THE KINETICS OF THE DEACTIVATION OF A NICKEL CATALYST
DURING THE HYDROGENATION OF CYCLOPROPANE

by

Edward M. Norin

B.S., University of Wisconsin
(1966)

Submitted in Partial Fulfillment

of the Requirements for the

Degree of Master of Science

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

January 15, 1968

Signature of Author..

Department of Chemical Engineering, Jan. 15,1968

Certified by:...

Thesis Supervisor

Accepted by:...

Chairman,
Departmental Committee on Graduate Theses

DEDICATION

To my father and mother, Albert and Dorothy Norin, for their unfailing gifts of love, aid, and guidance that have seen me through my entire life; I dedicate this thesis.

E. M. N.

ABSTRACT

THE KINETICS OF THE DEACTIVATION OF A NICKEL CATALYST
DURING THE HYDROGENATION OF CYCLOPROPANE

by

Edward M. Norin

Submitted to the Department of Chemical Engineering
on January 22, 1968, in partial fulfillment of the
requirements for the degree of Master of Science.

An experimental investigation into the kinetics of the deactivation of a nickel catalyst during the hydrogenation of cyclopropane was conducted. Information on the recoverability, the kinetics, and the theoretical significance of this deactivation is considered to be needed to facilitate other basic studies with this reaction system.

The reaction was carried out in an isothermal continuous flow reactor at near atmospheric pressure. Hydrogen and cyclopropane were mixed, diluted with helium up to a total flow rate of 1000 ml/min. and reacted over $1.64 \, m^2$ of nickel powder catalyst. The reaction products were analyzed by an on line gas chromatograph equipped with a hydrogen flame ionization detector.

Between each run, the catalyst was reactivated by heating first under high vacuum and then with flowing hydrogen. After deactivation, it was found that the activity of the nickel catalyst was completely recoverable by reactivating at temperatures above 350° C. From this it was concluded that the deactivation was due to the formation of a carbonaceous residue on the catalyst surface.

A study of the hydrogenation kinetics resulted in the following analytic expression for the rate of formation of cyclopropane:

$$-r_{cp} = k_o \exp(-13.8 \text{ kcal/gm mole}) \, (CP)^{0.4} (H_2)^{-0.6} \qquad \text{(A-1)}$$

This is in good agreement with previously reported kinetic data.

Studies of the deactivation kinetics showed that the rate of deactivation increased exponentially with increasing temperature. It was also found that, at 65° C, the rate of deactivation was essentially zero with a 300% excess of hydrogen in the reactant stream; increased linearly with the ratio of the partial pressure of cyclopropane to hydrogen up to a maximum value at the ratio at which there was no excess of either reactant; and then fell to a value of about half the maximum when there was a 25% excess of cyclopropane in the reactant stream.

It was finally found that the rate of deactivation, during any run, was constant over long times after an initial break-in period. From this it was concluded that the concentration of carbonaceous deposits increases linearly with time, independent of the amount of active surface remaining.

Thesis Supervisor: Max C. Deibert

Title: Assistant Professor of Chemical Engineering

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts   02139
January 22, 1968

Professor Edward N. Hartley
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge, Massachusetts   02139

Dear Professor Hartley:

In accordance with the regulations of the Faculty, I herewith submit a thesis, entitled "The Kinetics of the Deactivation of a Nickel Catalyst during the Hydrogenation of Cyclopropane" in partial fulfillment of the requirement for the degree of Master of Science in Chemical Engineering at the Massachusetts Institute of Technology.

Respectfully submitted,

Edward M. Norin

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. Summary

A. Experimental Objectives

Within the last decade, a need has arisen for information regarding the kinetics of the deactivation of a nickel catalyst during the hydrogenation of cyclopropane. This deactivation has made informative comparison of different investigations involving this reaction very difficult due to different methods used to interpret the data. Future planned work on the hydrogen-cyclopropane-nickel system has made the need for deactivation information critical. It is the basic object of this report to obtain this needed information.

The required information fell into three categories:

1) The conditions, if any, for completely reactivating the catalyst;

2) Determining the temperature and reactant concentration dependencies of the rate of deactivation;

3) Formulating a model that can explain the observed results

B. Apparatus and Procedure

In this investigation, purified hydrogen was mixed with cyclopropane and diluted with helium until the total flow rate was 1000ml/min. This final mixture was reacted over 1.64 m^2 of finely divided nickel powder catalyst at atmospheric pressure. The catalyst was supported by a glass fit in a 3/8 inch diameter glass tube. The reactor temperature was controlled by a thermostated oil bath. The incoming gases were preheated by looping through a foot of one-quarter inch glass tubing submerged in the oil bath. The gases then flowed downward through the catalyst bed and into the chromatograph.

All incoming gas streams were regulated both by pressure

regulators on the supply tank and needle valves in the manifold system. The flow rates were calibrated with a soap-film flow meter.

The effluent stream from the reactor was analyzed by means of a Model 700, F & M Scientific Corporation Gas Chromatograph equipped with a dual flame, hydrogen ionization detector and the appropriate electronics. Reaction product samples were injected into the chromatograph with an on-line gas sampling valve. The output of the chromatograph electrometer was tied into a Microcord 44 recorder.

The reactor system could be evacuated for catalyst reactivation purposes. A vacuum was drawn by means of a roughing pump in series with an oil diffusion pump and a liquid nitrogen cold trap. Pressures below 10^{-4} torr were reached.

An experimental run was initiated, after establishment of temperature equilibrium, by starting the flow of cyclopropane into the hydrogen-helium mixture. The effluent stream composition was periodically measured for between one and two hours. At this point the reaction was stopped and the catalyst reactivated. In reactivation, the catalyst was first evacuated at 400°C for four hours to remove any volatile material adsorbed on the catalyst surfaces. Then at the same temperature, hydrogen was allowed to flow over the catalyst to remove any organic deposits. The hydrogen flow was continued overnight after which a new run could be conducted. If the catalyst was not immediately used, it would be stored under a positive hydrogen pressure to prevent leaks into the system.

C. Results

The reversibility of the deactivation was first studied. It was found that the catalytic activity of the sample could be completely

restored using a combination of high vacuum, flowing hydrogen, and high temperature. The same level of activity resulted on reactivation at any temperature above 360°C, but below 360°C, activity of the treated catalysts fell off sharply.

By both varying reaction temperature and reactant stream composition independently of one another, it was possible to determine the kinetics for the disappearance of cyclopropane. This resulted in the analytic expression:

$$-r_{CP} = k_0 \exp(-13.8 \text{ kcal/gm mole})(CP)^{0.4}(H_2)^{-0.6} \qquad \text{(A-1)}$$

This is in good agreement with previously reported kinetic data [20], [21], [13].

The temperature, pressure, and concentration dependence of deactivation was next determined. It was found that the rate of deactivation increased exponentially with increasing temperature. It was also found that the rate of deactivation increased linearly with increasing ratio of cyclopropane partial pressure to hydrogen partial pressure, up to the ratio at which there were no excess of either reactants. The equilibrium rate of deactivation was essentially zero at 65°C with a 300% excess of hydrogen in the reactant stream; and reached a maximum value at the above mentioned upper limit. It was finally observed that during any run, the rate of deactivation was constant over long times after an initial break-in period.

D. Conclusions and Recommendations

It is concluded that the observed catalytic deactivation is completely reversible on treatment of the catalyst with high vacuum followed by flowing hydrogen at temperatures above 360°C. It was

also concluded that the rate of deactivation could be correlated as a function of the ratio of cyclopropane partial pressure to hydrogen partial pressure. It was recommended that more work be done on this correlation at ratios at and above that which produce no excess reactants.

It was further concluded that the concentration of carbonaceous deposits increases linearly with time, independent of the amount of active surface area. It was recommended that this conclusion be further tested by allowing the reaction to proceed until the catalyst activity reaches zero or levels off.

II. Introduction

A. Purpose

Within the last decade, there have appeared many studies of the catalytic hydrogenation of cyclopropane with the purpose of gaining fundamental knowledge about reactions, molecular structure, and sorption, rather than the purpose of collecting kinetic data for design work. In these studies, the accurate measurement of the specific catalyst activity has become necessary for meaningful interpretation of the data. Previous investigators, using this reaction as a tool to solve problems of a fundamental nature, have been hampered by the fact that the specific catalytic activity decreased with time. This deactivation has made informative comparison of different investigations very difficult.

