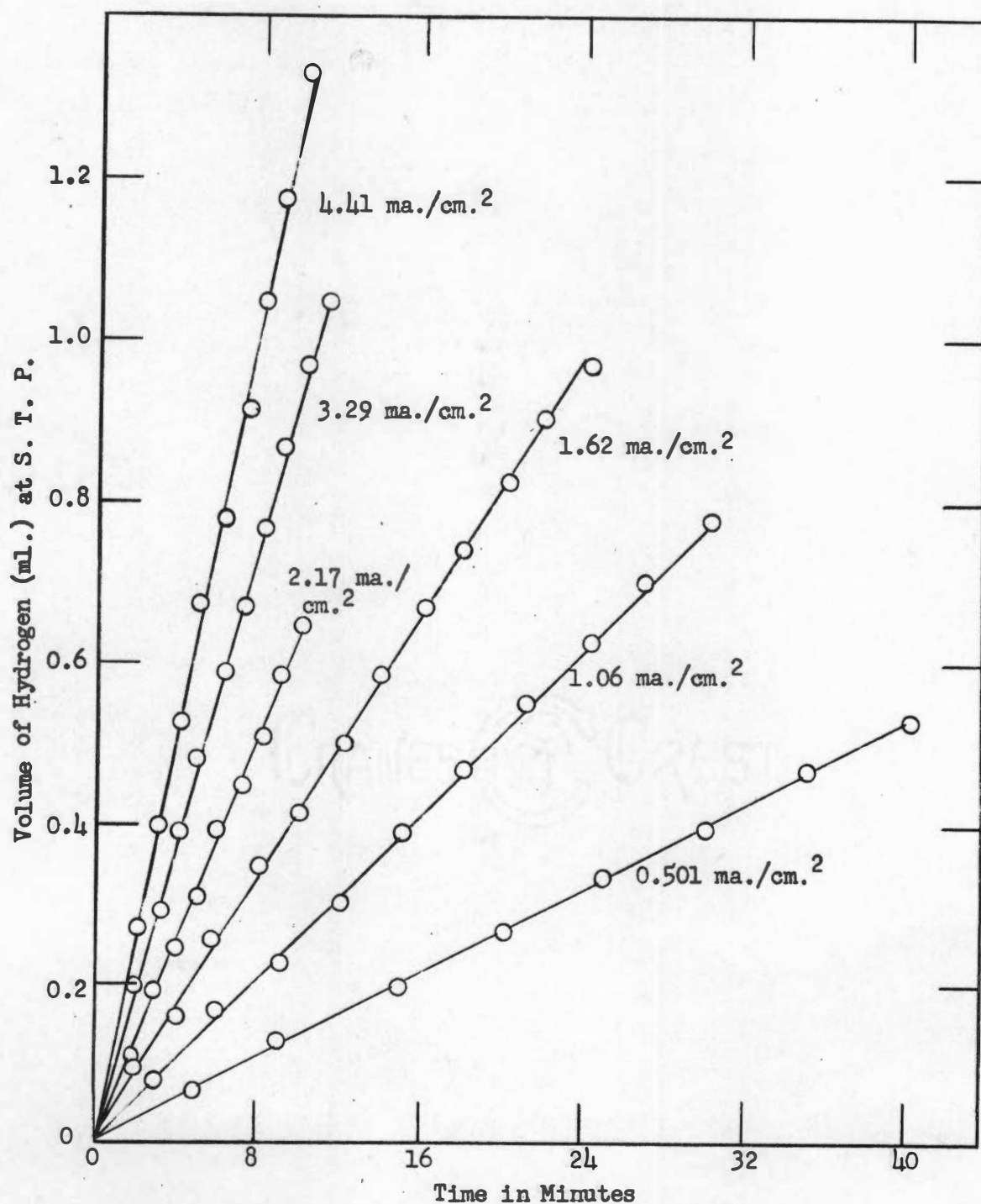


Figure 13. Volume of Hydrogen Transmitted Into System as a Function of Time at Various Current Densities

range studied. Hydrogen pressure within the system was not allowed to exceed 30 cm. Hg pressure.

In Figure 14 the hydrogen permeation rate is shown to be directly proportional to the current density at 30°. The equation for this line is

$$P = 5.41 \times 10^{-5} I$$

where P is the permeation rate in ml./cm.²/sec. and I is the current density in ma./cm.²

The per cent hydrogen transmission is plotted as a function of the temperature in Figure 15. At low temperatures the curve appears to approach a limiting value for the per cent of hydrogen diffusing through the metal, while at high temperatures almost all the hydrogen is transmitted through the palladium.

Two activation energy plots at different current densities are shown in Figure 16. The slopes of these lines in the temperature range from 30° to 70° were used to calculate the activation energy for the process. A value of 6.2 kcal./mole was obtained.

To determine the effect that certain gases, which are able to react with hydrogen on the inside of the thimbles, have on the diffusion rate of hydrogen, tritiated water was added to the electrolysis bath. Tritium as well as hydrogen diffused through the palladium under these circumstances. Figure 17 is a plot of the diffusion rate of hydrogen as a function of the amount of tritium which diffused through the palladium in ten minutes.

The per cent transmission of tritium was determined by measuring the tritium content of the solution. Dividing this into the per cent transmission of hydrogen gave a kinetic separation factor of 20 for hydrogen and tritium.

