May 23, 1950

To the Committee on Graduate Study:

I am submitting to you a thesis written by Norma Connell Bowen entitled "Rhenium and Rhenium-Nickel Alloys as Hydrogenation Catalysts." I recommend that it be accepted for eighteen quarter hours credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

A. D. McLaren
Major Professor

We have read this thesis and recommend its acceptance:

Wm. J. Smith, Jr.

Geo. K. Schweitzer

Accepted for the Committee

E. G. Wates
Dean of the Graduate School

RHENIUM AND RHENIUM-NICKEL ALLOYS AS HYDROGENATION CATALYSTS

A THESIS

Submitted to
The Committee on Graduate Study
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the Degree of
Master of Science

---

by

Norma Connell Bowen

June, 1950

ACKNOWLEDGEMENT

The author wishes to express her sincere appreciation to Dr. A. D. Melaven for the guidance and encouragement he has given in the direction of this research; to Dr. H. A. Smith for the use of the Navy Laboratory hydrogenation apparatus; and to Mr. William Bedoit for his advice on the use of this apparatus.

274158

TABLE OF CONTENTS

CHAPTER		PAGE
I.	INTRODUCTION AND HISTORY.	1
II.	EXPERIMENTAL.	7
	A. Preparation of Catalysts.	7
	1. Rhenium from Potassium Perrhenate . .	7
	2. Rhenium-Nickel Alloys	8
	a. From Reduction of Nickel Perrhenate.	8
	b. From Treatment with Carbon Monoxide.	10
	3. Electrolytic Rhenium.	11
	4. Raney Nickel.	12
	B. Preparation of Nitrobenzene	12
	C. Preparation of Methanol	12
	D. Source of Gases	13
	E. Hydrogenation Apparatus	13
	F. Procedure	14
III.	RESULTS	16
	A. Hydrogenation in the Presence of Raney Nickel.	16
	B. Hydrogenation in the Presence of Rhenium	17
	1. Rhenium from Potassium Perrhenate by Hydrogen Reduction	17
	2. Electrolytic Rhenium.	21

TABLE OF CONTENTS (CONTINUED)

CHAPTER PAGE

C. Hydrogenation in the Presence of Rhenium-Nickel Alloys. 21
1. Alloy Prepared at 150-200° 21
2. Alloy Prepared at 250-300° 25
3. Alloy Prepared at 350-400° 25
4. Alloy Prepared at 450-500° 32
D. Discussion 32
IV. SUMMARY 39
BIBLIOGRAPHY. 42
APPENDIXES. 45
I. ADDITIONAL DATA 46
II. CALCULATION OF PER CENT CONVERSION. 63
III. NICKEL ANALYSES 65

LIST OF TABLES

TABLE		PAGE
I.	Hydrogenation of Nitrobenzene Using Raney Nickel.	18
II.	Hydrogenation of Nitrobenzene Using Rhenium from Potassium Perrhenate	19
III.	Hydrogenation of Nitrobenzene Using Electrolytic Rhenium.	22
IV.	Hydrogenation of Nitrobenzene Using the Rhenium-Nickel Alloy Prepared at 150-200° . .	24
V.	Hydrogenation of Nitrobenzene Using Carbon Monoxide Treated 150-200° Rhenium-Nickel Alloy	26
VI.	Hydrogenation of Nitrobenzene Using the Rhenium-Nickel Alloy Prepared at 250-300° . .	28
VII.	Hydrogenation of Nitrobenzene Using Carbon Monoxide Treated 250-300° Rhenium-Nickel Alloy	29
VIII.	Hydrogenation of Nitrobenzene Using the Rhenium-Nickel Alloy Prepared at 350-400° . .	31
IX.	Hydrogenation of Nitrobenzene Using the Carbon Monoxide Treated 350-400° Rhenium-Nickel Alloy.	33

LIST OF TABLES (CONTINUED)

TABLE		PAGE
X.	Hydrogenation of Nitrobenzene Using the Carbon Monoxide Treated 450-500° Rhenium-Nickel Alloy.	35
XI.	Hydrogenation of Nitrobenzene Over Rhenium-Nickel Alloys	37
XII.	Data for Rhenium and Rhenium-Nickel Alloys as Catalysts for the Hydrogenation of Nitrobenzene.	40
XIII.	Hydrogenation of Nitrobenzene at 28° Using Rhenium Metal from Hydrogen Reduction of Potassium Perrhenate.	47
XIV.	Hydrogenation of Cyclohexene at 28° Using Rhenium from Hydrogen Reduction of Potassium Perrhenate.	50
XV.	Hydrogenation of Styrene at 28° Using Rhenium from Hydrogen Reduction of Potassium Perrhenate.	51
XVI.	Hydrogenation of Nitrobenzene Using Rhenium from Hydrogen Reduction of Potassium Perrhenate.	53
XVII.	Hydrogenation of Nitrobenzene Using a Rhenium-Nickel Alloy Prepared by Hydrogen Reduction of Nickel Perrhenate at 250-300?	55

LIST OF TABLES (CONTINUED)

TABLE		PAGE
XVIII.	Hydrogenation of Nitrobenzene Using a Rhenium-Nickel Alloy Prepared by Hydrogen Reduction of Nickel Perrhenate at 250-300°.	56
XIX.	Hydrogenation of Nitrobenzene Using a Rhenium-Nickel Alloy Prepared at 350-400°.	59
XX.	Hydrogenation of Nitrobenzene Using a Rhenium-Nickel Alloy Prepared at 150-200°.	61

LIST OF FIGURES

FIGURE		PAGE
1.	Hydrogenation of Nitrobenzene at 40-43°. . . .	20
2.	Hydrogenation of Nitrobenzene at 40-43°. . . .	23
3.	Hydrogenation of Nitrobenzene at 40-43°. . . .	27
4.	Hydrogenation of Nitrobenzene at 40-43°. . . .	30
5.	Hydrogenation of Nitrobenzene at 40-43°. . . .	34
6.	Hydrogenation of Nitrobenzene at 40-43°. . . .	36
7.	Hydrogenation of Nitrobenzene at 28° Using Rhenium from Hydrogen Reduction of Potassium Perrhenate	48
8.	Hydrogenation of Styrene and Cyclohexene at 28° Using Rhenium from Hydrogen Reduction of Potassium Perrhenate.	52
9.	Hydrogenation of Nitrobenzene at 36° Using Rhenium from Hydrogen Reduction of Potassium Perrhenate	54
10.	Hydrogenation of Nitrobenzene at 36° Using Rhenium-Nickel Alloys Prepared by Hydrogen Reduction of Nickel Perrhenate at 250-300° .	57
11.	Hydrogenation of Nitrobenzene at 40-43° Using a Rhenium-Nickel Alloy Prepared by Hydrogen Reduction of Nickel Perrhenate at 350-400° .	60

LIST OF FIGURES (CONTINUED)

FIGURE PAGE

12. Hydrogenation of Nitrobenzene at 40-43° Using a Rhenium-Nickel Alloy Prepared by Hydrogen Reduction of Nickel Perrhenate at 150-200°. . . 62

CHAPTER I

INTRODUCTION AND HISTORY

The use of the element rhenium and its compounds for catalytic work is suggested by the position of the metal in the periodic table. Very little experimental work has been done, however, in the field of rhenium catalysis. Compounds of rhenium, as well as the metallic form, both supported and unsupported have been tried for oxidation, dehydration, dehydrogenation and hydrogenation reactions.

In some of the earliest catalytic work, Siemens and Halske[1] obtained a patent for the use of rhenium and rhenium heptoxide as oxidation catalysts for the conversion of sulfur dioxide to trioxide, aniline to aniline black, and also in some chlorination processes. A patent was granted the Noddacks[2] for the use of rhenium oxide in a hydrochloric acid solution or the metal with a carrier for the sulfur dioxide to trioxide, sulfite to sulfate, nitrite to nitrate, and aniline to aniline black conversions. Siebert[3] used rhenium and some of its alloys to catalyze the oxidation of

---

(1) Siemens and Halske, A. G., Fr. Patent 682,446 (1929); (C. A., 24, 4362).

(2) Siemens and Halske, Noddack, W. and I., Brit. Patent 346,652 (1929); (C. A., 26, 569).

(3) Siebert, G., Fr. Patent 378,479 (1932); (C. A., 27, 1723).

ammonia, and Zenghelis and Stathis[4] found that the metal strongly catalyzed the synthesis of ammonia. They obtained a good yield of ammonia by bubbling hydrogen through a solution of ammonium chloride and sodium nitrite and passing the resultant mixture of nitrogen and hydrogen over the catalyst. They also found that the effectiveness of the catalyst was increased by the addition of iron.

Anisimov, Platonov and Tur[5] reported the dehydration of cyclohexanol vapor when it was passed over finely divided rhenium. Platonov and Tomilov[6] obtained 100 per cent decomposition of formic acid into carbon dioxide and water at 230° when they used metallic rhenium for the catalyst. The decomposition of ethanol was also studied. It was found that addition of hydrogen sulfide or arsenious oxide to the catalyst increased its activity. Platonov, Tomilov and Tur[7] found that "complete decomposition" of methanol would take place in the presence of rhenium, although in this case the addition of hydrogen sulfide or arsenious oxide would arrest

---

(4) Zenghelis, C., and Stathis, El., Osterr. Chem. Ztg., 40, 80-81 (1937); (C. A., 31, 4777).

(5) Anisimov, S. B., Platonov, M. S., and Tur, C. G., J. Gen. Chem. U. S. S. R., 7, 2895-8 (1937); (C. A., 32, 5383).

(6) Platonov, M. S., and Tomilov, V. I., J. Gen. Chem. U. S. S. R., 7, 776-777 (1937); (C. A., 31, 6189).

(7) Platonov, M. S., Tomilov, V. I., and Tur, E. V., J. Gen. Chem. U. S. S. R., 7, 1803-1804 (1937); (C. A., 31, 8341).

the reaction at the formaldehyde stage. Platonov[8] later reported that rhenium(IV) sulfide would catalyze the dehydrogenation of methyl and ethyl alcohol to the corresponding aldehydes and of isopropyl alcohol to acetone. Platonov, Anisimov and Krasheninnikova[9] studied the dehydrogenation of the propyl alcohols and found that rhenium on a ceramic carrier gave a better yield than copper under similar conditions. Platonov and Anisimov[10] reported that butyl alcohol gave the aldehyde very readily and iso-butyl alcohol gave methyl-ethyl ketone when rhenium was used as a catalyst. Platonov[11] studied the dehydrogenation of iso-amyl alcohol over rhenium and reported that the small amount of carbon monoxide and unsaturated hydrocarbons obtained indicated that some hydrogenation was taking place by the hydrogen split off from the alcohol in the presence of the catalyst. Rhenium appears to be a fairly good dehydrogenation catalyst because there are few side reactions. A patent for the preparation and use of rhenium in this connection was granted to Platonov and Anisimov.[12]

---

(8) Platonov, M. S., J. Gen. Chem. U. S. S. R., 11, 683-685 (1941); (C. A., 36, 3976).

(9) Platonov, M. S., Anisimov, S. B., and Krasheninnikova, V. M., Ber. 69B, 1050-1053 (1936); (C. A., 30, 4812).

(10) Platonov, M. S., and Anisimov, S. B., J. Gen. Chem. U. S. S. R., 7, 1360-1363 (1937); (C. A., 31, 1937).

(11) Platonov, M. S., J. Gen. Chem. U. S. S. R., 11, 590-591 (1941); (C. A., 35, 6924).

(12) Platonov, M. S., and Anisimov, S. B., Russ. Patent 52,780 (1938); (C. A., 34, 5467).

Zenghelis and Stathis[13,14] used a colloidal rhenium preparation in the decomposition of hydrogen peroxide and in the hydrogenation of maleic acid. A patent granted the N. V. DeBataafsche Petroleum Maatschappij[15,16] describes the use of colloidal rhenium or the sulfide on suitable carriers for hydrogenation, desulfurization, and like treatments of carbonaceous materials. The International Hydrogenation Patents Company[17] was granted a patent covering the use of colloidal rhenium for the production of antiknock fuels.

Tropsch and Kassler[18,19] reported the use of rhenium and rhenium-copper catalysts in the reduction of carbon monoxide to methane and ethylene to ethane and stated that the rhenium-copper catalyst seemed to retain its activity for a much longer time than pure rhenium. Rhenium trioxide

---

(13) Zenghelis, C., and Stathis, K., Atti X° congr. intern. chim., 2, 821-824 (1938); (C. A., 33, 8081).

(14) Zenghelis, C., and Stathis, C., Kolloid Z., 90, 129 (1940).

(15) N. V. DeBataafsche Petroleum Maatschappij, Brit. Patent 358,180 (1930); (C. A., 26, 4924).

(16) N. V. DeBataafsche Petroleum Maatschappij, Ger. Patent 693,707 (1940); (C. A., 41, 4941).

(17) International Hydrogenation Patents Company, Ltd., Fr. Patent 761,632 (1934); (C. A., 28, 4210).

(18) Tropsch, H., and Kassler, R., Ber. 63B, 2149-2151 (1930); (C. A., 25, 22).

(19) Tropsch, H., and Kassler, R., Mitt Kohlenforsch, Inst. Prag., 13-15 (1931); (Chem. Zentr., 2, 2420 (1932).

was used as a catalyst in the hydrogenation of acetone by Cabbage[20], who reported that it was comparable to copper chromite in this reaction. Platonov, Anisimov, and Krasheninnikova[21,22] found that metallic rhenium was a relatively weak catalyst for the hydrogenation of maleic acid and cyclohexene, but they also found that nitrobenzene was appreciably reduced to aniline around 250°. Supported copper or rhenium-copper catalysts were said to be as effective as the supported rhenium for these reactions. Rhenium, however, is not considered a very practical oxidation catalyst at temperatures over 100° due to the formation of volatile oxides.