Several different methods have been attempted to solve the problem of interpreting data with a deactivating catalyst. These include bracketing each rate measurement by a measurement under standard conditions, and then normalizing the results; applying long, many stepped pretreatment between each measurement and then have assumed that the catalyst has been regenerated to the same level of activity; running a series of identical runs and then extrapolating back to zero time; employing an elaborate statistical analysis of the data; and finally, trying to work under conditions where the deactivation process is slow compared to the length of their runs.

The best way to analyze data under the above circumstances would be to obtain the kinetics of the deactivation process, so as to enable reporting all measurements in terms of the catalyst's intrinsic activity. Desirable as this information would be, no previous investi-

gator has obtained it. Since the frequent use of the hydrogen-cyclopropane-nickel system justifies obtaining this data, such work was carried out in this thesis. It was the general purpose of this thesis to procure the kinetic expression for the deactivation of a nickel catalyst during the hydrogenation of cyclopropane under various conditions of temperature, reactant concentration ratios, and pretreatments. As a side study, the ability to regenerate the catalyst was also studied.

B. Results of Previous Works

1. Observed Deactivation

Many previous investigators have studied the hydrogenation of cyclopropane on nickel and other similar systems. Many investigators observed continuous deactivation of the catalyst and postulated mechanisms for poisoning. In fact, all the previous investigators reviewed, except for one (13), have reported deactivation to one degree or another.

The works of J. H. Sinfelt, et. al. (18), (20), (21), (24) were made in a flow reactor system very similar to the one used in this investigation. The first work reported by the group (19) was the hydrogenolysis of ethane over supported platinum. Decline in activity of 10 to 20% during any one run and large cumulative activity declines over extended periods of time were observed. In that study, as in later works (20), (21), (24), this catalyst deactivation was corrected by a bracketing technique. This involved making runs at a standard condition between the desired runs, and then dividing the rates by the average rate at standard conditions. This allows the comparison of different measurements on the same or similar

catalysts if the deactivation is close to linear and the reaction mechanism is constant with time and temperature. These assumptions hold when working under conditions of moderate variations in catalyst activity (23). However, this method cannot be used to compare measurements on different catalysts and does not yield the absolute activity required for many purposes.

Many other authors discussed the deactivation problem. Schuit and van Reijen (18) used an elaborate statistical analysis of their kinetic data on ethylene hydrogenation which only produced data of "doubtful utility" (24).

Benson and Kwan (3), who hydrogenated cyclopropane over a supported nickel catalyst, reported a slow poisoning of the catalyst during runs. To make all runs at the same conditions, they cleaned the catalyst surface with hydrogen at $350^{\circ}C$ for one hour; followed by evacuation of the catalyst for one-half hour at the reaction temperature between each run.

Bond and Sheridan (5) hydrogenated cyclopropane at 160-$180^{\circ}C$, a temperature considerably higher than that used by most investigators. They reported that deactivation of nickel occurred, but at rates sufficiently slow for reliable data to be obtained.

Douglas McKee investigated the hydrogen-cyclopropane system over platinum balck catalyst. He found a carbonaceous residue, which he calculated by material balances to be of approximate composition $CH_{1.1}$, on the surface. He was able to remove this residue only by reducing the catalyst in flowing hydrogen at $150^{\circ}C$ or above for at least two hours. He reported that this residue poisoned the metal surface and caused by-products to occur in the gas phase.

2. Postulated Mechanisms

The mechanism of the hydrogen-cyclopropane reaction has been developed from several studies $(\underline{1})$, $(\underline{6})$, $(\underline{15})$, $(\underline{22})$ and has recently been summarized $(\underline{12})$. It has been found that in the presence of hydrogen and transition metal catalysts, cyclopropane undergoes five reactions:

1. Hydrogenation
$$cy\text{-}C_3H_6 + H_2 = C_3H_8$$

2. Hydrogenolysis
$$cy\text{-}C_3H_6 + 2H_2 = C_2H_6 + CH_4$$

3. Cracking
$$cy\text{-}C_3H_6 = C_3H_6 + C_2H_6 + CH_4 + (CH_{1.1})_x$$
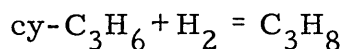
4. Isomerization
$$cy\text{-}C_3H_6 = CH_3\text{-}CH{=}CH_2$$
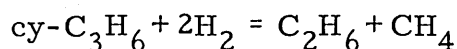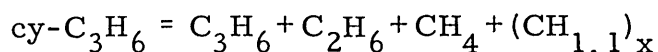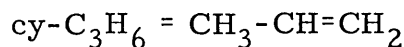
5. Polymerization
$$cy\text{-}C_3H_6 = (CH_2\text{-}CH_2\text{-}CH_2)_n$$
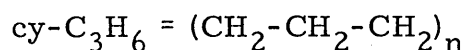
Under the reaction conditions used in this investigation, the hydrogenation and hydrogenolysis reactions will be the main reactions. Also of interest in this study will be the cracking reaction which lays down a deposit upon the catalyst surface and causes deactivation.

The nonstoichiometric cracking reaction takes place on most transition metals. It has even been observed during chemisorption of pure cyclopropane on nickel films $(\underline{13})$. McKee $(\underline{15})$ found that the reaction was no longer measurable above a hydrogen pressure of 25 mm of mercury on a platinum black catalyst, but the effect of hydrogen partial pressure over a nickel catalyst had not been investigated.

The reaction mechanism, after the cyclopropane has been

chemisorbed on the nickel surface, is probably the following:

$$\underset{*}{CH_2} \xrightarrow{\ 1\ } \underset{*}{\overset{\|}{CH_2}} + CH_3 \underset{\overset{\longleftarrow}{\longrightarrow}}{2} CH_3 + \underset{*}{\overset{\|}{CH_2}} \xrightarrow{\ 8\ } (CH_{1.1})_x$$

cyclopropane CH_2 ring with CH_2, CH_2, CH_2 (each attached to *)

reactions
3, 4, 5 connecting CH_2/CH_2

$$\underset{*}{H_2C} \text{---} \underset{*}{CH_2} \underset{\overset{\longleftarrow}{\longrightarrow}}{5} C_2H_6(g)$$

$$+$$

$$2\underset{*}{\overset{\|}{CH_2}} \xrightarrow{\ 6\ } 2\underset{*}{\overset{\|}{CH_3}} \xrightarrow{\ 7\ } 2CH_4(g)$$

$$\underset{*}{H_2C}\diagup \overset{CH_2CH_3}{|} \underset{\overset{\longrightarrow}{11}}{} CH_3CH_2CH_3(g)$$

10 (connecting top cyclopropane to CH_2CH_3 branch)

chemisorbed hydro-
gens not shown
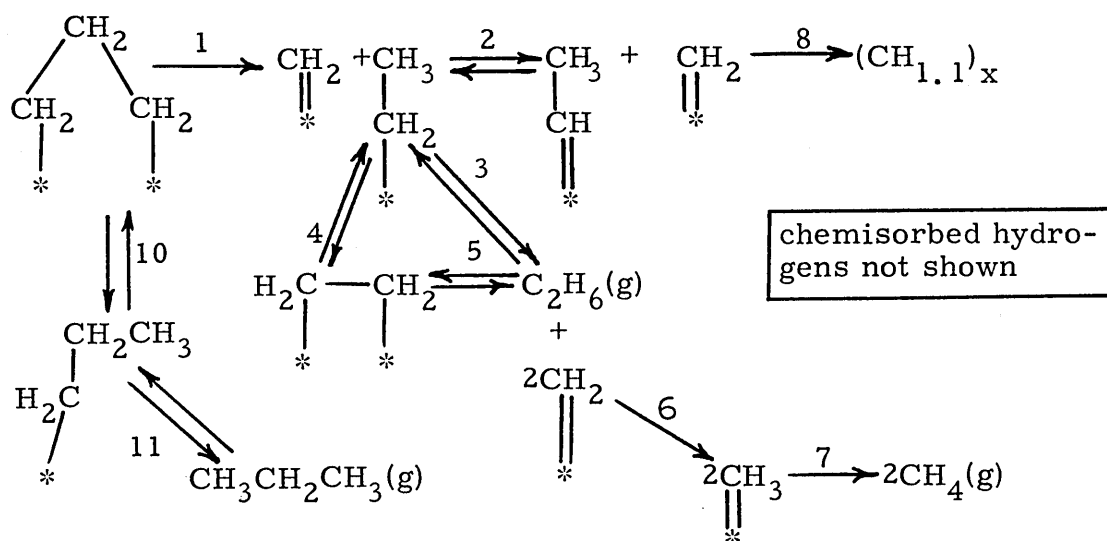
Reaction 1 is a cracking reaction where the two point adsorbed cyclopropane split into one and two carbon fragments. If the two carbon fragment loses a hydrogen atom, a double bonded radical occurs which could then polymerize and from the observed coke (reactions 2 and 9).