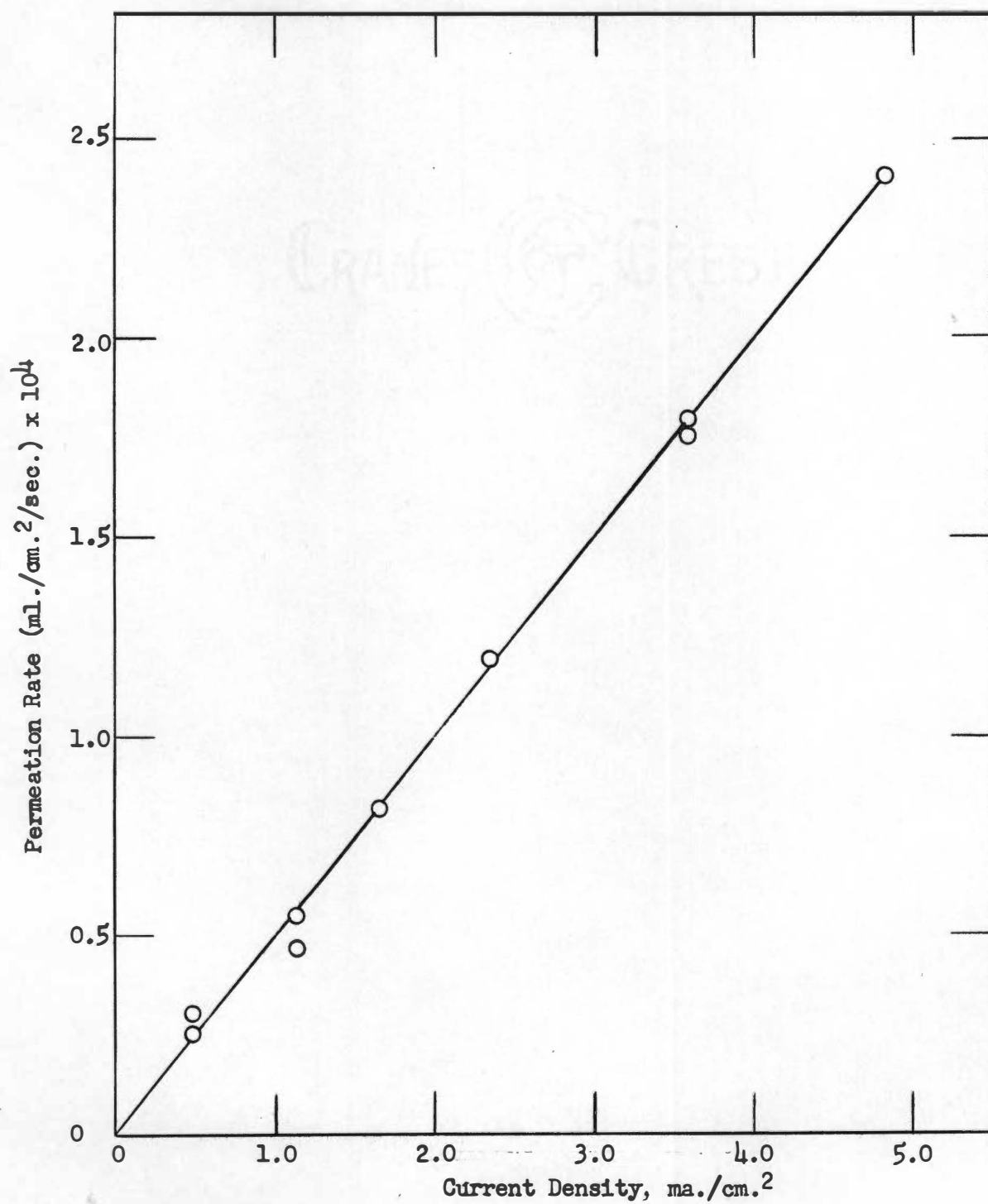


Figure 14. Permeation Rate versus Current Density for Hydrogen Diffusion at 30°

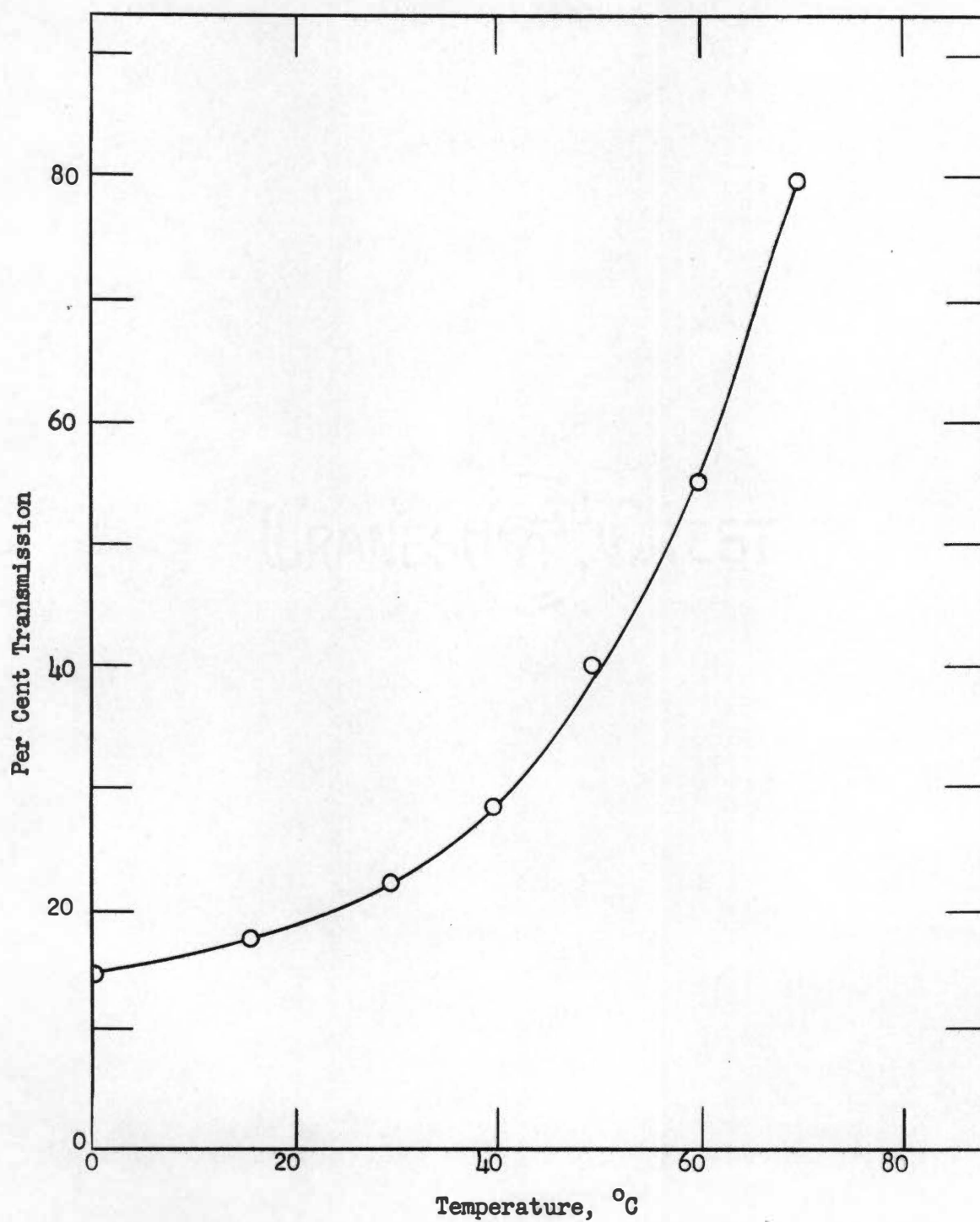


Figure 15. Per Cent Hydrogen Transmission as a Function of Temperature

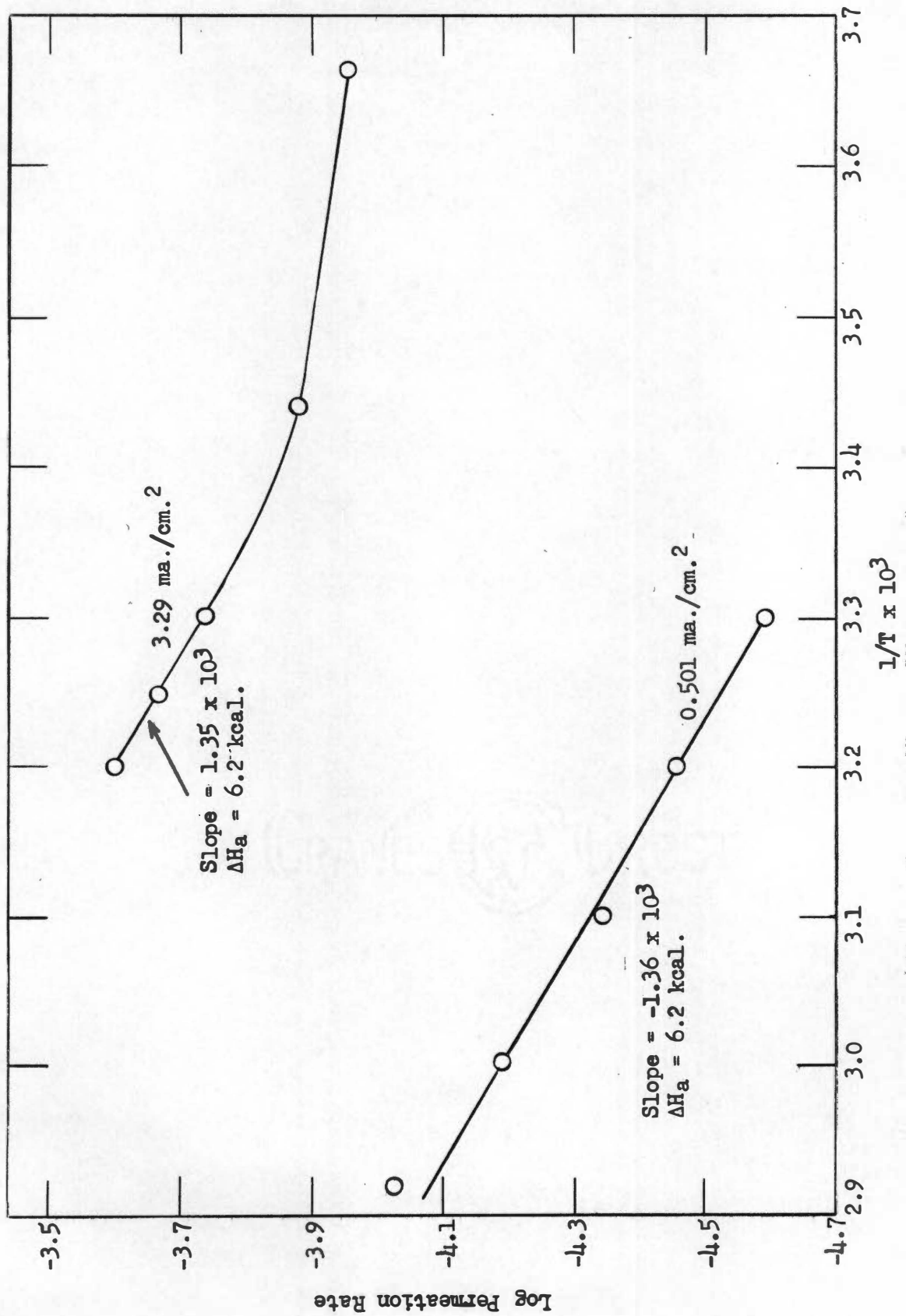


Figure 16. Activation Energy Plot for Hydrogen Diffusion

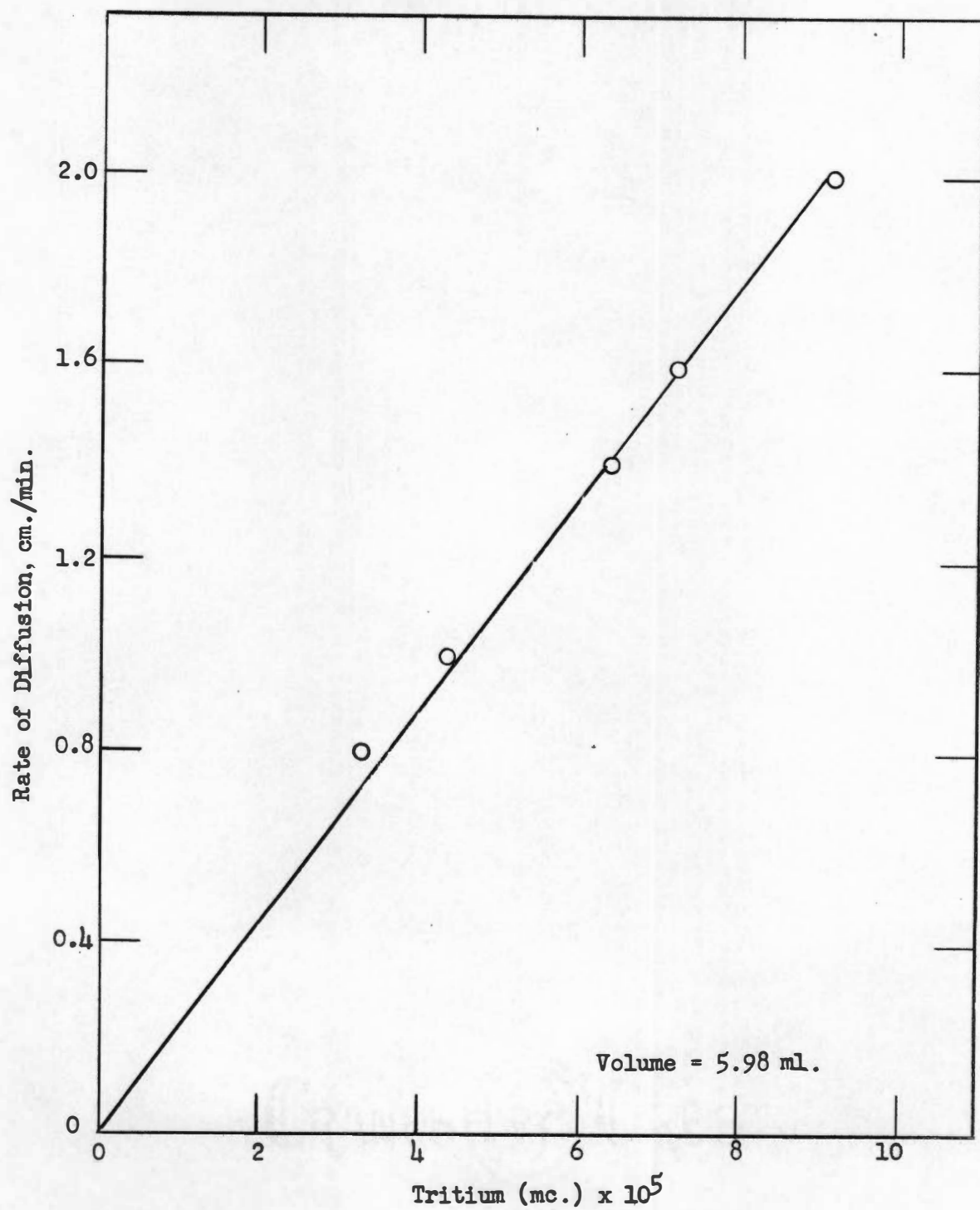


Figure 17. Rate of Hydrogen Diffusion versus Amount of Tritium Present in System After Ten Minutes

The effects of ethylene, acetylene and oxygen gas within the system on the rate of hydrogen diffusion are shown in Figures 18, 19 and 20 respectively. The rate of diffusion was generally lowered to a greater degree by ethylene and acetylene as the temperature was decreased. In Figure 18 the points for the diffusion rate at 40° , 35° and 30° lie very close together and, hence, only one line was drawn through these points. Similarly, one line was drawn through the data obtained at 18° and 0° . The presence of nitrogen within the system did not effect the diffusion rate to a measurable extent at 0° .

C. Gas Phase Hydrogenations

1. The Hydrogenation of Ethylene

The hydrogenation of ethylene was studied on three types of palladium catalysts. The first was a pure palladium thimble which contained no hydrogen. The second was a thimble through which hydrogen had been allowed to diffuse for a time, but the electrolysis had been discontinued and sufficient time was allowed for the diffusion of hydrogen to cease completely. This catalyst is referred to as beta palladium, although experimental evidence that its composition corresponded to $H_{0.6}Pd$ is lacking. The third type of catalyst studied was palladium through which hydrogen was diffusing.

In Figure 21 the logarithm of the hydrogen or ethylene pressure is plotted as a function of time for the reaction occurring on pure palladium. The slopes of the lines correspond to the rate constant of a first order reaction. The activation energy of the reaction on pure palladium was de-