The reported increase in the activity of rhenium as a catalyst upon the addition of copper and iron, in certain catalytic reactions, suggested the possibility that other metals might be as effective. Nickel has become very important in catalysis in recent years and it was thought that perhaps the addition of nickel to rhenium might give a

---

(20) Cabbage, A., "Catalytic Hydrogenation over Rhenium and the Production of Rhenium Metal," Master's Thesis, University of Tennessee, 1948, p. 1-35.

(21) Platonov, M. S., Anisimov, S. B., and Krasheninnikova, V. M., J. Gen. Chem. U. S. S. R., 5, 1059-1065 (1935); (C. A., 30, 944).

(22) Platonov, M. S., Anisimov, S. B., and Krasheninnikova, V. M., Ber. 68B, 761-765 (1935); (C. A., 29, 5005).

catalyst of greater activity than either of the single elements. It was the purpose of this research to prepare some rhenium-nickel alloys at various temperatures and compare their catalytic properties with rhenium and Raney nickel in hydrogenation.

CHAPTER II

EXPERIMENTAL

A. Preparation of Catalysts

1. Rhenium from Potassium Perrhenate

Rhenium was prepared using the standard method developed in this laboratory for obtaining the metal commercially.[1] This consisted of placing 50 g. of finely pulverized potassium perrhenate in a silver tube and inserting the tube and contents into a steel hydrogenation bomb. The bomb was filled with hydrogen to 1000 p.s.i. pressure, placed in a rocker type furnace and electrically heated to 500°. Reduction begins around 300° as represented by the following equation:

$$2KReO_4 + 7H_2 \longrightarrow 6H_2O + 2KOH + 2Re$$

After heating at 500° for one to two hours, the bomb was refilled with hydrogen at 700 p.s.i. pressure and left in the shaker overnight. After cooling to room temperature, the product was removed from the silver tube and washed five times with hot water to remove the potassium hydroxide, using a few drops of hydrochloric acid in the water after the third washing to prevent peptization of the metal. This was

---

(1) Cabbage, A., "Catalytic Hydrogenation over Rhenium and the Production of Rhenium Metal," Master's Thesis, University of Tennessee, 1948, p. 36-56.

followed by two washings with ethanol before the rhenium was placed in vacuo for drying.

Rhenium obtained from three such charges was pulverized and returned to the bomb for a second and a third overnight reduction at 500° and 700 p.s.i. pressure. The product obtained each time was washed and dried in the manner described above.

Approximately 60 g. of rhenium from the third overnight reduction was evenly distributed in a long silver tube which then was inserted into a four foot section of 35 mm. Vycor tubing. The tubes were placed in a high temperature furnace, and hydrogen dried by bubbling through sulfuric acid was passed through the system at 500° to dry the rhenium and to reduce any oxide which might have formed during the transfer and weighing of the metal. After this preliminary reduction, nitrogen was substituted for two hours to remove excess hydrogen. The system was evacuated and then refilled with nitrogen. The rhenium was transferred to a dry bottle as quickly as possible. During the transfer some oxidation took place, while the metal was exposed to air, in spite of the precautions taken.

2. Rhenium-Nickel Alloys

a. From reduction of nickel perrhenate. A weighed sample of rhenium was placed in a quartz boat for combustion. A Pyrex tube containing the boat was placed in a tube fur-

nace and heated to 300° in a stream of dry oxygen. Rapid oxidation of the rhenium took place between 275° and 300°, and the yellow oxide, accompanied by dense white fumes which have been reported previously as rhenium tetroxide[2], was collected and resublimed to obtain the yellow crystalline platelets of rhenium heptoxide. This oxide was dissolved in distilled water to obtain perrhenic acid.

Approximately 10 g. of Baker's C. P. nickel(II) carbonate was digested in 100 ml. of water at 50° for fifteen minutes. Perrhenic acid was added to the carbonate slowly with stirring, and the solution was left for fifteen hours to insure complete reaction before it was filtered to remove excess carbonate.

The filtrate obtained was placed on a steam bath and evaporated to the point of incipient crystallization before putting it in a refrigerator to cool. After cooling, the supernatant liquid was removed from the crystals. These crystals were dissolved and recrystallized twice from distilled water. The mother liquors from all three crystallizations were combined and further evaporated to obtain the remainder of the nickel perrhenate tetrahydrate. This salt was transferred to a watch glass and placed in an oven at

---

(2) Noddack, I. and W., Naturwissenschaften, 17, 93-4 (1939); (C. A., 23, 1833).

110° to obtain the dehydrated nickel perrhenate.[3]

Rhenium-nickel alloys were prepared by reducing dehydrated nickel perrhenate with hydrogen at temperatures of 150-200°, 250-300°, 350-400°, and 450-500°.

Portions of the salt were placed in a quartz boat which was inserted into a pyrex tube. Hydrogen gas, dried by bubbling through sulfuric acid, was passed over the sample for twenty-four to thirty-six hours depending upon the reduction temperature. After cooling to room temperature in an atmosphere of hydrogen, the samples were covered with methanol. This was accomplished by means of a piece of glass tubing inserted through the stopper at one end of the pyrex tube. The end outside the system was flanged above a right angle bend to facilitate the introduction of methanol and was closed during the reduction by means of rubber tubing and pinch clamp. The end of the glass tubing inside the system was drawn to a curved tip over the quartz boat. When the reduction was complete and the system had cooled, the rubber tubing was removed from the flanged end and methanol introduced immediately. The hydrogen flow was decreased, but not stopped, during this time.

b. From treatment with carbon monoxide. It was hoped that advantage could be taken of the following reaction for

---

(3) Smith, W. T., and Maxwell, G. E., J. Am. Chem. Soc., 71, 578-580 (1949).

the removal of nickel from the rhenium-nickel alloy:

$$2Re\text{-}Ni + 4CO \longrightarrow 2Re + Ni(CO)_4$$

A portion of each alloy was treated separately by placing it in a quartz boat, in the same system used for its preparation, and removing the methanol with hydrogen. Carbon monoxide was substituted for hydrogen for approximately forty-five hours at 50° in order to remove as much of the nickel as possible. At the end of this time, hydrogen was passed through the system to remove any excess carbon monoxide, and the alloys were covered with methanol, in the same manner as the original alloys.

3. Electrolytic Rhenium

The electrolytic rhenium was deposited from a solution which originally contained 50 g. of potassium perrhenate and 22 g. of sulfuric acid in a total volume of 2 l. The temperature of this solution during electrolysis varied from room temperature to 85° and the potential across the platinum electrodes was approximately 8 v. The current density was kept constant at 10 amp. per $dm.^2$ After deposition was complete, the platinum cathode with the deposited rhenium was removed from the solution and washed thoroughly with distilled water. The metallic rhenium was removed from the electrode, placed in a sintered-glass funnel, and washed eight times with hot distilled water. This was followed by three washings with absolute ethanol. Drying was completed in a

vacuum desiccator.

4. Raney Nickel

Raney nickel, for use as a standard in this research, was obtained from Mr. William C. Bedoit of the Office of Naval Research Fellowship Laboratory. It was prepared by the method outlined in Organic Syntheses[4] with some modifications.[5]

B. Preparation of Nitrobenzene

Nitrobenzene for hydrogenation was distilled from a 13 ft. 15 mm. Vigreaux column, equipped with a magnetic take off still head, at 109.4-109.5°/39 mm. Distillation of 100 ml. of the compound was carried out over a period of seven hours. The refractive index of nitrobenzene obtained was n_D^{27} 1.5492.

C. Preparation of Methanol

Methanol, for use as a solvent, was purified by distillation at atmospheric pressure and 64.5° from a 4 ft. 10 mm. column packed with glass helices and equipped with a

---

(4) Organic Syntheses, 21, 15 (1941).

(5) Bedoit, W. C., "Studies of Raney Nickel Catalysts," Master's Thesis, University of Tennessee, 1948, Appendix.

total condensation variable take off head. A reflux ratio of 15 to 1 was used.

D. Source of Gases

The hydrogen, oxygen, nitrogen and carbon monoxide gas used in these studies was of commercial grade. Each gas was taken directly from the cylinder and, with the exception of the hydrogen used in the hydrogenation runs, was dried by bubbling through sulfuric acid. Further purification was not attempted.

E. Hydrogenation Apparatus

Hydrogenations were performed in a high-pressure bomb and gauge assembly similar to that described by Fuzek[6], using a 50 ml. steel bomb (Navy cold-tested to 15000 p.s.i. pressure) with a bronze Duragauge. The bomb was placed in a rocker type furnace and electrically heated. The temperature was read from a Weston metal thermometer inserted into a well in the bottom of the bomb.

All low pressure work (see Appendix I) was performed in a standard low pressure hydrogenation apparatus made by Parr Instrument Company of Moline, Illinois.

---

(6) Fuzek, John F., "The Kinetics of Catalytic Hydrogenation of Terpenes," Doctoral Dissertation, University of Tennessee, 1947, p. 32.

F. Procedure

In this investigation, high pressure catalysis at 40-43° and approximately 800 p.s.i. pressure was used. Preliminary work at lower pressures, lower temperatures and with compounds other than nitrobenzene will be discussed in Appendix I.

Five ml. of methanol was pipetted directly into the steel bomb, which had been washed previously with methanol. Approximately 0.5 g. of the catalyst, wet with methanol, was transferred to the bomb. (Accurate weighing of the catalyst would have involved exposing it to air.) A second 5 ml. of methanol was pipetted into the bomb, making 10 ml. of solvent. One milliliter of nitrobenzene was added to the solvent, the bomb closed, and the pressure gauge connected. Hydrogen was added to approximately 800 p.s.i. pressure, and the bomb placed in the shaker furnace. The temperature was raised to 38°. Time, pressure, and temperature readings were recorded, starting at the time the bomb was put in motion. The temperature was kept in the range of 40-43°. Heat of reaction, time lag of temperature control, and difficulty encountered in reading the moving thermometer prevented closer regulation of the temperature. The pressure gauge was tapped sharply before each reading to eliminate, as much as possible, the sticking common to commercial gauges.

The shaker was stopped at the end of each run, with

the bomb in the nearly upright position, and allowed to stand in order to test for any hydrogen leaks. If none were found, the solution and catalyst were washed from the bomb with methanol and filtered, using a sintered-glass funnel. The catalyst was washed with methanol and dried for twenty-four hours over calcium chloride before weighing.

CHAPTER III

RESULTS

A. Hydrogenation in the Presence of Raney Nickel

Raney nickel was used as a standard of comparison for determining the effectiveness of rhenium and rhenium-nickel alloy catalysts in the hydrogenation of nitrobenzene in methanol.

It has been found that hydrogenation in the presence of Raney nickel[1] is zero order with respect to the hydrogen acceptor and first order with respect to hydrogen pressure. The integrated expression for a first order reaction is

$$k = 1/t \ln a/a-x = 1/t\ 2.303 \log a/a-x$$

where k represents the velocity constant, a the initial concentration of reacting substance, and a-x the concentration at time t.[2] When a gas is the reactant, the integrated expression for a first order reaction is

$$k = 1/t\ 2.303 \log P_o/P$$

where P_o is the initial pressure and P the pressure at time t.

---

(1) Bedoit, W. C., "Kinetics of the Catalytic Hydrogenation of the Nitre Group on Adams Platinum and Raney Nickel Catalysts," Doctoral Dissertation, University of Tennessee, 1950, p. 134.

(2) Glasstone, S., "Textbook of Physical Chemistry," Second Edition, D. Van Nostrand Company, New York, N. Y., 1946.

From this it can be seen that a plot of log P_o/P versus time t will give a straight line whose slope, when multiplied by 2.303, will be the velocity constant for the reaction. The velocity constants found in this manner were divided by the catalyst weights to obtain the constant per gram of catalyst.

The data for the hydrogenation of nitrobenzene using Raney nickel as a catalyst are given in Table I. A plot of log P_o/P versus t is shown as Curve 1 in Figures 1-6. Calculation of the velocity constant from these data gives a value for k of 198×10^{-4}. Hydrogenation stopped at the end of fifty minutes, as denoted by the break in the curve, with only 61 per cent conversion. The method used for calculating per cent conversion is discussed in Appendix II.

B. Hydrogenation in the Presence of Rhenium

1. Rhenium from Potassium Perrhenate by Hydrogen Reduction

Metallic rhenium, prepared by hydrogen reduction of potassium perrhenate, gave a velocity constant of 16.7×10^{-4} as compared to the value of 198×10^{-4} obtained with Raney nickel under the same conditions. The conversion using rhenium was 66 per cent although it required seven hours as compared to fifty minutes for the 61 per cent conversion with Raney nickel. The data obtained using this sample of rhenium are given in Table II and are plotted as Curve 2 in Figure 1.