As seen by reactions 3 and 4, the two carbon fragments could also go to methane or ethane gas which are observed products of the reaction system.

3. Poisons

Cambell and Thomson (8) showed that mercury vapor is a poison for hydrogen-cyclopropane reactions. Their conclusion was that mercury displaces hydrogen from the catalyst surface, inhibiting the reaction. Because mercury is a poison, only oil diffusion pumps were used.

Oxygen has also been found to be a poison for this system.

Knor, et. al. (13), reported that the preadsorption of oxygen on a
nickel film decreases the rate of hydrogenation approximately to the
same degree as it decreases the extent of hydrogen chemisorption.
Care has been taken to keep all oxygen out of the system.

C. Method of Investigation

The main part of the investigation was the determination of the
kinetics for the deactivation of the catalyst. The reaction was
carried out in a flow reactor which contained a nickel powder catalyst.
The catalyst was regenerated before every run. During the run, the
reaction was monitored so that the rate of hydrogenation of cyclopro-
pane could be determined as a function of time.

A secondary study of the regeneration process was also made.
Time, temperature, and hydrogen flow rate were varied, starting
from the most severe conditions, until the catalyst no longer reached
its former level of initial activity.

III. Experimental Apparatus and Procedure

Research grade hydrogen and cyclopropane were diluted with helium, preheated, and reacted over a nickel powder catalyst in a thermostated, differential, continuous flow reactor. The reaction products were then analyzed with a gas chromatograph equipped with a flame ionization detector. All the gas streams for both the reaction and the gas chromatograph were controlled by one central manifold board. A standard catalyst preparation and chromatograph standardization were carried out before each experimental run.

A. Reagents and Catalyst

The "ultra Pure" grade of hydrogen was purchased from the Matheson Company, Inc., East Rutherford, New Jersey, and was further purified with a Deoxo®Gas Purifier from Engelhard Industries, Inc. and with molecular sieve desiccants. These purifiers are claimed by their manufacturers to lower the oxygen and water vapor concentrations to less than one part per million.

Cyclopropane of 99.6% purity was also purchased from the Matheson Company.General laboratory grades of hydrogen and helium were obtained from MIT laboratory supplies. These three gases were used without further purification.

A standard gas mixture for use in standardization of the gas chromatograph was obtained from the Matheson Company, Inc. Their analysis, done by their Morton, Georgia, laboratory was recorded in Appendix A-1. Natural gas was also used for standardization. A laboratory analysis, by the Boston Gas Company, of the mixture used can also be found in Appendix A-1.

An International Nickel Company, New York, N. Y., Mond Nickel Powder - Grade 255 was used as a catalyst. This powder was composed of irregularly shaped particles averaging between 2.6 and 3.4 microns in size. It had a porosity of between 85-90% as measured in Appendix B-8. Five and one-half grams of this catalyst was used giving a BET measured surface area of 1.5 meters^2.

B. Reactor and Bath

The catalyst was supported on a glass frit in a thin walled glass reactor tube (Fig. 6). The reactor was 3.5 inches high with an 0.5 inch outside diameter. The reactor was placed vertically with the gases entering from the top. A thermocouple junction was taped to the outer edge to record temperature.

The reactor was placed in a well-insulated Nujall bath (Fig. 2 and 5). The bath was agitated by a large magnetic stirrer. Temperature in the bath was controlled by a YSI Thermistemp® Model 71 temperature controller. Cooling water was allowed to flow continuously through a copper coil in the bath. One 250 watt infrared, immersion heater was operated continuously while a second was activated by the Thermistemp.

Before entering the reactor, the gases were preheated and mixed by passing through a 21 inch loop of glass tubing submerged in the oil bath. This preheated the gases to within 1°C of the bath temperature.

C. Manifold System

All the gas cylinders were connected directly to one central control panel (Fig. 1 and 4). The gas flow rates were controlled by
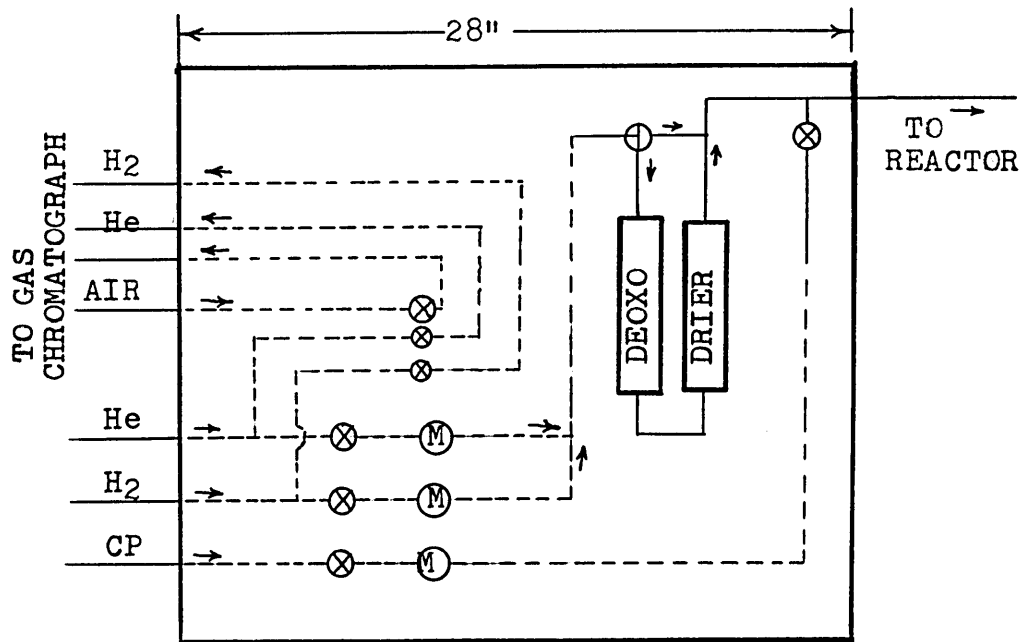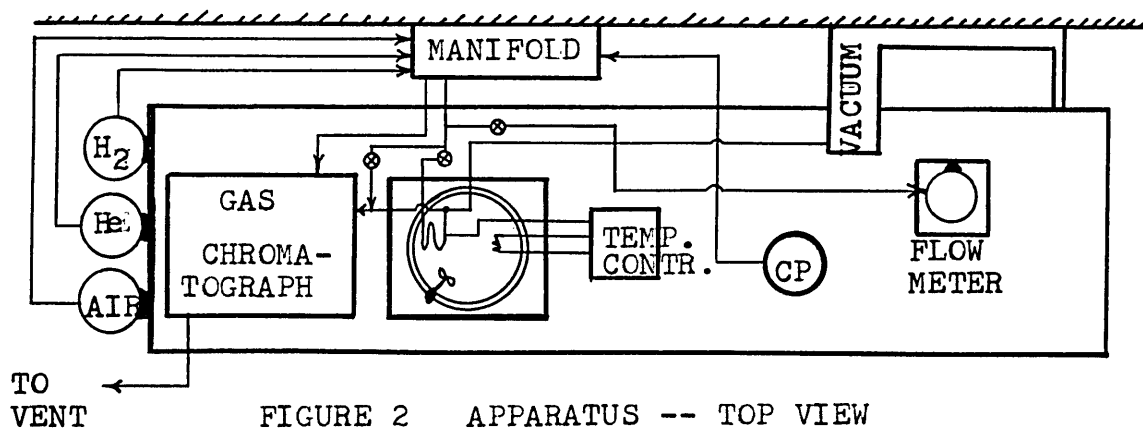
FIGURE 1   GAS MANIFOLD
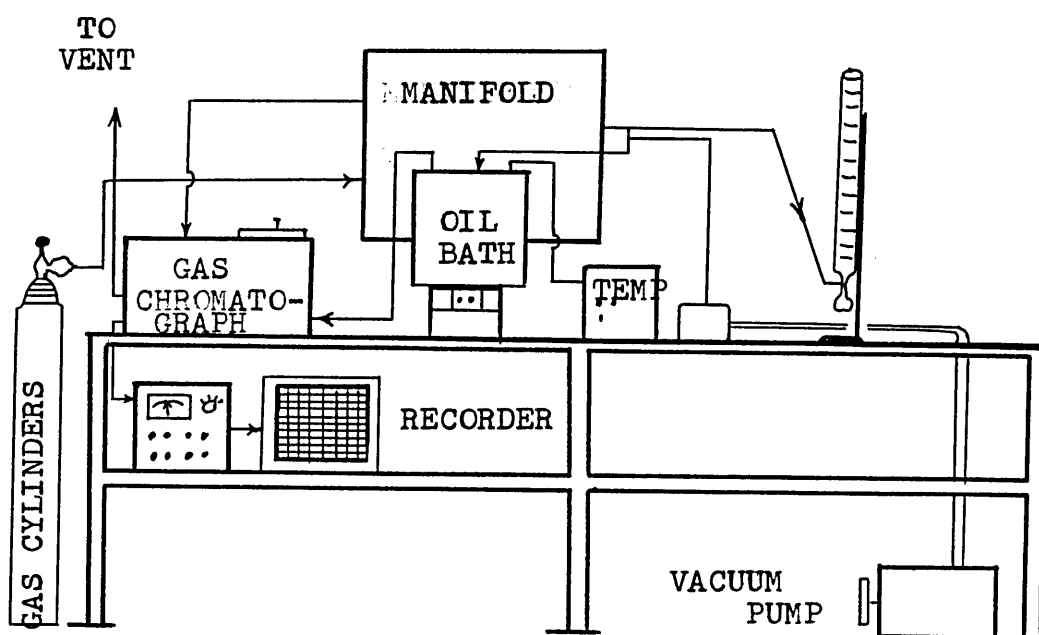