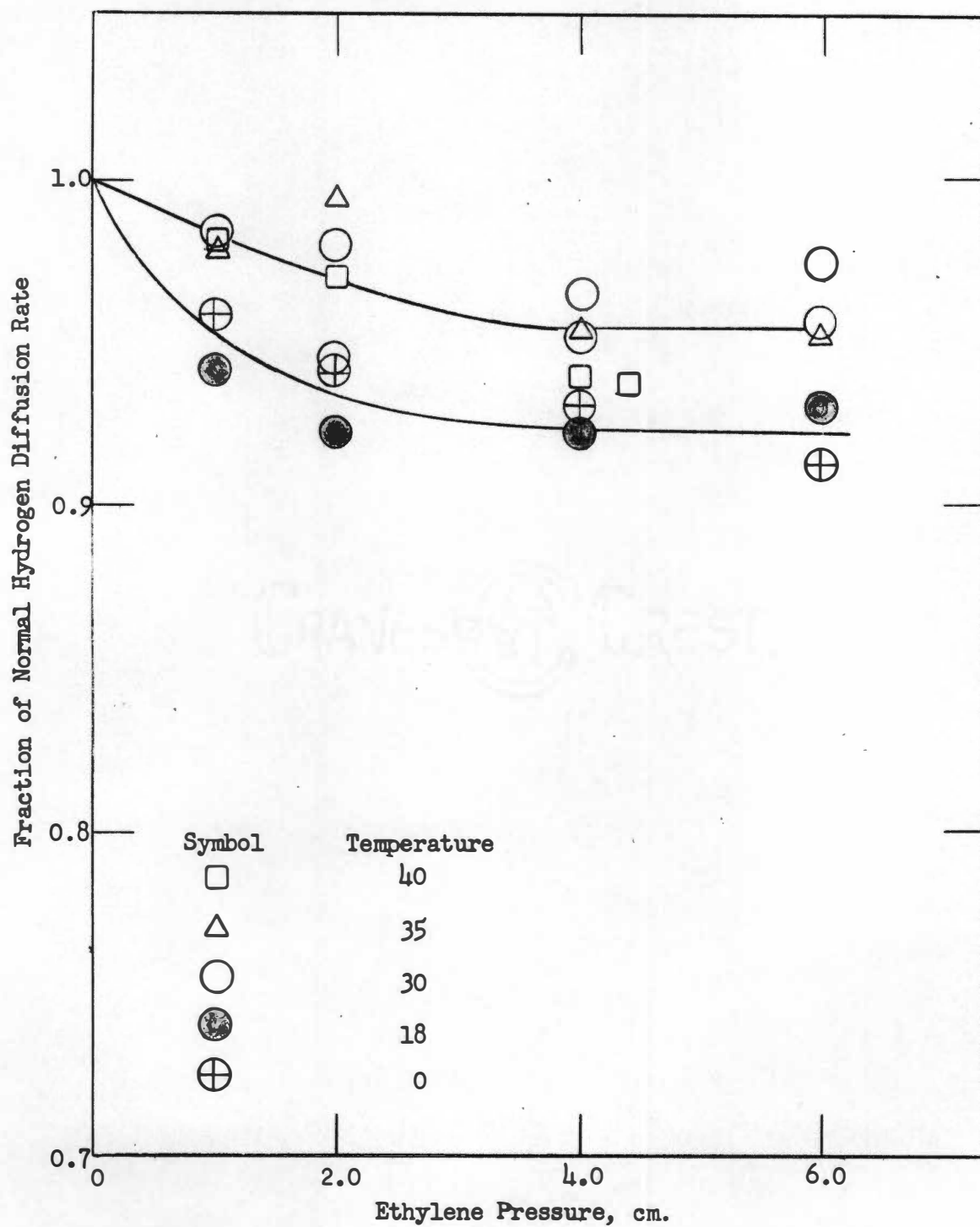


Figure 18. Effect of Ethylene on the Hydrogen Diffusion Rate

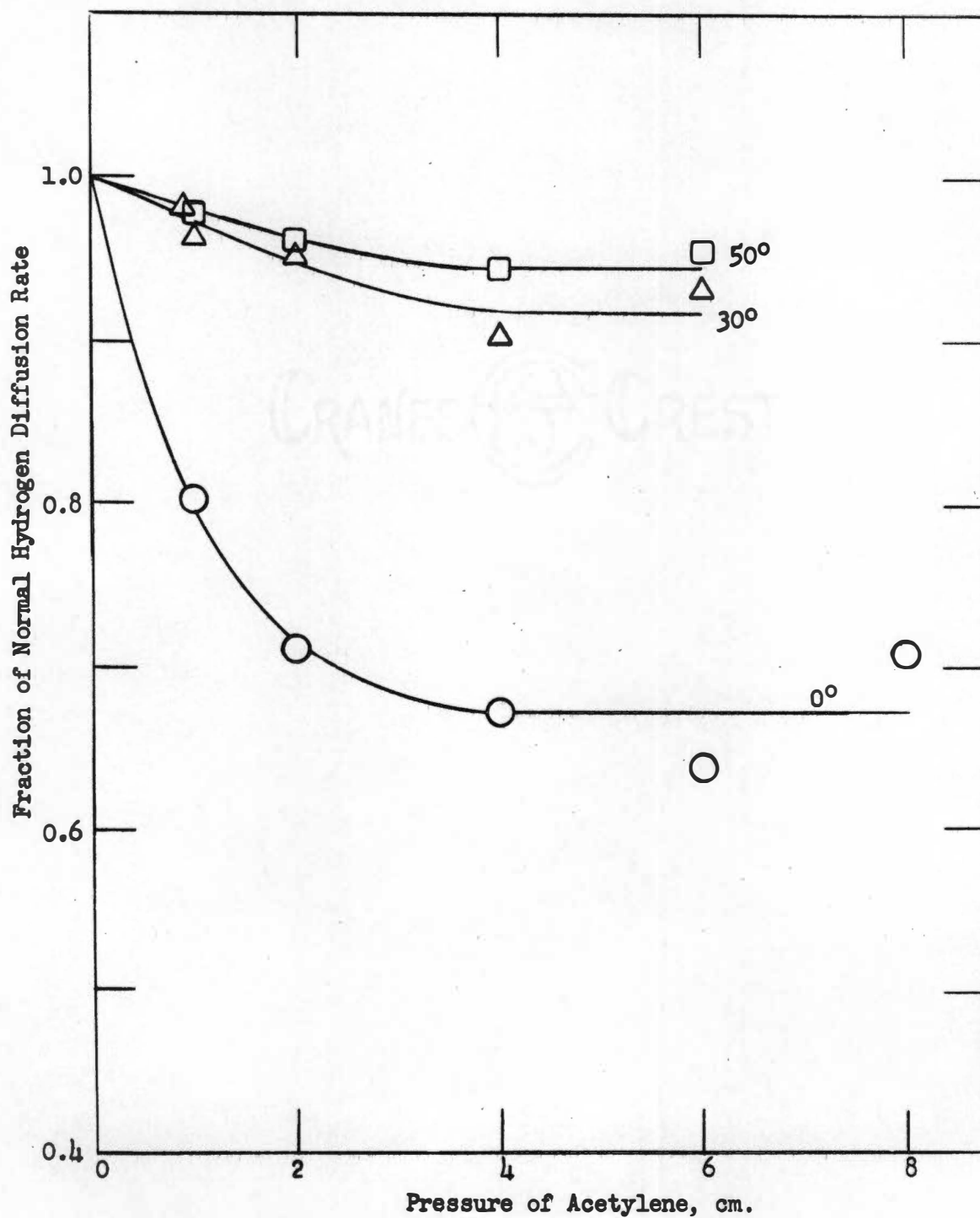


Figure 19. Effect of Acetylene on the Hydrogen Diffusion Rate

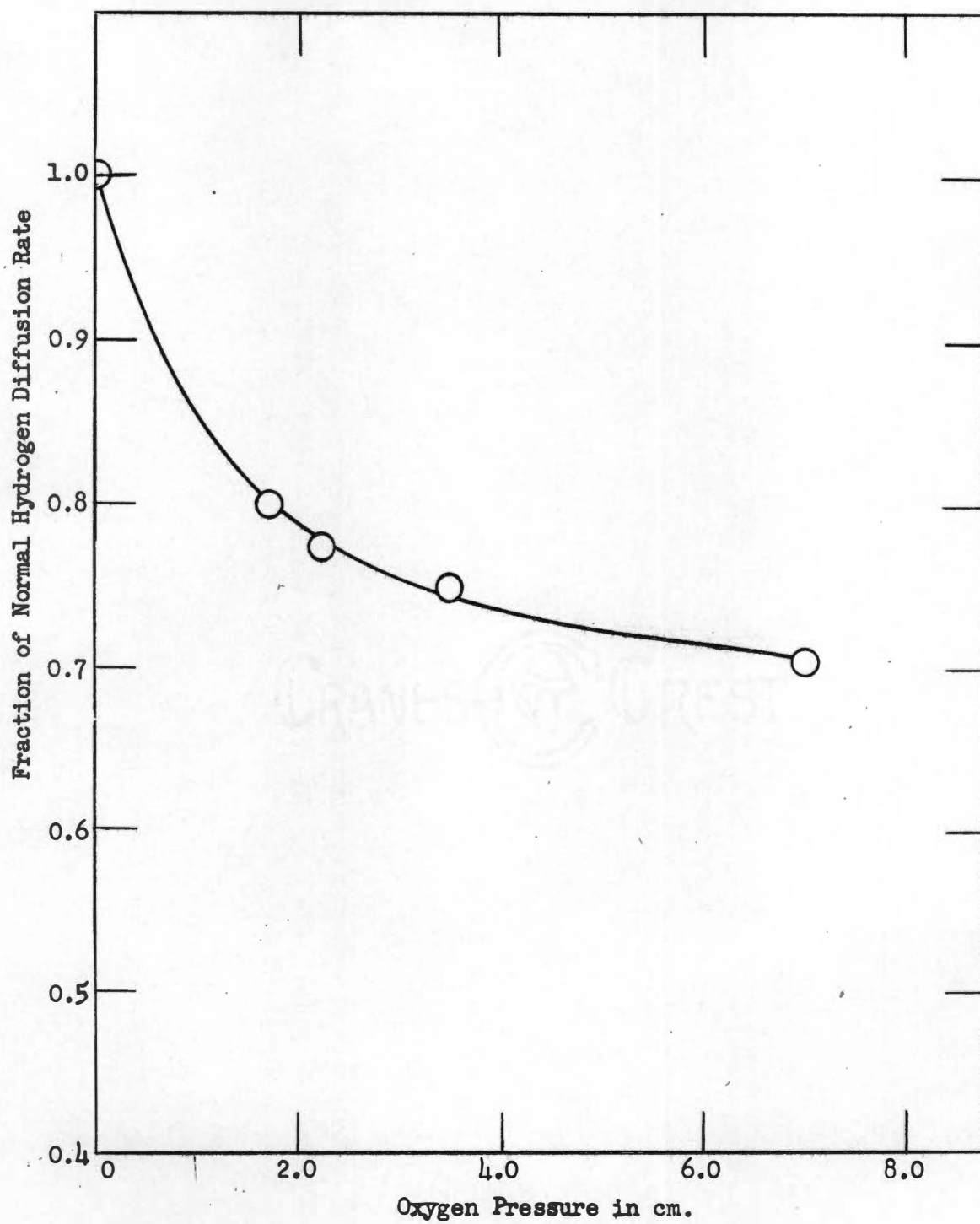


Figure 20. Effect of Oxygen on Hydrogen Diffusion at 70°

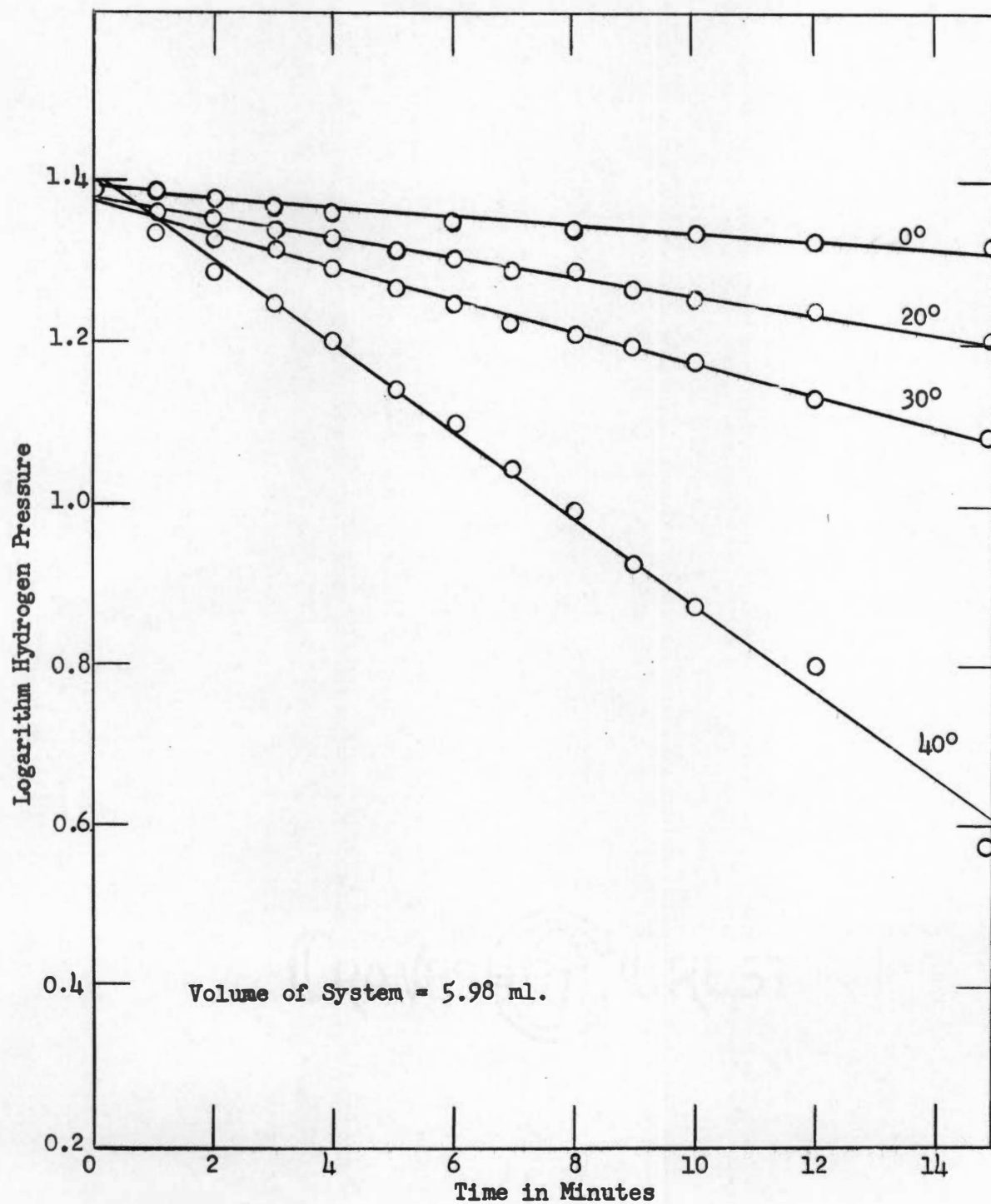


Figure 21. The Natural Logarithm of the Partial Pressure of Hydrogen versus Time for the Hydrogenation of Ethylene on Pure Palladium

terminated to be 10.6 kcal./mole (Figure 22).

In Figure 23 the rates of the reaction on beta palladium catalyst at the same hydrogen pressure but at different pressures of ethylene, i.e., 2, 4, 6 and 8 cm. Hg, are shown. The rate of the reaction is essentially independent of ethylene pressure. The logarithm of the hydrogen pressure is plotted as a function of time for various initial pressures of hydrogen at 40° in Figure 24. The slopes of these lines correspond to the rate constant for a first order reaction. Hence, it was concluded that the reaction on beta palladium is first order with respect to hydrogen pressure and zero order with respect to the pressure of ethylene. In Figure 25 the rate constants for the reaction were determined at several temperatures and these were used to construct the activation energy plot in Figure 26. The activation energy of the hydrogenation of ethylene on this catalyst was calculated to be 5.2 kcal./mole from the slope of this line.

In Figure 27 some results are shown for the hydrogenation of ethylene at 0° with hydrogen diffusing through the catalyst. Lines for the normal hydrogen diffusion rate as well as the actual diffusion rate in the presence of ethylene are given. The line obtained for the pressure change due to combined reaction and diffusion was subtracted from the actual diffusion rate to obtain the fourth line shown which corresponds to the pressure drop due to the reaction alone.

Figure 28 and Figure 29 are the pressure-time plots obtained in like manner at 30° and 40°. The slopes of these curves at any particular point give the rate of reaction, dp/dt , at the time corresponding to that point. At zero time the hydrogen pressure within the system was zero.

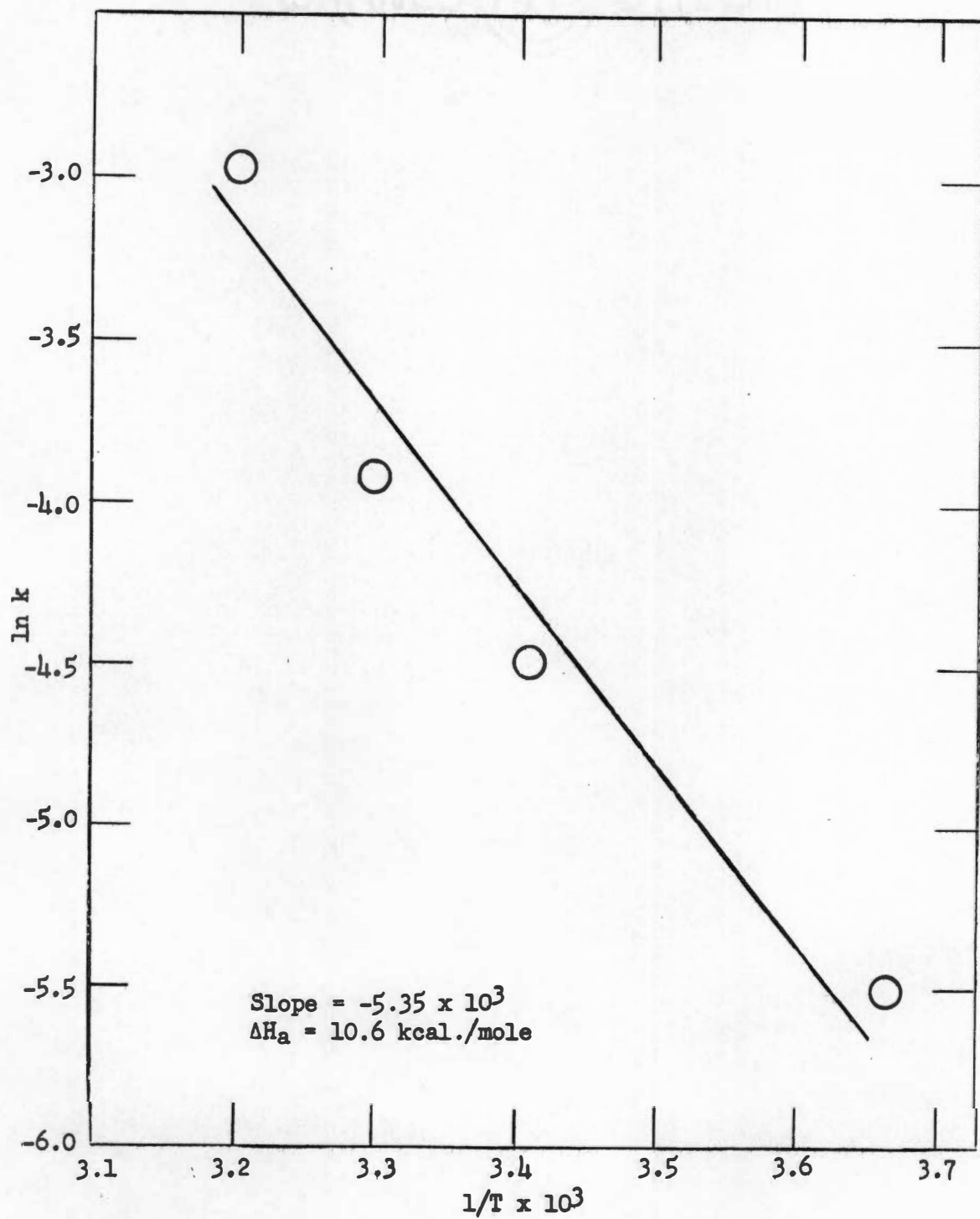


Figure 22. Activation Energy Plot for the Hydrogenation of Ethylene on Pure Palladium

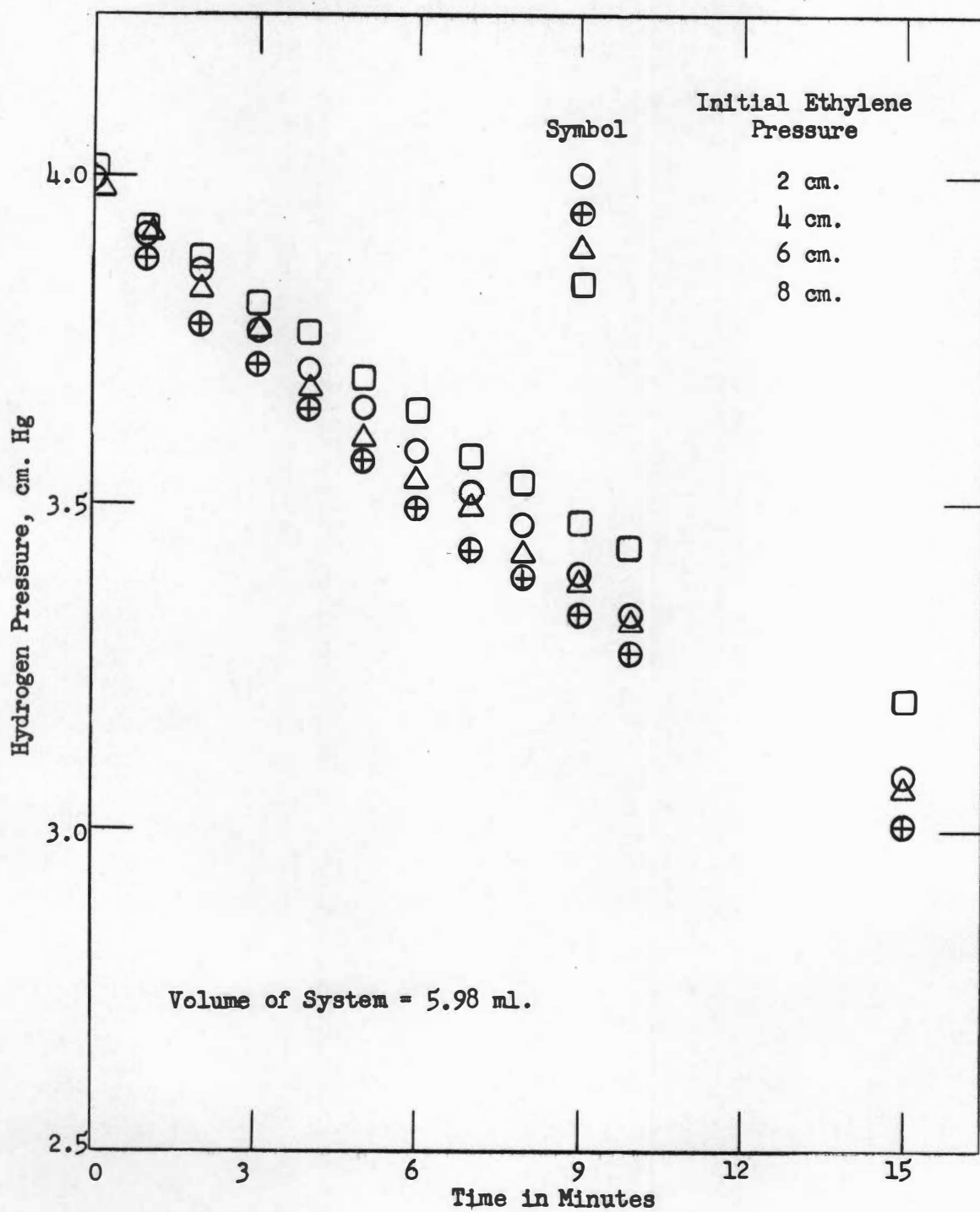


Figure 23. The Effect of Initial Ethylene Pressure on Beta Palladium at 40°

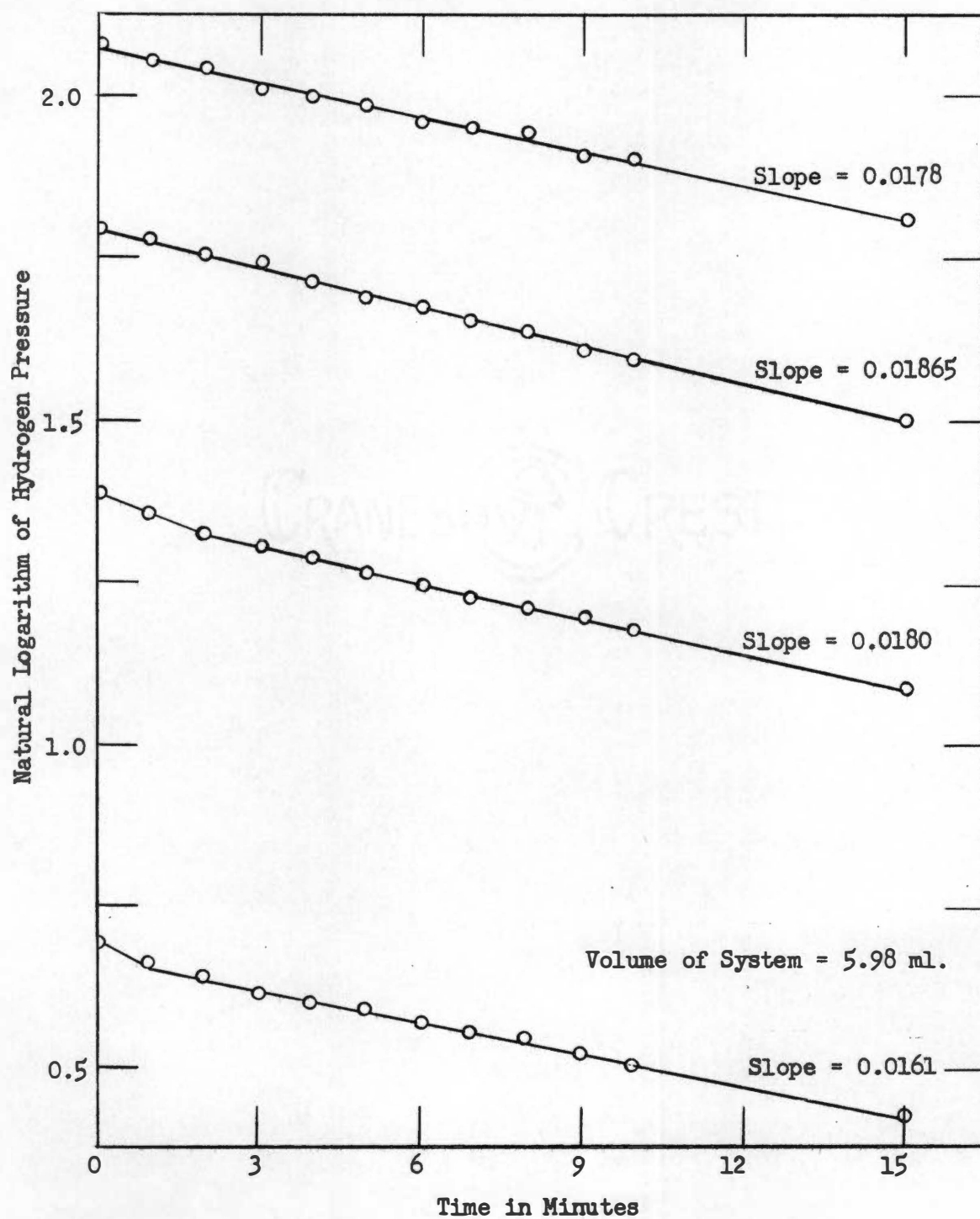


Figure 24. Natural Logarithm of Hydrogen Pressure versus Time for Hydrogenation of Ethylene on Beta Palladium at 40°

