

MODIFICATIONS OF ADAMS' PLATINUM CATALYST

I. THE HYDROGENATION OF BENZOIC ACID

A THESIS

Presented to

the Faculty of the Division of Graduate Studies

Georgia Institute of Technology

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemistry

by

Ralph Hervey Earle, Jr.

September 1950

Original Page Numbering Retained.

MODIFICATIONS OF ADAMS' PLATINUM CATALYST

I. THE HYDROGENATION OF BENZOIC ACID

Approved:

[Handwritten signature]

[Handwritten signature]

[Handwritten signature]

Date Approved by Chairman September 27, 1950

ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to Dr. James A. Stanfield for proposing this problem to me, for his many suggestions in its execution, and for innumerable small actions that made the work run more smoothly.

I would also like to express my appreciation to Mr. John A. Brown for his help in preparing the bibliography for this study.

Finally, I would like to thank the School of Chemistry and the Graduate Division for their cooperation in making this study possible.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION.	1
II. THEORETICAL DISCUSSION.	3
A. MECHANISM OF CATALYSIS.	3
B. THE ROLE OF PROMOTERS AND INHIBITORS.	6
C. THE RATE CONSTANT	9
D. FACTORS AFFECTING CATALYST ACTIVITY	11
III. EXPERIMENTAL.	12
A. MATERIALS	12
B. APPARATUS	14
C. PROCEDURE	15
IV. DISCUSSION OF RESULTS	20
A. EXPERIMENTAL RESULTS.	20
B. CONCLUSIONS OF SIMILAR INVESTIGATIONS	23
C. CONCLUSIONS	24
V. SUGGESTIONS FOR FURTHER STUDIES	25
APPENDIX I. TABLES	26
APPENDIX II. GRAPHS.	28
BIBLIOGRAPHY.	37

LIST OF GRAPHS

GRAPH	PAGE
I. Sample Hydrogenation Curve for Benzoic Acid . . .	28
II. Effect of Iron.	29
III. Effect of Cobalt.	30
IV. Effect of Nickel.	31
V. Effect of Manganese	32
VI. Effect of Zinc.	33
VII. Effect of Chromium.	34
VIII. Effect of Aluminum.	35
IX. Effect of Palladium	36

LIST OF TABLES AND FIGURES

FIGURE	PAGE
1. Construction of Heating Unit.	16

TABLES	
I. Activity of Modified Adams' Platinum Catalyst in the Reduction of Benzoic Acid	26
II. Effect of Added Salts in Solution on the Activity of Adams' Platinum Catalyst	27

ABSTRACT

A study has been made of the effect of the addition of various metallic elements to Adams' platinum catalyst used in the reduction of the aromatic nucleus of benzoic acid in glacial acetic acid solution. A standard Parr hydrogenation apparatus was employed.

The elements were incorporated into the catalyst surface by introducing a water solution of a salt of the element into the fusion mixture of platinum chloride and sodium nitrate from which the catalyst was prepared. The catalyst was fused at 550° C. for thirty minutes.

The metals investigated may be considered in two classes on the basis of their effect on the rate of the above-mentioned reaction:

1. Elements which promote the reaction at concentrations on the order of 0.01 milli-mole per 0.2 gram of catalyst and then inhibit the reaction with increasing concentration. Into this class fall nickel, iron, zinc, cobalt, and manganese; nickel being the most effective promoter and manganese the least.

2. Elements which promote the reaction and whose effect is relatively constant to concentrations on the order of 0.2 milli-mole per 0.2 gram of catalyst. In this group are palladium, aluminum, chromium, and silver; palladium being the most effective promoter and silver the least.

CHAPTER I

INTRODUCTION

MODIFICATIONS OF ADAMS' PLATINUM CATALYST

I. THE HYDROGENATION OF BENZOIC ACID

CHAPTER I

INTRODUCTION

Since the first use of Adams' platinum catalyst, prepared by the fusion of chloroplatinic acid with sodium nitrate (3), as a hydrogenation catalyst, numerous studies have been made of its use in the reduction of different types of compounds. Very early in these studies it was noted that certain metallic salts when introduced into the reduction mixture had the ability to promote the reaction (1,13). In some cases reductions which had not been possible using Adams' catalyst were accomplished quite readily in the presence of these metallic salts (33, 50,61). In other cases the addition of these salts had no effect or even retarded the reduction (14,29,30,31).

Carothers and Adams (14) studied the effect of a variety of metallic salt solutions when added to the reaction mixture for the reduction of benzaldehyde to benzyl alcohol. The maximum promoting effect was found to exist in the region of low concentration of the added salt (approximately 0.1 milli-mole of salt per 0.1725 gram of catalyst). As the concentration of the salt was increased, the activity of the platinum catalyst was suppressed in most cases.

One of the most useful applications of Adams' platinum catalyst has been in the reduction of aromatic nuclei at room temperature and

low pressures. Prior to this discovery, the reduction had been accomplished only at high temperatures and pressures in the presence of a nickel catalyst.

It was found by Trimble of this laboratory (62) that the benzene nucleus and the pyridine nucleus of quinoline were hydrogenated at different rates by different catalyst preparations. In addition, the ratio of the reduction of the two nuclei was not constant. Upon spectrographic analysis it was found that minor traces of various elements were present in differing amounts in each sample of catalyst. Although several other factors may have caused this difference in the activity, it is quite probable that these impurities played an important role in determining the rate of reduction of the two nuclei.

In an unpublished work, Cox (16) of this laboratory investigated the effects of several metallic salts in solution on the reduction of the aromatic nucleus of benzoic acid. He found no promoting effect by these metals.

It is generally conceded that the catalyst surface is the site of its activity. It was felt, therefore, that a study should be made of the effect of various elements when incorporated into the catalyst surface on the reduction of the aromatic nucleus. Benzoic acid was chosen as the reference standard because of its ready availability in a pure state.

CHAPTER II

THEORETICAL DISCUSSION

CHAPTER II

THEORETICAL DISCUSSION

Despite the great number of studies made on heterogeneous contact catalysis, the exact mechanism whereby the various types of reactions proceed and the role which promoters and inhibitors play have not been satisfactorily explained. Several conflicting theories have been advanced, but none of them is universally applicable. It seems unlikely that any one theory will be able to explain all catalytic phenomena since experimental evidence to date seems to indicate that the role of the catalyst may vary from reaction type to reaction type.

A. MECHANISM OF CATALYSIS

Although the exact mechanism of catalysis is unknown, the basic steps of the reaction are generally agreed upon as (a) the diffusion of the reactants to the catalyst surface, (b) the action of activation on the catalyst surface, (c) the dissociation of the products from the surface, and (d) the diffusion of the products away from the catalyst (53). It is the nature of the action in (b) and (c) which is of greatest interest.

Faraday postulated that the hydrogen and substance to be hydrogenated were adsorbed onto the catalyst surface and hence brought into close contact permitting more rapid reaction (52). It has also been suggested that by holding the reactants in contact for longer time intervals than would be the case if the reaction proceeded purely through molecular collisions, the probability of reaction is increased

(55). In light of this theory, it is difficult to explain why charcoal, which has the ability to adsorb molecules, fails to display any catalytic activity.

Closely related to this is the "tunnel theory" proposed by Born and Franck (55). According to wave mechanics it is not necessary for the energy of two molecules to be sufficient to surmount the energy barrier between the two for them to unite. The reaction may occur by means of a "tunneling through" the energy barrier. This is particularly true when the potential energy wall is thin (in \AA units) and the two molecules are of similar energy states. By this theory, the catalyst serves to hold the molecules in contact for such a time that the probability of passing through a "tunnel" in the potential wall becomes marked.

The formation of metallic hydrides with the catalyst through chemisorption has been advanced by Sabatier and his co-workers (9,11,52). They also recognize the possibility of the formation of organometallic complexes. Either the metallic hydrides or organic complexes could be the reactive intermediate.

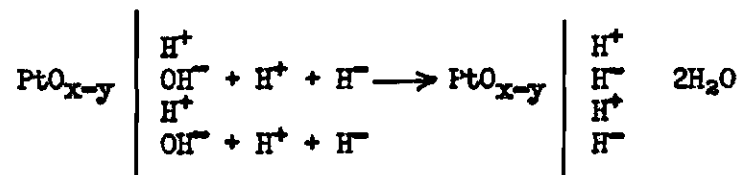
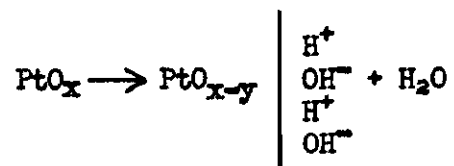
Atomic hydrogen has been proposed as the active intermediate by Winkelmann and Goehn (54). They reached this conclusion from certain mathematical considerations of the nature of gaseous adsorption. Langmuir (11,19,53) also postulated this same mechanism empirically.

Taylor (45,53) assumed that catalytic activity is found only at certain "active points" on the catalyst surface. At these "active points," caused by displacement of a metallic atom from the normal crystal structure, chemisorption occurs and the reaction proceeds as

indicated by Sabatier.

The idea of "active lines" such as occur at crystal edges, grain boundaries, etc., has been developed by Schwab and his collaborators (53). Maxted's work (45) on poisoning experiments has led him to support this theory. Instead of chemisorption occurring at these points, he proposed the formation of ionic hydrogen with the catalyst serving as an "electron sink." The "active lines" are located as the sites of ionization. This view would be in harmony with the theory of acid-base catalysis based on the concept of Lewis acids and bases (55). This theory is also supported by Schmidt (54), who postulates hydride formation then ionization of the hydrogen accompanied by diffusion into the interior of the catalyst.