TABLE I

HYDROGENATION OF NITROBENZENE USING RANEY NICKEL

Catalyst Weight = 0.272 g.
k = 198 x 10^{-4}
Conversion = 61 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
42	0	810	824	---
42	0.5	800	814	0.0053
42	1.0	796	810	0.0074
42	2.0	790	804	0.0106
42	3.0	782	796	0.0150
42	4.0	778	792	0.0172
42	5.0	772	786	0.0205
42	8.0	760	774	0.0272
42	10.0	751	765	0.0322
42	15.0	730	744	0.0443
42	20.0	711	725	0.0556
42	25.0	693	707	0.0665
42	30.0	674	688	0.0783
42	40.0	638	652	0.1017
42	50.0	635	649	0.1037
42	60.0	635	649	0.1037

TABLE II

HYDROGENATION OF NITROBENZENE USING RHENIUM FROM POTASSIUM PERRHENATE

Catalyst Weight = 0.484 g.
k = 16.7×10^{-4}
Conversion = 66 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
38	0	800	814	---
40	0.5	794	808	0.0032
41	1.0	794	808	0.0032
42	5.0	792	806	0.0043
42	6.0	790	804	0.0053
42	10.0	788	802	0.0064
42	15.0	784	798	0.0086
42	20.0	780	794	0.0108
42	30.0	770	784	0.0163
42	40.0	763	777	0.0202
42	50.0	759	773	0.0224
42	80.0	740	764	0.0275
42	100.0	728	742	0.0392
42	120.0	713	727	0.0491
42	150.0	697	711	0.0587
42	180.0	682	696	0.0680
42	210.0	666	680	0.0781
42	345.0	620	634	0.1085
42	390.0	618	632	0.1099
42	420.0	618	632	0.1099

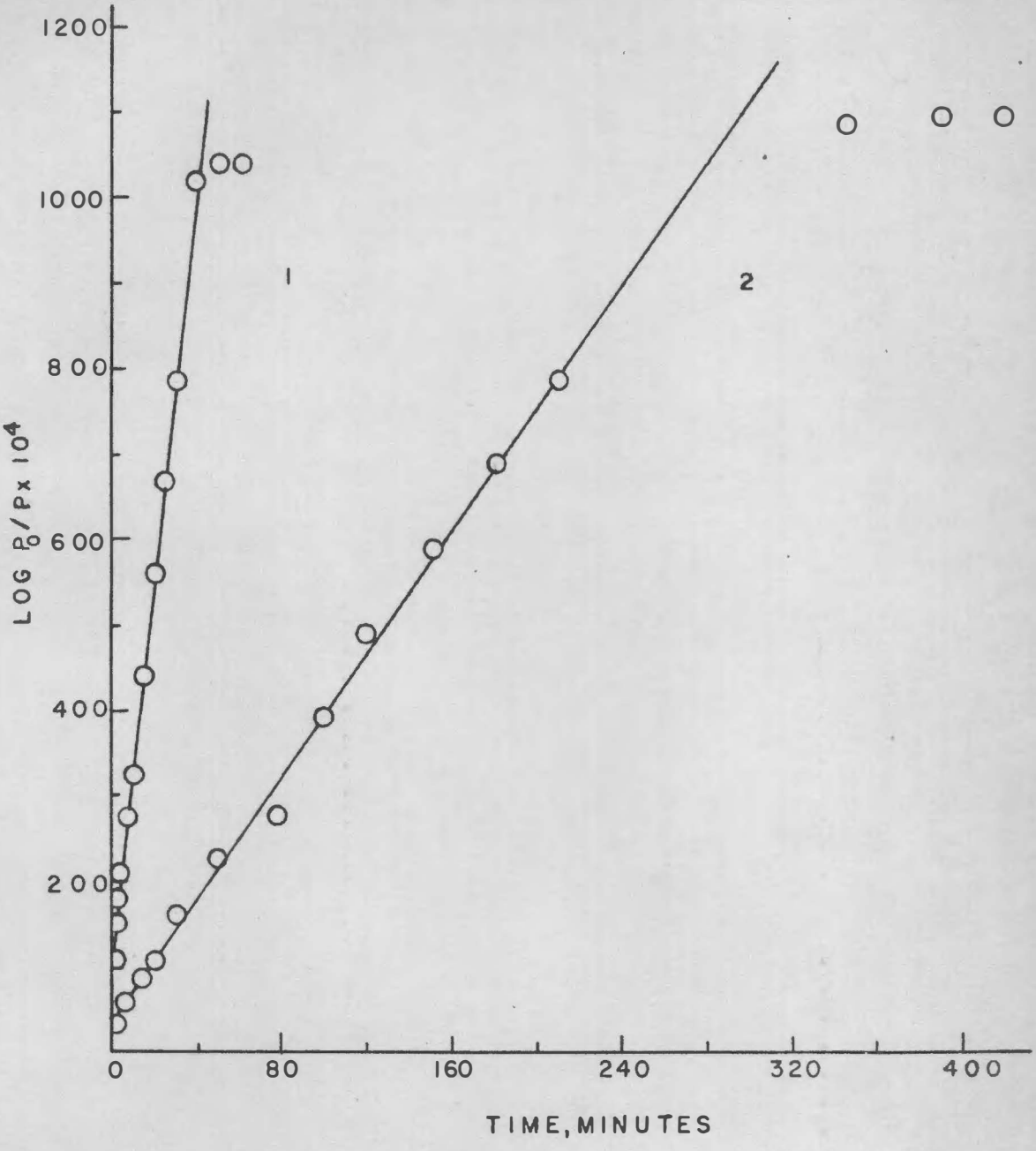

Figure 1. Hydrogenation of nitrobenzene at 40-43°: (1) Raney nickel, k = 198 x 10^{-4}; (2) rhenium from hydrogen reduction of potassium perrhenate, k = 16.7 x 10^{-4}.

2. Electrolytic Rhenium

The velocity constant for the hydrogenation of nitrobenzene using electrolytic rhenium as a catalyst was found to be 10.8×10^{-4}. The data for this reaction are given in Table III and are plotted in Figure 2. Rhenium prepared in this manner was not as effective as that from the hydrogen reduction of potassium perrhenate. Fifty per cent conversion was achieved in the four hours before the catalyst was rendered inactive.

C. Hydrogenation in the Presence of Rhenium-Nickel Alloys

1. Alloy prepared at 150-200°

A sample of rhenium-nickel alloy, reduced from nickel perrhenate at 150-200°, was used as a catalyst in the hydrogenation of nitrobenzene on each of two consecutive days. The velocity constants for these runs checked closely, but a difference in the per cent conversion was found (See Appendix I). Hydrogenation using this alloy immediately after its preparation gave a velocity constant of 12.8×10^{-4} and the reaction was still incomplete at the end of seven and one-half hours. The conversion was 75 per cent. The data for this reaction are shown in Table IV.

After treatment of the alloy with carbon monoxide, the velocity constant for the hydrogenation decreased to 7.15×10^{-4}. A conversion of 34 per cent was effected over

TABLE III

HYDROGENATION OF NITROBENZENE USING ELECTROLYTIC RHENIUM

Catalyst Weight = 0.645 g.
$k = 10.8 \times 10^{-4}$
Conversion = 50 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Absolute	Log P_o/P
34	0	795	809	---
40	10	795	809	---
40	20	780	802	0.0037
40	30	780	794	0.0081
40	40	772	786	0.0125
40	50	763	777	0.0175
40	60	753	767	0.0231
40	70	748	762	0.0259
40	80	742	756	0.0294
40	90	734	748	0.0340
40	100	729	743	0.0369
40	110	724	738	0.0388
40	120	719	733	0.0428
40	130	714	728	0.0458
40	140	709	723	0.0488
40	150	704	718	0.0518
40	160	700	714	0.0542
40	170	697	711	0.0560
40	180	693	707	0.0585
40	190	690	704	0.0603
40	200	687	701	0.0622
40	210	682	696	0.0653
40	220	679	693	0.0672
40	230	676	690	0.0691
40	240	673	687	0.0709
40	250	670	684	0.0728

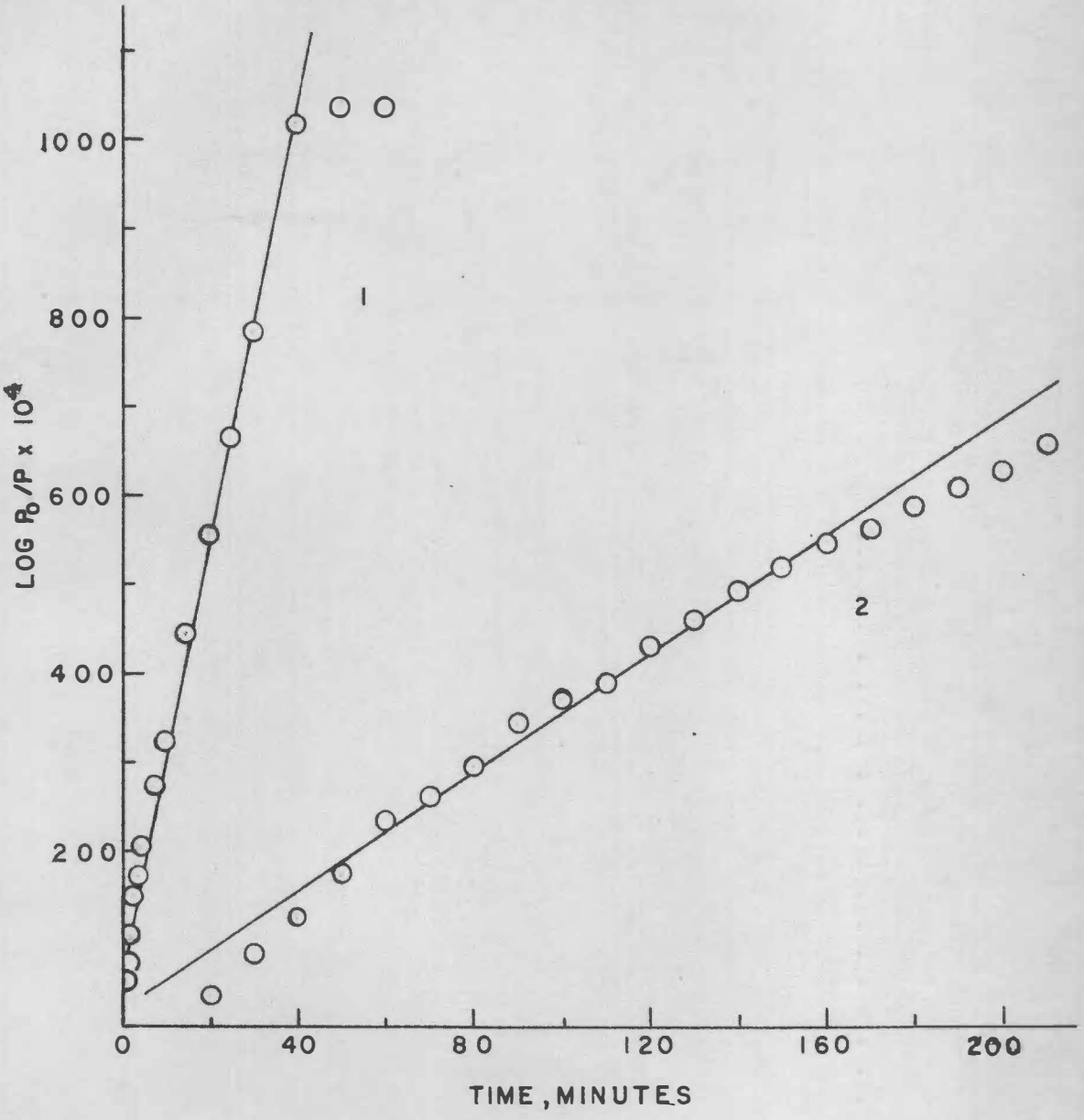

Figure 2. Hydrogenation of nitrobenzene at 40-43°: (1) Raney nickel, $k = 198 \times 10^{-4}$; (2) electrolytic rhenium, $k = 10.8 \times 10^{-4}$.

TABLE IV

HYDROGENATION OF NITROBENZENE USING THE RHENIUM-NICKEL ALLOY PREPARED AT 150-200°

Catalyst Weight = 0.499 g.
k = 12.8×10^{-4}
Conversion = 75 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
38	0	772	786	---
42	2.0	770	784	0.0011
42	15.0	758	772	0.0078
42	20.0	754	768	0.0100
42	25.0	749	763	0.0129
42	30.0	744	758	0.0157
42	35.0	740	754	0.0180
42	40.0	738	752	0.0192
42	45.0	735	749	0.0209
42	50.0	732	746	0.0227
42	55.0	729	743	0.0244
42	60.0	727	741	0.0256
42	70.0	722	736	0.0285
42	80.0	719	733	0.0303
42	90.0	715	729	0.0327
42	100.0	711	725	0.0351
42	110.0	706	720	0.0381
42	120.0	700	714	0.0417
42	135.0	692	706	0.0466
42	150.0	686	700	0.0503
42	165.0	680	694	0.0540
42	180.0	674	688	0.0578
42	195.0	669	683	0.0610
42	210.0	662	676	0.0655
42	225.0	655	669	0.0700
42	240.0	650	664	0.0732
42	255.0	645	659	0.0765
42	270.0	638	652	0.0812
42	300.0	625	639	0.0899
42	345.0	607	621	0.1023
42	390.0	587	601	0.1165
42	450.0	570	584	0.1290

a period of nine and one-half hours. See Table V.

Curves representing both of these hydrogenation reactions are shown in Figure 3.

2. Alloy prepared at 250-300°

Using the alloy prepared at 250-300° as a catalyst, a velocity constant of 14.3×10^{-4} was obtained. Nineteen per cent conversion was obtained in the two hours before hydrogenation ceased as shown by the data in Table VI.

When this alloy was treated with carbon monoxide, a velocity constant of 13.9×10^{-4} was obtained and hydrogenation ceased at the end of fifty minutes with 14 per cent conversion. The data for this reaction are found in Table VII.

Graphical representation for comparison of these catalysts is shown in Figure 4.

3. Alloy prepared at 350-400°

Using the alloy prepared at 350-400° as a catalyst, a velocity constant of 6.43×10^{-4} was found for the hydrogenation of nitrobenzene. This reaction ceased at the end of ninety minutes with 9 per cent conversion. See data in Table VIII.

After treating this alloy with carbon monoxide, a large increase in the velocity constant was found, and a greater conversion took place before hydrogenation ceased.