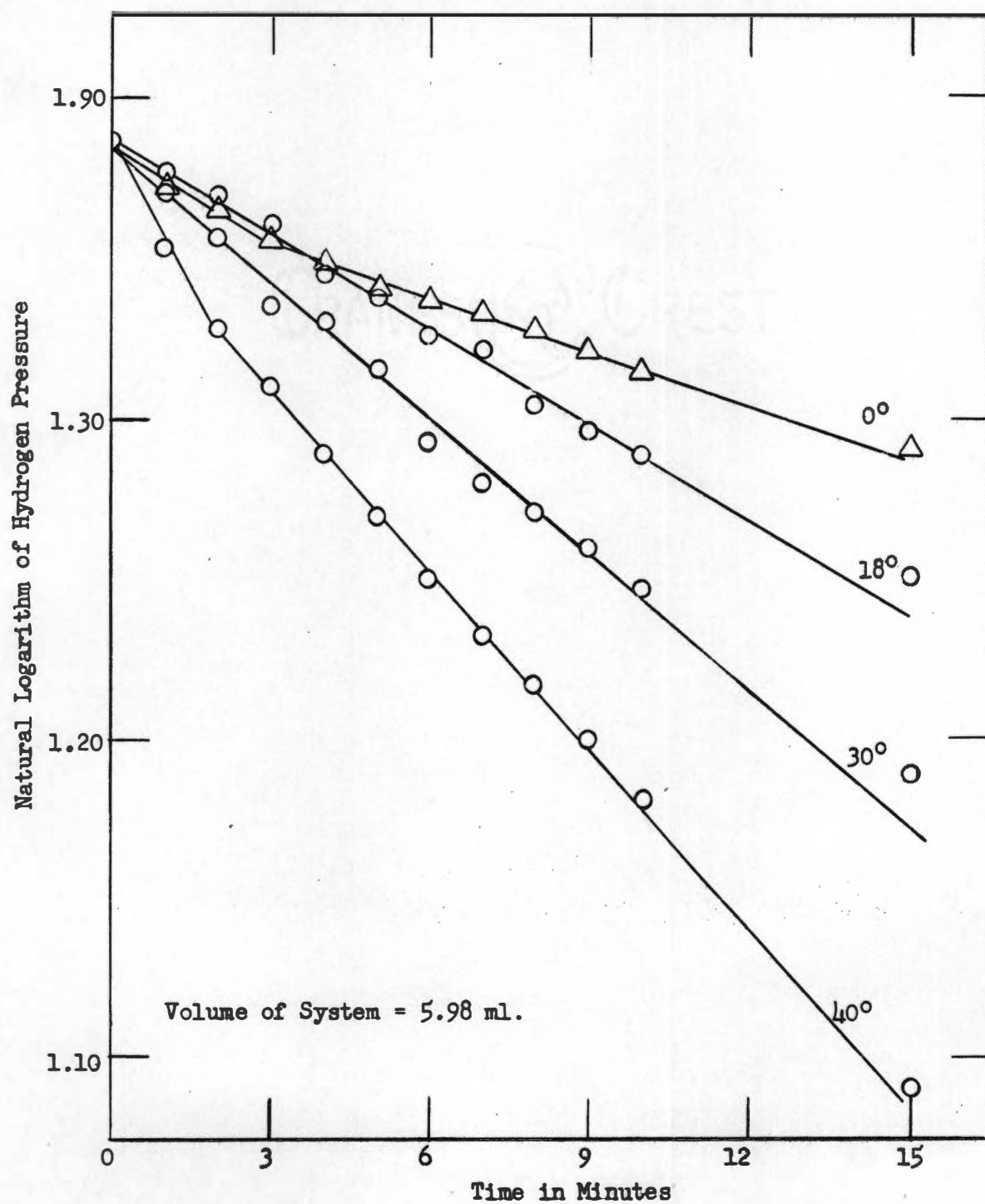


Figure 25. Natural Logarithm of Hydrogen Pressure versus Time for Hydrogenation of Ethylene on Beta Palladium at Various Temperatures

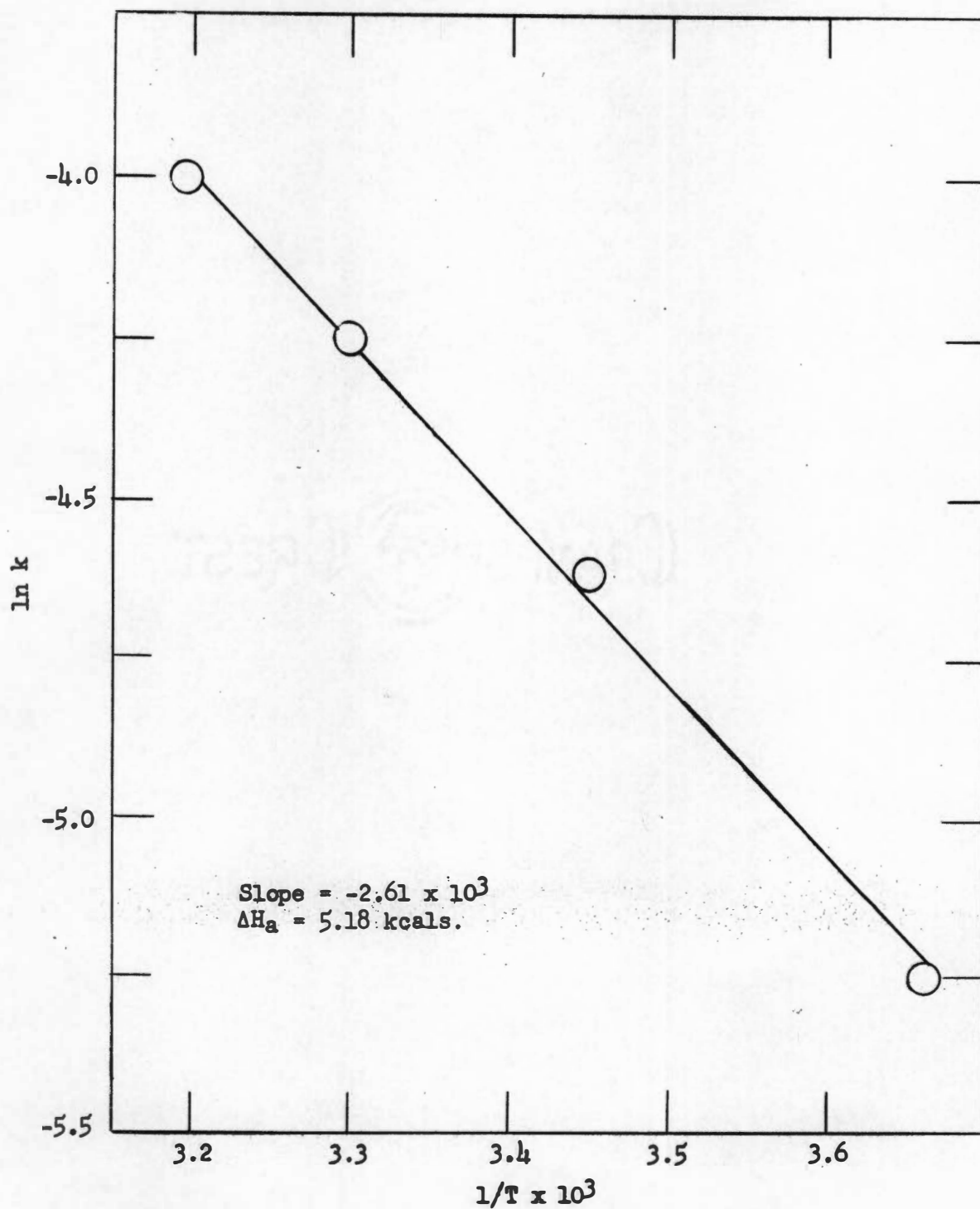


Figure 26. Activation Energy Plot for Hydrogenation of Ethylene on Beta Palladium

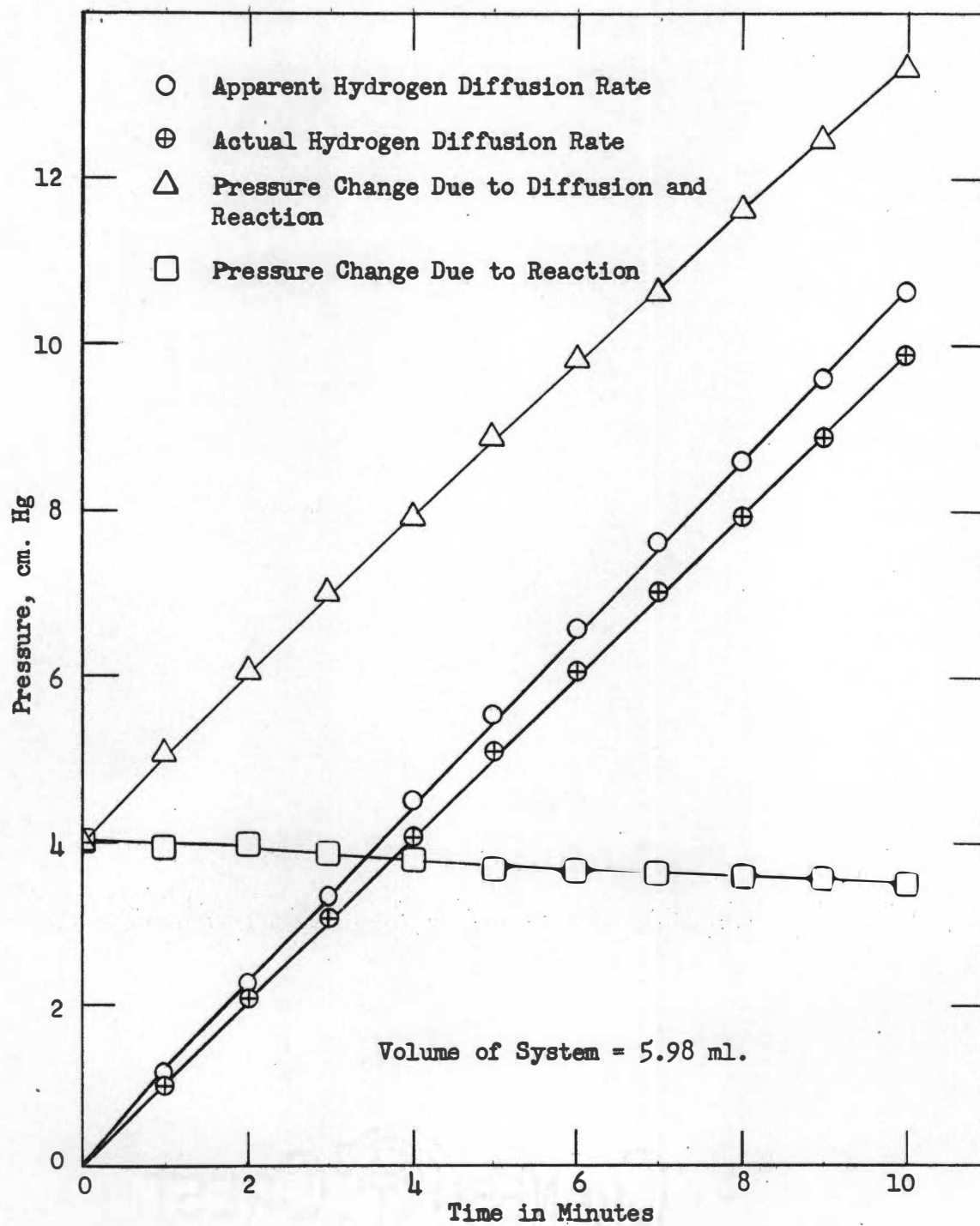


Figure 27. Hydrogenation of Ethylene at 0° With Hydrogen Diffusing Through the Palladium

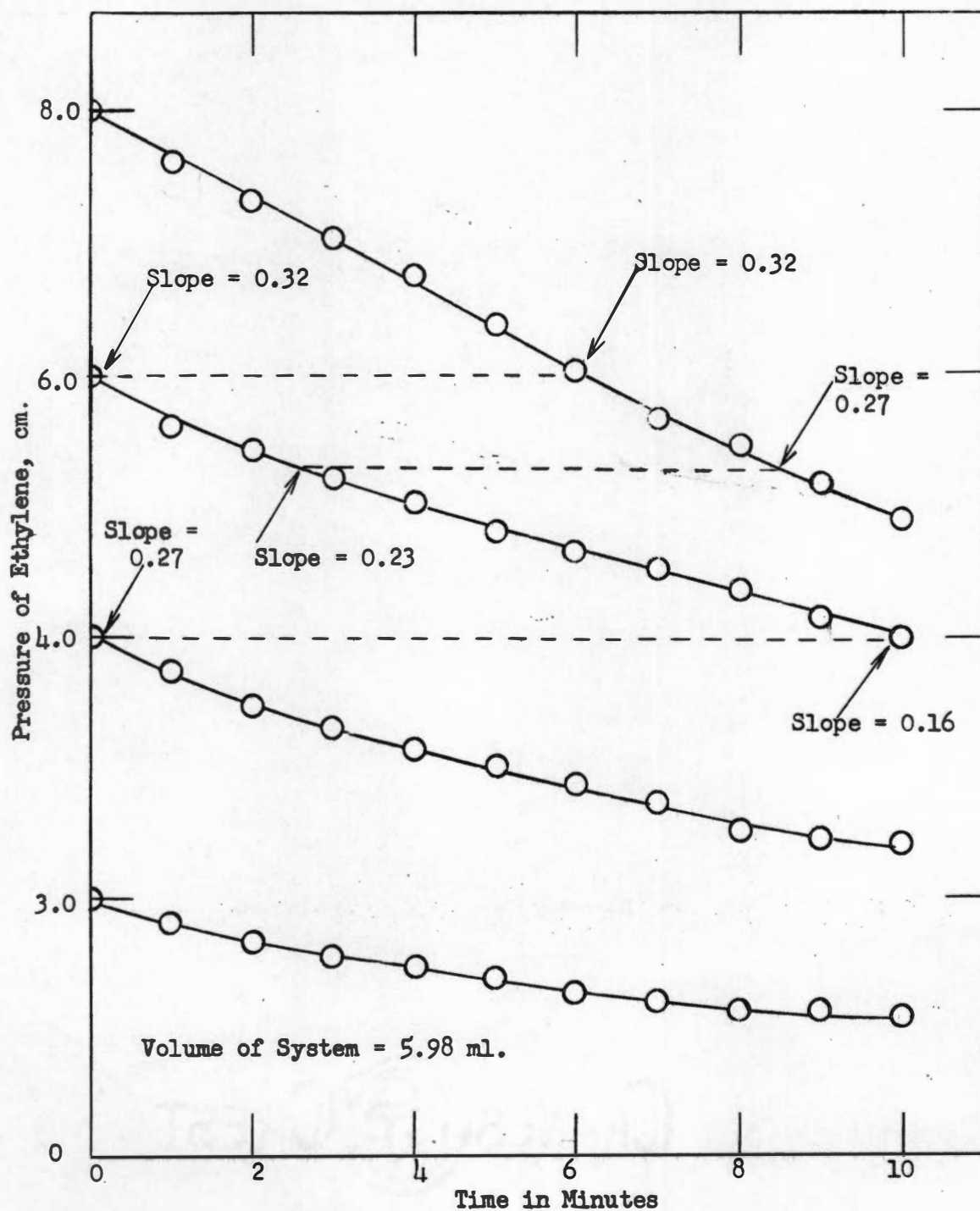


Figure 28. Pressure of Ethylene versus Time for Hydrogenation at 30° With Hydrogen Diffusing Through the Palladium

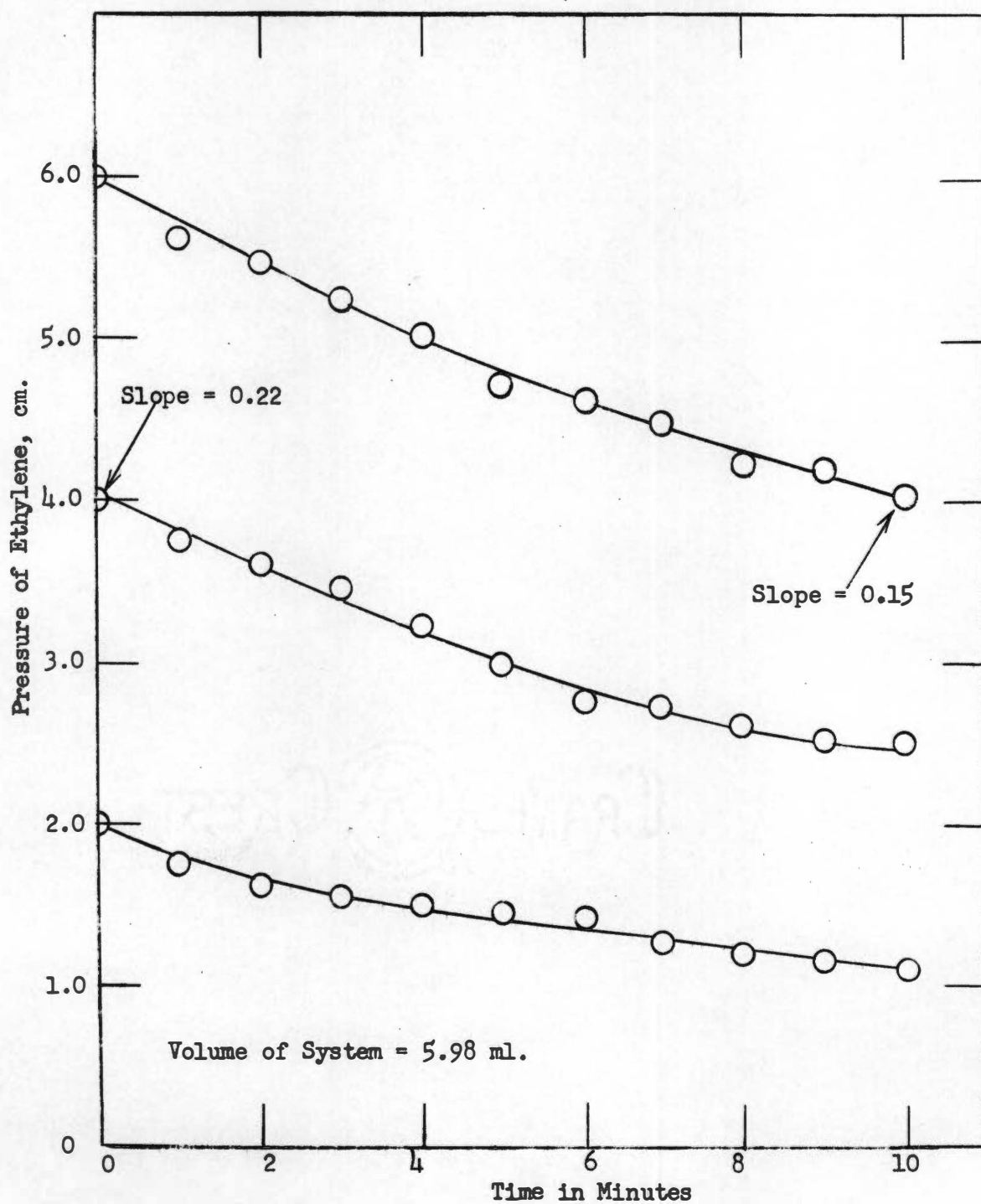


Figure 29. Pressure of Ethylene versus Time for Hydrogenation at 40° With Hydrogen Diffusing Through the Palladium

The diffusion rates at 30° and 40° were 1.34 and 1.79 cm./min. of hydrogen respectively. Thus, the hydrogen pressure is increasing inside the reaction volume with time. To establish the effect of the hydrogen pressure, the slopes of the curves in Figure 28 and Figure 29 were measured at the same ethylene pressure but at different pressure of hydrogen. The dotted lines in Figure 28 connect points of like ethylene pressure. Slopes obtained at the two points connected by these dotted lines were compared.