FIGURE 2   APPARATUS -- TOP VIEW

FIGURE 3   APPARATUS -- FRONT VIEW
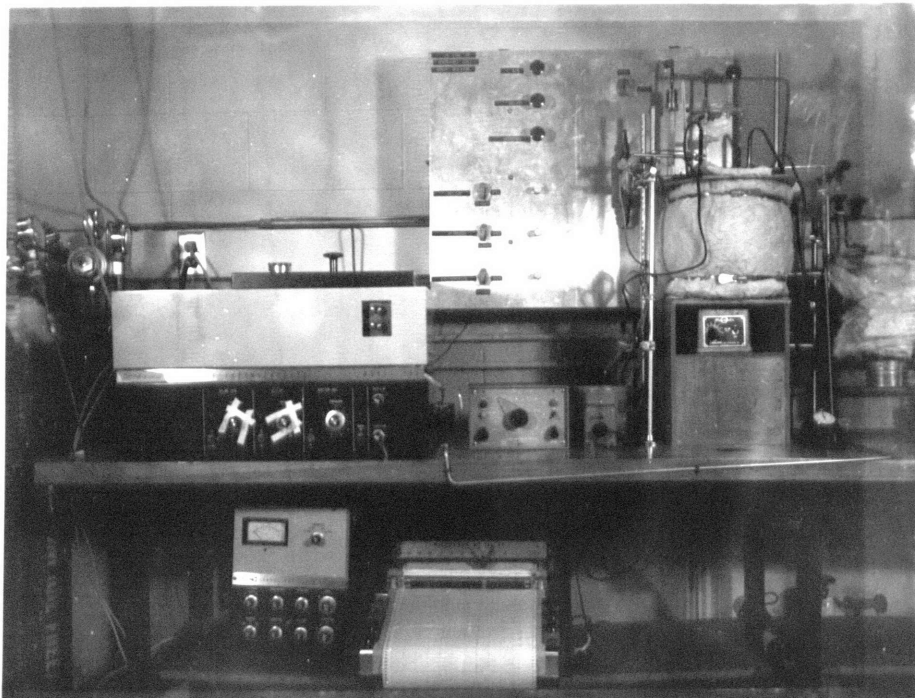
FIGURE 4   APPARATUS - PHOTOGRAPH
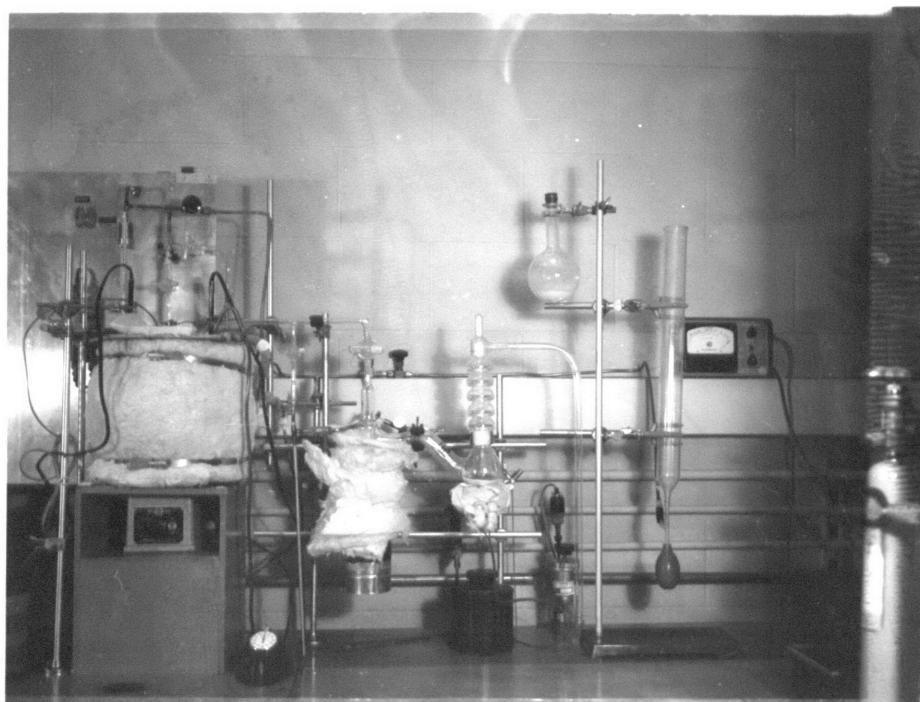
FIGURE 5   APPARATUS - PHOTOGRAPH
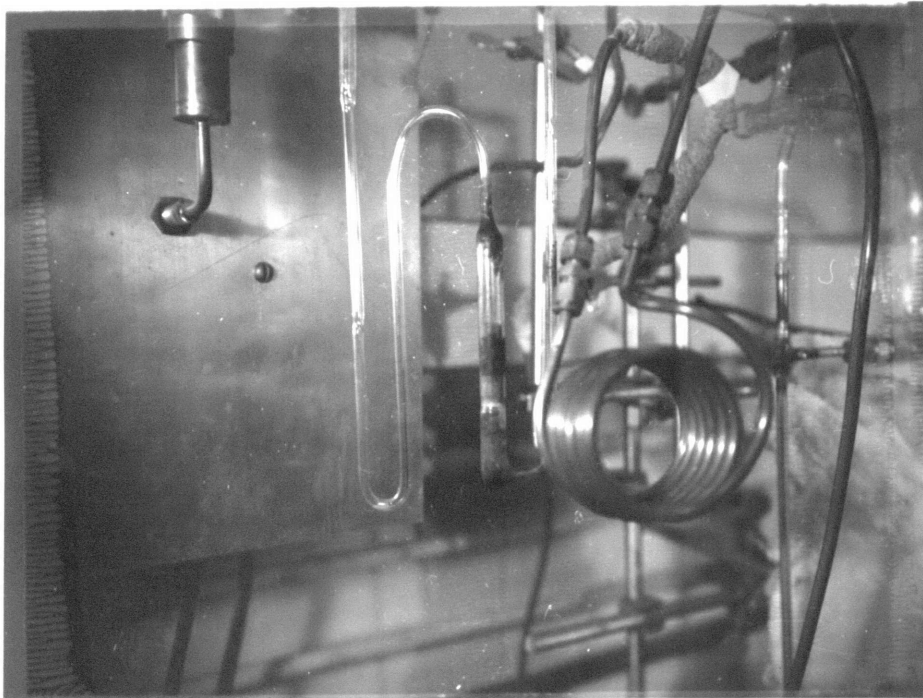
FIGURE 6   REACTOR - PHOTOGRAPH

means of micrometer-dialed needle valves which were set before each run with a soap film flow meter. In order that the flow rates be independent of small changes in down stream pressure drops, stainless steel capillary tubes were placed in the manifold system. It was determined that the flow rates were independent of each other; of the down stream resistances caused by the hydrogen purifying system; and of flow through the side stream feeding the gas chromatograph.

The manifold system was also connected up to the vacuum system. During the initial activation of the catalyst and during all subsequent reactivations, a high vacuum was needed. To obtain this vacuum, a roughing pump, an oil diffusion pump, and a liquid nitrogen cold trap were connected in series. An oil diffusion pump was used instead of the more efficient mercury pumps, because mercury is a catalyst poison.

The oil diffusion pump was a Consolidated Vacuum Corporation (Rochester, New York) type G-4 that was supplied with Octoil pump fluid. The vacuum, as measured with a type 518, NRC Equipment Corporation ionization gauge, was less than 5×10^{-5} torr.