TABLE V

HYDROGENATION OF NITROBENZENE USING CARBON-MONOXIDE TREATED 150-200° RHENIUM-NICKEL ALLOY

Catalyst Weight = 0.253 g.
$k = 7.15 \times 10^{-4}$
Conversion = 34 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
39	0	790	804	---
40	0.5	788	802	0.0011
42	15.0	787	801	0.0017
42	20.0	780	794	0.0055
42	25.0	778	792	0.0066
42	30.0	775	789	0.0082
42	40.0	770	784	0.0110
42	50.0	768	782	0.0121
42	60.0	765	779	0.0138
42	80.0	760	774	0.0166
42	100.0	758	772	0.0177
42	120.0	755	769	0.0194
42	150.0	752	766	0.0211
42	180.0	749	763	0.0226
42	240.0	740	754	0.0279
42	375.0	720	734	0.0396
42	420.0	715	729	0.0426
42	480.0	710	724	0.0456
42	540.0	702	716	0.0504
42	565.0	700	714	0.0546

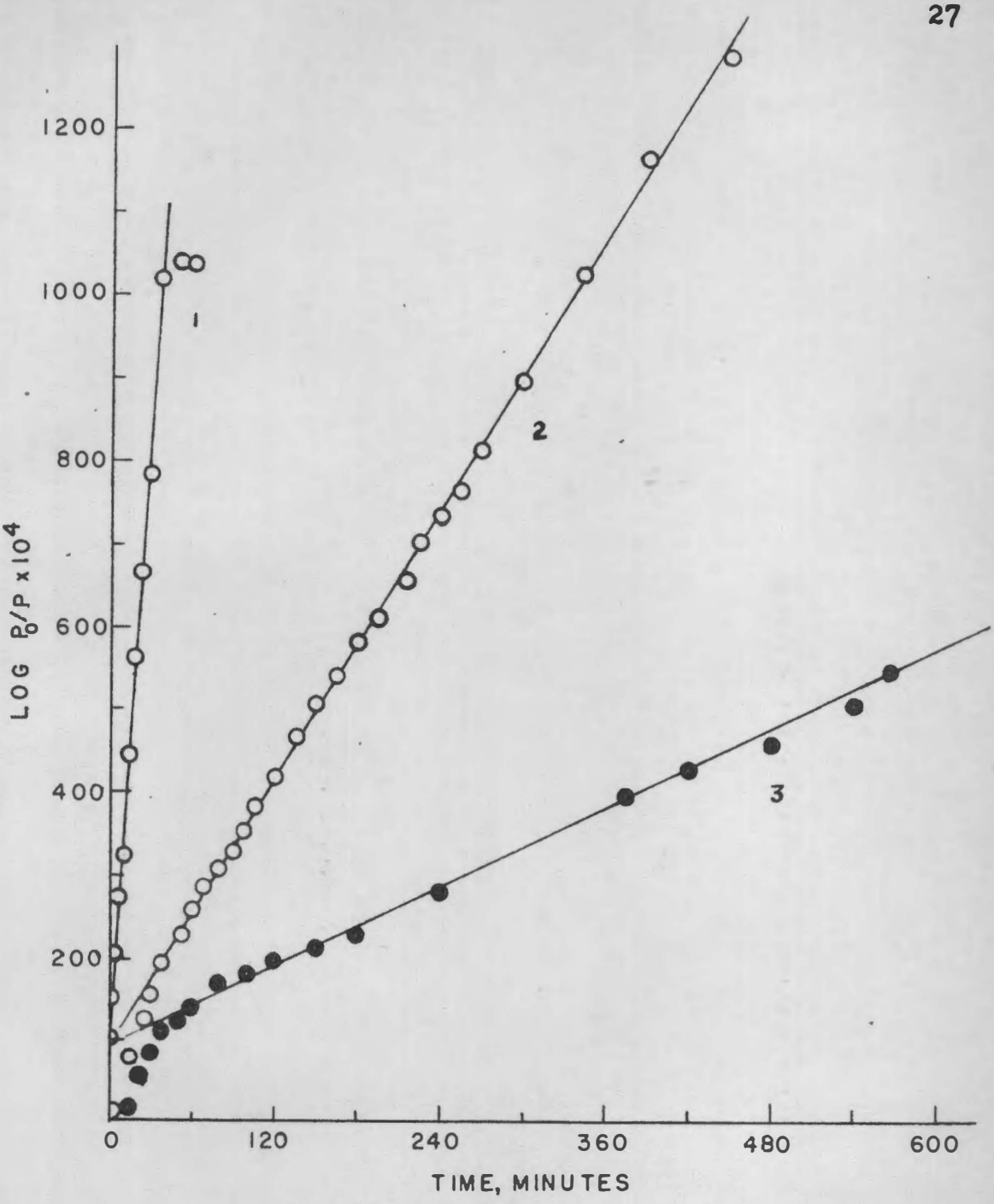

Figure 3. Hydrogenation of nitrobenzene at 40-43°: (1) Raney nickel, $k = 198 \times 10^{-4}$; (2) the rhenium-nickel alloy prepared at 150-200°, $k = 12.8 \times 10^{-4}$; (3) the carbon monoxide treated 150-200° rhenium-nickel alloy, $k = 7.15 \times 10^{-4}$.

TABLE VI

HYDROGENATION OF NITROBENZENE USING THE RHENIUM-NICKEL ALLOY PREPARED AT 250-300°

Catalyst Weight = 0.350 g.
$k = 14.3 \times 10^{-4}$
Conversion = 19 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
35	0	797	811	---
38	1.0	795	809	0.0016
40	5.0	795	809	0.0016
41	10.0	790	804	0.0037
41	15.0	790	804	0.0037
42	20.0	790	804	0.0037
41	30.0	784	798	0.0070
41	35.0	780	794	0.0092
41	40.0	780	794	0.0092
41	45.0	780	794	0.0092
42	50.0	778	792	0.0103
41	55.0	775	789	0.0119
41	60.0	770	784	0.0147
41	65.0	770	784	0.0147
41	75.0	770	784	0.0147
41	90.0	760	774	0.0203
41	120.0	755	769	0.0231
41	130.0	755	769	0.0231
41	140.0	755	769	0.0231

TABLE VII

HYDROGENATION OF NITROBENZENE USING CARBON-MONOXIDE TREATED 250-300° RHENIUM-NICKEL ALLOY

Catalyst Weight = 0.498 g.
$k = 13.9 \times 10^{-4}$
Conversion = 14 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
38	0	800	814	---
39	0.5	795	809	0.0027
40	1.0	795	809	0.0027
43	5.0	795	809	0.0027
42	10.0	795	809	0.0027
42	15.0	790	804	0.0053
42	20.0	786	800	0.0075
42	25.0	781	795	0.0102
42	30.0	779	793	0.0113
42	40.0	775	789	0.0135
42	50.0	770	784	0.0163
42	60.0	770	784	0.0163
42	70.0	770	784	0.0163

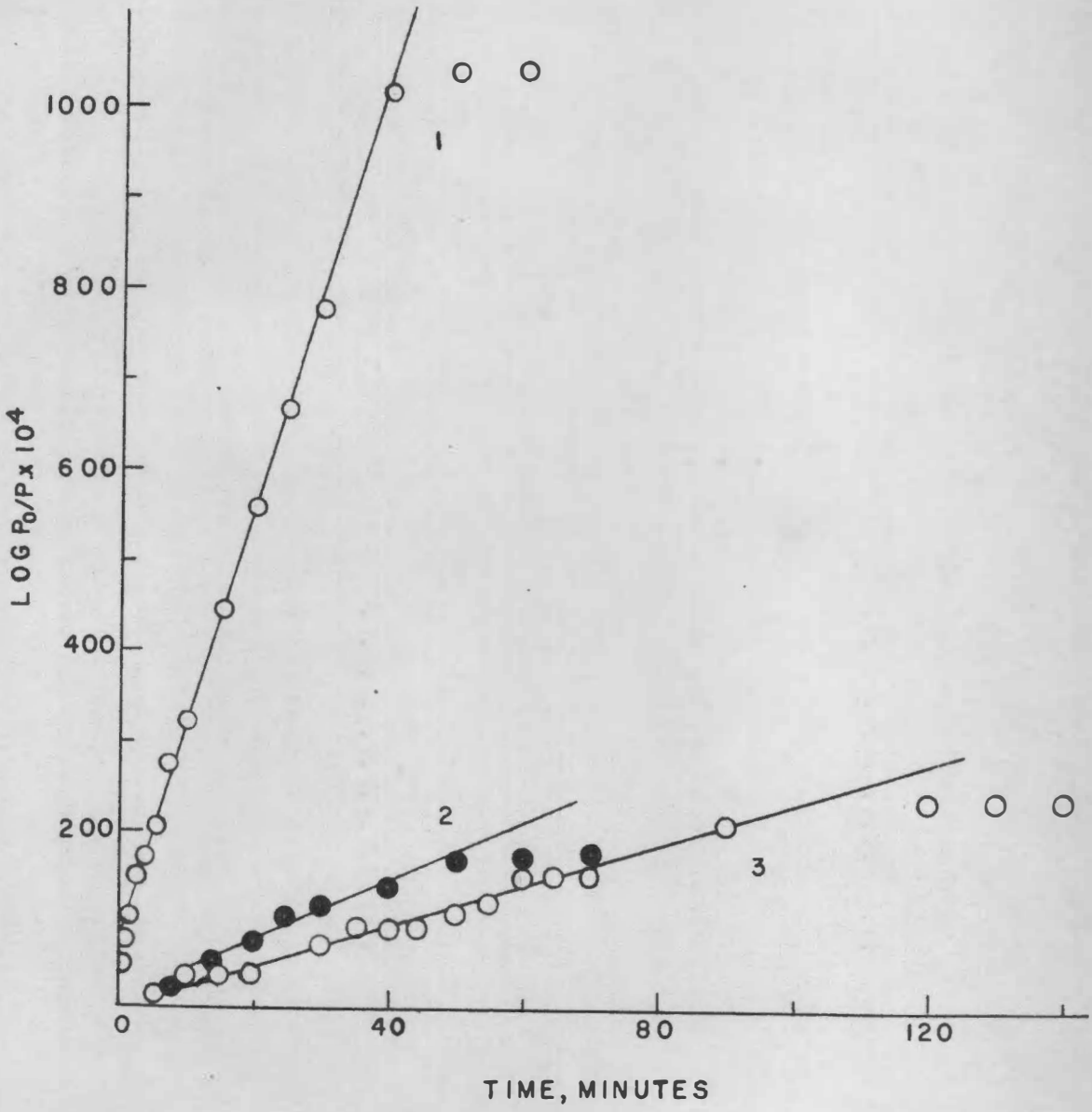

Figure 4. Hydrogenation of nitrobenzene at 40-43°: (1) Raney nickel, $k = 198 \times 10^{-4}$; (2) the rhenium-nickel alloy prepared at 250-300°, $k = 14.3 \times 10^{-4}$; (3) the carbon monoxide treated 250-300° alloy, $k = 13.9 \times 10^{-4}$.

TABLE VIII

HYDROGENATION OF NITROBENZENE USING THE RHENIUM-NICKEL ALLOY PREPARED AT 350-400°

Catalyst Weight = 0.345 g.
$k = 6.43 \times 10^{-4}$
Conversion = 9 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
35	0	790	804	---
37	1.0	787	801	0.0017
40	20.0	790	804	0.0000
40	30.0	788	802	0.0011
40	45.0	785	799	0.0028
40	60.0	782	796	0.0044
40	75.0	780	794	0.0055
40	90.0	779	793	0.0060
40	105.0	778	792	0.0061
40	120.0	778	792	0.0061
40	135.0	778	792	0.0061
40	165.0	778	792	0.0061

The constant in this case was 107 x 10^{-4} and a 38 per cent conversion was obtained in forty-five minutes. The data for this reaction are shown in Table IX.

The data of Table VIII and IX are shown graphically in Figure 5.

4. Alloy prepared at 450-500°

No measurable hydrogenation was obtained using the alloy prepared at 450-500° for a catalyst.

When a sample of this preparation was treated with carbon monoxide, some hydrogenation did take place and a velocity constant of 120 x 10^{-4} was found for the reaction. The catalyst was rendered inactive at the end of forty minutes, but a conversion of 30 per cent was effected during this length of time. Data for this reaction are found in Table X and plotted in Figure 6. In respect to velocity constants, this catalyst compared more favorably with Raney nickel than any of the other preparations.