The logarithm of the ethylene pressure is plotted as a function of time in Figures 30, 31, 32 and 33 for the temperatures 0° , 18° , 30° and 40° , respectively. The slopes of these lines correspond to rate constants for a first order reaction. The averages of the rate constants obtained at each temperature were used in the activation energy plot shown in Figure 34. An activation energy of 5.0 kcal./mole was obtained for the reaction on this third type of catalyst.

Table II gives a summary of the rate constants obtained on the three types of palladium catalysts at 0° , 18° , 30° and 40° .

2. The Hydrogenation of Acetylene

The hydrogenation of acetylene was also studied on the three types of palladium catalysts described previously. Figures 35 and 36 show the pressure drops due to reaction on pure and beta palladium, respectively, at three temperatures. No attempts were made to determine the order of the reaction since the gas mixtures were not analyzed during the course of the reaction. The rates of pressure changes are used only for comparison purposes for the three types of catalysts. For these studies initial

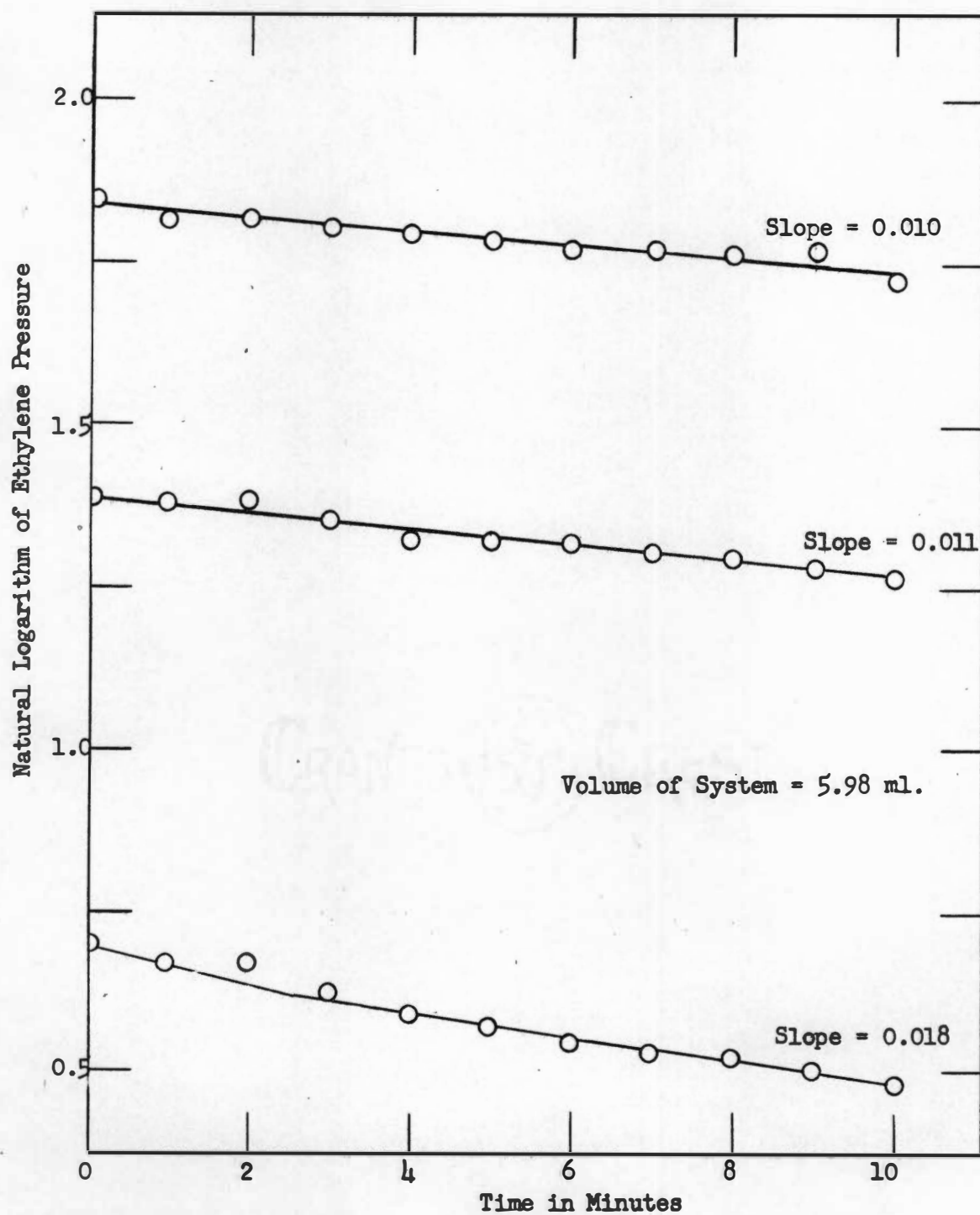


Figure 30. Natural Logarithm of Ethylene Pressure versus Time for Hydrogenation at 0° With Hydrogen Diffusing Through the Palladium

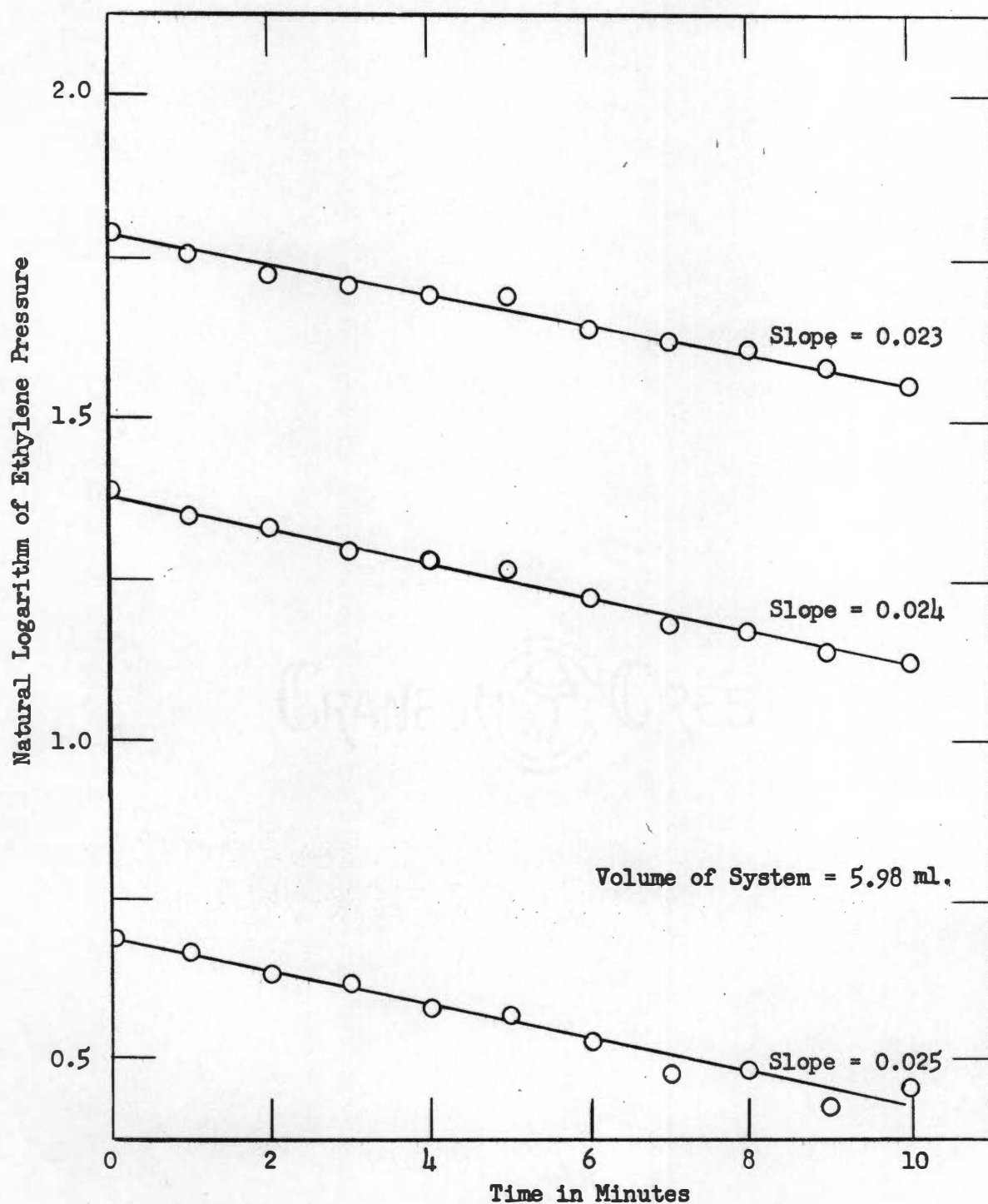


Figure 31. Natural Logarithm of Ethylene Pressure versus Time for Hydrogenation at 18° With Hydrogen Diffusing Through the Palladium

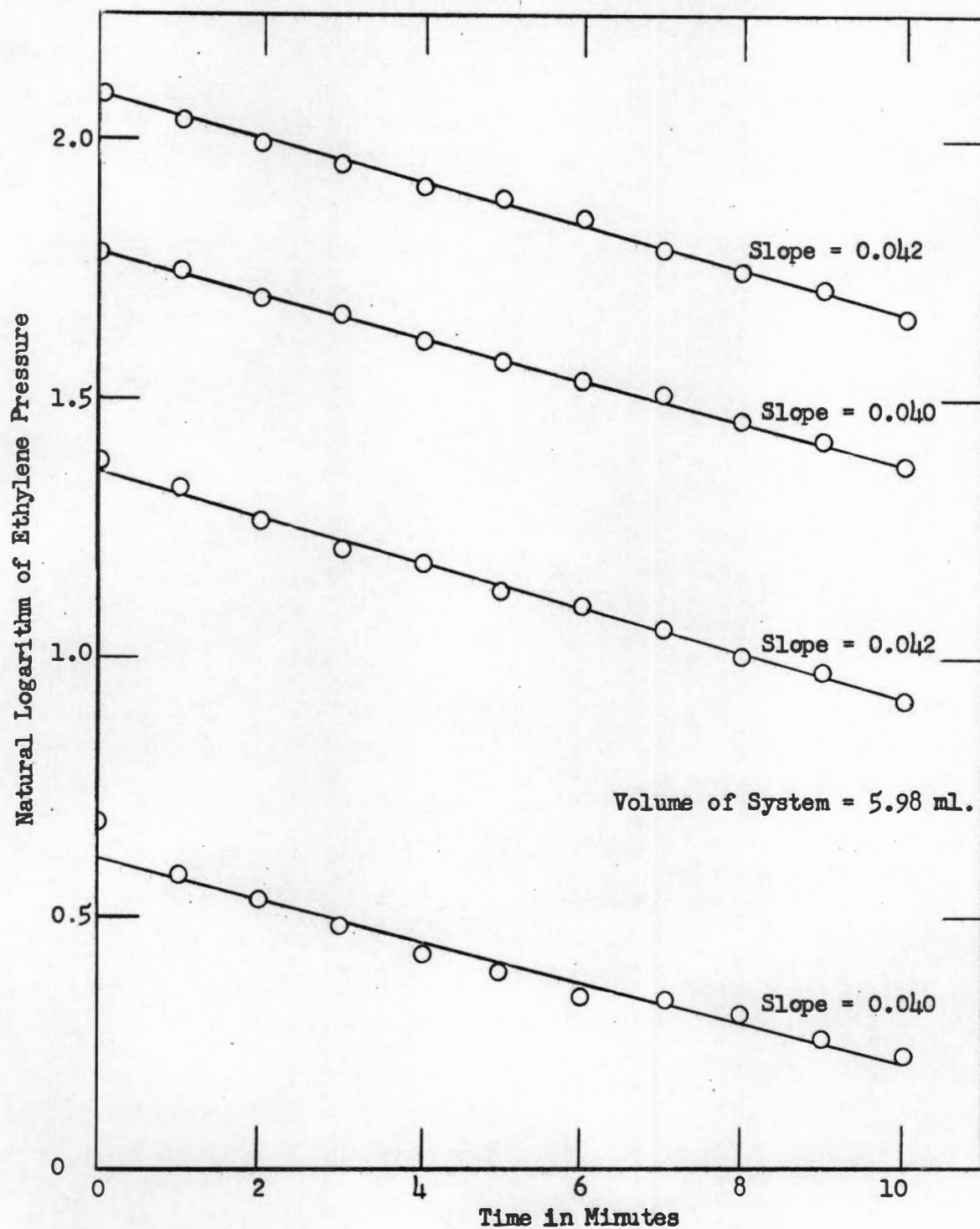


Figure 32. Natural Logarithm of Ethylene Pressure versus Time for Hydrogenation at 30° With Hydrogen Diffusing Through the Palladium

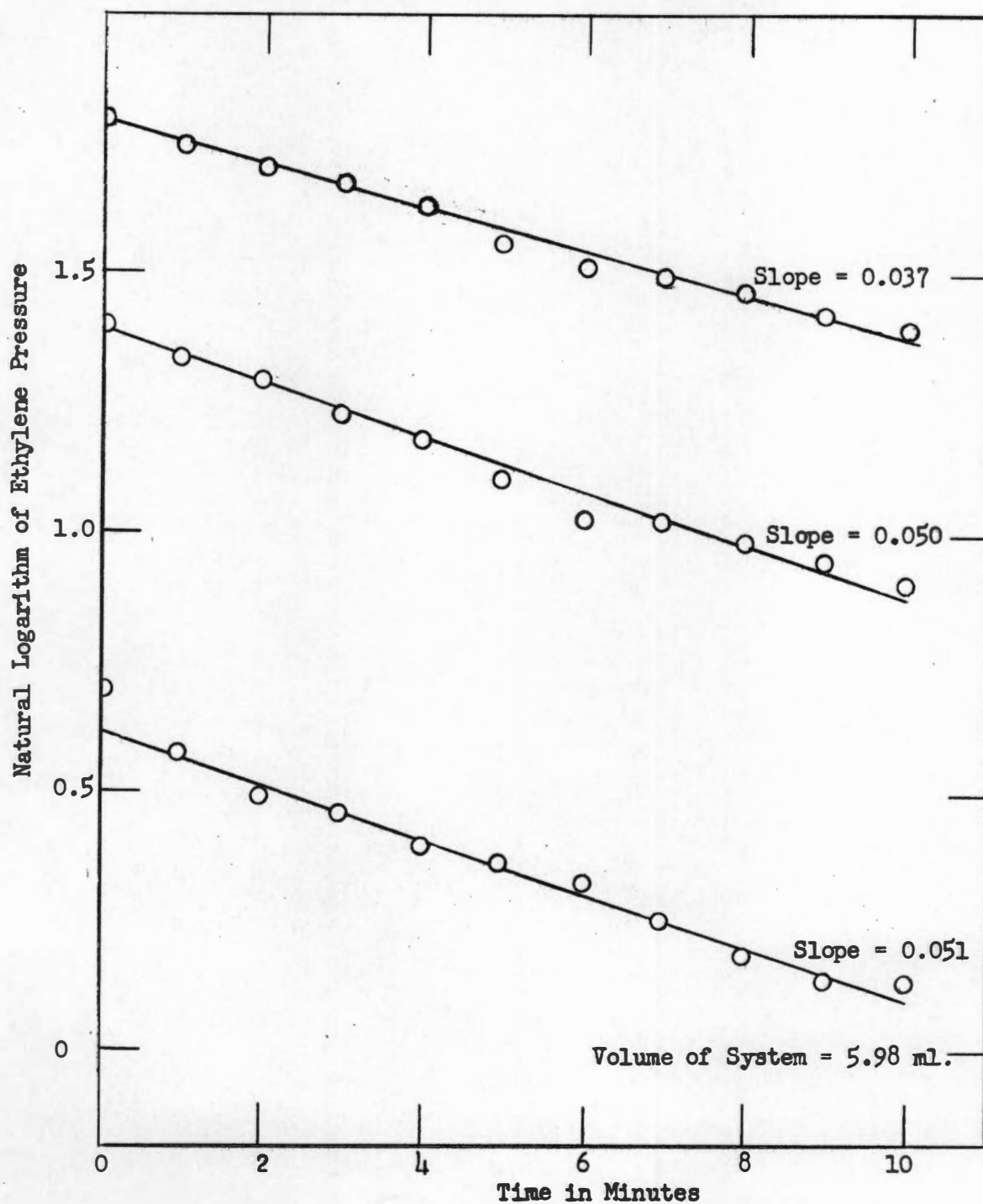


Figure 33. Natural Logarithm of Ethylene Pressure versus Time for Hydrogenation at 40°C With Hydrogen Diffusing Through the Palladium