As a result of their study of the composition of active nickel and platinum catalysts, Boswell et al. (9,10,11) have also proposed an ionic mechanism. However, instead of the pure metal being the catalyst, the metallic oxide is suggested as the active component. They found that if the metal was completely reduced, the catalyst was inactive. This was also found by Voorhees and Adams (64). In this mechanism it is thought that the oxide is reduced and the water which is formed ionizes on the catalyst surface. Hydrogen molecules are adsorbed as a secondary layer and polarized by the OH^- radical. The OH^- radical combines with a proton forming water, and the space it occupied is taken by a negative hydrogen ion. Oxygen in the interior of the catalyst slowly reacts with these ions repeating the cycle. In addition, the water formed during the cycle may be re-adsorbed. The cycle may be diagramed:



The positive and negative hydrogen ions are postulated as the active intermediates.

This mechanism would account for the necessity for the presence of oxygen in the catalyst and for the gradual decrease in the activity of the catalyst during the course of a hydrogenation.

B. THE ROLE OF PROMOTERS AND INHIBITORS

For this discussion a promoter is defined as any substance which, when added to the catalyst or a reduction mixture, results in an increase in activity of the catalyst. This includes both catalytically active and catalytically inert materials. An inhibitor is any substance which, when added to the catalyst or the reduction mixture, results in a decrease in activity of the catalyst.

As in the case of catalytic mechanisms, the exact role of promoters is not known. The several theories which have been proposed depend on the acceptance of one or another of the theories of heterogeneous catalysis.

Several experimental observations have been made by several investigators which might be of assistance in considering the theories

of promoter action:

1. the addition of one promoter to a catalyst at maximum activity due to the presence of another promoter decreases the activity (29);
2. if a promoter is extracted from a catalyst, the catalyst then exhibits approximately its normal activity (26);
3. a mixture of two catalysts is not necessarily superior to one or either of them (7);
4. the incorporation of a promoter in a catalyst does not affect the size or shape of the crystal lattice (29);
5. the optimum concentration of a promoter is a function of the catalyst and not the promoter (29).

It has been postulated by Nyrop (47) that the promoter preserves the "accessible" area during catalytic processes by preventing the sintering of the catalyst with a resulting loss of the "active points." Since the catalyst surface contains only relatively few "active points," only a small amount of promoter is necessary to be effective.

This theory is supported by Taylor (49) who suggests, in addition, the possibility of the promoter creating additional active surface or altering the proportions in which the reactants and products are adsorbed. He has also suggested that the promoter may form a new type of "active point" on the catalyst for which the activation energy of the reactants is lowered.

The possibility has also been recognized that the promoter may form more reactive intermediates with the reactants (20). If this were true, it is difficult to see why the promoter becomes an inhibitor

above the regions of very low concentration.

In a paper by Dupont and Piganiol (18) it is stated that the metal adsorbs and activates hydrogen while the promoter adsorbs and activates the organic compound. They also indicate that the "active points" in this case are not the points of abnormal distribution of the atoms in the crystal structure, but the contact points between the promoter and catalyst.

In explaining the effect of promoters for his theory of ionic catalysis, Boswell (10) proposes that the promoter enables the catalyst to hold a greater concentration of ions on its surface and has found this to be substantiated for the promotion of platinum black by potassium hydroxide. In addition, he believes that the promoter decreases the rate of loss of water from the catalyst surface, accelerates the transfer of oxygen from the interior to the surface, increases film stability, and hastens film formation.

The phenomenon of catalytic inhibition is generally considered to be caused by two main factors. Either the inhibitor is strongly adsorbed onto the catalyst, effectively shielding the surface, or it forms unreactive complexes with the intermediates.

Boswell (10) attributes the effect of inhibitors, in addition to the above effects, to their power to destroy the surface film in which ionization occurs.

In a series of studies by Maxted and co-workers (31-38) the nature of catalytic poisoning has been considered. As a result of their work they have found that, in general, the decrease of activity is a linear function of the concentration of the inhibitor to regions

of high concentration, at which point incipient poisoning of the catalyst occurs.

C. THE RATE CONSTANT

For a first order reaction, the rate of reaction may be expressed as (28):

$$-\frac{dc}{dt} = kc \quad (1)$$

where c is the concentration of the reactant, t is the time, and k a constant.

Integration of equation (1) between the limits of c_1 at t_1 and c_2 at t_2 and converting to logarithms to the base 10 gives:

$$k = \frac{2.303}{t_2 - t_1} \log \frac{c_1}{c_2} \quad (2)$$

At t_0 , the concentration is c_0 , and one finds on rearrangement of (2):

$$\log \frac{c_0}{c} = \frac{kt}{2.303} \quad (3)$$

For the case in which the substance involved is a gas, the pressure of the gas is proportional to its concentration, and one may substitute pressures for concentration in equation (3):

$$\log \frac{p_0}{p} = \frac{kt}{2.303} \quad (4)$$

By plotting $\log p_0/p$ as a function of time, the graph will be a straight line of slope $k/2.303$ (graph I). From this, k , the rate constant, is readily calculated.

From studies on the hydrogenation of the benzene nucleus, Smith et al. (57-60) concluded that the reaction is first order with respect to hydrogen and zero order with respect to the organic compound. Thus, the above equations may be applied for this study. They have also shown that the rate constant is directly proportional to the quantity of catalyst.

In addition, the rate constant is affected by the reaction temperature, the solvent employed, and the volume of the system. The volume of the system for this investigation was 4.65 liters. The rate constant was checked for each new batch of glacial acetic acid to insure reproducible results.

In order to correct for temperature, the integrated form of the Arrhenius Equation was employed to correct all results to 30° C (28):

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where k is the rate constant, R is the universal gas constant, T is the absolute temperature, and E_a the activation energy of benzoic acid. By taking the value of 8000 calories per mole for the activation energy of benzoic acid (57) which is constant over the temperature range encountered, it is possible to make a plot of k_2/k_1 as a function of the temperature. From this it is possible to obtain the value of k_2 directly.

All rate constants used in this work are in units of reciprocal minutes per gram of catalyst.

D. FACTORS AFFECTING CATALYST ACTIVITY

The activity of the catalyst is known to be affected by several factors (4). First, the manner of preparation can greatly affect the activity. For example, platinum black prepared by the treatment of chloroplatinic acid with formaldehyde followed by the addition of alkali (64) is much less active than Adams' platinum catalyst. The manner of preparation in a large measure fixes the size of the catalyst particles and hence their surface area, the chemical composition of the catalyst, its nature (whether colloidal or a solid), etc.

Next, the fusion temperature determines the activity of the catalyst. Adams (4) found that the most active catalyst resulted from a fusion temperature of 500 to 550° C.

Finally, as has already been stated, the activity of the catalyst is affected by the presence of trace impurities.

CHAPTER III

EXPERIMENTAL

CHAPTER III

EXPERIMENTAL

Because of the sensitivity of the reaction to poisoning, and because of the number of factors affecting the rate constant, it is necessary to standardize all procedures, to use the best available reagents, and to clean all apparatus thoroughly in order to secure reproducible results. Except for the specific factor under investigation, it has been attempted to keep all conditions constant or to correct for any variations from the standard.

A. MATERIALS

1. Benzoic Acid

The benzoic acid (m.p. 121-2° C.) used for this study was of reagent grade obtained from Merck and Company, Rahway, New Jersey, and contained no more than 0.5 per cent impurities. Only one lot was used to prevent any variation in the reference standard.

2. Acetic Acid

The acetic acid was purified by distilling technical grade glacial acetic acid through a five-foot column packed with single-turn glass helices of 1/8 inch diameter. The still had approximately 40 theoretical plates. The constant boiling fraction distilling at 116.6° C. at 740 mm. pressure was collected. This corresponds to a boiling point of 118.2° C. at 760 mm.

3. Hydrogen

The hydrogen was obtained from the National Cylinder Gas Company of Atlanta, Georgia, and used without further purification.

4. Platinum Chloride

The platinum chloride used throughout this work was from one lot (No. 122848) of c. p. chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) secured from the J. T. Baker Chemical Company of Phillipsburg, New Jersey. The platinum chloride was dissolved in water (3.5 grams per 10 ml. of solution) for use in catalyst preparation. One sample (A') was possibly contaminated by a metal spatula used in removing the platinum chloride from its container. Later determinations of the rate constant for pure catalyst prepared from this sample were slightly higher which tends to substantiate the fact that it was contaminated.

5. Metallic Salts

All of the metallic salts were dissolved in water solution, and the desired quantity for each preparation was obtained by using appropriate portions of the solution. For preparations in which only very small portions of the salt were desired, a portion of the standard solution was diluted with water, and appropriate quantities of this dilute solution used.

- a. Ferric Nitrate - Merck's reagent grade $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
- b. Cobalt Nitrate - Merck's reagent grade $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
- c. Nickel Nitrate - Fischer Scientific Company, c.p. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
- d. Palladium Chloride - Coleman and Bell Company, Norwood, Ohio, c.p. PdCl_2 (It was necessary to use 0.5 ml. of HCl for 25 ml.

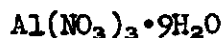
of 0.05 M PdCl₂ solution in order to dissolve the palladium chloride.)

e. Manganous Chloride - J. T. Baker Chemical Company, c.p.



f. Silver Nitrate - Merck's c.p. AgNO₃

g. Aluminum Nitrate - J. T. Baker Chemical Company, c.p.



h. Chromic Nitrate - J. T. Baker Chemical Company, c.p.



i. Zinc Nitrate - J. T. Baker Chemical Company, c.p. Zn(NO₃)₂·6H₂O

6. Sodium Nitrate

One lot of Merck's reagent grade sodium nitrate was used for preparation of all catalyst samples.