D. Discussion

As the reduction temperature used for the preparation of the original alloys from nickel perrhenate was increased, the per cent conversion of nitrobenzene to aniline and the length of time elapsing before poisoning took place decreased. This trend can be seen from the values in Table XI. The velocity constants for the reaction, in the presence of the

TABLE IX

HYDROGENATION OF NITROBENZENE USING THE CARBON MONOXIDE TREATED 350-400° RHENIUM-NICKEL ALLOY

Catalyst Weight = 0.287 g.
$k = 107 \times 10^{-4}$
Conversion = 38 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
38	0	802	816	---
40	1.0	797	811	0.0027
40	5.0	790	804	0.0064
40	10.0	778	792	0.0130
40	15.0	765	779	0.0202
40	20.0	752	766	0.0275
40	25.0	742	756	0.0332
40	30.0	731	745	0.0395
40	35.0	720	734	0.0460
40	45.0	700	714	0.0580
40	50.0	700	714	0.0580
40	55.0	700	714	0.0580

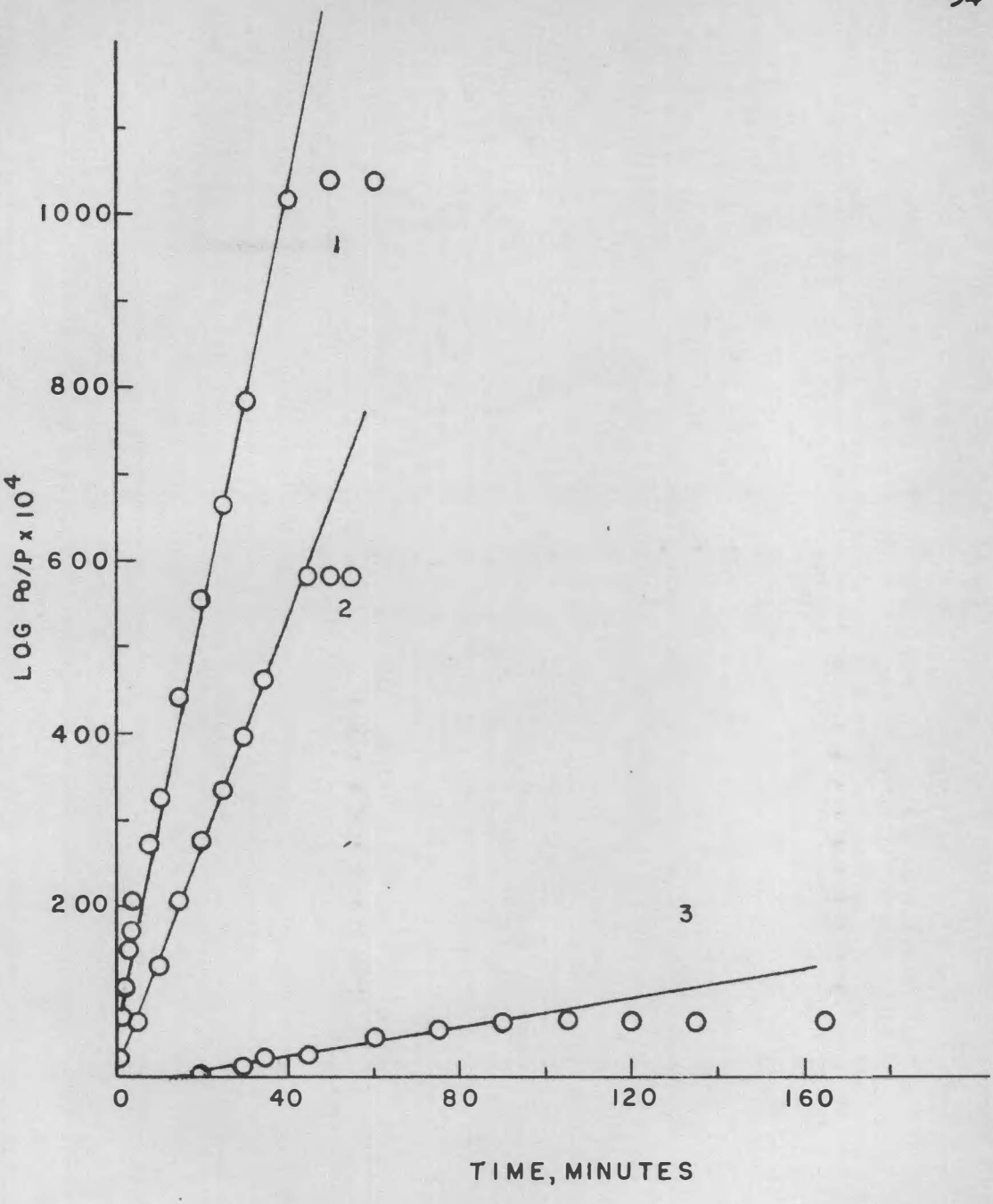

Figure 5. Hydrogenation of nitrobenzene at 40-43°: (1) Raney nickel, k = 198 x 10^{-4}; (2) the rhenium-nickel alloy prepared at 350-400°, k = 6.43 x 10^{-4}; (3) the carbon monoxide treated 350-400° rhenium-nickel alloy, k = 107 x 10^{-4}.

TABLE X

HYDROGENATION OF NITROBENZENE USING THE CARBON MONOXIDE TREATED 450-500° RHENIUM-NICKEL ALLOY

Catalyst Weight = 0.221 g.
k = 120 x 10^{-4}
Conversion = 30 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
37	0	800	814	---
39	0.5	793	807	0.0037
40	1.0	792	806	0.0043
40	5.0	788	802	0.0064
40	10.0	778	792	0.0119
40	20.0	756	770	0.0241
40	30.0	736	750	0.0355
40	40.0	722	736	0.0437
40	50.0	722	736	0.0437
40	60.0	722	736	0.0437

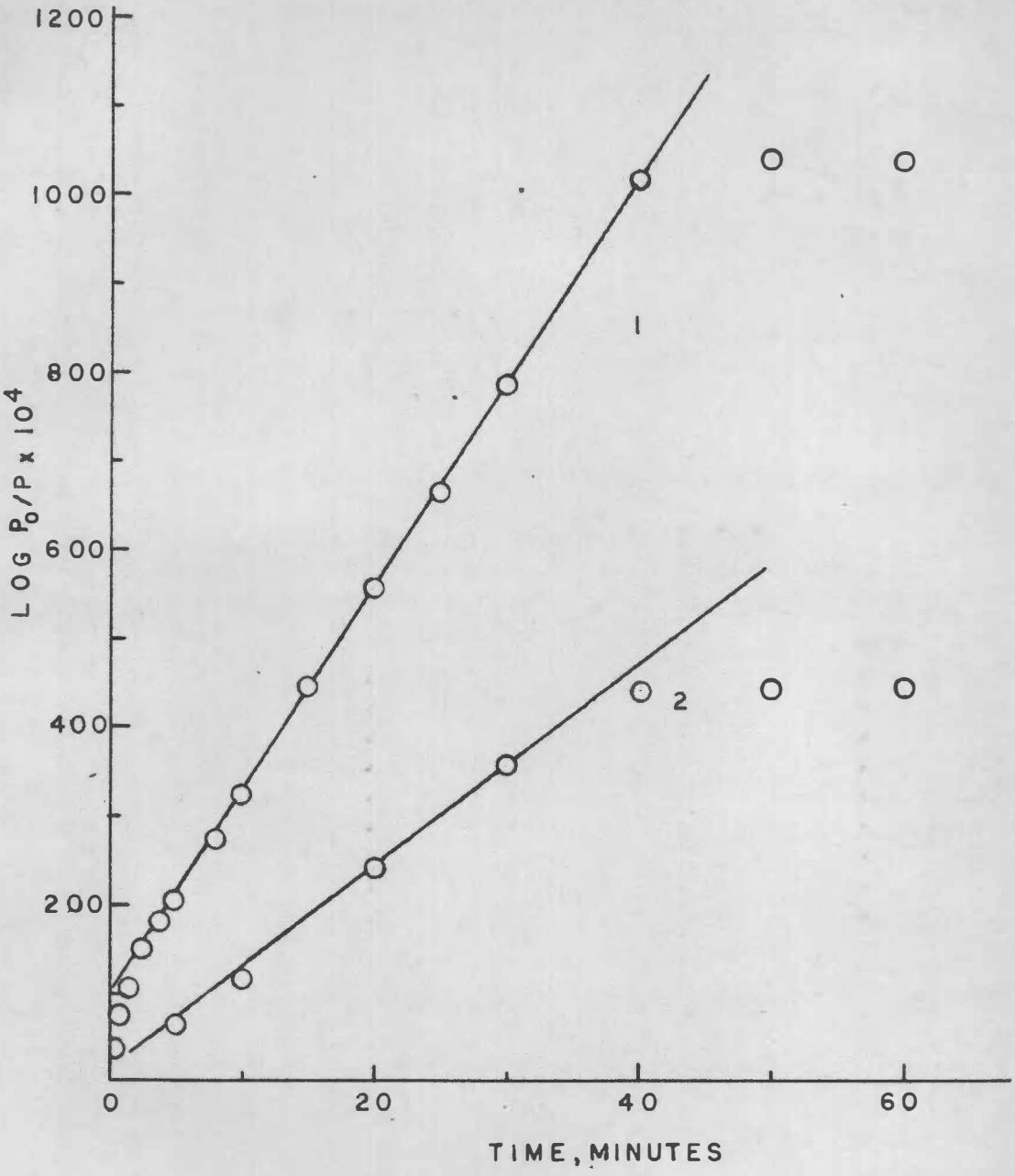

Figure 6. Hydrogenation of nitrobenzene at 40-43°: (1) Raney nickel, k = 198 x 10^{-4}; (2) carbon monoxide treated 450-500° rhenium-nickel alloy, k = 120 x 10^{-4}.

TABLE XI

HYDROGENATION OF NITROBENZENE OVER RHENIUM-NICKEL ALLOYS

Rhenium-Nickel Alloy	Velocity Constant k x 10^4	Per Cent Conversion	Time in Minutes[a]
150-200°[b]	12.8	75	450[d]
250-300°[b]	14.3	19	120
350-400°[b]	6.43	9	90
450-500°[b]	---	---	---
150-200°[c]	7.15	34	570[d]
250-300°[c]	13.9	14	50
350-400°[c]	107	38	45
450-500°[c]	120	30	40

[a]Represents time elapsed before poisoning occurred.

[b]Prepared by hydrogen reduction of nickel perrhenate at the temperature indicated.

[c]The original alloys, prepared at the temperature indicated, after treatment with carbon monoxide.

[d]The hydrogenation run stopped before poisoning occurred.

various alloys, reach a peak for the catalyst prepared at 250-300°. The fact that the alloy prepared at 150-200° gave a lower value for the velocity constant may be due to incomplete reduction at this temperature.

Table XI also gives the comparison of similar data obtained for the carbon monoxide treated alloys. Analyses of these showed that the method of removing nickel from the alloys was very inefficient (See Appendix III), but after treatment with carbon monoxide, in an attempt to remove the nickel, the velocity constant increased rapidly as the reduction temperature used in the preparation of the original alloys increased. The time elapsing before poisoning occurred decreased here, as it did in the previous set of alloys. The per cent conversion seemed to take no definite trend, but was lowest for the alloy prepared at 250-300°.

None of the alloys prepared were better catalysts for the hydrogenation of nitrobenzene than Raney nickel, although rhenium prepared by hydrogen reduction of potassium perrhenate and the alloy prepared at 150-200° from nickel perrhenate gave higher per cent conversions over a long period of time.

CHAPTER IV

SUMMARY

A series of rhenium-nickel alloys was prepared by hydrogen reduction of nickel perrhenate at 150-200°, 250-300°, 350-400°, and 450-500°. These alloys were used as catalysts in the hydrogenation of nitrobenzene at 40-43° and approximately 800 p.s.i. pressure of hydrogen. A second series of alloys was prepared by treating each of the original alloys with carbon monoxide to effect a partial removal of the nickel. In addition to the alloys, samples of metallic rhenium, prepared by electrolysis of a potassium perrhenate solution and by hydrogen reduction of the solid salt, were used. Raney nickel was taken as a standard for this work.

The velocity constant for the hydrogenation taking place in the presence of each catalyst, calculated from a plot of time versus log P_o/P, and the per cent conversion effected by each of these catalysts were calculated. The results are summarized in Table XII.

The rhenium-nickel alloys, prior to treatment with carbon monoxide, were no more effective as catalysts than pure rhenium and were not nearly so effective as Raney nickel under the same conditions. Over a long period of time, the alloy prepared at 150-200° and rhenium from the

TABLE XII

DATA FOR RHENIUM AND RHENIUM-NICKEL ALLOYS AS CATALYSTS FOR THE HYDROGENATION OF NITROBENZENE

Catalyst	Method of Preparation	Velocity Constant k x 10^4	Per Cent Conversion	Time in Minutes[a]
Raney nickel	Standard[b]	198	61	50
Rhenium	From hydrogen reduced $KReO_4$ at 500°[c]	16.7	66	420
Rhenium	Electrolytic	10.8	50	250[e]
Ni-2Re	150-200°[c]	12.8	75	450[e]
Ni-2Re	250-300°[c]	14.3	19	120
Ni-2Re	350-400°[c]	6.43	9	90
Ni-2Re	450-500°[c]	---	---	---
Ni-Re	150-200°[d]	7.15	34	570[e]
Ni-Re	250-300°[d]	13.9	14	50
Ni-Re	350-400°[d]	107	38	45
Ni-Re	450-500°[d]	120	30	40

[a]Represents time elapsed before poisoning occurred.

[b]Organic Syntheses, 21, 15, 1941.

[c]Prepared by hydrogen reduction of nickel perrhenate at the temperature indicated.

[d]Original alloy treated with carbon monoxide at 50° for forty-five hours.

[e]Hydrogenation run stopped before poisoning occurred.

hydrogen reduction of potassium perrhenate, gave higher per cent conversions than the other alloys or electrolytic rhenium. After treatment with carbon monoxide, however, the alloys prepared at 350-500° showed more promise for use as hydrogenation catalysts than the other alloys or the pure rhenium metal. None of the catalysts prepared were found to be as effective as Raney nickel in the hydrogenation of nitrobenzene.

BIBLIOGRAPHY

BIBLIOGRAPHY

Anisimov, S. B., Platonov, M. S., and Tur, C. G., J. Gen. Chem. U. S. S. R., 7, 2895-8 (1937); (C. A., 32, 5383).

Bedoit, W. C., "Studies of Raney Nickel Catalysts," Master's Thesis, University of Tennessee, 1948, Appendix.

Bedoit, W. C., "Kinetics of the Catalytic Hydrogenation of the Nitro Group on Adams Platinum and Raney Nickel Catalysts," Doctoral Dissertation, University of Tennessee, 1950, p. 134.

Cabbage, A., "Catalytic Hydrogenation over Rhenium and the Production of Rhenium Metal," Master's Thesis, University of Tennessee, 1948, p. 1-56.

Fuzek, John F., "The Kinetics of Catalytic Hydrogenation of Terpenes," Doctoral Dissertation, University of Tennessee, 1947, p. 32.

Glasstone, S., "Textbook of Physical Chemistry," Second Edition, D. Van Nostrand Company, New York, N. Y., 1946.

Kolthoff, I. M., and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," Revised Edition, Macmillan Company, New York, N. Y., 1945.

Noddack, I. and W., Naturwissenschaften, 17, 93-4 (1929); (C. A., 23, 1833).

N. V. DeBataafsche Petroleum Maatschappij, Brit. Patent 358,180 (1930); (C. A., 26, 4924).

N. V. DeBataafsche Petroleum Maatschappij, Ger. Patent 693,707 (1940); (C. A., 41, 4941).

Organic Syntheses, 21, 15 (1941).