D. Chromatograph and Recorder

The effluent stream from the reactor was analyzed for all reaction products and also for cyclopropane. The analysis system was composed of an on-line gas chromatograph with associated electronics and a strip chart recorder (Fig. 4). The gas chromatograph was placed on-line with a gas sampling valve (Model GV-10, F & M Scientific Corporation, Avondale, Penna.). These valves provided a convenient method of introducing reproducable amounts of sample into the chromatograph. The valve was designed to operate

without leaks at pressures more than two and a half times greater than used. Details of the operation of this valve will be found in Appendix A-3.

The analysis of reactor product stream samples was done on a laboratory gas-liquid chromatograph (700 Series, F & M Scientific Corporation) that was fitted with a dual flame, ionization detector and the appropriate electronics. The column used was a 30 foot one-quarter inch stainless steel tubing packed with 20% dimethylsufolane on 60-80 mesh chromosorb W.

The separated gases from the column were then burned in a flame ionization detector. A description of this detector may be found in Appendix A-4 and Reference 9 presents a more detailed analysis of the subject.

The electric signal produced by the detector was attenuated and balanced against background noise by an F & M Model 700 Electrometer (See Appendix A-2 for details of operation). From the electrometer, the signal was sent into a Microcord 44 (Photovolt Corporation, New York, N. Y.) self balancing, potentiometric strip recorder. During operation the recorder was set at full scale equal to one millivolt, and at a chart speed of two inches per minute.

E. Reactivation Procedure

After a kinetic run, the catalyst activity was generally much lower than its original activity. However, this activity could be completely restored by the reactivation procedure. The sixteen hour reactivation process was accomplished overnight.

The first step of reactivation was heating the sample under a high vacuum. With all flows turned off, the oil bath was removed from the reactor, and the reactor was wound with heating tape. The vacuum was

turned on as the temperature was allowed to rise to 400 ± 10°C. This was continued for four hours.

After heating in high vacuum to remove all gaseous adsorption products, the catalyst was heated under flowing hydrogen to remove carbonaceous deposits. The hydrogen flow was set at 50-70 cc/min and was held at 400°C for 10 to 16 hours. After this time, the catalyst was cooled in flowing hydrogen. At this point, it was concluded that the catalyst was fully reactivated. If the catalyst was not to be used immediately, it was stored under a positive pressure of 20 psig of hydrogen to assure against leaks into the system.

F. Kinetic Data Collecting Procedure

The experimental procedure began by cooling the freshly reactivated catalyst sample and placing the reactor in the oil bath. While the bath was equilibrating at the desired reaction temperature, the gas flow rates were set with a soap film flow meter, and then a blank was run through the analysis system.

When the desired temperature was reached, the hydrogen and helium flows were started. The reaction was started when the cyclopropane was mixed with the hydrogen. Samplings were then taken at regular intervals - every four minutes at the start of a run and every fifteen minutes near the end of the run. After enough data was taken (ninety to one hundred-fifty minutes), the hydrogen and cyclopropane flows were closed and the system was purged with helium. This purge was analyzed for catalyst desorption products. Finally the reaction rates were calculated for each sample taken.

G. Chromatograph Standardization Procedure

Although the output from a flame ionization detector was reported

to be linear (9), such an assumption did not produce the required accuracy. Chromatograph standardization was based upon the fact that at constant detector temperature and constant carrier gas flow rate, the ratio of the electrical outputs from each component remained constant. The mathematics behind this standardization technique is worked out in detail in Appendix B-1 and B-2. The equipment was standardized on three different occasions. Results of these standardizations are shown in Table III.

IV. Results

A. Hydrogenation Kinetics

The temperature and concentration dependence of the hydrogenation reaction kinetics were determined on catalysts activated at $400 \pm 10^{\circ}C$. The reaction rates were measured for temperatures of 55°, 75°, and $90^{\circ}C$ at a concentration of 0.03 atm. of CP, 0.09 atm. of hydrogen, and 0.88 atm. helium. These results are summarized in Figs. 8 and 9.

Determination of the concentration dependence of the rate of disappearance of cyclopropane was done at $65^{\circ}C$. The work was done in two parts. As summarized in Fig. 10, the concentration of CP was held constant at 0.04 atm. while the hydrogen concentration was varied between 0.04 and 0.20 atm. As the partial pressure of hydrogen increased, the initial rate of reaction decreased.

Next the hydrogen concentration was held constant at 0.09 atm. and the CP flow rate was varied from between 0.015 to 0.060 atm. As seen in Fig. 11, as the partial pressure of CP increased, the initial rate of reaction - as determined by extrapolating the linear portion of the curves back to time equals zero - increased.

B. Deactivation Kinetics

The effects of temperature and concentration of reactants upon the rate of deactivation of the nickel catalyst were measured. It was noted that the reaction rate versus time curves became linear at long times. The slope of this linear portion was defined as the rate of deactivation. For ease of comparison, all such data were fitted by the best straight line visually determinable.

The same runs that were used to study the effect of temperature

REACTION RATE vs. TIME
CP FLOW = 30 cc/min
H2 FLOW = 90 cc/min
☐ REACTION TEMP = 75°C.
⊙ REACTION TEMP = 55°C.

TIME (MIN)

FIGURE 8

-rcp (10⁻⁷ moles/sec/meter²)

REACTION RATE vsTIME
CP FLOW = 30 cc/min
H_2 FLOW = 90 cc/min
REACTION TEMP = 90°C.