B. APPARATUS

1. Hydrogenation Apparatus

For this study, a standard low pressure hydrogenation apparatus manufactured by the Parr Manufacturing Company of Moline, Illinois, was used for all rate constant determinations. The apparatus consists essentially of a hydrogen storage tank connected to a heavy pyrex reaction bottle. The storage tank is equipped with a special pressure gauge capable of being read to within 0.05 p.s.i. The reaction bottle is surrounded by a perforated metal shield and held in an oscillating mount connected to a shaker arm. All connections are of heavy duty rubber tubing. The shaker operates at approximately 280 cycles per minute.

A two-way valve is placed in the line from the hydrogen tank to the reaction bottle. This valve is connected by a line to an acid-gas trap and thence to a vacuum pump. The volume of the tank and reaction bottle is approximately 4.65 liters.

2. Heating Unit

After several unsuccessful attempts to prepare catalyst samples of reproducible rate constants, it was found necessary to construct a special heating unit for catalyst preparations (Figure I). The heating unit was made from an iron hemisphere lined with pyrex-wool and asbestos insulation in which was cast a refractory lining of limonite cement shaped to fit a No. 400 porcelain casserole. Imbedded in the refractory lining was an 8 1/2 foot length of No. 25 B. and S. gauge nichrome resistance wire in 3/16 inch coils to provide more efficient heating. The temperature of the fusion mixture was recorded by means of a chromel-alumel thermocouple connected to a pyrometer. The thermocouple was equipped with a removable pyrex jacket.

C. PROCEDURE

1. Hydrogenation

As mentioned above, in order to prevent poisoning of the reaction, the greatest of care was necessary in cleaning all apparatus.

All rubber connections and stoppers were treated by boiling for 20 minutes in a 20 per cent sodium hydroxide solution; washed and boiled 20 minutes in distilled water; rinsed again with distilled water and dried with acetone. When a new stopper was placed on the apparatus

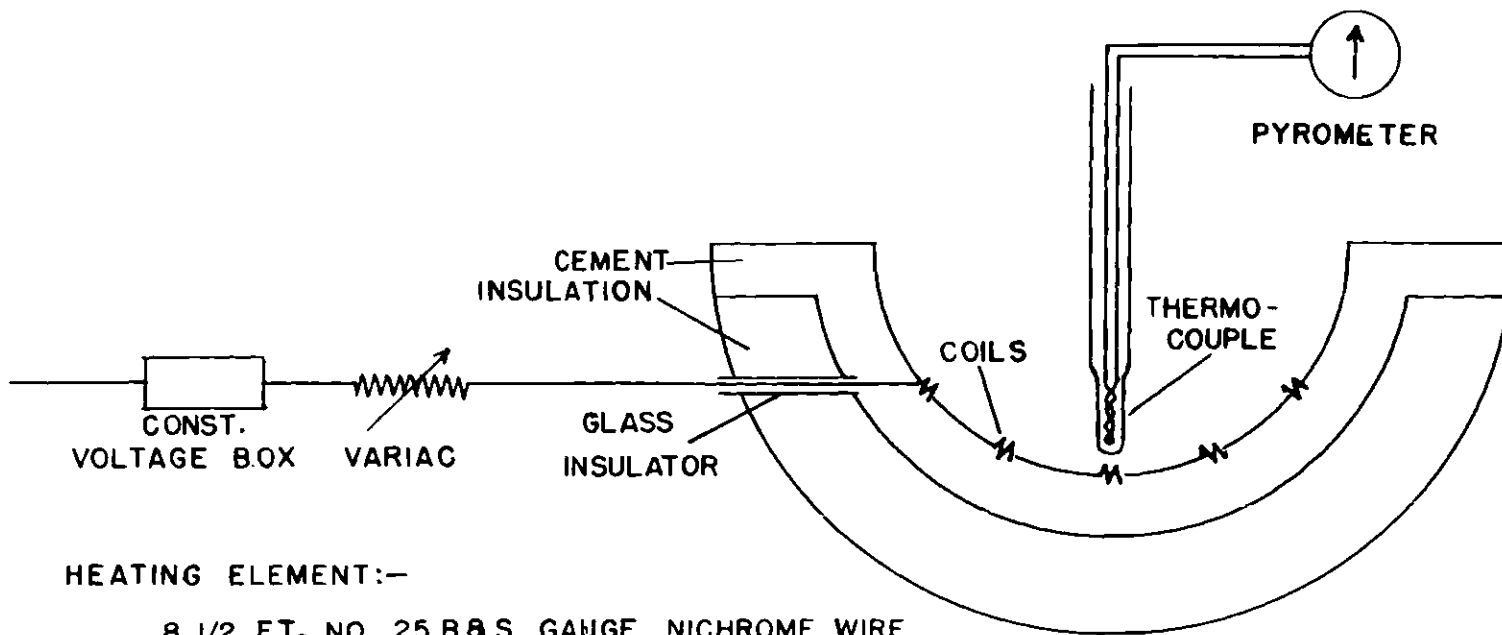


FIGURE 1.
CONSTRUCTION OF HEATING UNIT

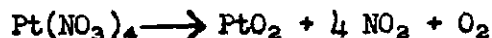
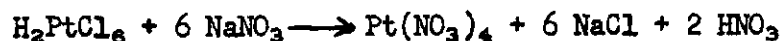
a blank run was made to remove any possible remaining traces of contamination.

The reaction bottles were prepared by washing with soap and water, rinsed, then allowed to stand full of sulfuric acid - potassium dichromate cleaning solution for at least 30 minutes. After rinsing well with tap water followed by rinsing several times with distilled water, all bottles were dried in an electric oven at 115° C.

Prior to each run, the metal tube connecting the reaction bottle to the line from the hydrogenation tank was cleaned with a pipe cleaner moistened with c. p. methanol. Then 0.200 gram of the catalyst sample and 2.442 gram (0.02 mole) of benzoic acid, both weighed on an analytical balance, were placed in the reaction bottle with 50 ml. of glacial acetic acid. The reaction bottle was clamped onto the apparatus and alternately evacuated and filled with hydrogen three times. The line to the reaction bottle from the storage tank was opened, and the system filled with hydrogen to a gauge pressure of 50 p.s.i. corresponding to an absolute pressure of approximately 64.3 p.s.i. The stop-watch and shaker were started simultaneously. During each run the gauge pressure and the temperature of the storage tank were recorded at regular time intervals.

2. Preparation of Catalyst

The procedure followed for preparation of the catalyst was based on Adams' directions (4) with certain modifications. The reactions involved may be summarized as follows:



Ten ml. of the chloroplatinic acid solution (3.5 grams in 10 ml. of solution) were placed in a porcelain casserole with 35 grams of sodium nitrate. To this was added the appropriate quantity of metallic salt solution and sufficient distilled water to bring the total liquid volume of the reaction mixture to 27.5 ml.

The mixture was evaporated to dryness and the temperature raised until the entire mass was melted. Over a 20 minute period the temperature was then raised to the fusion temperature of 550° C. During this step vigorous stirring was necessary to prevent frothing from the rapid evolution of gases. The mixture was held at 550 ± 10° C for 30 minutes, then allowed to cool.

The fused mass was dissolved in 50 ml. of distilled water, and the platinum oxide allowed to settle. The supernatant liquid was decanted, and the process repeated with 25 ml. of distilled water. The catalyst was washed with 15 ml. of distilled water and transferred to a small Büchner funnel. After washing with three 10 ml. portions of distilled water, the sample was dried in a vacuum dessicator over calcium chloride.

For some of the runs, 15 ml. of the chloroplatinic acid solution with respectively larger amounts of all other materials was used. It was found that this did not affect the rate constant within the

experimental error.

Throughout the fusion, the temperature was recorded by means of the thermocouple in a pyrex jacket immersed in the reaction mixture.

CHAPTER IV

DISCUSSION OF RESULTS

CHAPTER IV

DISCUSSION OF RESULTS

A. EXPERIMENTAL RESULTS

In the course of this investigation the following metals were introduced into the catalyst in varying concentrations: iron, cobalt, nickel, manganese, zinc, chromium, aluminum, palladium, and silver. With the exception of silver, all of these metallic nitrates decompose into the oxide below the fusion temperature employed. Silver decomposes into its elementary state (21).

The concentrations were based on the number of milli-moles of added element in 0.2 gram of catalyst.

From Table I it appears, in general, that the metals may be divided into two classes:

1. Elements which promote the catalyst at low concentration and then inhibit the activity as concentration increases. In this group belong iron, cobalt, nickel, manganese, and zinc.

2. Elements which promote the catalyst and whose effect is relatively constant to high concentrations. In this group belong chromium, aluminum, palladium, and silver.

The rate of the pure catalyst used as a reference point was based on a series of three catalyst preparations.

Catalyst IV	$230 \times 10^{-4} \text{ min}^{-1} / \text{ gm. catalyst}$
Catalyst V	219×10^{-4}
Catalyst VI	<u>227×10^{-4}</u>
Average	225×10^{-4}

Group 1

All of those elements showing a "normal" promoting curve, i.e. one with a maximum in the region of low concentration and then falling off rapidly, with the exception of manganese show a maximum promoting effect in the region of 0.001 milli-mole of promoter per 0.2 gram of catalyst. (Graphs II,III,IV,V) The maximum for the manganese curve may also be in this region (Graph VI), but because of the failure of the data to fall on a relatively smooth curve, it is difficult to say. This data would be in agreement with Griffith's statement (29), "The optimum promoter concentration is a function of the catalyst and not of the promoter."

The general order of the maximum promoter activity for these metals from the highest activity to the lowest is nickel, iron, zinc, cobalt, and manganese.