Platonov, M. S., J. Gen. Chem. U. S. S. R., 11, 683-685 (1941); (C. A., 36, 3976).

Platonov, M. S., J. Gen. Chem. U. S. S. R., 11, 590-591 (1941); (C. A., 35, 6924).

Platonov, M. S., and Anisimov, S. B., J. Gen. Chem. U. S. S. R., 7, 1360-1363 (1937); (C. A., 31, 1937).

Platonov, M. S., and Anisimov, S. B., Russ. Patent 52,780 (1938); (C. A., 34, 5467).

Platonov, M. S., Anisimov, S. B., and Krasheninnikova, V. M., Ber. 68B, 761-765 (1935); (C. A., 29, 5005).

Platonov, M. S., Anisimov, S. B., and Krasheninnikova, V. M., Ber. 69B, 1050-1053 (1936); (C. A., 30, 4812).

Platonov, M. S., Anisimov, S. B., and Krasheninnikova, V. M., J. Gen. Chem. U. S. S. R., 5, 1059-1065 (1935); (C. A., 30, 944).

Platonov, M. S., and Tomilov, V. I., J. Gen. Chem. U. S. S. R. 7, 776-777 (1937); (C. A., 31, 6189).

Platonov, M. S., Tomilov, V. I., and Tur, E. V., J. Gen. Chem. U. S. S. R., 7, 1803-1804 (1937); (C. A., 31, 8341).

Siebert, G., Fr. Patent 378,479 (1932); (C. A., 27, 1723).

Siemens and Halske, A. G., Fr. Patent 682,446 (1929); (C. A., 24, 4362).

Siemens and Halske, Noddack, W. and I., Brit. Patent 346,652 (1939); (C. A., 26, 569).

Smith, W. T., and Maxwell, G. E., J. Am. Chem. Soc., 71, 578-580 (1949).

Tropsch, H., and Kassler, R., Ber. 63B, 2149-2151 (1930); (C. A., 25, 22).

Tropsch, H., and Kassler, R., Mitt Kohlenforsch, Inst. Prag., 13-15 (1931); (Chem. Zentr., 2, 2420 (1932).

Zenghelis, C., and Stathis, C., Kolloid Z., 90, 129 (1940).

Zenghelis, C., and Stathis, El., Osterr. Chem. Ztg., 40, 80-81 (1937); (C. A., 31, 4777).

Zenghelis, C., and Stathis, K., Atti X° congr. intern. chim., 2, 821-824 (1938); (C. A., 33, 8081).

APPENDIXES

APPENDIX I

ADDITIONAL DATA

Attempts were made to hydrogenate nitrobenzene at low pressures and temperatures. In this connection, portions of the rhenium-nickel alloy prepared at 250-300° and 350-400° were used for hydrogenation at room temperature and approximately 60 p.s.i. pressure. No measurable hydrogenation was obtained under these conditions.

Some hydrogenations were tried at room temperature and 1000 p.s.i. pressure using the alloy prepared at 450-500°, this same alloy after treatment with carbon monoxide, and rhenium metal as catalysts. Very little hydrogenation was obtained using the alloys. The velocity constant for the hydrogenation using metallic rhenium under these conditions was 6.8×10^{-4} with a 31 per cent conversion over a period of three hours. Hydrogenation was still taking place as can be seen from the graph in Figure 7 plotted from the data in Table XIII.

The hydrogenation of other compounds, in addition to nitrobenzene, was attempted. Redistilled cyclohexene and Eastman white label styrene, stabilized with tertiary butyl catechol, were tried using rhenium, prepared by hydrogen reduction of potassium perrhenate, as the catalyst. Velocity constants and data calculated for the two compounds gave

TABLE XIII

HYDROGENATION OF NITROBENZENE AT 28° USING RHENIUM METAL FROM HYDROGEN REDUCTION OF POTASSIUM PERRHENATE

Catalyst Weight = 0.535 g.
$k = 6.8 \times 10^{-4}$
Conversion = 31 per cent

Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
0	968	982	---
0.5	950	964	0.0080
1.0	948	962	0.0089
5.0	945	959	0.0103
15.0	939	953	0.0130
45.0	928	942	0.0180
75.0	917	931	0.0232
105.0	908	922	0.0274
135.0	899	913	0.0316
165.0	888	902	0.0369
180.0	883	897	0.0393

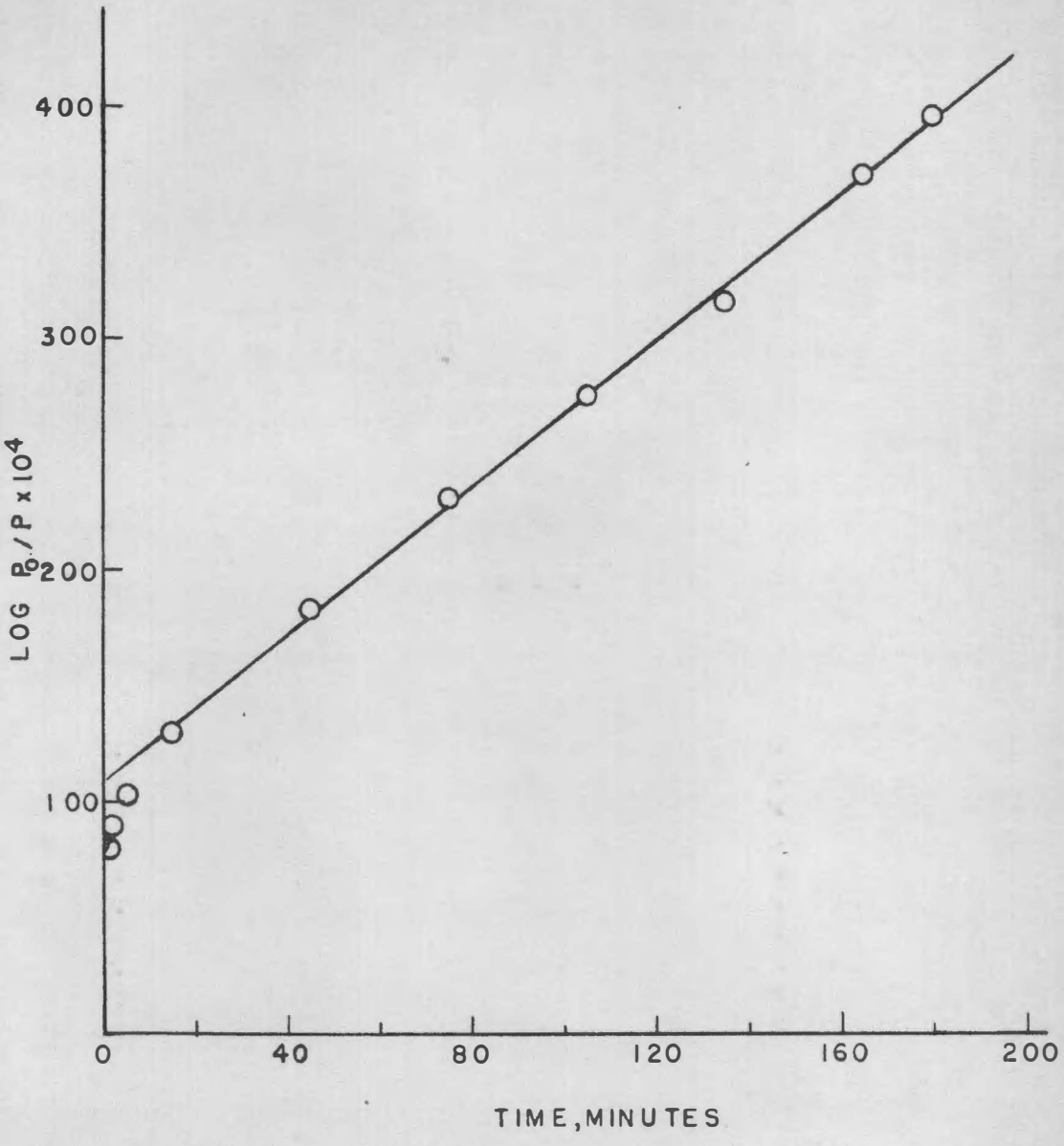

Figure 7. Hydrogenation of nitrobenzene at 28° using rhenium from the hydrogen reduction of potassium perrhenate, k = 6.8 x 10^{-4}.

9.56×10^{-4} and 21 per cent conversion in ten minutes for cyclohexene and 16.5×10^{-4} with 35 per cent conversion in thirty minutes for styrene. The data in Table XIV for cyclohexene and Table XV for styrene are plotted in Figure 8.

A few runs at 36-38° and approximately 800 p.s.i. pressure were made with nitrobenzene using rhenium prepared by hydrogen reduction of potassium perrhenate. The velocity constant was 46.4×10^{-4} and a 69 per cent conversion was obtained in two hours. The data for this reaction are given in Table XVI and plotted in Figure 9. Two samples of the 250-300° alloy were also tried under these conditions. The first sample was used immediately after reduction and a velocity constant of 8.4×10^{-4} was obtained. When the reaction stopped at the end of two hours, 10 per cent of the nitrobenzene had been hydrogenated. A second sample was placed in a desiccator for two months and then reduced a second time and placed under methanol for use. The velocity constant obtained using this alloy was 7.55×10^{-4} with a 23 per cent conversion in two and three-quarter hours. Data for these runs are shown in Tables XVII and XVIII and are plotted in Figure 10. In this case a second reduction showed a lowering of the velocity constant, but an increase in per cent conversion and length of time elapsing before the catalyst was poisoned.

A similar trend was noted in another set of alloys treated in the same manner, but prepared at 350-400°.

TABLE XIV

HYDROGENATION OF CYCLOHEXENE AT 28° USING RHENIUM FROM HYDROGEN REDUCTION OF POTASSIUM PERRHENATE

Catalyst Weight = 0.511 g.
$k = 9.56 \times 10^{-4}$
Conversion = 21 per cent

Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
0	880	894	---
0.5	865	879	0.0073
1.0	865	879	0.0073
5.0	863	877	0.0083
10.0	861	875	0.0093
30.0	861	875	0.0093

TABLE XV

HYDROGENATION OF STYRENE AT 28° USING RHENIUM FROM HYDROGEN REDUCTION OF POTASSIUM PERRHENATE

Catalyst Weight = 0.508 g.
$k = 16.5 \times 10^{-4}$
Conversion = 35 per cent

Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
0	900	914	---
0.5	880	894	0.0096
1.0	880	894	0.0096
5.0	877	891	0.0110
10.0	873	887	0.0130
30.0	872	886	0.0135
60.0	872	886	0.0135
90.0	872	886	0.0135

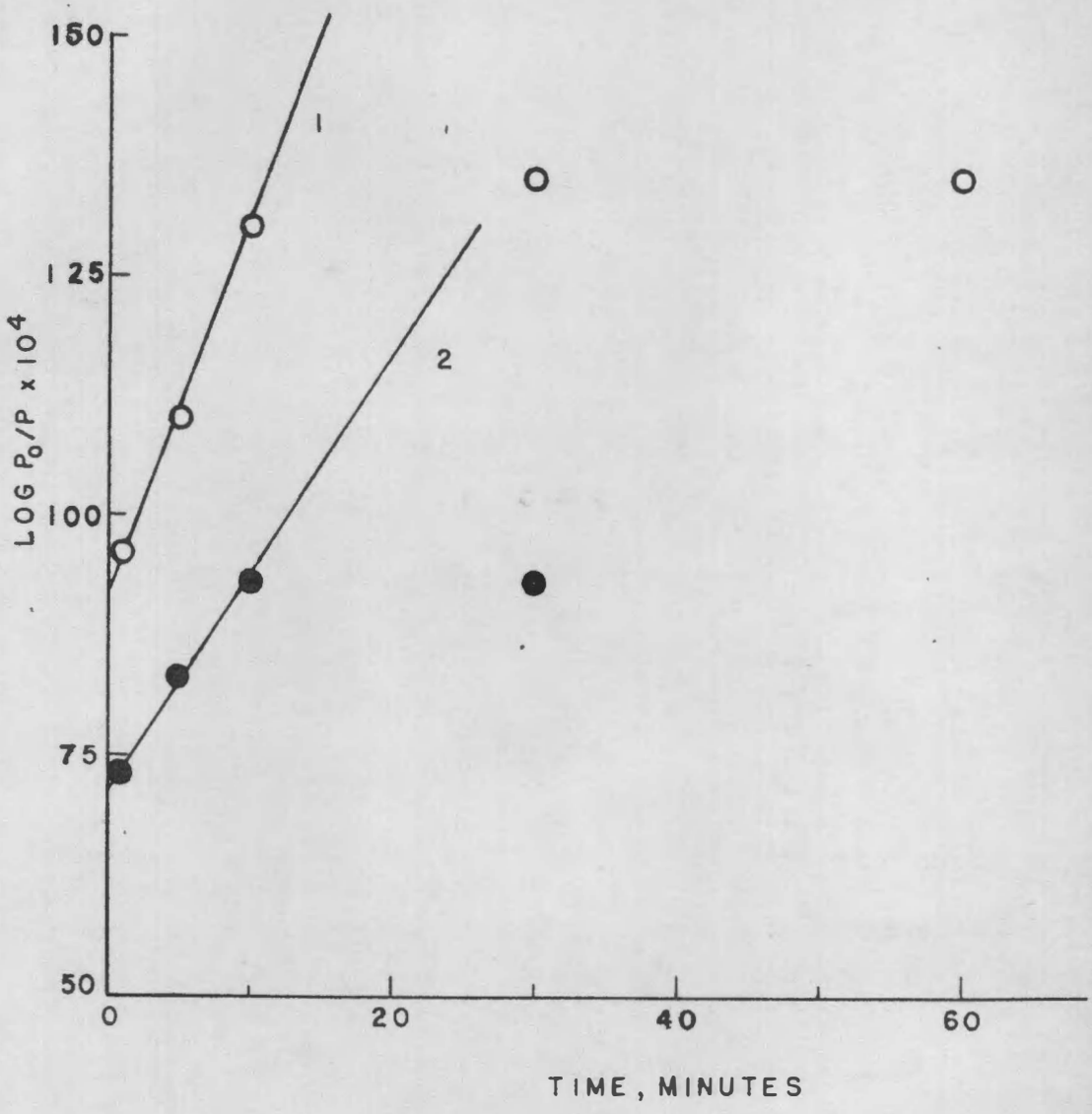

Figure 8. Hydrogenation of styrene and cyclohexene at 28° using rhenium from hydrogen reduction of potassium perrhenate: (1) styrene, k = 16.5 x 10^{-4}; (2) cyclohexene, k = 9.56 x 10^{-4}.