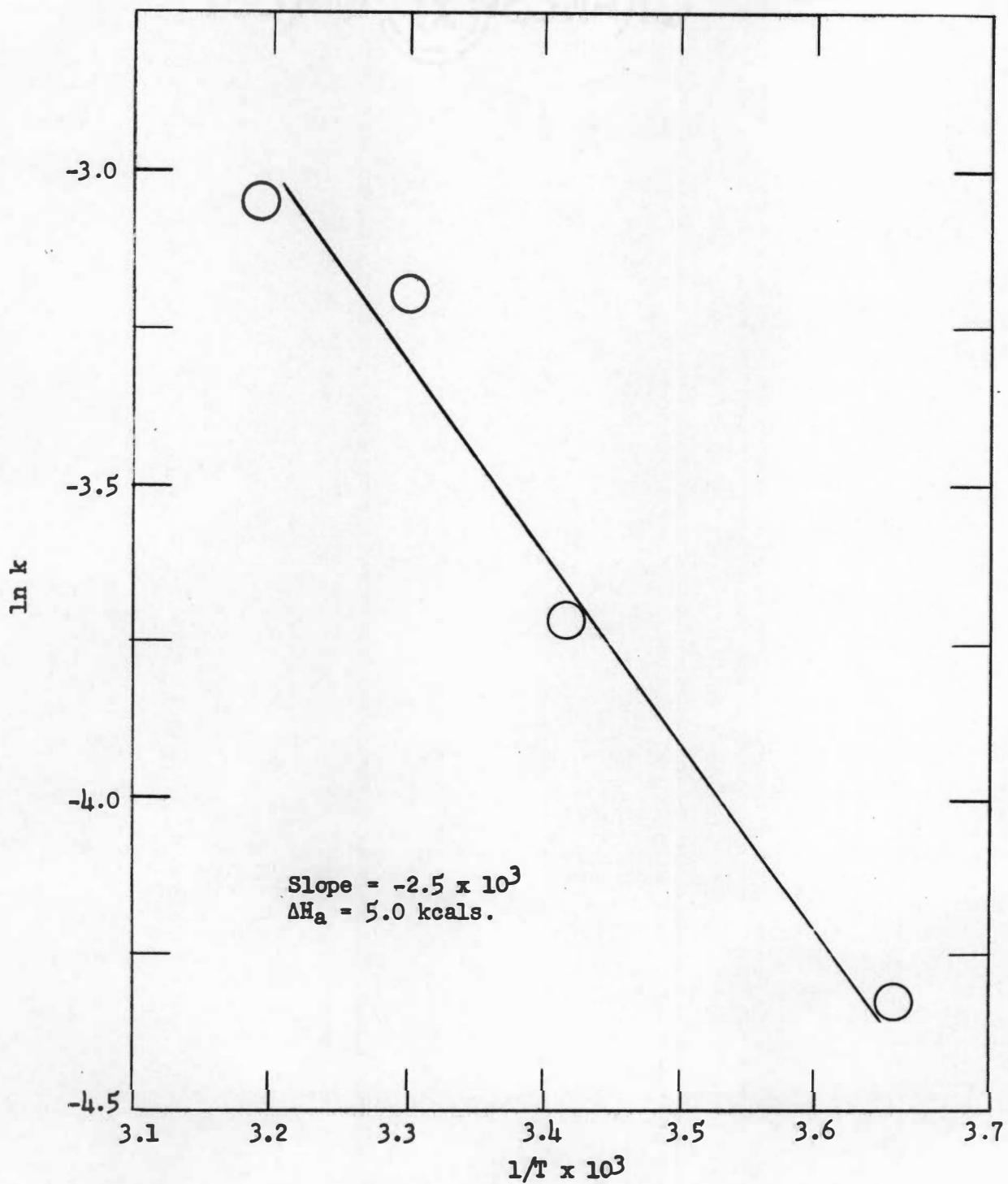


Figure 34. Activation Energy Plot for Hydrogenation on Ethylene With Hydrogen Diffusing Through the Catalyst

TABLE II

HYDROGENATION OF ETHYLENE ON PALLADIUM

Temperature	Rate Constant, min. ⁻¹			Hydrogen Diffusion Rate cm./min.
	Pure Palladium	Beta Palladium	Palladium With Hydrogen Diffusion	
0°	0.0042	0.0052	0.012	1.00
18°	0.0113	0.0098	0.024	1.09
30°	0.0203	0.0144	0.041	1.34
40°	0.0523	0.0180	0.046	1.79

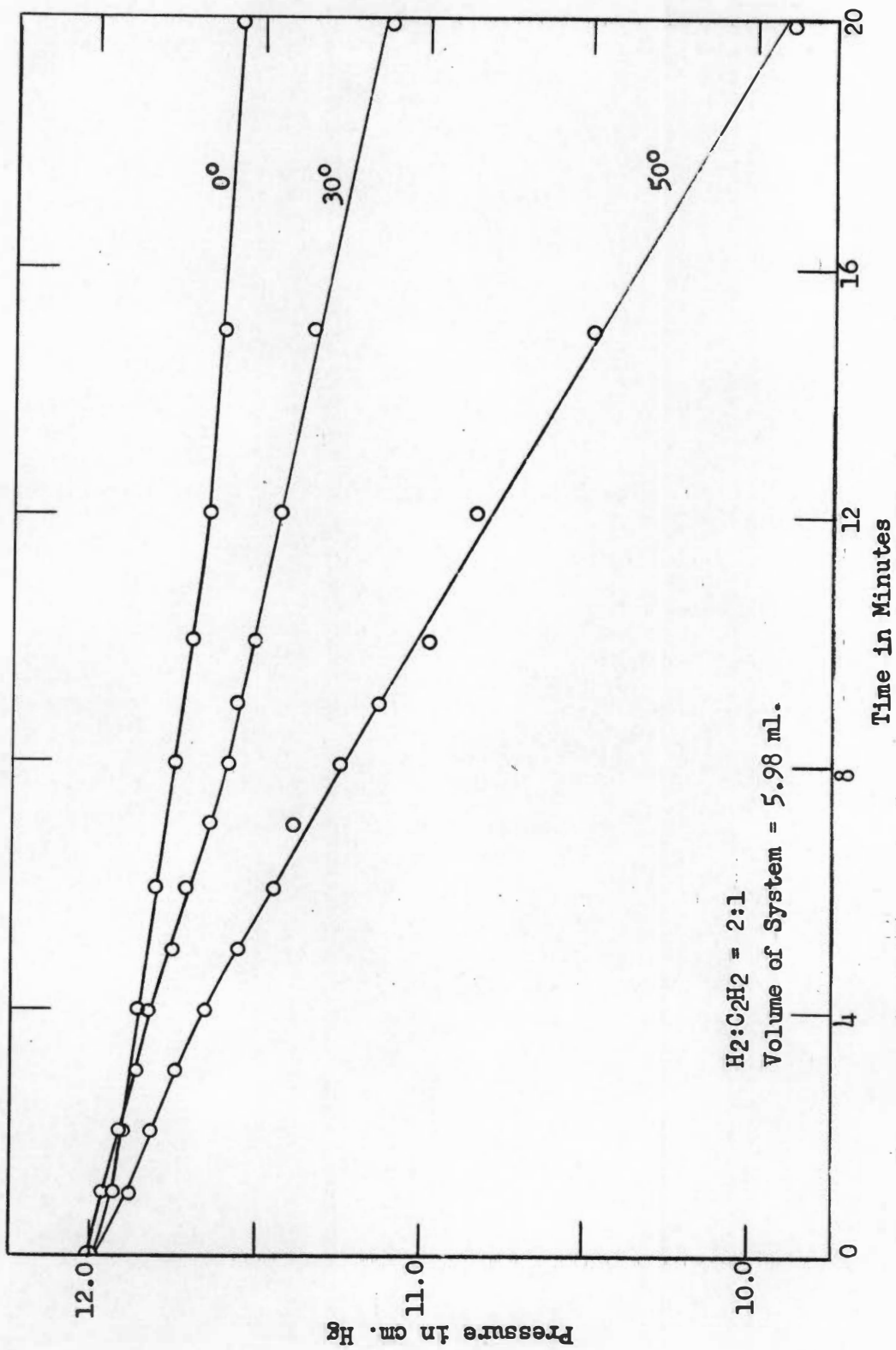


Figure 35. Hydrogenation of Acetylene on Pure Palladium

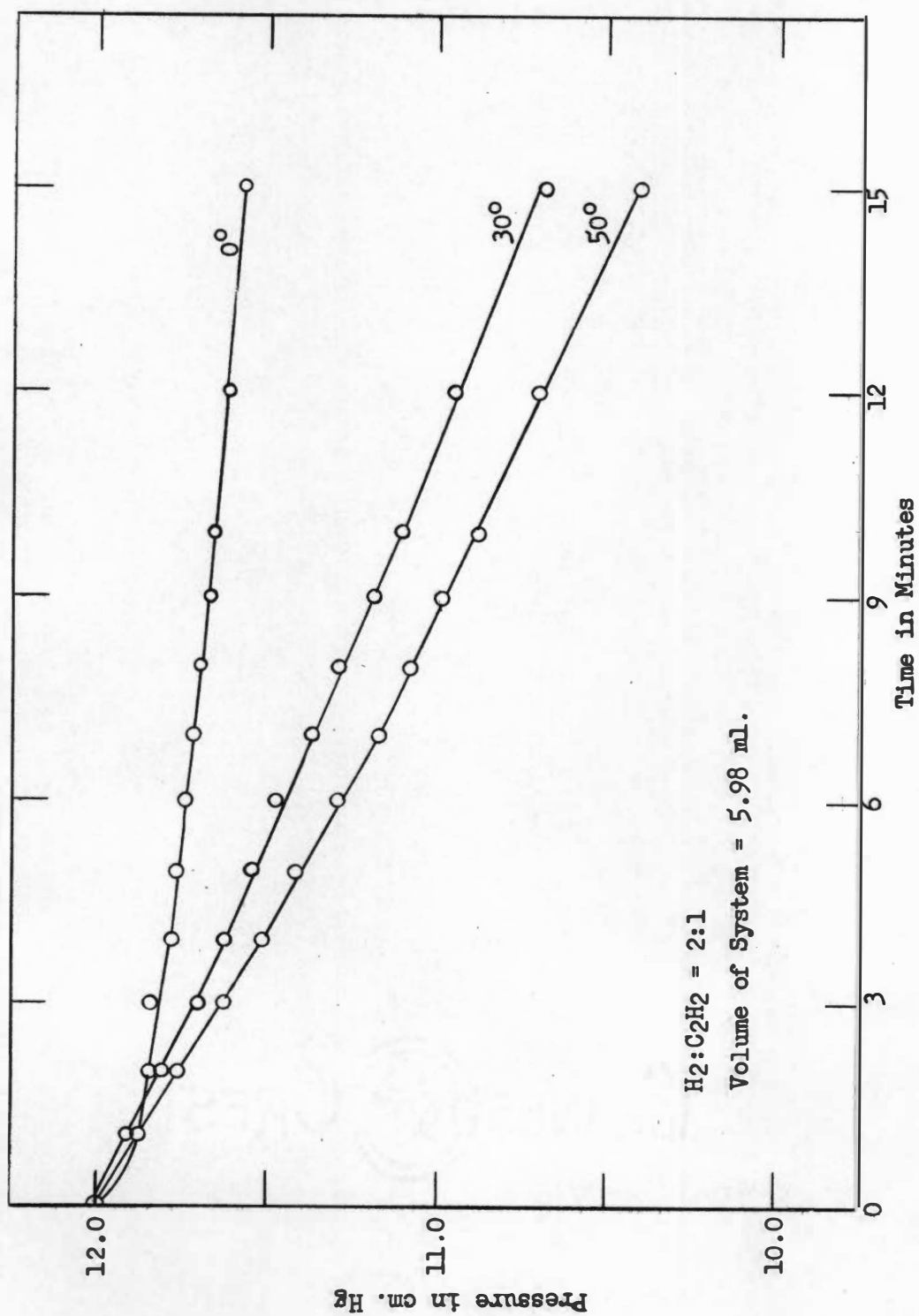


Figure 36. Hydrogenation of Acetylene on Beta Palladium

pressures of hydrogen and acetylene were 8 and 4 cm. Hg, respectively.

In Figure 37 results are shown for the determination of the reaction rate at 0° with hydrogen diffusing through the palladium. The pressure change due to reaction plus diffusion was subtracted from the actual hydrogen diffusion rate to obtain the curve representing the drop in pressure due to reaction. Figure 38 includes the complete results determined in a like manner for pressure changes due to hydrogenation on this type of catalyst. The rates of hydrogen diffusion at 0° , 30° and 50° were 0.70, 1.28 and 1.95 cm./min., respectively.

In Table III the values of the slopes are tabulated for various times of reaction for the three types of catalysts. Also, the pressure drops due to reaction for ten minutes are given.

3. The Hydrogen-Oxygen Reaction

Hydrogen and oxygen were catalytically combined at 68° on pure palladium and palladium through which hydrogen was diffusing. In Figure 39 the results obtained for each case are given. The top curve represents the pressure drop due to reaction on pure palladium with an initial oxygen pressure of 4 cm. Hg. Only the temperature of the catalyst was held at 68° to prevent the water formed from condensing on its surface. The remainder of the reaction volume was at room temperature, 26° , with the exception of the Dry-Ice, acetone trap at -78° . If the total amount of water formed as the product of the reaction had remained in the vapor phase, the total pressure drop corresponding to a complete combination should have been only 4 cm. Hg. Since the pressure drop evidenced is greater than this, it is concluded that some of the water condensed in

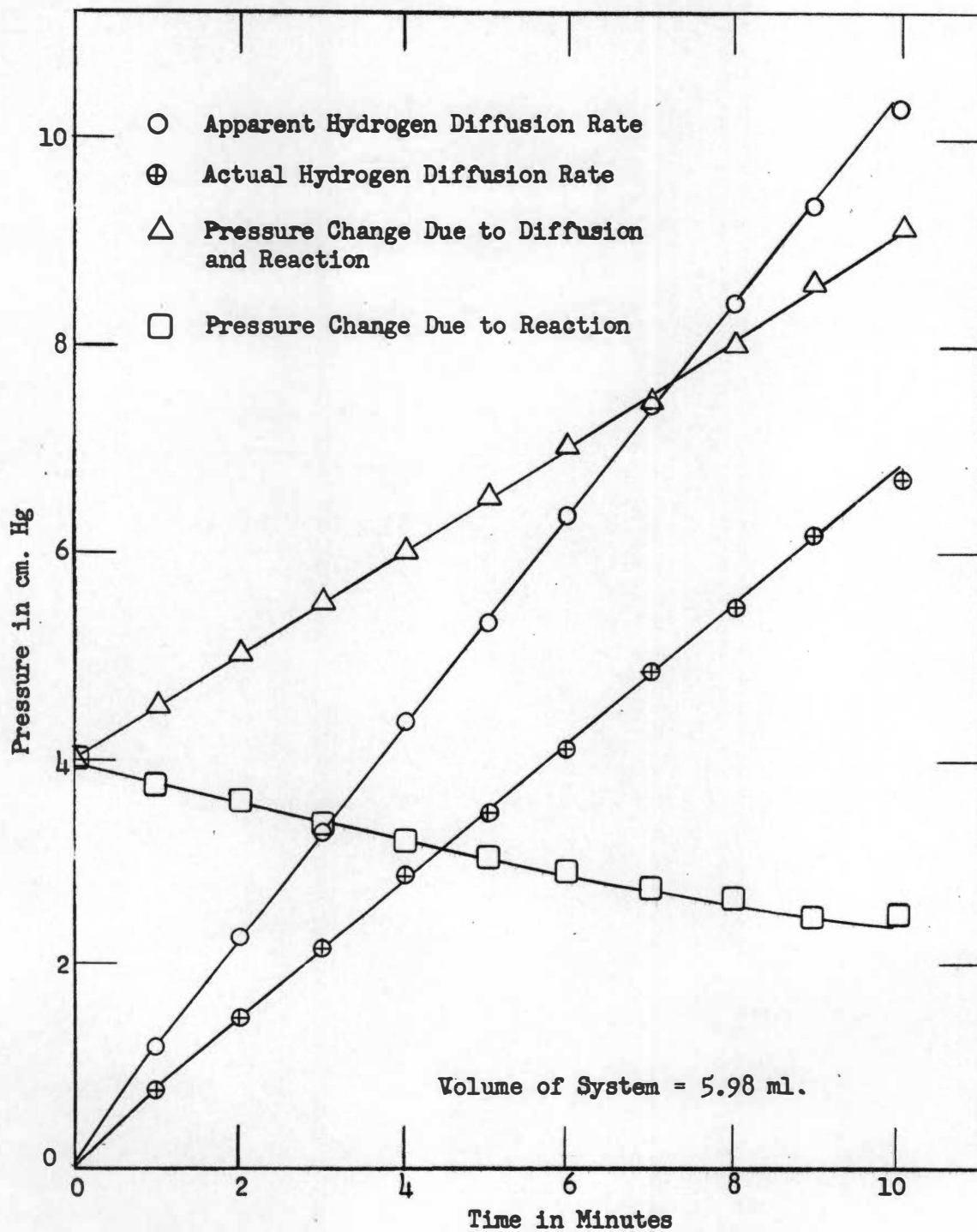


Figure 37. Hydrogenation of Acetylene at 0° With Hydrogen Diffusing Through the Catalyst