The activity of the catalyst is almost completely suppressed in the region of 0.1 to 0.2 milli-mole of promoter per 0.2 gram of catalyst by these metals. Manganese inhibits the catalyst most rapidly with concentration followed by nickel, zinc, iron, then cobalt. It is interesting to note that all of these elements have two electrons in their outer orbital, which are s orbitals in all cases.

Group 2

The elements in this group seem to have a relatively constant effect on the activity of the catalyst with increasing concentration. For the region studied in this investigation, no inhibiting effect was found except for perhaps the case of aluminum at 0.4 mmole per gram of catalyst (Graphs VII,VIII,IX).

With the exception of palladium, all of these elements have a

single electron in their outer orbital. Palladium has $4d^{10}$ electrons in its outer orbital, but since the energy difference between a $4d$ and $5s$ orbital is small, it can be easily excited to a configuration of $4d^9$, $5s^1$ in which case its configuration would fall into the same classification as the others.

Shriner and Adams (57) report that PdO prepared by sodium nitrate fusion is an active catalyst for the reduction of the carbonyl group and for the reduction of maleic acid to succinic acid. Pure PdO , when prepared in the same manner in this study, showed only slight activity in the reduction of the aromatic nucleus. ($k = 2 \times 10^{-4} \text{ min}^{-1} / \text{gm. of catalyst}$)

Difficulty was encountered in the introduction of silver into the catalyst due to the formation and precipitation of silver chloride from the reaction mixture. In an attempt to avoid this, the platinum chloride - sodium nitrate mixture was evaporated to dryness to drive off all HCl before the addition of the silver nitrate. A catalyst prepared in this same manner was found to show a slightly lower activity than that prepared by the normal procedure. To check the effect of the modification, a sample of 0.1 mmole of aluminum per 0.2 gram of catalyst was prepared in the manner just described. It, too, showed a slightly lower activity (Table I). For this reason, further study of the effect of silver was not undertaken.

B. CONCLUSIONS OF SIMILAR INVESTIGATIONS

In a study by Carothers and Adams (15) of the effect of metallic salt solutions on the reduction of benzaldehyde to benzyl alcohol in 95 per cent alcohol it was found that certain elements promoted the reaction. Iron, nickel, cobalt, manganese, zinc, and chromium gave maximum promotion in the region of 0.1 mmole of salt per 0.1725 gram of catalyst. The relative efficiency of the metals varied with the cation with which they were combined.

In some cases as the concentration was increased to 1 millimole, the catalyst was inhibited to varying degrees, and in other cases the activity remained almost constant.

Palladium was very effective as a promoter for all concentrations studied. Aluminum and silver had no effect.

As mentioned in the introduction, an unpublished work by Cox, of this laboratory, indicated no promotion by several metallic salts in solution when used in the reduction of the aromatic nucleus of benzoic acid in glacial acetic acid. In this investigation, Cox studied the effects of nickel nitrate, nickel chloride, cobalt nitrate, cobalt chloride, ferric chloride, ferric sulfate, palladium chloride, and platinum chloride. (Table II)

Although no indications of promotion were found, as in the case of the work by Carothers and Adams, it was noticed that the effect of the cation of the salt had a noticeable effect on the activity of the catalyst.

C. CONCLUSIONS

From a consideration of the results of these three studies, it would seem that the effect of the various elements as promoters is specific for each type of reduction. It would also seem that the effect depends on the manner in which the promoter is introduced (i.e., as salt in solution or in the catalyst), the compound as which it is introduced, and its concentration; each of these effects varying independently.

CHAPTER V

SUGGESTIONS FOR FURTHER STUDIES

CHAPTER V

SUGGESTIONS FOR FURTHER STUDIES

1. Effect of modified catalysts on the reduction of benzaldehyde

It would be interesting to compare the results of this investigation with a similar study of the reduction of benzaldehyde to benzyl alcohol in 95 per cent ethanol. These results could then be considered in light of the work of Carothers and Adams (15) on the effect of metallic salt solutions.

2. Effect on the reduction of the pyridine nucleus

As has already been noted, Trimble (62) found that trace impurities in the catalyst caused a change in the ratio of the reduction of the aromatic nucleus and the pyridine nucleus. This investigation has considered the reduction of the aromatic nucleus by modified catalysts. A similar study for the pyridine nucleus should be undertaken to find the effect of the same modified catalyst on these two compounds.

3. Effect of the second group of metals over a wider range of concentrations

During the course of this study, no noticeable catalytic inhibition was found for the Group 2 elements in the concentration range covered. It was found that in the case of palladium, the pure PdO was of negligible activity. Evidently there must be some point at which inhibition is initiated in mixed platinum-palladium catalysts. Further investigation should reveal this point as well as the corresponding points for the other elements in this series.

APPENDIX I

TABLES

TABLE I

ACTIVITY OF MODIFIED ADAMS' PLATINUM CATALYST IN
THE REDUCTION OF BENZOIC ACID

Salt Conc. mmole	Rate Constant $k_{30} \times 10^4 \text{ min}^{-1}/\text{g.}$								
	Fe	Co	Ni	Mn	Zn	Cr	Al	Pd	Ag
0.0005	257								
0.001	246	238	281	231	246			278	
0.01	206	221	237	231	245	228	256	269	
0.02		205							
0.05	166		148	52					
0.1	87	101		33	48	253	258 237 ^a	285	226 198 ^a
0.2	4					225	254	285	
0.4	2						209		

Note: All rate constants referred to pure catalyst $k = 225 \times 10^{-4}$

^aSample evaporated to dryness before addition of the salt solution

TABLE II

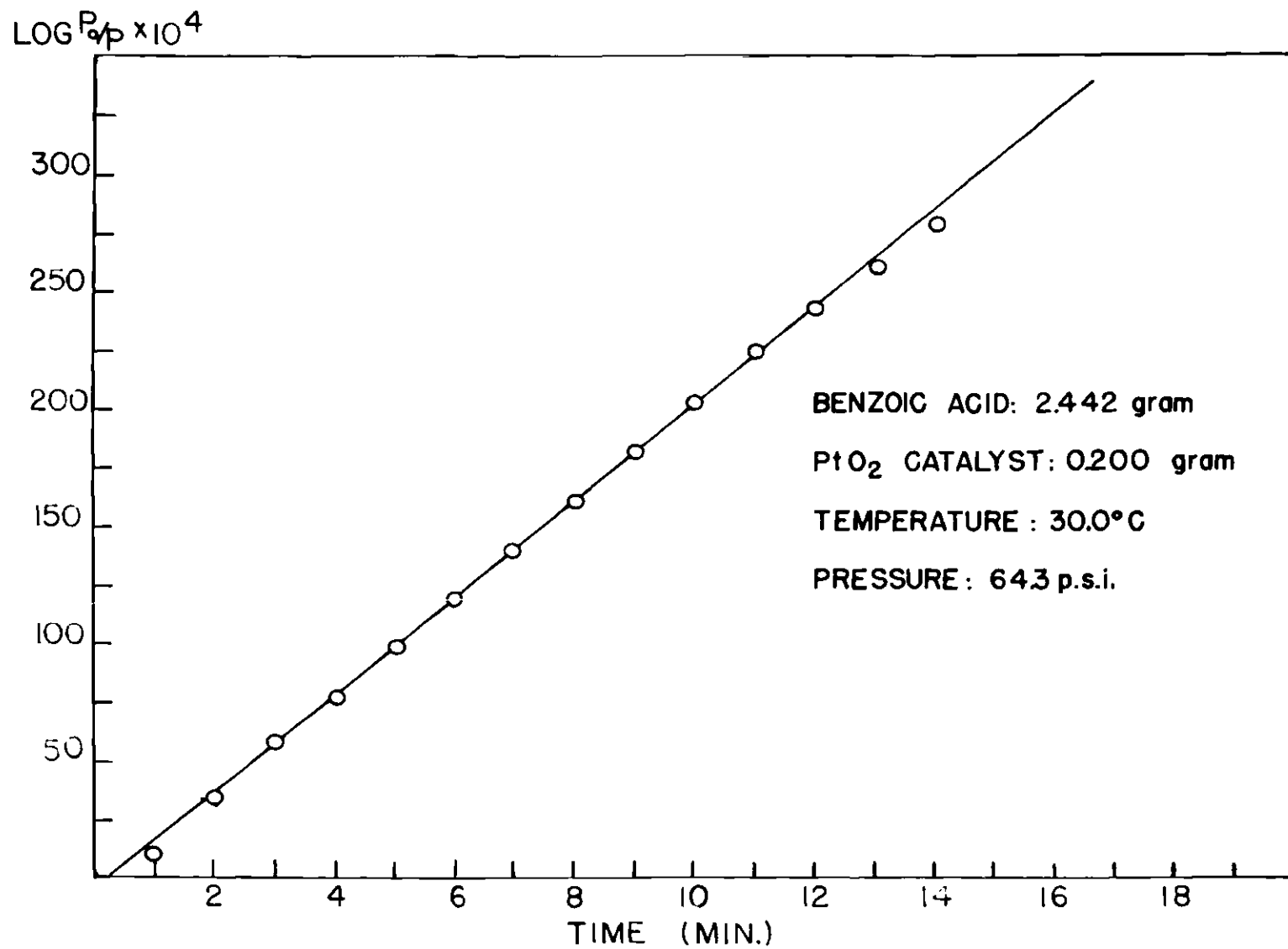
EFFECT OF ADDED SALTS IN SOLUTION ON THE ACTIVITY OF
ADAMS' PLATINUM CATALYST (16)