TABLE XVI

HYDROGENATION OF NITROBENZENE USING RHENIUM FROM HYDROGEN REDUCTION OF POTASSIUM PERRHENATE

Catalyst Weight = 0.616 g.
k = 46.4×10^{-4}
Conversion = 69 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
32	0	799	813	---
35	0.5	790	804	0.0048
37	1.0	790	804	0.0048
37	5.0	780	794	0.0103
37	10.0	769	783	0.0163
37	15.0	758	772	0.0225
37	20.0	746	760	0.0293
36	25.0	735	749	0.0356
36	30.0	725	739	0.0415
36	35.0	715	729	0.0474
36	40.0	705	719	0.0534
36	45.0	696	710	0.0598
36	60.0	672	686	0.0738
36	90.0	626	640	0.1039
36	120.0	615	629	0.1114
36	150.0	615	629	0.1114

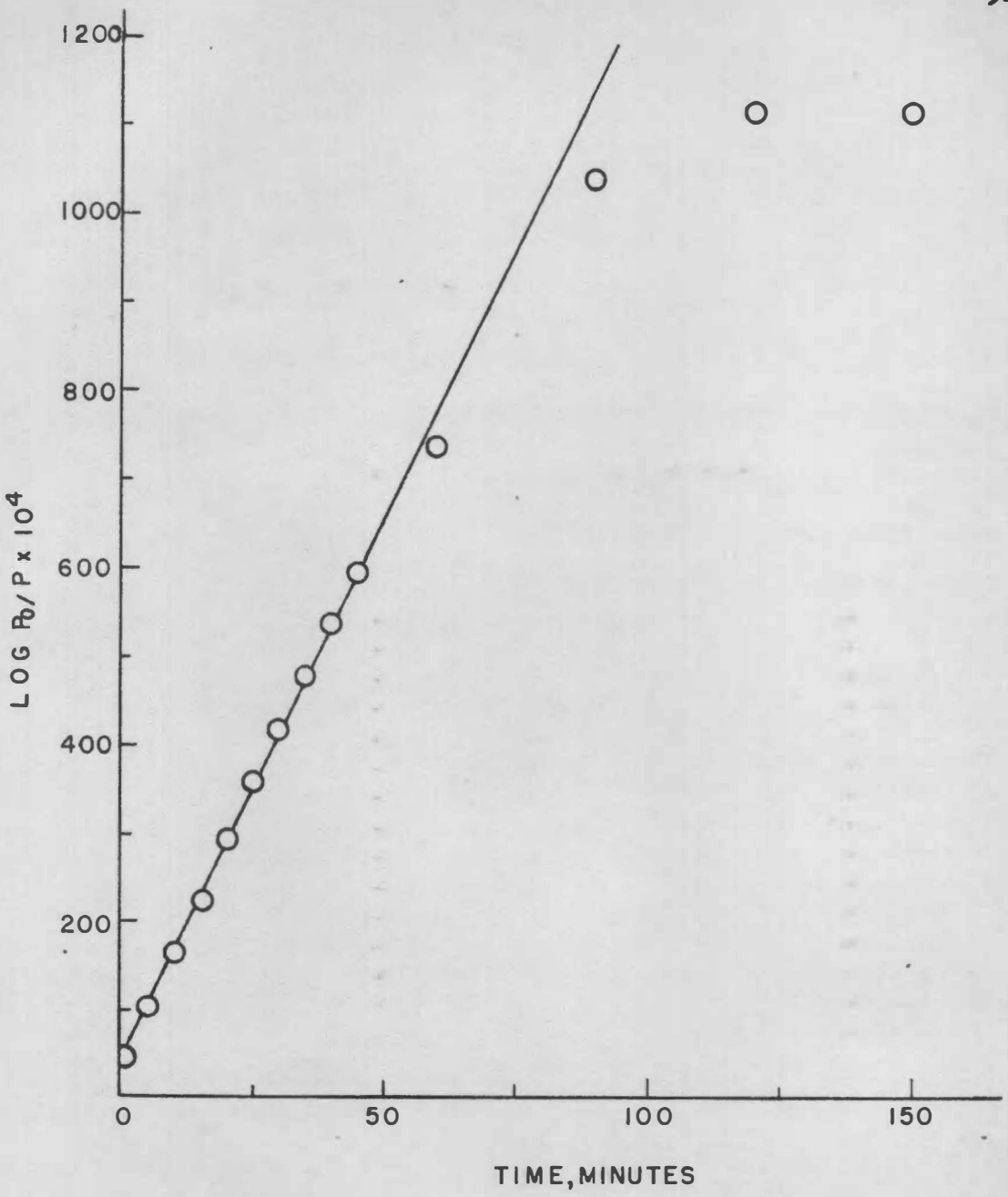

Figure 9. Hydrogenation of nitrobenzene at 36° using rhenium from hydrogen reduction of potassium perrhenate, $k = 46.4 \times 10^{-4}$.

TABLE XVII

HYDROGENATION OF NITROBENZENE USING RHENIUM-NICKEL ALLOY PREPARED BY HYDROGEN REDUCTION OF NICKEL PERRHENATE AT 250-300°[a]

Catalyst Weight = 0.347 g.
k = 8.4×10^{-4}
Conversion = 9.6 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
32	0	758	772	---
35	0.5	752	766	0.0034
35	1.0	752	766	0.0034
36	5.0	756	770	0.0011
36	10.0	756	770	0.0011
36	20.0	756	770	0.0011
36	30.0	754	768	0.0022
36	45.0	754	768	0.0022
36	60.0	752	766	0.0034
36	75.0	749	763	0.0051
36	90.0	745	759	0.0074
36	105.0	742	756	0.0091
36	120.0	740	754	0.0102
36	135.0	740	754	0.0102
36	150.0	740	754	0.0102
36	180.0	740	754	0.0102

[a]This sample was used immediately after reduction.

TABLE XVIII

HYDROGENATION OF NITROBENZENE USING RHENIUM-NICKEL ALLOY PREPARED BY HYDROGEN REDUCTION OF NICKEL PERRHENATE AT 250-300°[a]

Catalyst Weight = 0.457 g.
$k = 7.55 \times 10^{-4}$
Conversion = 23 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
32	0	745	759	---
34	0.5	738	752	0.0040
35	1.0	738	752	0.0040
36	5.0	738	752	0.0040
36	10.0	735	749	0.0057
36	20.0	728	742	0.0093
36	30.0	719	733	0.0151
36	45.0	716	730	0.0169
36	60.0	712	726	0.0193
36	75.0	708	722	0.0217
36	90.0	704	718	0.0214
36	105.0	701	715	0.0259
36	120.0	699	713	0.0271
36	150.0	695	709	0.0296
36	165.0	690	704	0.0326

[a]This sample was placed in desiccator for two months and reduced a second time before using.

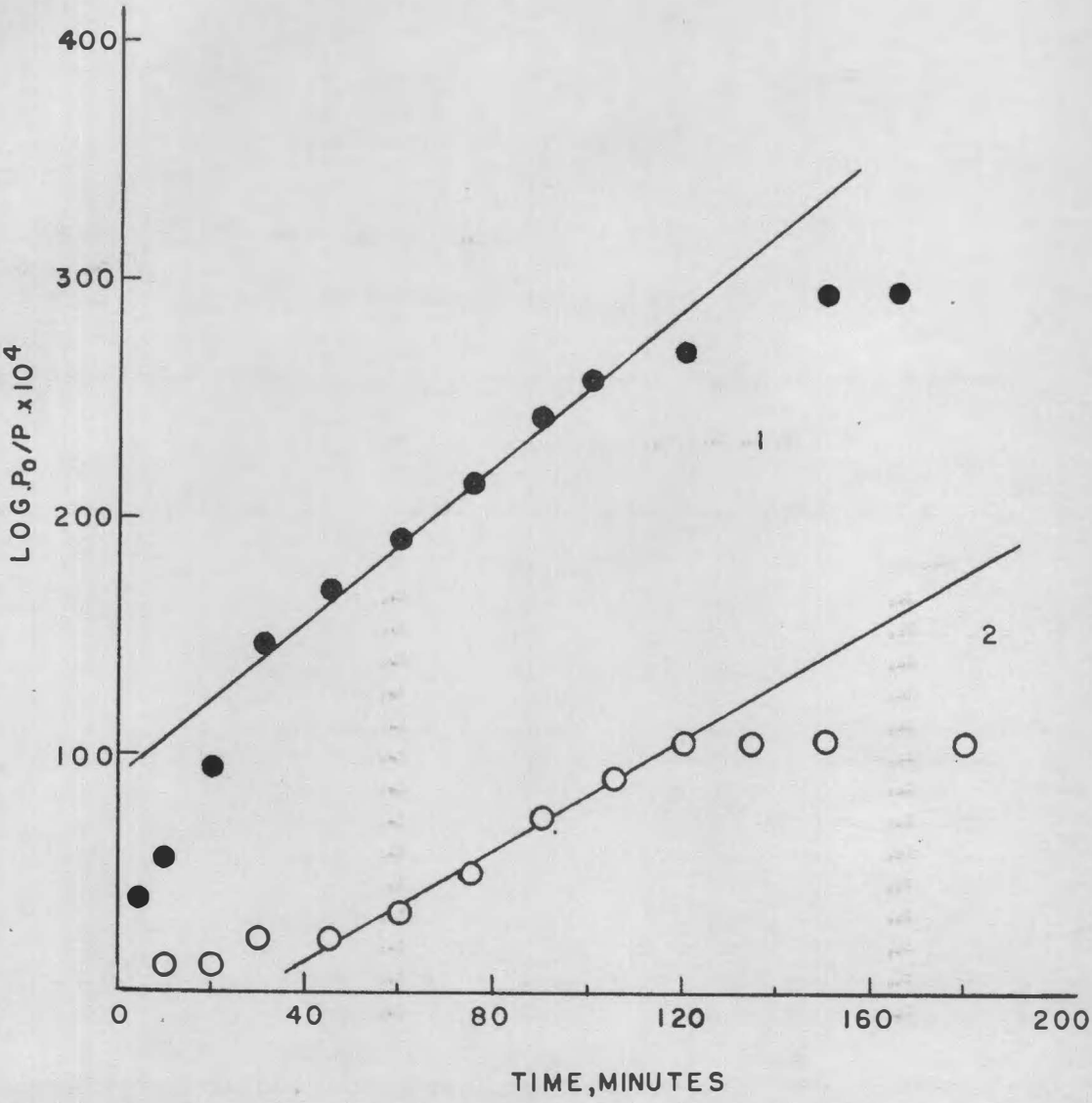

Figure 10. Hydrogenation of nitrobenzene at 36° using rhenium-nickel alloys prepared by hydrogen reduction of nickel perrhenate at 250-300°: (1) Sample reduced a second time after standing, k = 7.55 x 10^{-4}; (2) sample used immediately after first reduction, k = 8.4 x 10^{-4}.

This set was used for the hydrogenation of nitrobenzene at 40-45° and 800 p.s.i. pressure. Data for the first reduction sample are given in Table VIII, page 31, and are plotted in Figure 5 on page 34. The sample from the second reduction gave a constant of 4.63×10^{-4} and 20 per cent conversion in four hours with hydrogenation still taking place. The data found in Table XIX were plotted in Figure 11 for this reaction.

Two samples of the alloy prepared at 150-200° were used on consecutive days to note any difference which standing for a period of twelve hours might make. The velocity constants were very nearly the same, but the conversion and time elapsing before poisoning occurred were different. The sample used the first day was discussed on page 21, and the data for the reaction in Table IV, page 24, were plotted in Figure 3, page 27. The sample used the second day gave a velocity constant of 12.9×10^{-4} and a 67 per cent conversion in five and one-half hours. The data for this sample in Table XX are plotted in Figure 12.

TABLE XIX

HYDROGENATION OF NITROBENZENE USING A RHENIUM-NICKEL ALLOY PREPARED AT 350-400°[a]

Catalyst Weight = 0.537 g.
$k = 4.63 \times 10^{-4}$
Conversion = 20 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
34	0	830	844	---
35	0.5	825	839	0.0025
36	1.0	825	839	0.0025
40	15.0	830	844	0.0000
40	30.0	825	839	0.0025
40	45.0	822	836	0.0041
40	60.0	820	834	0.0051
40	75.0	819	833	0.0057
40	90.0	813	827	0.0088
40	105.0	809	824	0.0104
40	120.0	805	819	0.0130
40	150.0	800	814	0.0157
40	165.0	798	812	0.0167
40	180.0	794	808	0.0189
40	195.0	790	804	0.0210
40	210.0	789	803	0.0216
40	225.0	788	802	0.0221
40	240.0	785	799	0.0238

[a]This sample was placed in desiccator for two months and reduced a second time before using.