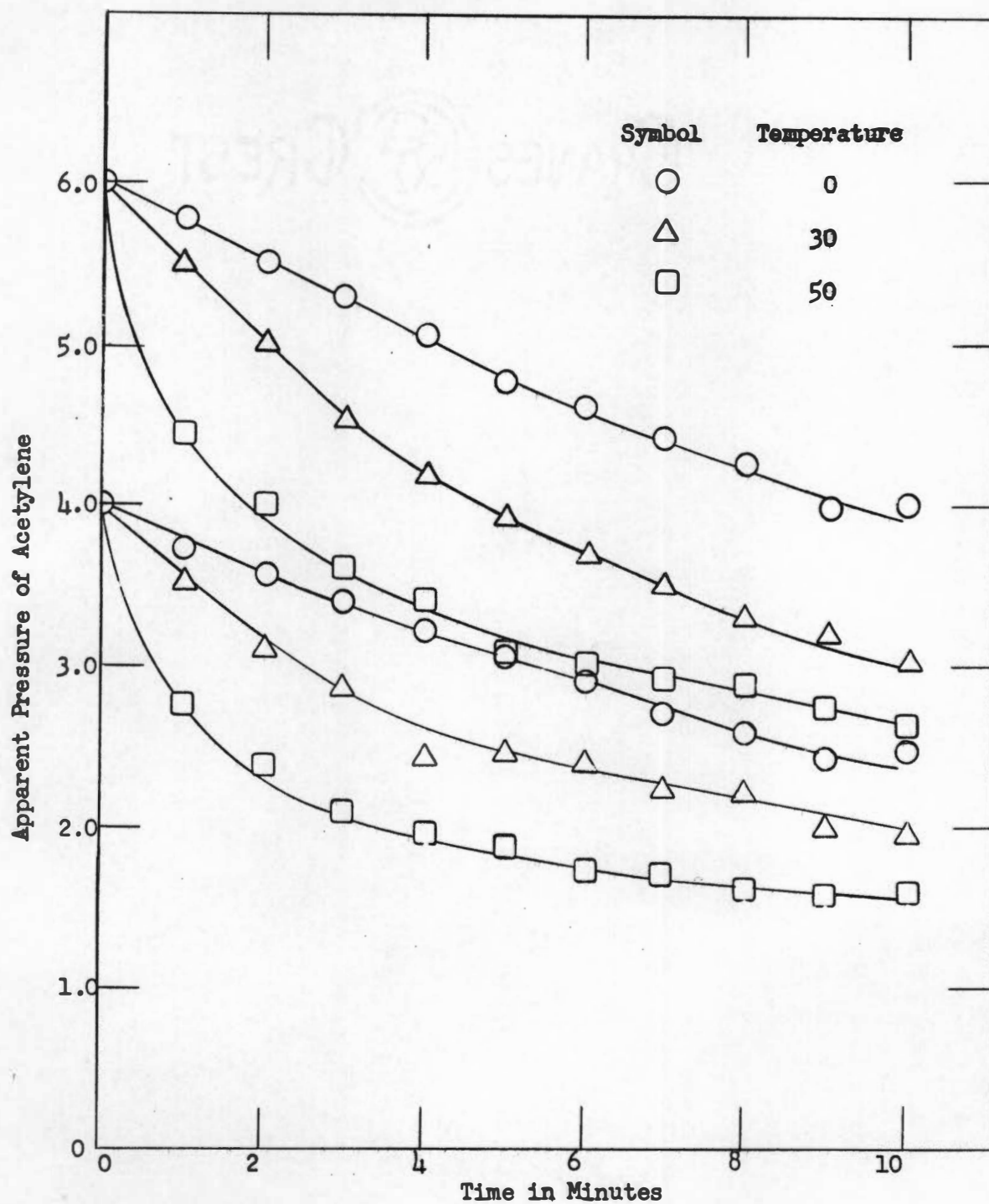


Figure 38. Pressure of Acetylene versus Time for Hydrogenation With Hydrogen Diffusing Through the Palladium

TABLE III

HYDROGENATION OF ACETYLENE

Temperature	Pressure Drop in 10 min. (cm.)	dp/dt at Various Times, min.		
		2	6	10
Pure Palladium (Initial Pressure of Acetylene = 4 cm. Hg)				
50°	0.98	0.068	0.093	0.137
30°	0.57	0.052	0.052	0.038
0°	0.30	0.025	0.025	0.023
Beta Palladium (Initial Pressure of Acetylene = 4 cm. Hg)				
50°	1.10	0.122	0.108	0.095
30°	0.80	0.097	0.086	0.086
0°	0.33	0.027	0.020	0.020
Palladium Through Which Hydrogen is Diffusing (Initial Pressure of Acetylene = 4 cm. Hg)				
50°	2.4	0.37	0.08	0.05
30°	2.0	0.36	0.11	0.11
0°	1.6	0.17	0.15	0.10
(Initial Pressure of Acetylene = 6 cm. Hg)				
50°	3.4	0.46	0.14	0.11
30°	3.0	0.48	0.20	0.16
0°	2.1	0.23	0.20	0.18

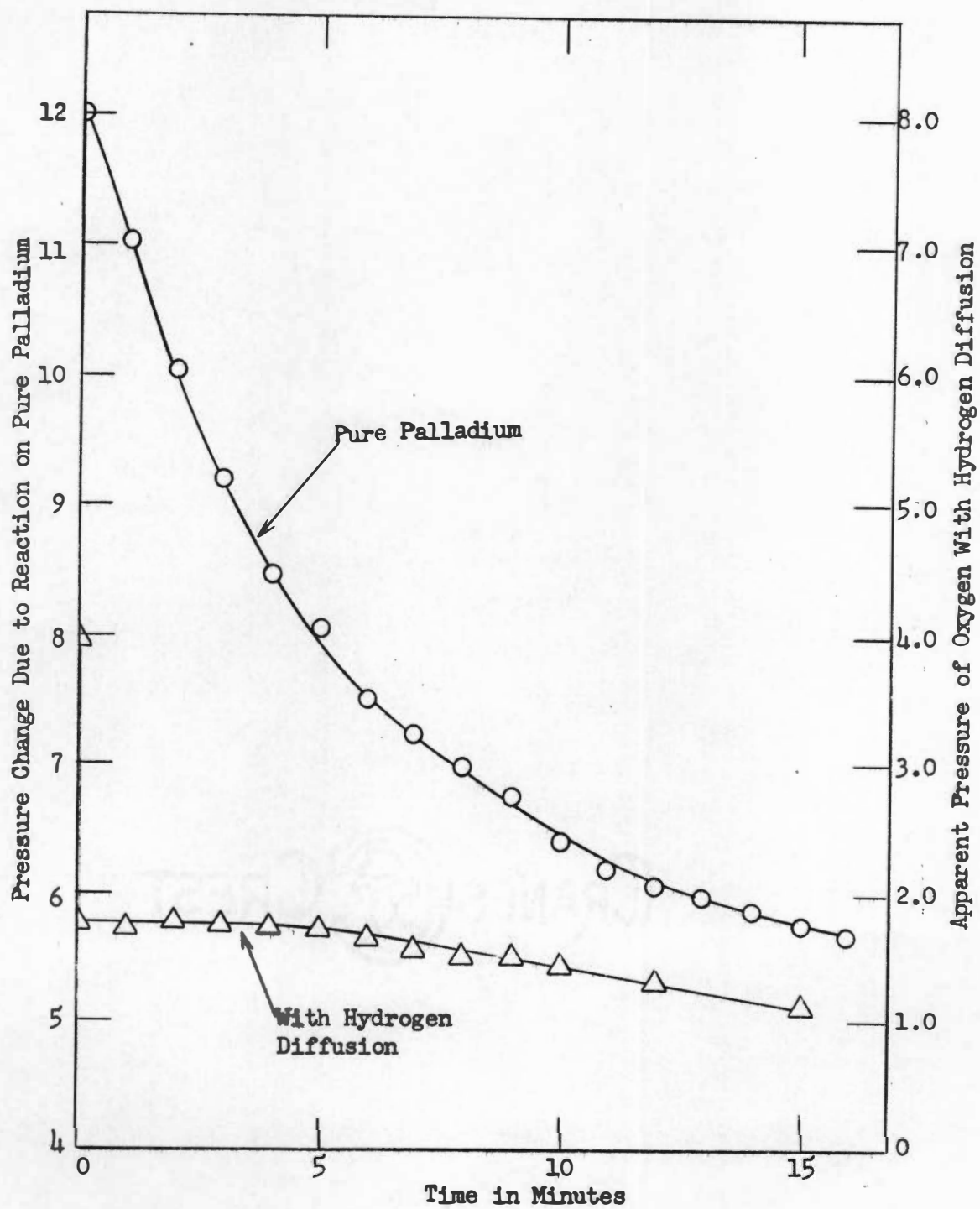


Figure 39. Hydrogen-Oxygen Reaction at 68°

the cooler portion of the system. For this reason the results obtained are useful only for comparison purposes under similar conditions.

The bottom curve represents the pressure change due to reaction with hydrogen diffusing through the palladium at a rate of 0.57 cm./min. The initial oxygen pressure was 4 cm. Hg. Following a very rapid decrease in pressure, the reaction appeared to be very slow at first but increased in rate as the pressure of hydrogen increased within the system. Apart from this study it was observed that if air was allowed in the system while hydrogen was diffusing through the palladium, it was impossible to rid the catalyst of oxygen by drawing a vacuum on the system overnight. However, if the reaction volume were closed off allowing hydrogen pressure to build up over the catalyst, the oxygen reacted with the hydrogen to form water. This water was observed to freeze out in the trap. In the case of a very low hydrogen pressure in the system, no water was observed in the trap.

CHAPTER IV

DISCUSSION

A. Liquid Phase Hydrogenations

The results obtained for the hydrogenation of allyl alcohol with regard to polarization of the catalysts are different in some respects from those of the hydrogen-oxygen reaction. No periodicity was observed in the reaction rate upon direct polarization for the former reaction. The potential difference between the two platinum electrode catalysts was observed in a few instances to change periodically. These few occurrences can possibly be explained by the presence of oxygen in the system which was not removed by flushing out the system sufficiently with hydrogen. However, several generalities can be made regarding the effects of polarization on the reaction rates for both hydrogenations. For neither reaction did anodic polarization of a platinized-platinum electrode produce changes in the catalytic activity except at high polarization currents in which cases the activity declined. For both reactions the catalytic activity was enhanced by the following means:

1. alternating current polarization;
2. changing the polarity of the electrodes suddenly, which, in effect, is an abbreviated version of the first procedure;
3. stopping anodic polarization of a platinized-platinum electrode.

In each of these cases the potentials of each of the two electrodes are changed suddenly due to the mechanics of the process.

A sharp change in the anodic potential was also observed to occur just prior to the rise in catalytic activity of the electrodes which were subjected to direct current polarization in the hydrogen-oxygen reaction. The anodic potential rose suddenly followed usually by a sharp drop. In cases in which the potential remained at the high value long enough for any change in activity to be observed, it was found that the catalytic activity decreased. Therefore, it is concluded that the sudden drop in the anodic potential, i.e., to a more negative value with respect to the saturated calomel electrode, is necessary for the enhanced activity. Since the potential of the cathode remained constant during this periodic behavior, it is likely that the phenomenon which causes this periodicity occurs on the anode. Hydrogen gas in the system and a low pH are also believed necessary for the phenomenon since periodicity of the anodic potential and reaction rate does not occur in their absence. To confirm that the hydrogen ion concentration was a factor in the periodic behavior rather than sodium sulfate, (which when used as an electrolyte in neutral solution hindered the process) solutions containing both sulfuric acid and sodium sulfate were tried. The periodicity was observed in these solutions also. It was not determined with certainty whether or not oxygen is essential for this phenomenon, although usually it was not observed in the hydrogenation of allyl alcohol experiments.

Joncich and Hackerman⁶ studied the relation between the catalytic activity and the potential between the two catalysts when a platinized-platinum electrode was an anode. They observed a periodic change in catalytic activity which corresponded to simultaneous changes in the

E. M. F. between the two electrodes. In the present study, the periodicity was observed only when smooth platinum was made the anode and either smooth or platinized-platinum was made the cathode. Impurities in the platinized-platinum electrodes used in this work may be responsible for the differences in the two investigations. It was found, however, that the rise in catalytic activity in each cycle was greater with platinized-platinum than smooth platinum cathodes (see Figures 9 and 10).

In summary, enhanced activity of platinum electrodes upon electrolytic polarization in the two reactions studied, occurred only when the potential of one or both of the catalyst was suddenly changed.

Hofmann⁴² believed that alternating current polarization increased the activity of the catalyst because a surface free of hydride and oxide formation would lend itself to a more active state and that alternating polarization prevented their formation.

Joncich and Hackerman⁶ proposed that the periodic behavior of the catalytic activity and the potential between the two electrodes was caused by formation of platinum oxides on the anode. El Wakkud and Emara¹⁰⁸ previously reported that when a platinum electrode is brought to a potential at which hydrogen is evolved to that at which oxygen is evolved, platinum monoxide is first formed over the platinum surface. This state is followed by the formation of platinum dioxide, and by the evolution of oxygen. Platinum dioxide is unstable and decomposes into platinum monoxide. Hence, the periodic behavior in the catalytic activity and anodic potential was believed by Joncich and Hackerman to be due to a buildup and breakdown of oxide films on the anode with the maximum activity

of the anode reached when a critical mixture of the two oxides occurred. This proposal does not explain the increased activity observed upon alternating polarization, however. Further it does not involve the presence of hydrogen gas and a high hydrogen ion concentration which were found by the present study to be necessary for the periodicity.

The results of this work appear to favor the proposal by Hofmann, although an explanation for the periodicity in the case of the hydrogen-oxygen reaction cannot be given.

B. Electrolytic Hydrogen Diffusion Through Palladium

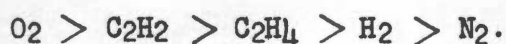
Preliminary experiments of hydrogen diffusion through palladium are not reported in Chapter III. These results were not reproducible and in most cases the diffusion rate decreased with time after the initial period required to fill the palladium with hydrogen. At other times no hydrogen could be observed to permeate the metal. However, this initial work did show the necessity for purity on both sides of the palladium wall through which hydrogen was diffusing.

Very reproducible results were obtained by using no pretreatment of the thimbles other than anodic oxidation and protecting the inside surface from the vapors of mercury and stopcock grease. Diffusion rates measured under similar conditions of temperature and current density did not vary more than 5 per cent from one thimble to another. Hydrogen pressure on the inside of the system did not effect the rates as shown in Figure 13. In agreement with an earlier study by Heath,⁵⁷ the permeation rate was found to be proportional to the current density at

current densities less than 4.5 ma./cm.^2 (see Figure 13). Furthermore, hydrogen was observed to diffuse through the palladium at the lowest current density tried, 0.5 ma./cm.^2 . This gives added support to Heath's argument that the threshold value of the current density proposed by Borelius and Lindblom⁵⁴ does not exist. The rates obtained in this study are five times faster than those reported by Heath⁵⁷ and approximately ten times faster than those given by Joncich and Kowaka.⁷ The thickness of the palladium in Heath's work was 0.030 cm. compared to a thickness of 0.025 cm. in the present study and the work of Joncich and Kowaka.

The significance of the activation energy found for the hydrogen diffusion process is uncertain. The higher diffusion rates at higher temperatures can be attributed to the higher mobility of hydrogen atoms inside the metal, the activation energy of atomic hydrogen recombination on the exit surface of the palladium, or to a higher rate of desorption of the molecular hydrogen. Barrer⁵⁵ reports activation energies of 8.5 and 9.2 kcals. for electrolytic hydrogen diffusion compared to 6.2 kcals. found in this study.