Salt Conc. mmole	Rate Constant $k_{30} \times 10^4 \text{ min}^{-1}/\text{g.}$							
	$\text{Ni}(\text{NO}_3)_2$	NiCl_2	$\text{Co}(\text{NO}_3)_2$	CoCl_2	FeCl_3	$\text{Fe}_2(\text{SO}_4)_3$	PdCl_2	PtCl_4
0.001	190		193					
0.005	187		182	174	203			
0.01	155	167	179	164	208			227
0.05	100	112	113		130	228		
0.1	28		63	53	27	212	218	169

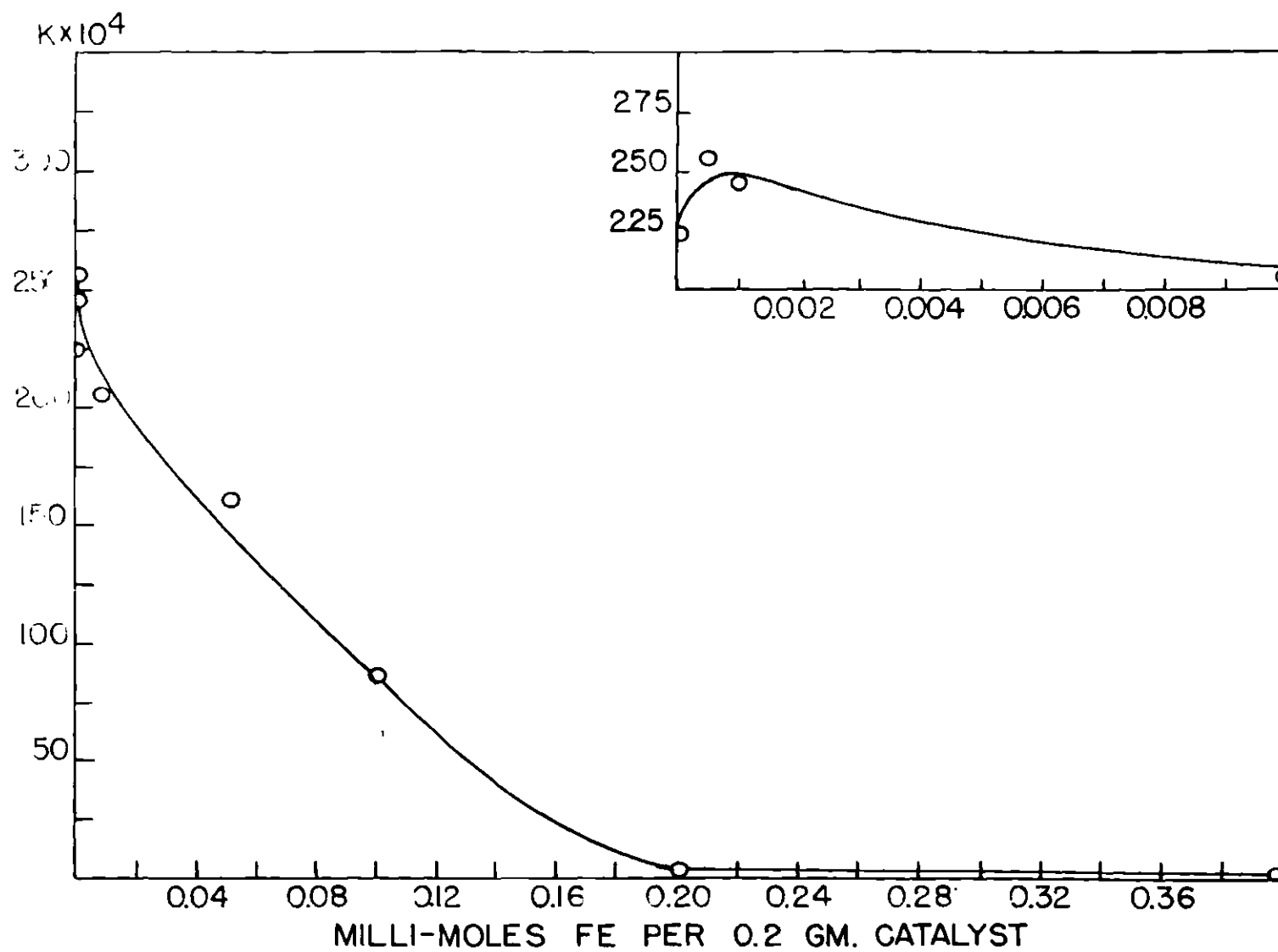
Note: All rate constants referred to pure catalyst $k = 225 \times 10^{-4}$