TIME (MIN)
FIGURE 9

REACTION RATE vs. TIME

AT T = 65° C. AND CP FLOW = 40cc/min

HYDROGEN FLOW RATES

X = 40 cc/min
O = 90 cc/min
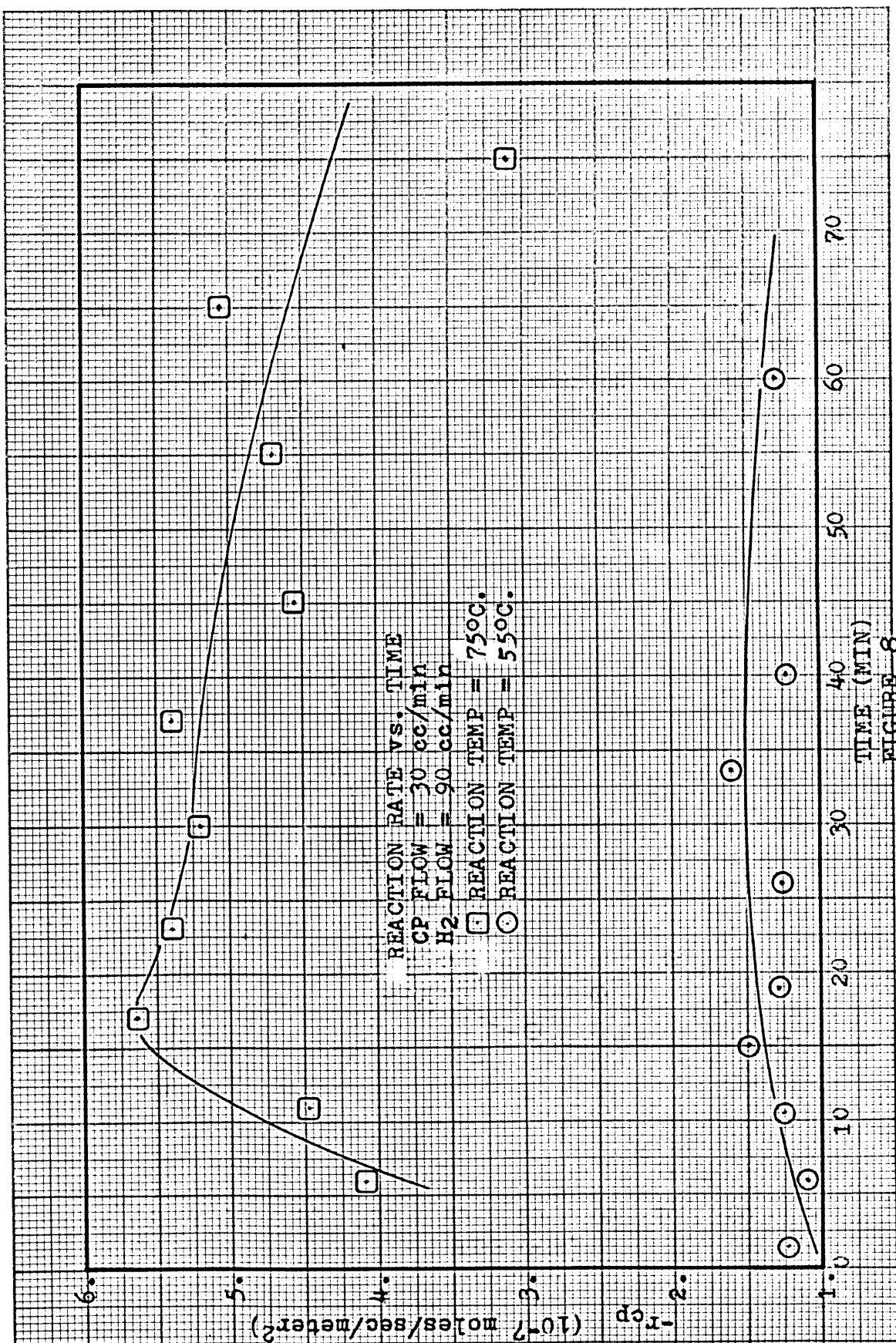△ = 120 cc/min
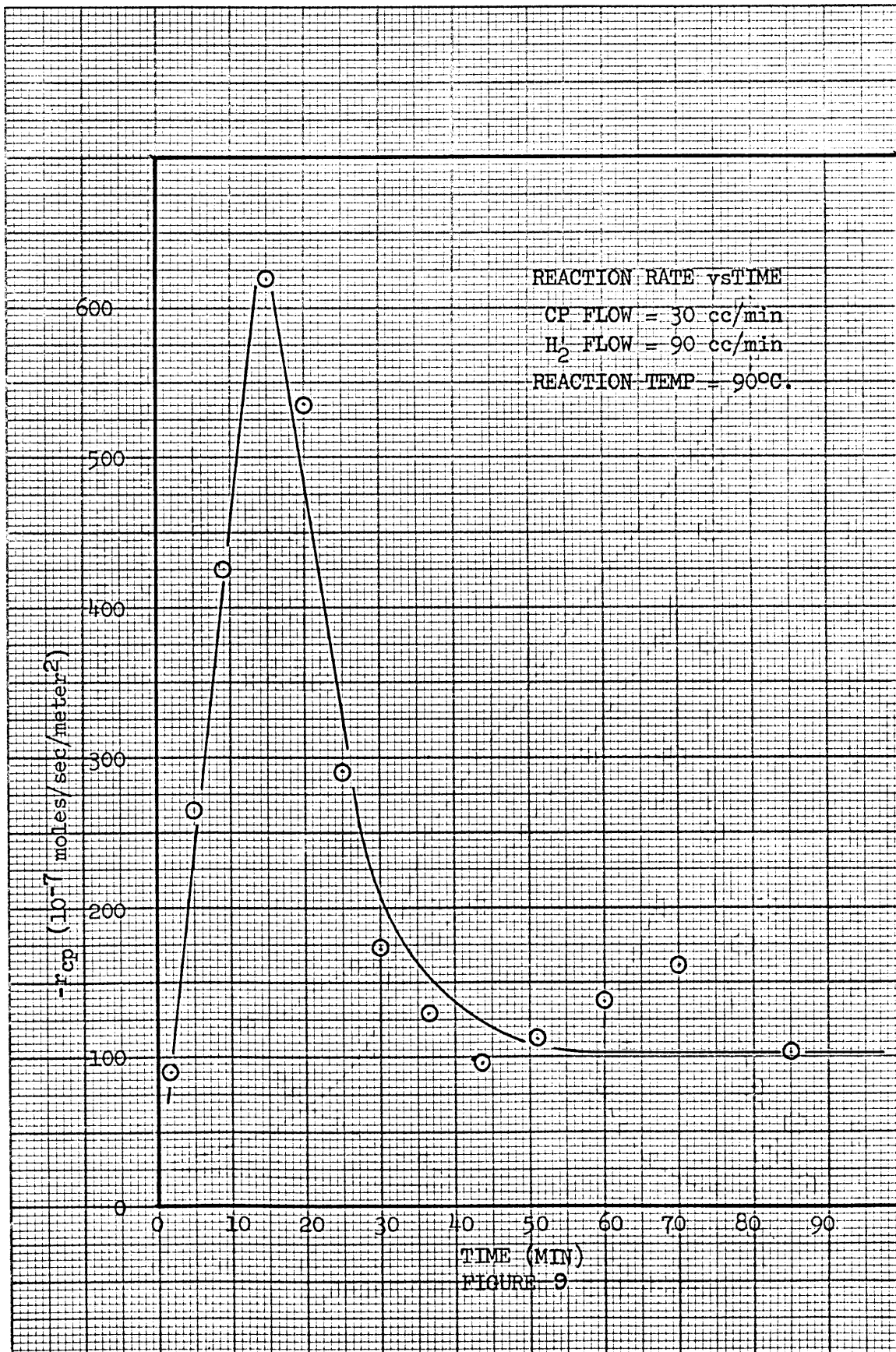⊕ = 200 cc/min

-rcp (10⁻⁷ moles/sec/meter²)

TIME (MIN)