The effect of gases exposed to the downstream surface of the palladium on the hydrogen diffusion rate can be correlated with the heats of chemisorption of the gases. Trapnell¹⁰⁷ reports that nickel, palladium, rhodium and platinum chemisorb hydrogen, ethylene, acetylene and oxygen but do not chemisorb nitrogen at room temperature. The reported order of affinity is



In the present study oxygen was found to decrease the hydrogen diffusion rate to an extent greater than the other gases studied. It was followed by acetylene and ethylene in that order. Hydrogen and nitrogen did not have a measurable effect on the diffusion rate. This correlation can be explained by assuming the chemisorbed gas occupies surface sites on the exit surface of the palladium on which atomic hydrogen normally recombines to molecular hydrogen after it diffuses through the metal.

C. Gas Phase Hydrogenation

1. Hydrogenation of Ethylene

It has been well established^{1,7,72,76} that the hydrogenation of ethylene on metal catalysts including palladium is first order with respect to hydrogen pressure and zero order with respect to ethylene. For this reason a detailed study of the reaction on pure palladium was not made to determine the order of the reaction with respect to hydrogen and ethylene. The rate constants at 40°, 30°, 18° and 0° were determined on untreated palladium for comparison with those obtained on beta palladium and palladium through which hydrogen was diffusing. Figure 21 shows that the reaction follows a first order rate expression, since the logarithm of the hydrogen or ethylene pressure is linear when plotted as a function of time. The pressure drop due to reaction can be attributed to the fall in hydrogen or ethylene pressure, since the combination of one mole of each of these gases gives one mole of ethane. The activation energy found for the reaction agrees well with Beeck's value of

10.7 kcals./mole.¹ However, the experimental error in the present reported value is ± 2.0 kcals./mole.

The hydrogenation reaction was studied more extensively on beta palladium, since results of similar works were not found in the literature. The reaction was concluded to be zero order with respect to ethylene from the results presented in Figure 23. Different initial ethylene pressures and the same initial hydrogen pressure were used in this study and a maximum deviation of 3.0 per cent was observed from the mean value of the pressure of hydrogen plotted as a function of time of reaction. The reaction is shown to be first order with respect to hydrogen in Figure 24. The rate constants obtained for the reaction on beta palladium are much lower than those obtained on pure palladium. It has been observed previously⁷ that initial hydrogen treatment will lower the activity of pure palladium. The calculated activation energy, 5.2 kcals./mole, is approximately half of that observed on pure palladium.

The results for the hydrogenation of ethylene on palladium through which hydrogen was diffusing differ from those observed on pure or beta palladium. The hydrogen gas pressure over the catalyst was found not to affect the reaction rate to a great degree as shown in Figures 28 and 29. The variation in the rate of reaction at different hydrogen pressures but identical ethylene pressure is probably within the experimental error of the data and the determination of the slopes. The reaction is shown to be first order in Figures 30, 31, 32 and 33. Since hydrogen pressure did not affect the reaction rates, the reaction is concluded to be first order with respect to ethylene.

The current density of the palladium cathode was held constant at 3.3 ma./cm.² for each temperature at which the reaction was studied. Therefore, the diffusion rate of hydrogen increased as the temperature was raised. Joncich and Kowaka⁷ found that the reaction rate generally increased as the diffusion rate of hydrogen increased. Hence, the true activation energy of the reaction is probably lower than the value of 5.0 kcals./mole determined in Figure 34.

It is concluded from the summary of rate constants presented in Table II that palladium through which hydrogen is diffusing is a more active catalyst for the reaction than pure palladium which, in turn, is a more active catalyst than beta palladium. This statement is made with the assumption that the only reaction which occurred on each of the catalysts was the hydrogenation of ethylene to form ethane. To prevent polymer formation, an excess of ethylene was avoided for the hydrogenations on pure palladium. Also, the rates of hydrogen diffusion were found to be the same before and after hydrogenation of ethylene on the third type of catalyst. For this reason it is not believed that poisoning polymers were formed on this type of catalyst.

Since the rate constants for the reaction on beta palladium are less than those found on pure palladium, it is believed that the filling of the d-bands of palladium does not promote the catalytic activity of the metal. Rather, this and/or the increased spacings on the palladium surface lead to a decreased activity. The lattice constant for pure palladium is 3.883, while that for beta palladium is 4.018.⁵⁶ Hence, it is concluded that changes in these metallic properties are not re-

sponsible for the increased activity of palladium through which hydrogen is diffusing.

A different reaction mechanism must be operating on this third type of catalyst than on pure or beta palladium, since the rate of reaction is dependent on the ethylene pressure over the catalyst but independent of the hydrogen pressure. The heat of chemisorption of ethylene falls from 58 to 25 kcals./mole with increasing surface coverage on nickel.¹ Similar behavior should be expected in the case of palladium. If ethylene is unable to adsorb on the palladium surface through which hydrogen is diffusing, it must react from the gas phase or a van der Waals layer. Since the reaction rate was found essentially independent of hydrogen in the gas phase of the system, the reacting hydrogen is believed to be in or on the palladium. It is furthermore believed that hydrogen forming the beta phase of palladium is too strongly bound to the metal to react. This conclusion is supported by the low activity of beta palladium and the fact that the reaction is first order with respect to hydrogen pressure on this metal.

The other possibility is that ethylene reacts from the gas phase with hydrogen which is emerging in some form from the palladium surface. Most investigators^{52, 64} believe that hydrogen diffuses through palladium in the atomic state. After reaching the downstream surface, the atomic hydrogen is thought to be recombined catalytically to molecular hydrogen which desorbs from the surface and passes into the gas phase. It is likely that ethylene reacts with either atomic hydrogen or freshly formed molecular hydrogen which is adsorbed on the metallic surface.

2. Hydrogenation of Acetylene

As pointed out in Chapter I, kinetic data obtained for the hydrogenation of acetylene without simultaneous analysis of the reaction products are of little value due to the possibility of several reactions occurring. Many investigators^{87,88,94,95} believe that most of the acetylene is converted to ethylene and polymers before the ethylene reduction begins. For these reasons, no attempt was made to elucidate the order of the reaction or the rate constants. The pressure drops observed due to reaction are plotted as a function of time, and these pressure drops as well as the slopes of the curves are compared for the three types of catalysts studied (see Table III).

Very little difference was noted in the results obtained on pure versus beta palladium. This agrees with Sheridan's observation that large amounts of hydrogen occluded on palladium did not change the mechanism of the reaction.⁹³ The heat of adsorption of acetylene on nickel, 67 kcal.,⁸⁵ has been found to be much greater than that for ethylene, 25 kcal.,¹ at high surface coverage. Hence, it seems likely that acetylene can adsorb much easier on beta palladium than can ethylene. This may explain why the rate of hydrogenation of ethylene was low on beta palladium, while the rate of acetylene hydrogenation is near that on pure palladium.

Initially the pressure drop due to reaction of acetylene on palladium through which hydrogen was diffusing was much larger than that observed on the other two catalysts. If this change in pressure corresponds to the hydrogenation of acetylene, this third type of catalyst is initially more active than pure or beta palladium. Also, as observed in

the case of ethylene, the rate of hydrogen diffusion was the same before and after the reaction of acetylene on the palladium surface.

If polymeric materials are formed on the surface to any large extent, it would seem likely that the hydrogen diffusion rate would be less after reaction unless these polymers can be pulled off the surface by a vacuum.

3. The Hydrogen-Oxygen Reaction

When oxygen was introduced over a palladium catalyst through which hydrogen was diffusing, a large instantaneous uptake of the gas was observed. Since the heat of adsorption of oxygen on palladium is high, 75 kcal.,¹⁰⁹ oxygen may be able to preferentially replace adsorbed hydrogen on the surface of the metal. Very little pressure change was observed thereafter until the pressure of hydrogen in the gas phase of the system became large (5 cm. Hg). This observation as well as the fact that oxygen could be removed from the surface only by increasing the hydrogen pressure over the catalysts leads to the conclusion that oxygen adsorbed on the surface reacts with molecular hydrogen in the gas phase rather than hydrogen which is diffusing onto the catalytic surface. Other investigators^{3,21-23,32} have reported that adsorbed hydrogen inhibited the reaction on palladium and platinum.

D. Suggestions for Further Work

No explanation of the periodic behavior of the anodic potential and the catalytic activity in the hydrogen-oxygen reaction is reached in

this study. Further work should first ascertain whether oxygen gas in the reaction solution is necessary for this phenomenon. When all the factors which influence this behavior are studied, it may be possible to elucidate the mechanism for the periodicity. Also, it would be interesting to study the catalytic activity of the electrodes as a function of fixed constant potentials.

Further work on the hydrogenation of compounds on which hydrogen is diffusing should include simultaneously analysis of the reaction products to determine the specificity of the three types of catalysts, particularly for acetylene hydrogenation.

CHAPTER V

SUMMARY

Two methods of generating reactants on a catalytic surface were used to investigate the effect of this procedure on the activity of the platinum and palladium catalysts.

In the first method the effect of electrolytic polarization on the catalytic activity of platinized and smooth platinum electrodes was measured in the hydrogenations of allyl alcohol and oxygen in solution. The catalysts were subjected to both direct and alternating polarization in acid, basic and neutral solutions. A reaction system was constructed such that the hydrogenations could be studied for unlimited lengths of time. It was completely automatic, and very slow reactions could be followed. The potentials of the electrode catalysts were also measured with respect to a reference electrode.

The catalytic activity of the platinum electrodes was observed to be enhanced in both reactions by the following means: 1. alternating polarization; 2. changing the polarity of the catalysts suddenly; and 3. stopping anodic polarization of a platinized-platinum catalyst. This increased activity was not observed in basic solutions. In the case of the hydrogen-oxygen reaction, periodic behavior of the catalytic activity and the potential of the anode was observed for anodic polarization of smooth platinum electrodes in acid solutions.

In the other method hydrogen was caused to diffuse electrolytically through a palladium thimble, the inside of which was used as a catalyst

for low pressure hydrogenation reactions. Untreated and hydrogen pretreated palladium thimbles were also studied as catalysts for the hydrogenation of ethylene, acetylene and oxygen. The diffusion rate of hydrogen through the palladium was studied as a function of the temperature, current density and the pressure of the reactant gases on the inside surface.

The permeation rate of hydrogen was found to be proportional to the current density at low currents. The presence of ethylene, acetylene and oxygen on the inside surface of the metal lowered the rate of diffusion. This effect was correlated with the heats of chemisorption of the gases on palladium.

The activity of the palladium through which hydrogen was diffusing was observed to be higher than that of pure palladium, which, in turn, was higher than that of beta palladium for the hydrogenation of ethylene and acetylene. The hydrogenation of ethylene on palladium through which hydrogen was diffusing was found to be first order with ethylene pressure and zero order with hydrogen pressure. The order was reversed on beta palladium. It was proposed that ethylene in the gas phase reacts with active hydrogen which emerges from the catalytic surface due to diffusion.

In the case of the hydrogen-oxygen reaction, a palladium surface with hydrogen diffusing through it was found to be less active than a pure palladium surface. Oxygen adsorbed on the surface was believed to react with hydrogen in the gas phase on the former type of catalyst.

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APPENDIX

APPENDIX

A. Sample Calculation of the Determination of the Volume of the Gas Phase System

The theory and procedure has been described in Chapter II. An illustration of the calculations involved will be given here. The atmospheric pressure was 74.81 cm. Hg.

<u>Reference Point</u>	<u>Atmospheric Pressure-P</u>	<u>P, cm.</u>	<u>V₀, ml.</u>	<u>PV₀</u>
z	70.95	3.86	13.00	50.1
y	68.82	5.99	6.27	37.5
x	66.72	8.09	2.92	23.6
w	64.62	10.19	1.02	10.4
u	62.90	11.91	0	0

PV_b is plotted as a function of P in Figure 40. The slope of the line, -6.20 ml., is the negative of the volume, V₀ + V₁. The volume between mark u and the stopcock S₁, V₁, was determined to be 0.22 ml. Therefore, the volume of the reaction system is 6.20 minus 0.22 or 5.98 ml.

B. Sample Calculation of Change in Hydrogen Diffusion Rate With Acetylene in the System

The tritium content of a sample of hydrogen gas was measured by the number of seconds required for the microammeter dial of the vibrating reed electrometer to travel seven-tenths of the distance across the dial with the gas sample in the ionization chamber. The averages of seven readings taken with samples which were taken with and without acetylene in the system at 30° are 29.10 and 30.42 seconds respectively. These

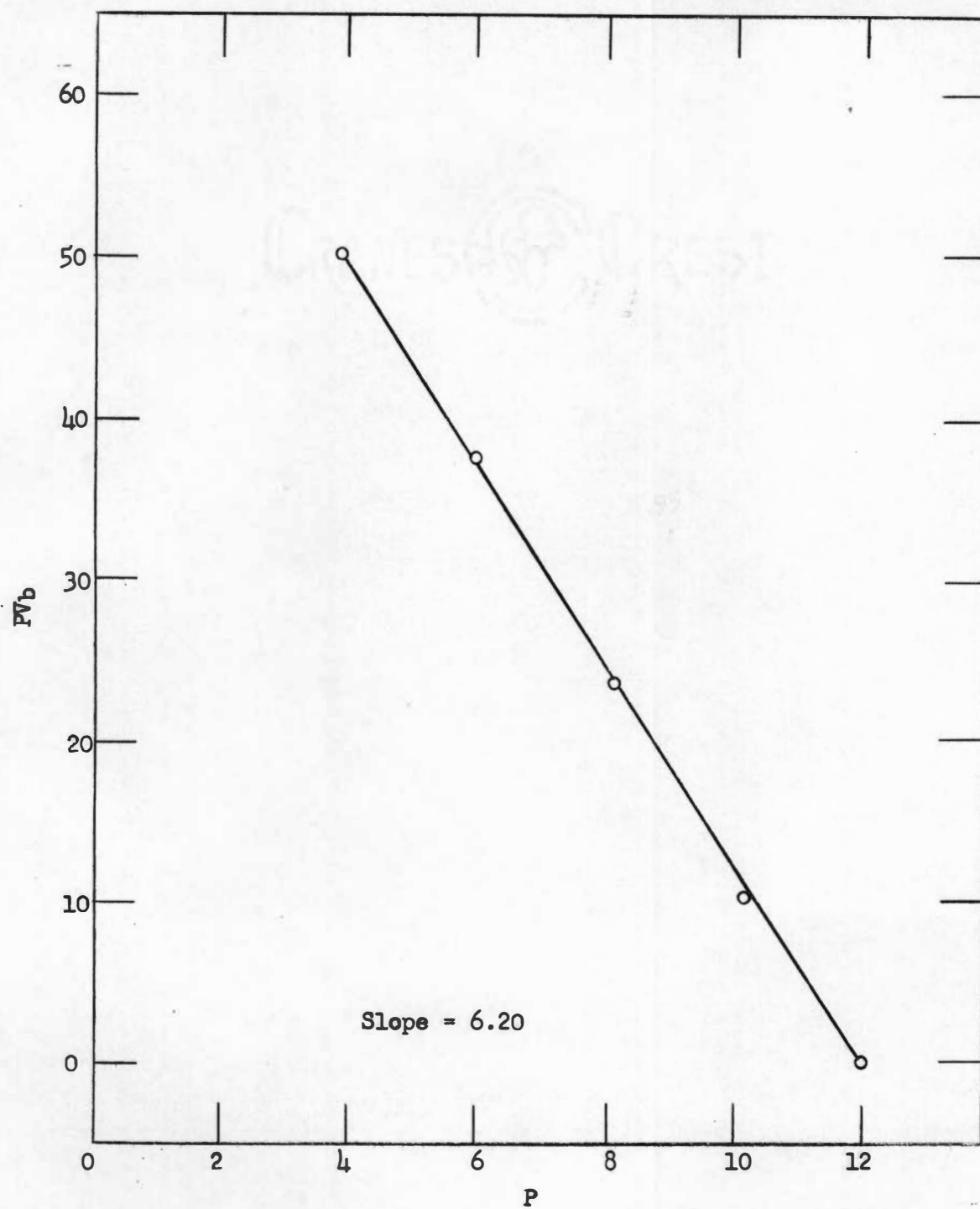


Figure 40. Plot of PV_b versus P for Determination of Volume of the System

readings were obtained with the instrument on the 300 mv. scale. The reading for background radiation with the ionization chamber filled with non-radioactive hydrogen was 21.86 seconds on the 30 mv. scale. This is equivalent to 218.6 seconds on the 300 mv. scale. The activity of each sample can be calculated by the expression given in Chapter II:

$$a = k \left(\frac{1}{t_1} - \frac{1}{t_2} \right) .$$

The ratio of these activities will be equal to the fraction of hydrogen which normally diffuses through the palladium.

$$\frac{a_1}{a_2} = \frac{\left(\frac{1}{30.42} - \frac{1}{218.6} \right)}{\left(\frac{1}{29.10} - \frac{1}{218.6} \right)} = 0.95$$

VITA

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