APPENDIX II

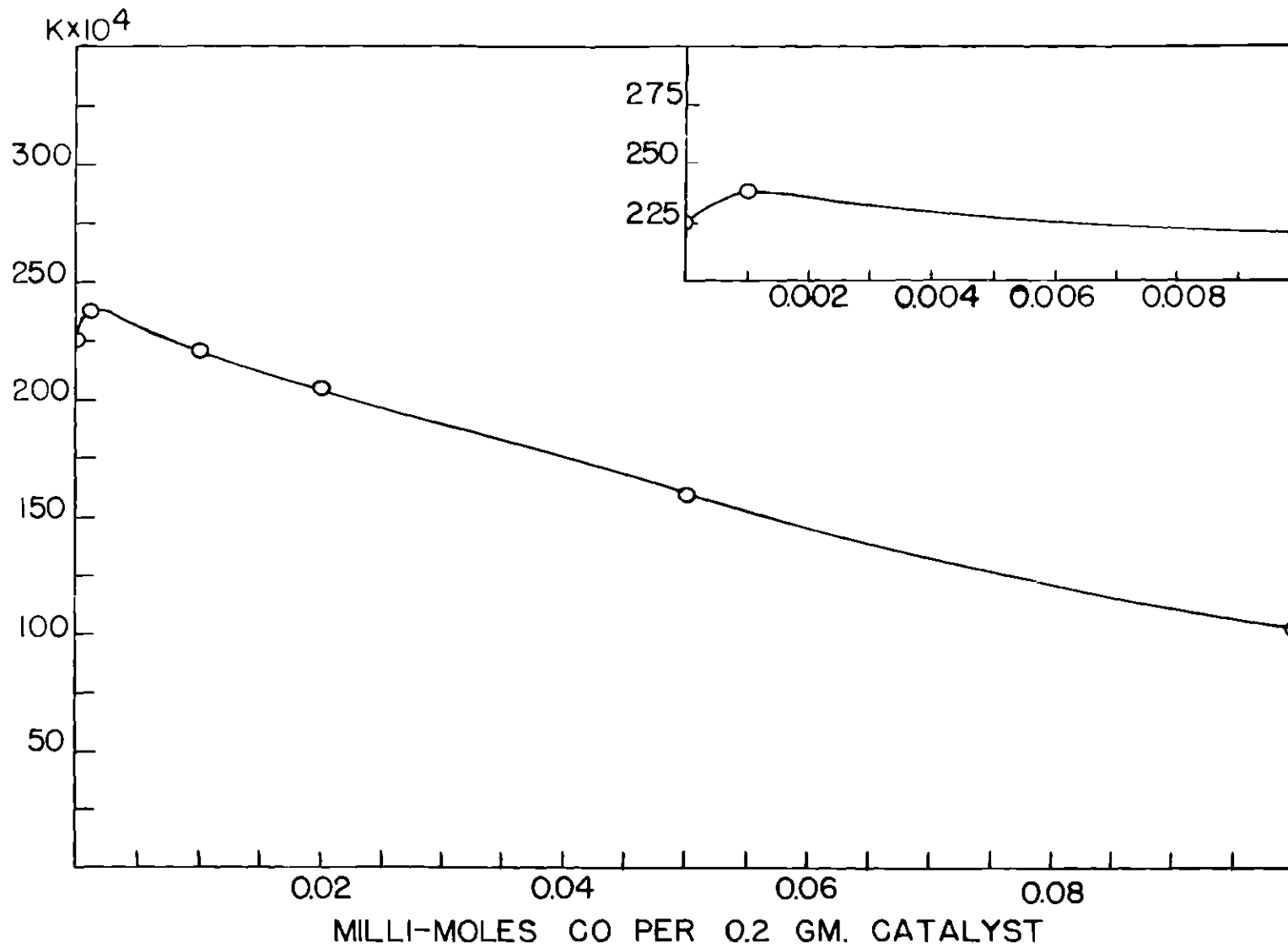
GRAPHS



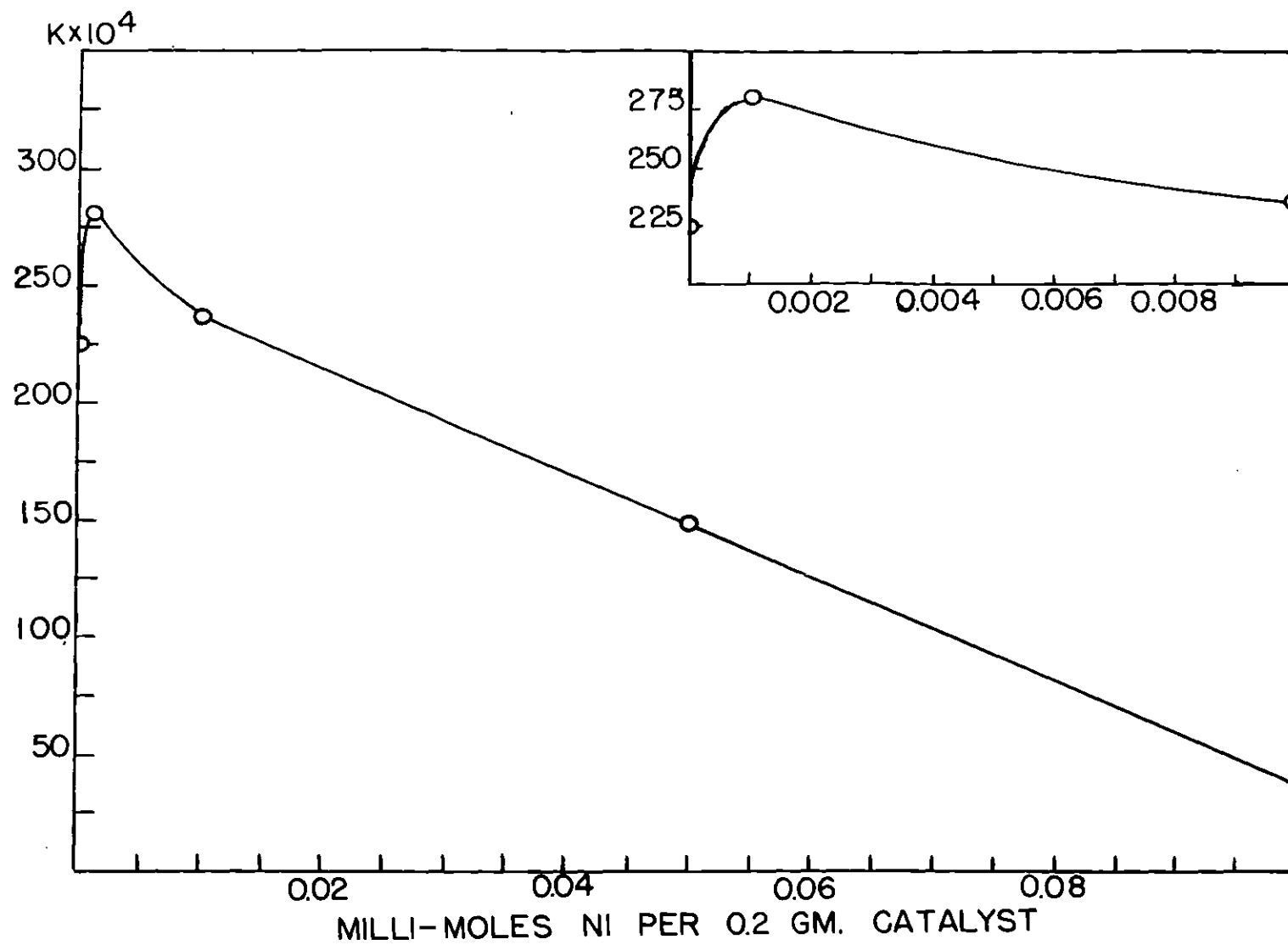
GRAPH I
SAMPLE HYDROGENATION CURVE FOR BENZOIC ACID



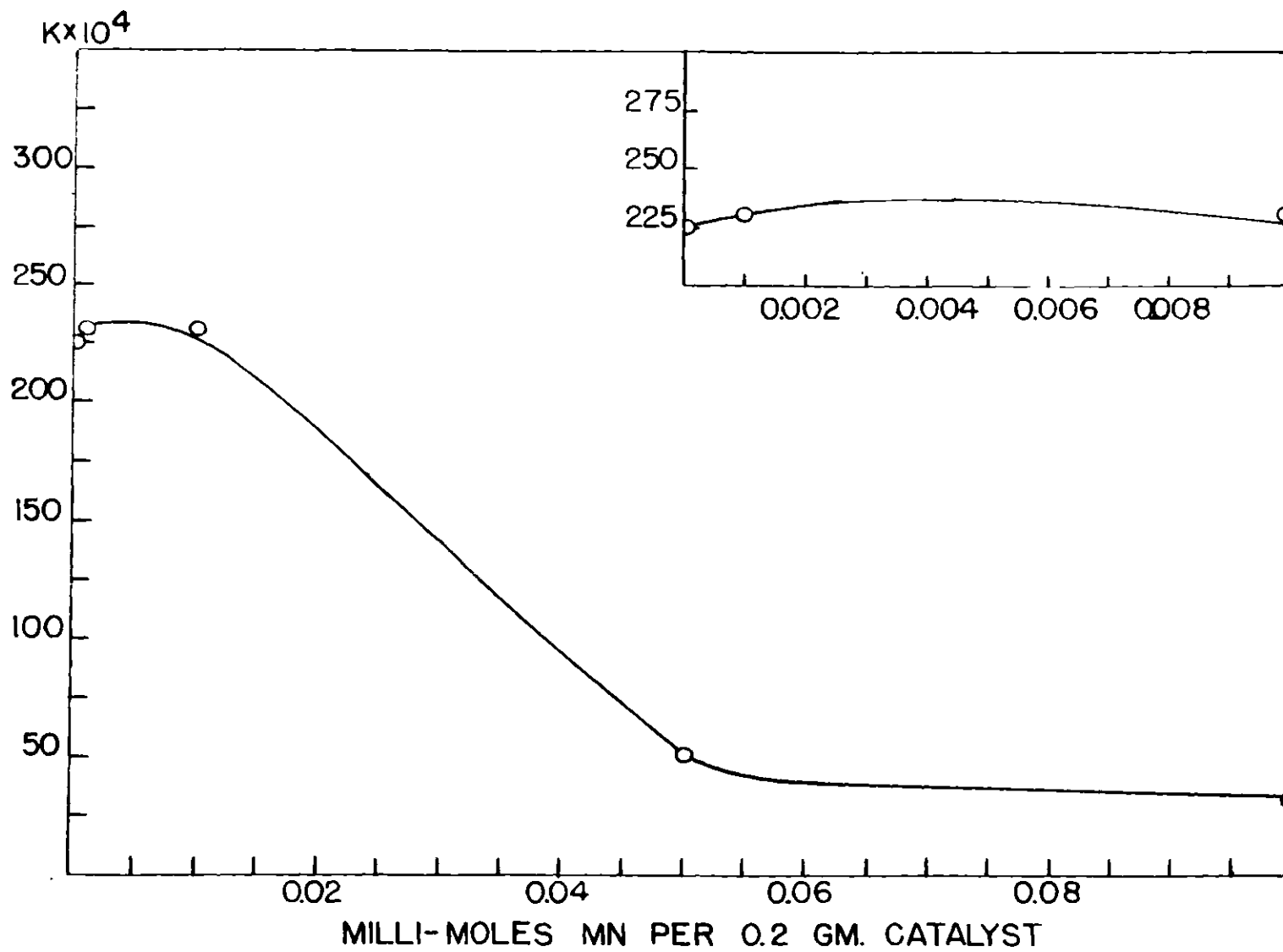
GRAPH II
EFFECT OF IRON



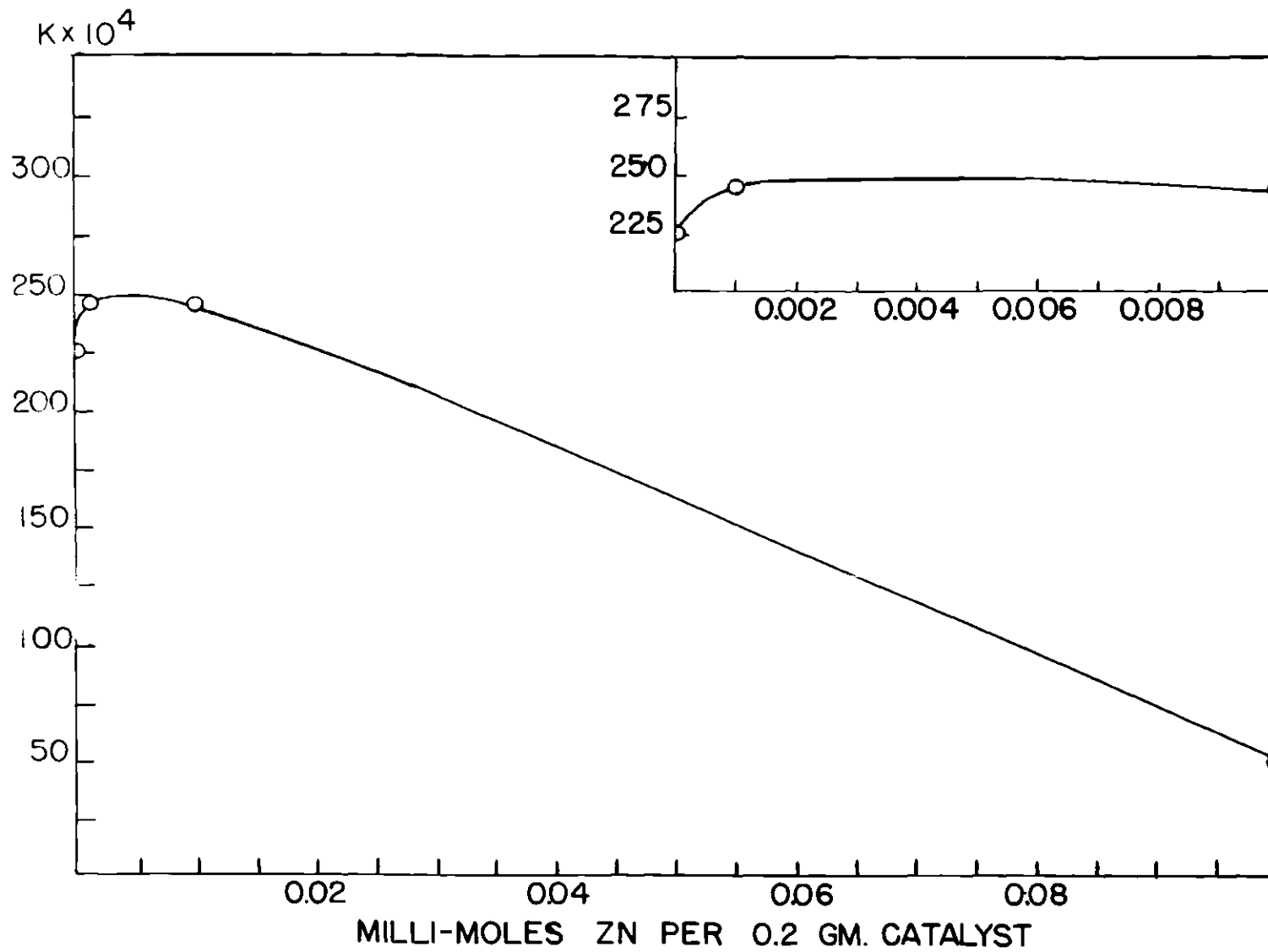
GRAPH III
EFFECT OF COBALT



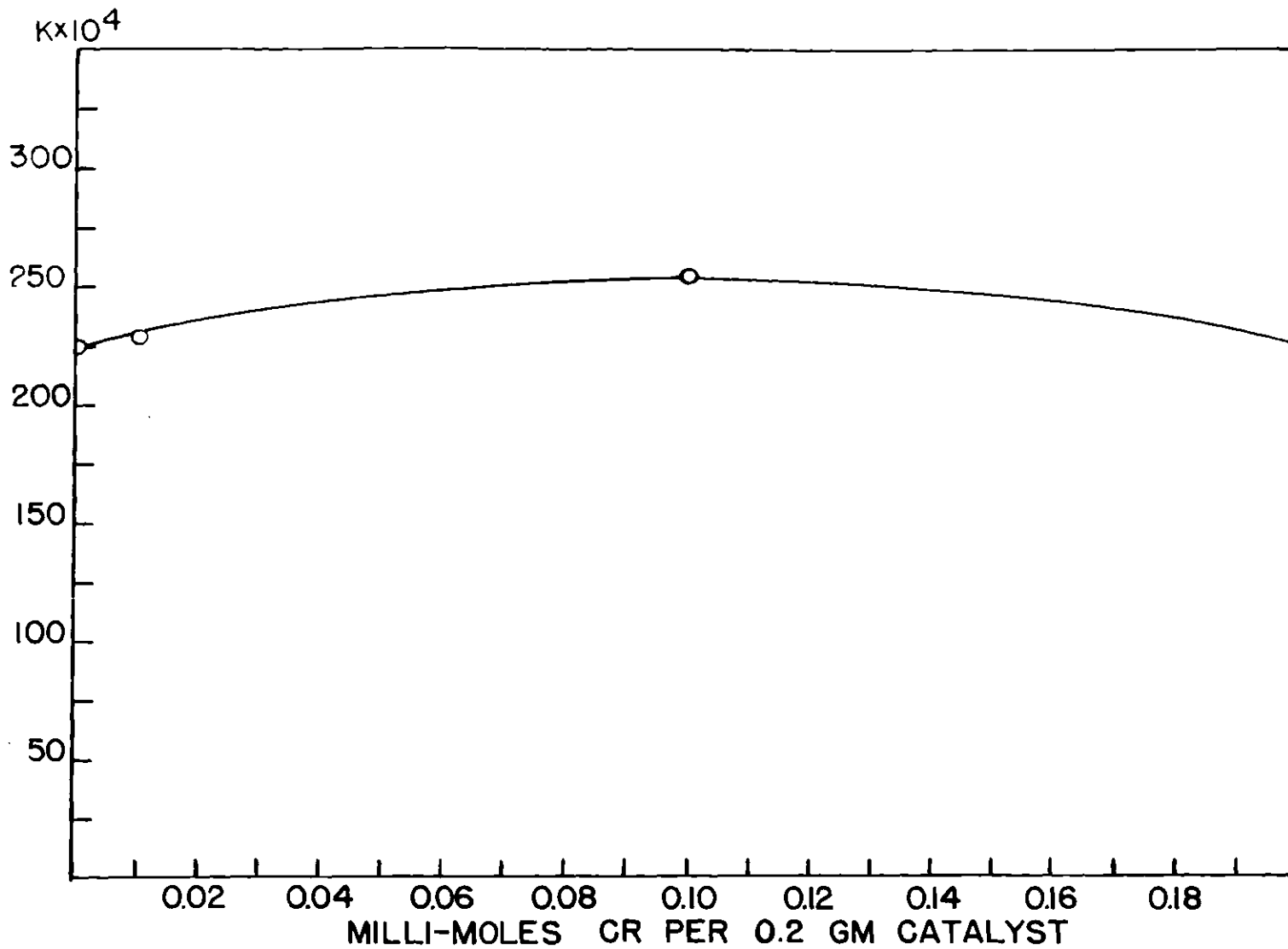
GRAPH IV
EFFECT OF NICKEL



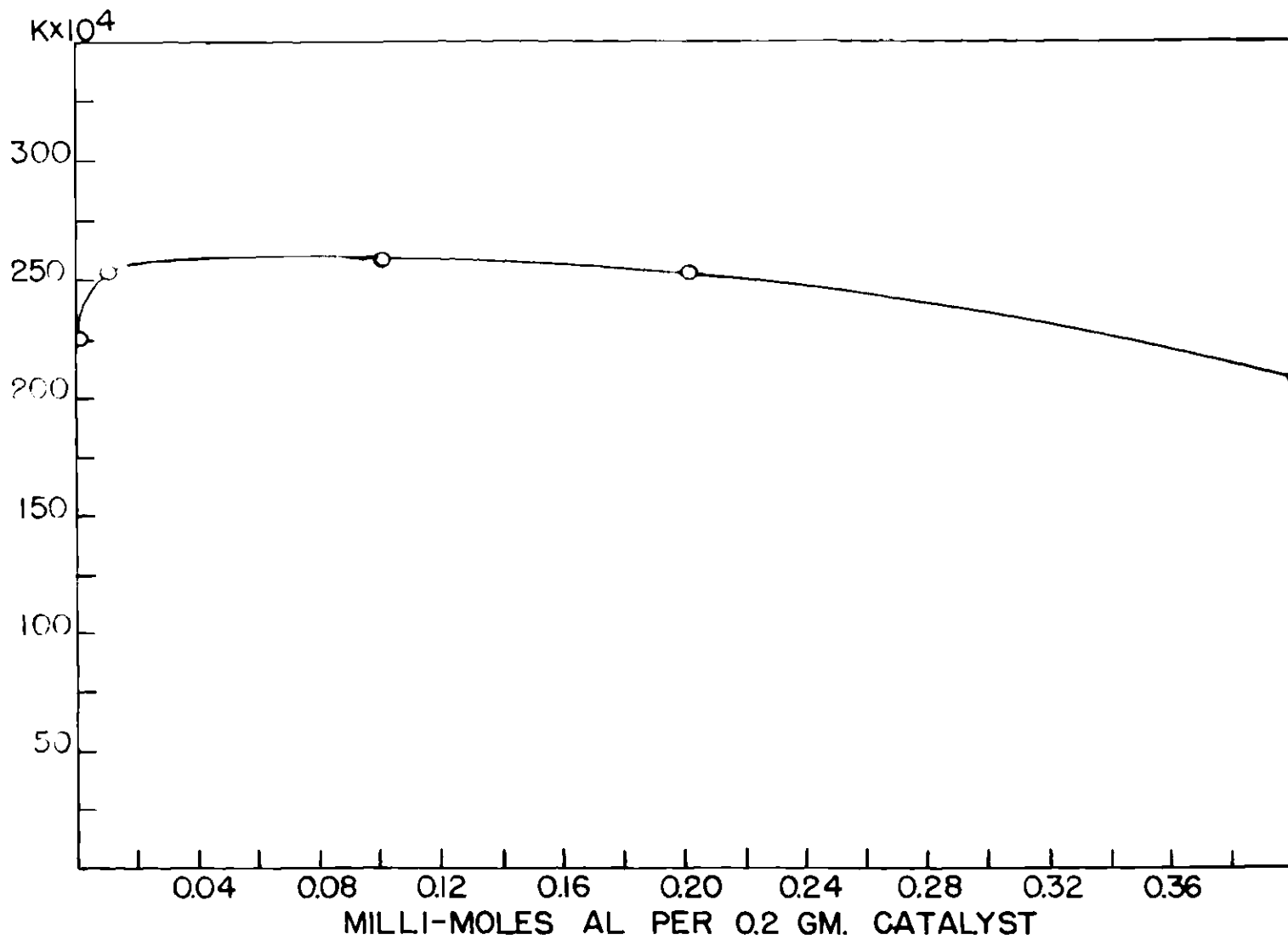
GRAPH V
EFFECT OF MANGANESE



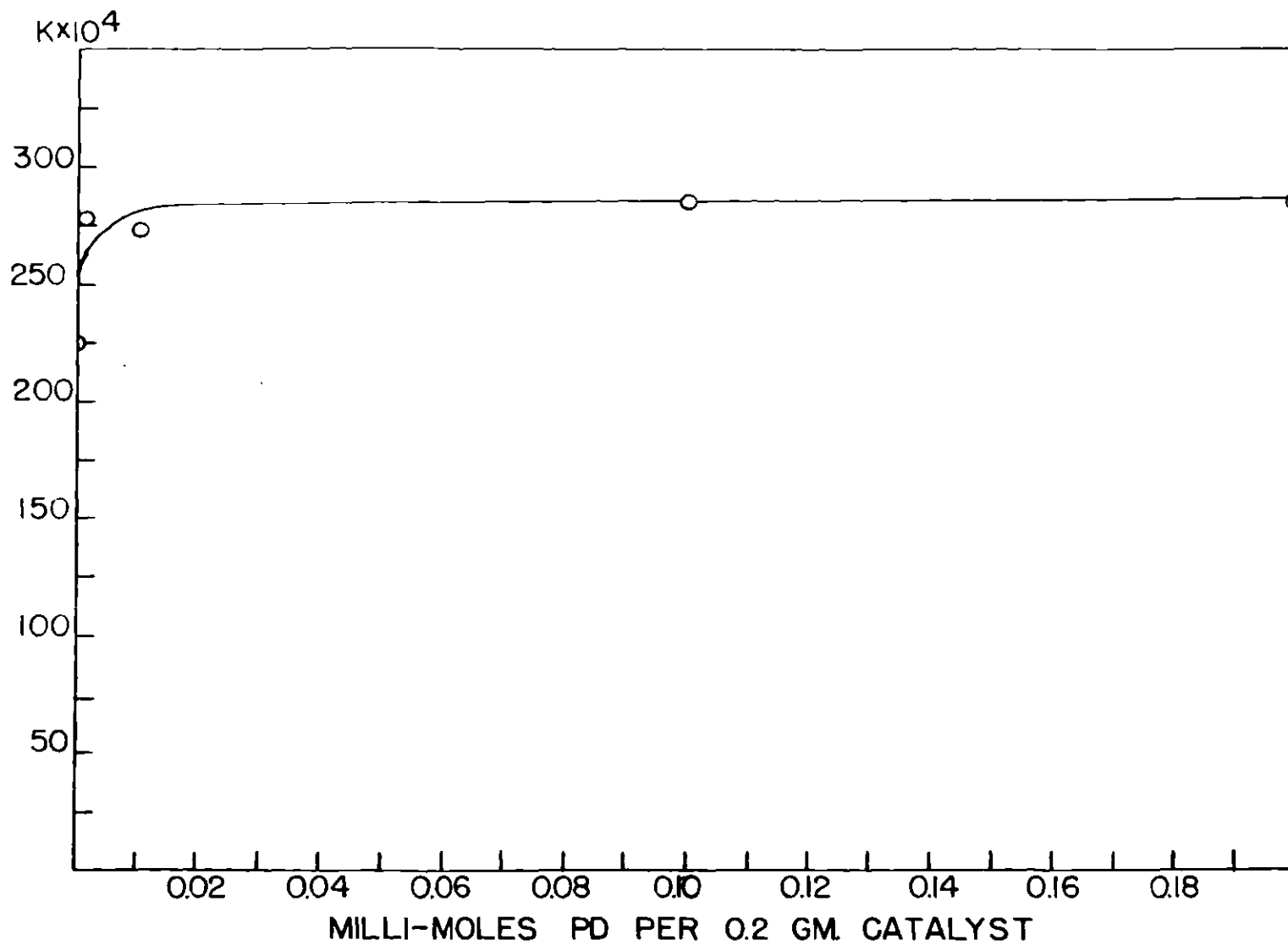
GRAPH VI
EFFECT OF ZINC



GRAPH VII
EFFECT OF CHROMIUM



GRAPH VIII
EFFECT OF ALUMINUM



GRAPH IX
EFFECT OF PALLADIUM

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Adams, R., and B. S. Garvey, Journal of the American Chemical Society, 48: 477-82 (1926).
2. Adams, R., and J. R. Marshall, Journal of the American Chemical Society, 50: 1970 (1928).
3. Adams, R., and R. L. Shriner, Journal of the American Chemical Society, 45: 2171-9 (1923).
4. Adams, R., V. Voorhees, and R. L. Shriner, Organic Synthesis, Collective Volume I. New York: John Wiley and Sons, Ed. 2, 1944. 463-70 pp.
5. Anderson, V. G., Chemical Engineering and Mining Review, 15: 365-9 (1923).
6. Bancroft, W. D., The Journal of Industrial and Engineering Chemistry, 14: 326-31, 14: 44-7, 545-8, 642-6 (1922).
7. Berkman, S., J. C. Morrell, and G. Egloff, Catalysis. New York: Reinhold Publishing Corporation, 1940.
8. Born, M., and J. Franck, Göttingen Nachrichten, II: 77 (1930).
9. Boswell, M. C., Proceedings of the Royal Society of Canada, 16: III (1922).
10. Boswell, M. C., and C. H. Bailey, The Journal of Physical Chemistry, 29: 679-92 (1925).
11. Boswell, M. C., and R. R. McLaughlin, Transactions of the Royal Society of Canada, 17: III (1923).
12. Brown, J. H., H. W. Durnad, and C. S. Marvel, Journal of the American Chemical Society, 58: 1594-96 (1936).
13. Carothers, W. H., and R. Adams, Journal of the American Chemical Society, 45: 1071-86 (1923).
14. _____, Journal of the American Chemical Society, 46: 1675-83 (1924).
15. _____, Journal of the American Chemical Society, 47: 1047-63 (1925).