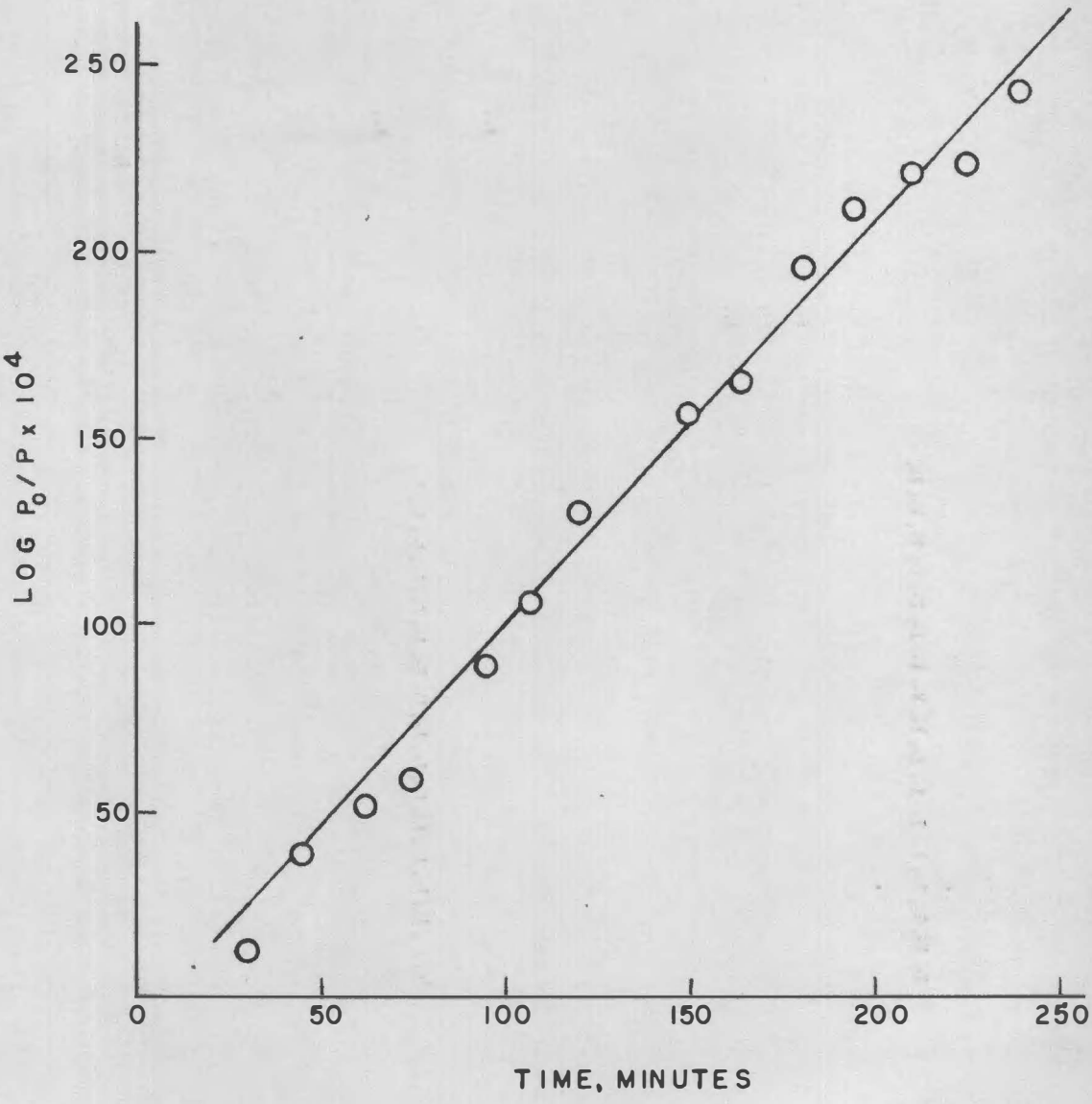

Figure 11. Hydrogenation of nitrobenzene at 40-43° using a rhenium-nickel alloy prepared by hydrogen reduction of nickel perrhenate at 350-400°, k = 4.63 x 10^{-4}.

TABLE XX

HYDROGENATION OF NITROBENZENE USING A RHENIUM-NICKEL ALLOY PREPARED AT 150-200°[a]

Catalyst Weight = 0.532 g.
$k = 12.9 \times 10^{-4}$
Conversion = 67 per cent

Temperature °C	Time, Minutes	Pressure, p.s.i. Gauge	Pressure, p.s.i. Absolute	Log P_o/P
38	0	830	844	---
42	1.0	828	842	0.0010
42	5.0	825	839	0.0025
42	10.0	820	834	0.0031
42	20.0	809	823	0.0109
42	30.0	800	814	0.0157
42	40.0	795	809	0.0184
42	50.0	790	804	0.0210
42	60.0	785	799	0.0238
42	75.0	778	792	0.0276
42	90.0	768	782	0.0331
42	105.0	760	774	0.0376
42	120.0	752	766	0.0421
42	150.0	738	752	0.0501
42	180.0	725	739	0.0577
42	210.0	710	724	0.0666
42	240.0	694	708	0.0763
42	270.0	679	693	0.0856
42	300.0	665	679	0.0944
42	330.0	650	664	0.1041
42	360.0	650	664	0.1041
42	420.0	650	664	0.1041

[a]This sample was allowed to stand twelve hours under methanol before using.

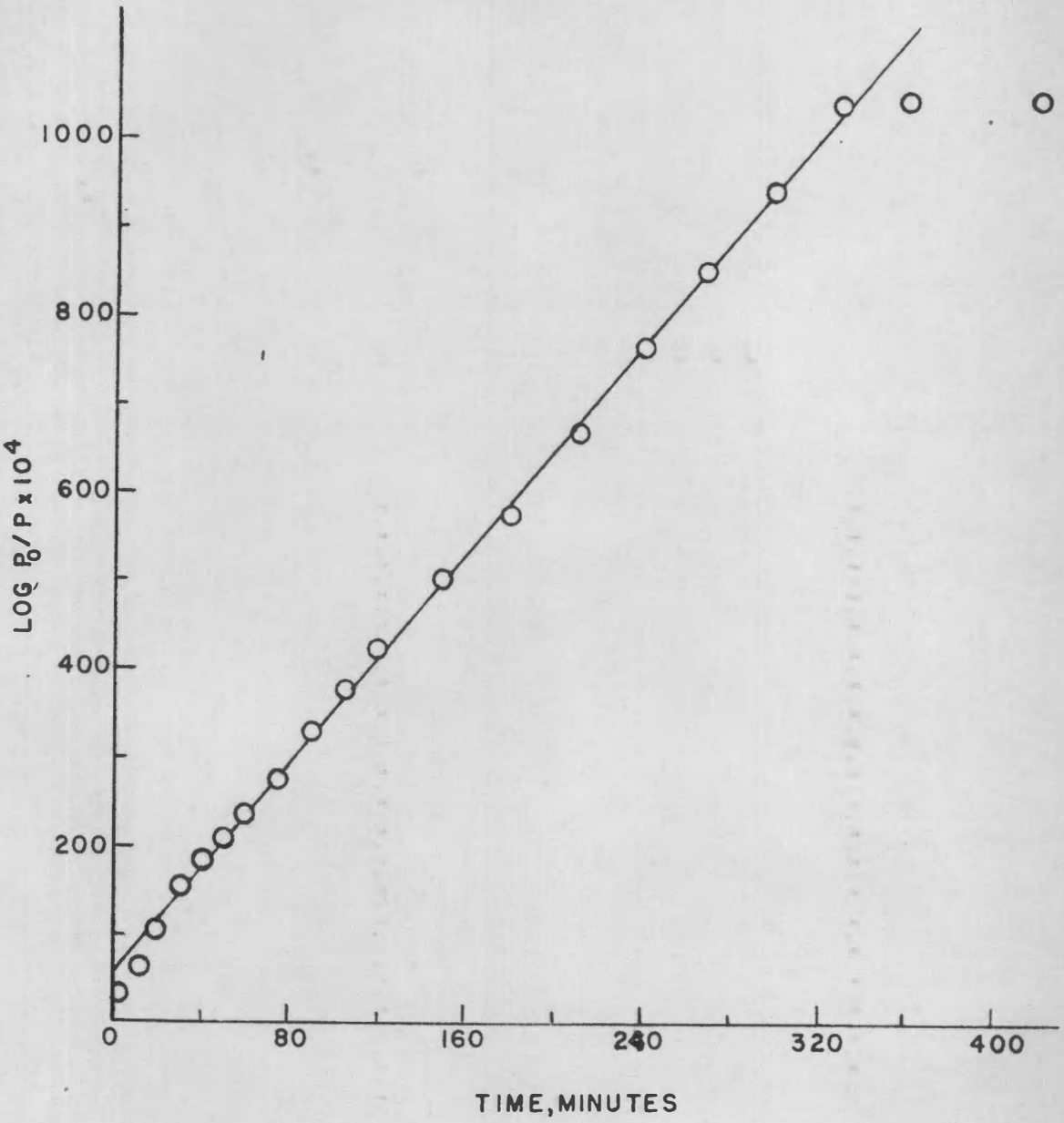

Figure 12. Hydrogenation of nitrobenzene at 40-43° using a rhenium-nickel alloy prepared by hydrogen reduction of nickel perrhenate at 150-200°, k = 12.9 x 10^{-4}.

APPENDIX II

CALCULATION OF PER CENT CONVERSION

The per cent conversion for the hydrogenation of nitrobenzene to aniline was obtained by dividing the measured drop by the theoretical pressure drop for the complete conversion and multiplying by one hundred.

The actual or measured drop in pressure was obtained by subtracting the final pressure reading from the initial reading which had been corrected for the initial T_i and final T_f temperature difference by the following relationship:

$$\frac{\text{(Initial gauge pressure) } T_f}{T_i} = \text{Initial gauge pressure at } T_f$$

All pressures were measured in pounds per square inch. A factor of 14 p.s.i., representing the average existing barometric pressure at the time the hydrogenation runs were made, was added to the initial gauge pressure at T_f to obtain the absolute initial pressure, P_i, at the final temperature. If P_f represents the absolute final pressure, then

$$P_i - P_f = P_{ad} \text{ (measured absolute pressure drop)}$$

To find the theoretical drop in pressure for the reaction, it was necessary to calculate the volume V_H occupied by one mole of hydrogen under the conditions of

the reaction.

$$V_H = \frac{(82.05)\ (14.7)\ (T_f)}{P_i}$$

The total capacity of the bomb used was 50 ml. Neglecting the volume occupied by the catalyst, and subtracting 11 ml. for the volume occupied by the methanol and nitrobenzene from this value gave 39 ml. of free space for the hydrogen gas.

$\frac{39\ ml.}{V_H}$ = M_i(The original number of moles of H_2 in the bomb)

The density of the nitrobenzene used in the hydrogenations was 1.20 g./ml. One milliliter of nitrobenzene would be equivalent to 0.0098 moles and hence would require 0.0294 moles of hydrogen according to the reaction

$$C_6H_5NO_2 + 3H_2 \longrightarrow C_6H_5NH_2 + 2H_2O$$

The number of moles of hydrogen M_r remaining in the bomb after the theoretical hydrogenation had taken place would be equal to

M_i - 0.0294 moles = M_r

$\frac{(M_r)\ (P_i)}{M_i}$ = P_t(theoretical final pressure)

$P_i - P_t = P_{td}$(theoretical pressure drop)

$\frac{P_{ad}}{P_{td}} \times 100$ = Per Cent Conversion

APPENDIX III

NICKEL ANALYSES

The rhenium-nickel alloys before and after treatment with carbon monoxide and the anhydrous nickel perrhenate were analyzed for nickel using the dimethylglyoxime method outlined in Kolthoff and Sandell.[1] The results of these analyses are given in Table XXI.

These analyses showed that the removal of nickel as the carbonyl was very inefficient. A more efficient method for partial or total removal of the nickel might result in more effective rhenium catalysts for the hydrogenation of nitrobenzene.

---

(1) Kolthoff, I. M., and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," Revised Edition, Macmillan Company, New York, N. Y., 1945.

TABLE XXI

ANALYSES OF NICKEL IN RHENIUM-NICKEL ALLOYS AND ANHYDROUS NICKEL PERRHENATE

Sample		Per Cent Nickel (Theoretical)	Weight of Dimethyl-glyoxime nickel salt, g.[a]	Per Cent Nickel Found
$Ni(ReO_4)_2$	I	10.5	0.1186	9.82
	II		0.1185	9.94
Ni-2Re(150-200°)		13.6[b]	------	-----
Ni-2Re(250-300°)	I	13.6[b]	0.1140	12.6
	II		0.1063	11.8
Ni-2Re(350-400°)	I	13.6[b]	0.1247	12.5
	II		------	-----
Ni-2Re(450-500°)	I	13.6[b]	0.1363	13.5
	II		0.1994	12.7
Ni-Re(150-200°)[c]	I	----	0.0719	12.2
	II		0.0565	11.9
Ni-Re(250-300°)[c]	I	----	0.0649	12.3
	II		0.0726	12.2
Ni-Re(350-400°)[c]	I	----	0.1100	12.3
	II		0.0713	12.1
Ni-Re(450-500°)[c]	I	----	0.0645	13.1
	II		0.0623	12.8

[a]Multiply by a factor of 0.2031 to obtain weight of nickel in sample.

[b]Calculated on basis of a 1:2 nickel to rhenium ratio.

[c]Carbon monoxide treated.

VITA

VITA

Norma Connell Bowen was born in Elizabeth City, North Carolina, on September 28, 1926. She attended the elementary school of Bel Air, Maryland, until 1935 when she moved to Baltimore, Maryland. Her elementary school education was completed in the Baltimore City Public Schools and she was graduated from Western Senior High School of that city in 1943. The following September she entered Lynchburg College, Lynchburg, Virginia, having been awarded a partial scholarship by that college, and received the Bachelor of Science degree, *cum laude*, in June 1947. Following graduation she taught at Lynchburg college until September 1948, when she entered the Graduate School of The University of Tennessee. She was granted a graduate assistantship for the school years 1948-1949 and 1949-1950.

The author is a member of the American Chemical Society.