FIGURE 10

36.
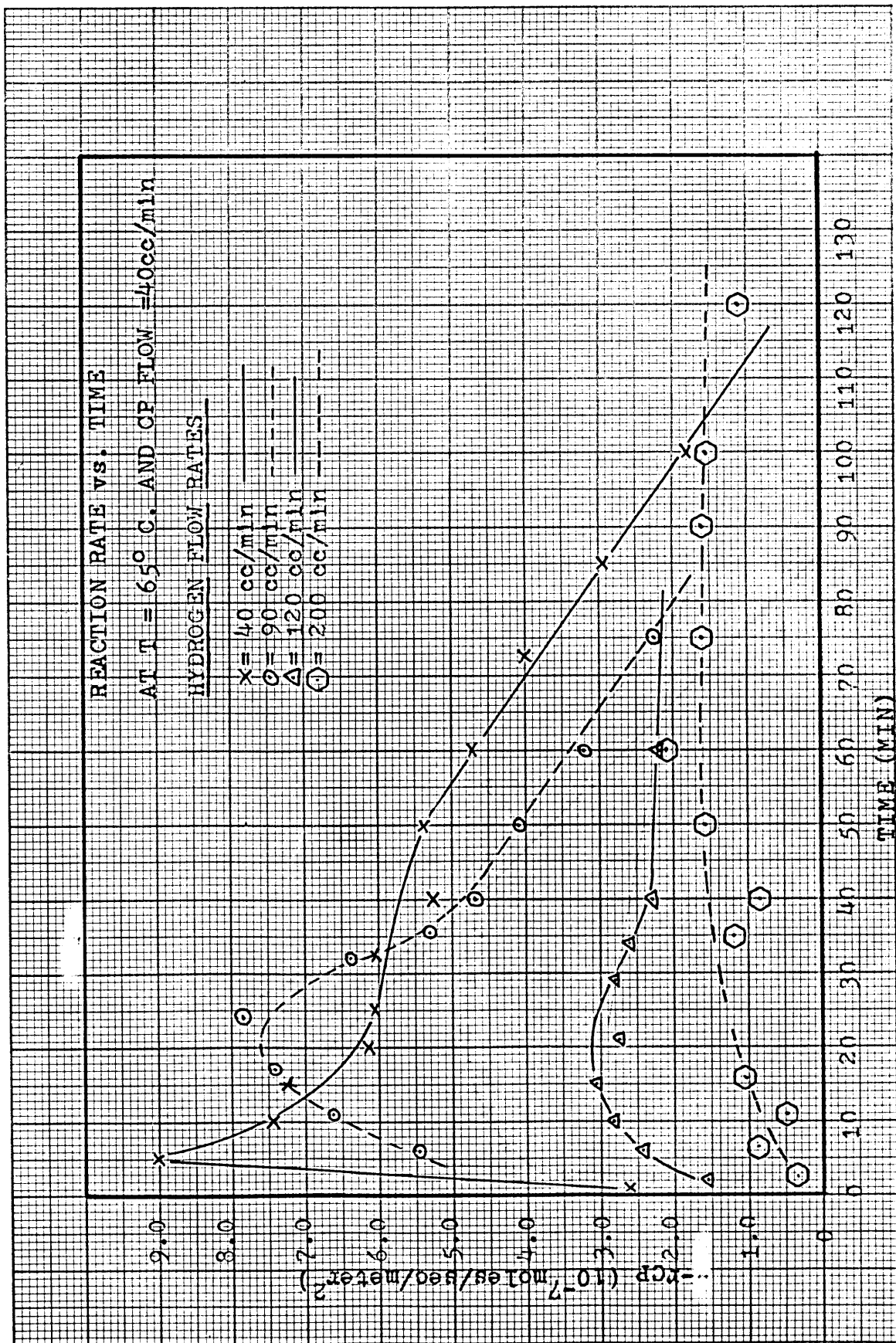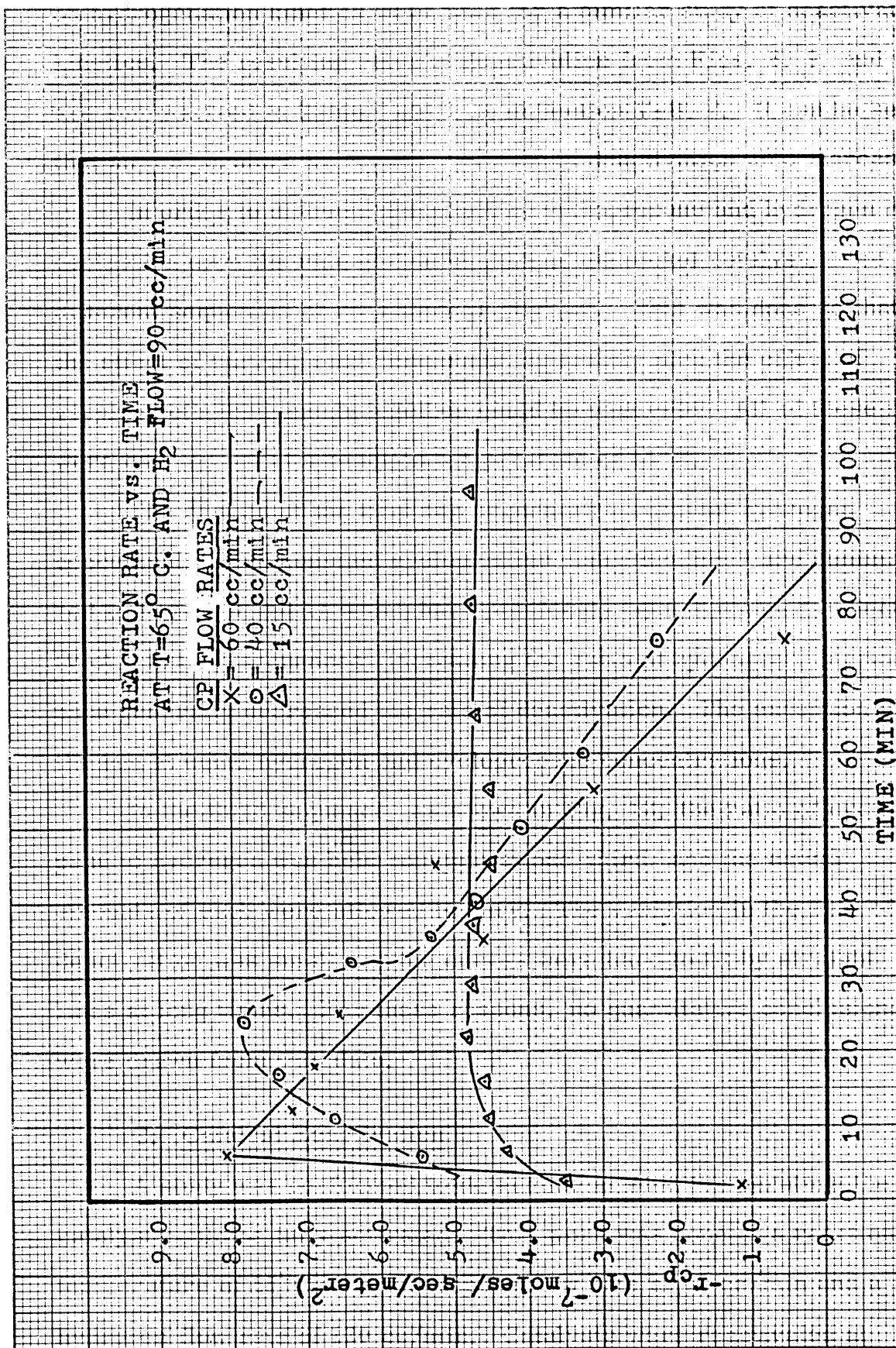
FIGURE 11

on hydrogenation kinetics were used for a similar study of deactivation kinetics. The resulting rates of deactivation from Figs. 8, 9, and 12 are summarized in Table I which is in Section V-B. 2. It can be seen that as temperature increases, the rate of deactivation also increases.

In order to discover the effect of cyclopropane and hydrogen concentration upon the rate of deactivation of the nickel catalyst, three different sequences of runs were performed. This was done so that the effect of varying each component separately plus the effect of varying both components together could be observed. All of these runs were carried out at a reaction temperature of 65°C.

The results of the first two sequences - constant hydrogen concentration and constant cyclopropane concentration - are summarized in Figs. 10 and 11 which have previously been discussed in Section IV-A. In both sequences, increasing the ratio of hydrogen to cyclopropane generally decreased the rate of deactivation. The exception being the run at equal hydrogen and cyclopropane concentrations.

In the third sequence, as shown in Fig. 12, the ratio of cyclopropane to hydrogen was held constant at one-third, and the actual amounts of each were allowed to vary. The variation in the rate of deactivation was small and the curves were hard to fit by straight lines at long times. For these reasons, no quantitative conclusions were drawn from this data.

C. Catalyst Reactivation

A study was performed to determine at what temperature the catalyst could be fully activated. This work was done at a reaction temperature of 65°C, a cyclopropane flow rate of 40 cc/min and a hydrogen flow rate of 120 cc/min. Catalysts were reactivated at

38.

REACTION RATE vs. TIME
AT T = 65°C. AND (CP/H2) = 0.33

○ CP = 50 cc/min   H2 = 150 cc/min
⊡ CP = 40 cc/min   H2 = 120 cc/min

-rCP (10⁻⁷ moles/sec/meter²)

TIME (MIN)
FIGURE-12
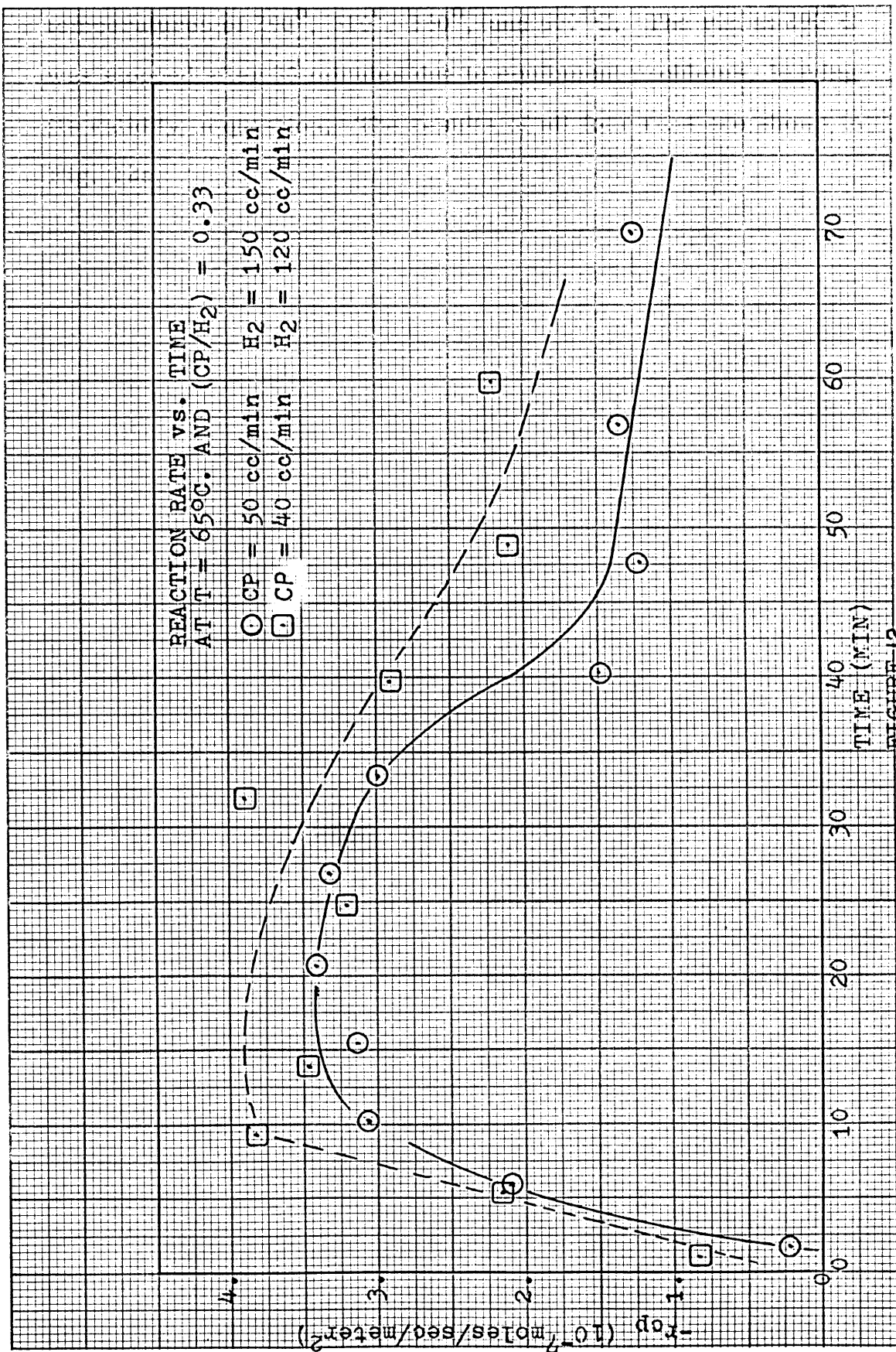
temperatures of 290°, 310°, 360°, and 400°C. The run at 290°C

was stopped after 30 minutes due to equipment problems, leaving

its validity in question. The results of all four runs are shown in

Fig. 12a.