16. Cox, E. F., Senior Problem, Georgia Institute of Technology, Atlanta, Georgia (1949).

17. Dowden, D. A., Research (London), 1, 239-40 (1948).
18. Dupont, G., and P. Piganiol, Bulletin de la société chimique de France, 6: 322-31 (1939).
19. Eley, D. D., Quarterly Reviews, 3: No. 3, 209-25 (1949).
20. Reid, E. E., Journal of Industrial and Engineering Chemistry, 14: 838-9 (1922).
21. Ephriam, F., Inorganic Chemistry. New York: Nordeman Publishing Company, 1943. 694-700 pp.
22. Emmet, P. H., Colloid Chemistry, 6: 214-42 (1946).
23. Faillebin, M., Comptes rendus hebdomadaires des séances de l'academie des sciences, 175: 1077-9 (1922).
24. _____, Comptes rendus hebdomadaires des séances de l'académie des sciences, 177: 118-20 (1923).
25. _____, Annales de chimie, 4: 156-82, 410-96 (1925).
26. _____, Comptes rendus hebdomadaires des séances de l'académie des sciences, 182: 138-40 (1926).
27. Fuzek, J. F., and H. A. Smith, Journal of the American Chemical Society, 70: 3743 (1948).
28. Glasstone, S., Textbook of Physical Chemistry. New York: D. Van Nostrand Company, Ed. 1, 1940. 1026, 1068 pp.
29. Griffith, R. H., The Mechanism of Contact Catalysis. London: Oxford University Press, 1936.
30. Hamilton, T. S., and R. Adams, Journal of the American Chemical Society, 50: 2260-63 (1928).
31. Heckel, H., and R. Adams, Journal of the American Chemical Society, 47: 1712 (1925).
32. Hiers, G. S., and R. Adams, Berichte der deutschen chemischen Gesellschaft, 59B: 162-70 (1926).
33. Juliard, A., and Cl. Herbo, Bulletin de la société chimique de Belgique, 47: 717-69 (1938).
34. Kaufmann, W. E., and R. Adams, Journal of the American Chemical Society, 45: 3029-44 (1923).

35. Kodji, Suzuki, The Chemical News and Journal of Industrial Science, 139: 153 (1929).
36. Korozynski, A., Bulletin de la société chimique de France, 29: 283-90 (1921).
37. Lohse, H. W., Catalytic Chemistry. New York: Chemical Publishing Company, Incorporated, 1945.
38. Maxted, E. B., The Industrial Chemist and Chemical Manufacturer, 1: 449-52 (1925).
39. _____, Journal of the Chemical Society, 117: 1501-6 (1920).
40. _____, Journal of the Chemical Society, 119: 225-33 (1921).
41. _____, Journal of the Chemical Society, 127: 73-7 (1925).
42. _____, Journal of the Chemical Society, 1945: 205.
43. Maxted, E. B., and A. Marsden, Journal of the Chemical Society, 1940: 469-74.
44. Maxted, E. B., and R. W. D. Morrish, Journal of the Chemical Society, 1940: 252-6.
45. Maxted, E. B., and V. Stone, Journal of the Chemical Society, 1934, 26-9.
46. National Research Council, Twelfth Report of the Committee on Catalysis. New York: John Wiley and Sons, Incorporated, 1940.
47. Nyrop, J. E., Chemistry and Industry, 50: 752-5 (1931).
48. Patel, C. K., Journal of the Indian Institute of Science, 7: 197-204 (1924).
49. Pease, R. N., and H. S. Taylor, The Journal of Physical Chemistry, 24: 241-47 (1920).
50. Pickles, A., Chemical Age (London), 7: 232-3 (1922).
51. Pierce, J. S., and R. Adams, Journal of the American Chemical Society, 47: 1098 (1925).
52. Rideal, E. K., Chemistry and Industry, 62: 335-38 (1943).
53. Russell, W. W., The Journal of Chemical Education, 22: 163-8 (1945).
54. Schmidt, O., Chemical Reviews, 12: 363-417 (1933).

55. Schwab, G. M., Catalysis. New York: D. Van Nostrand Company, 1937.
56. Short, W. F., Journal of the Society of Chemical Industry, 55:
11T (1936).
57. Shriner, R. L., and R. Adams, Journal of the American Chemical Society, 46: 1683-93 (1924).
58. Smith, H. A., D. M. Alderman, and F. W. Nadig, Journal of the American Chemical Society, 67: 272 (1945).
59. Smith, H. A., and H. T. Meriwether, Journal of the American Chemical Society, 71: 413 (1949).
60. Smith, H. A., and E. F. H. Pennekamp, Journal of the American Chemical Society, 67: 276 (1945).
61. Smith, H. A., and J. A. Stanfield, Journal of the American Chemical Society, 71: 81 (1949).
62. Trimble, A. T., Jr., Master's Thesis, Georgia Institute of Technology, Atlanta, Georgia (1949).
63. Tuley, W. F., and R. Adams, Journal of the American Chemical Society, 47, 3061-8 (1925).
64. Voorhees, V., and R. Adams, Journal of the American Chemical Society, 44: 1397-405 (1922).