40.

REACTION RATE vs. TIME FOR VARIOUS REACTIVATION TEMPERATURES

$(CP/H_2) = 0.33$ $T = 65°C.$

⊙ $T = 360°C$
▢ $T = 400°C$
✕ $T = 310°C$
⬡ $T = 290°C$

TIME (MIN)

FIGURE-12a

$-r_{CP}$ (10^{-7} moles/sec/meter^2)
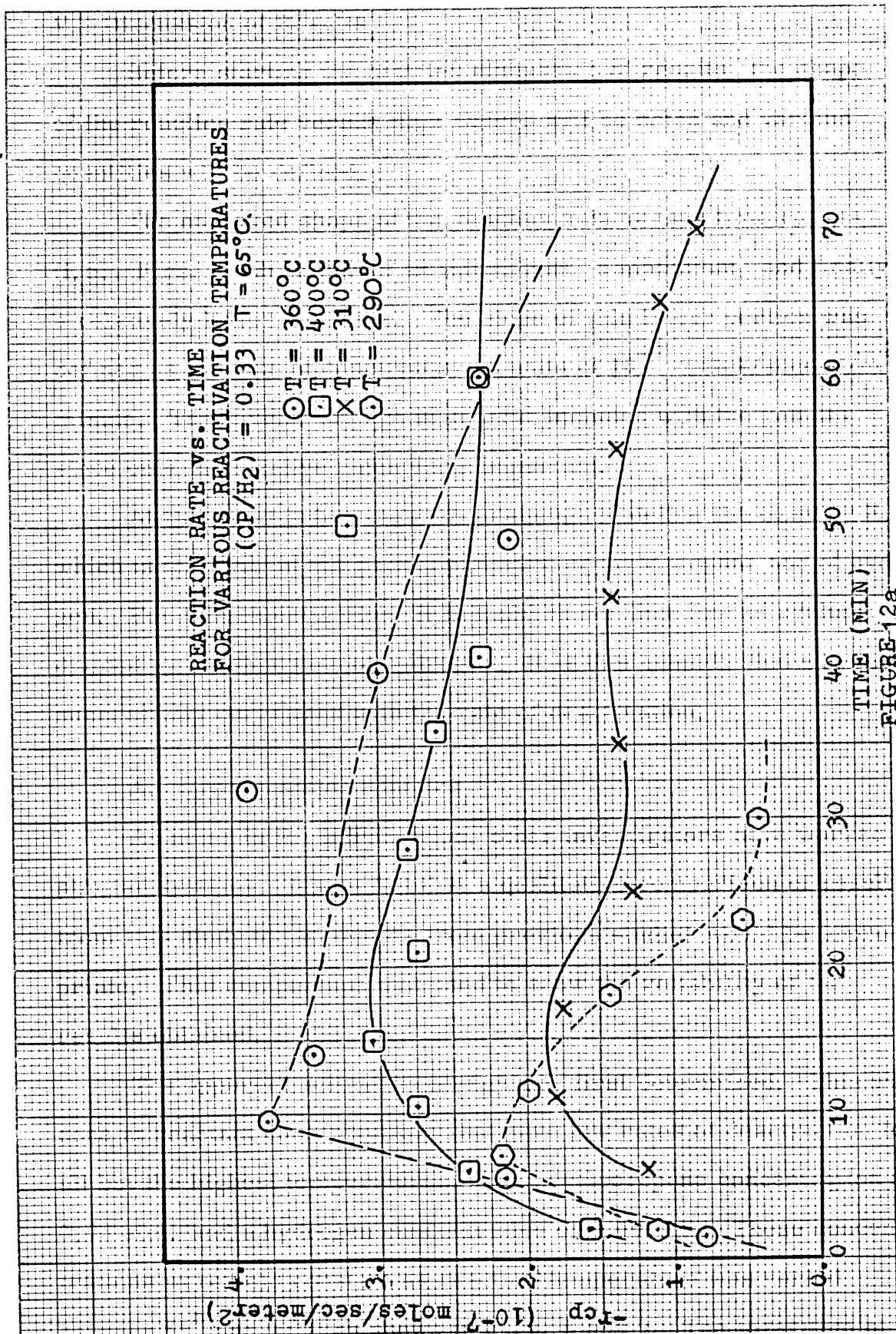
V. Discussion of Results

Before starting the detailed discussion of results, the shape of the reaction rate versus time curves will be noted and various quantities will be defined.

The observed shape of the reaction rate versus time curves (i.e., Figs. 7-12) is that of an initial rise, a maximum, and finally a relatively linear decrease. The slope of this linear portion was defined as the rate of deactivation in units of 10^{-7} moles/second/m^2/ minute. These units are not in general included with the results since only the relative rates were important.

At this point it becomes advantageous to define the quantity R, which is the ratio of the partial pressure of cyclopropane and of hydrogen. For this investigation, R is equal to the flow rate of cyclopropane divided by the flow rate of hydrogen. It is this quantity that was most successfully correlated with the rate of deactivation.

A. Hydrogenation Kinetics

As noted in the introduction, other investigators have worked on similar systems. It was felt that a qualitative comparison of results from this study to the results from previous studies would be appropriate. This comparison was used to show the reliability of the results obtained.

The apparent activation energy was first determined. This was done at reactant concentrations that gave low rates of deactivation for all but the highest temperatures, i.e., cyclopropane concentration of 0.03 atm. and a hydrogen concentration of 0.09 atm. These concentrations were held constant as reaction temperature was varied between 55° and 90^oC as shown in Figs. 8 and 9. The logarithm of

the rate at 70 minutes of reaction time was plotted versus the reciprocal of the reaction temperature in Fig. 13. From the slope of the resulting straight line, the apparent activation energy is 13.8 kcal/gm mole. This value compares well with a range of 13.0 - 15.2 kcal/gm mole obtained by J. H. Sinfelt, et. al. (20), (21) for various types of supported nickel catalysts.

By extrapolation, kinetic data for the hydrogenation of cyclopropane is commonly reported at $0^{\circ}C$. Thus for comparative purposes, some of the reaction rates determined in this investigation were referred to the above temperature. This was done by assuming that the apparent activation energy was independent of temperature down to $0^{\circ}C$. Although this assumption is probably in error, the error is small and also the same assumption has been used by all other investigators for comparison purposes.

Sinfelt, et. al. (20), (21) reported rates of reaction of between $3.5 - 250 \times 10^{-10}$ moles/sec/m^2 referred to $0^{\circ}C$, at a hydrogen partial pressure of 0.20 atm., and at a cyclopropane partial pressure of 0.03 atm. These rates were determined on various supported nickel catalysts. On the pure nickel powder used in the present investigation, it was found that the rate under similar conditions to those described above, the reaction rate is 6.1×10^{-10} moles/sec/m^2.

Knor, Ponec, et. al. (13) have carried out the hydrogenation of cyclopropane on a nickel powder catalyst similar to the one used in this investigation. They reported a rate of 3.0×10^{-10} moles/sec/m^2 for an equal mixture of cyclopropane and hydrogen referred to $0^{\circ}C$. The comparison value found in the present investigation is 14.0×10^{-10} moles/sec/m^2. The factor of five difference in these values may be due to differences in experimental procedure. Knor, Ponec, et. al.

REACTION RATE vs (TEMPERATURE)$^{-1}$
CP FLOW = 30 cc/min
H_2 FLOW = 90 cc/min
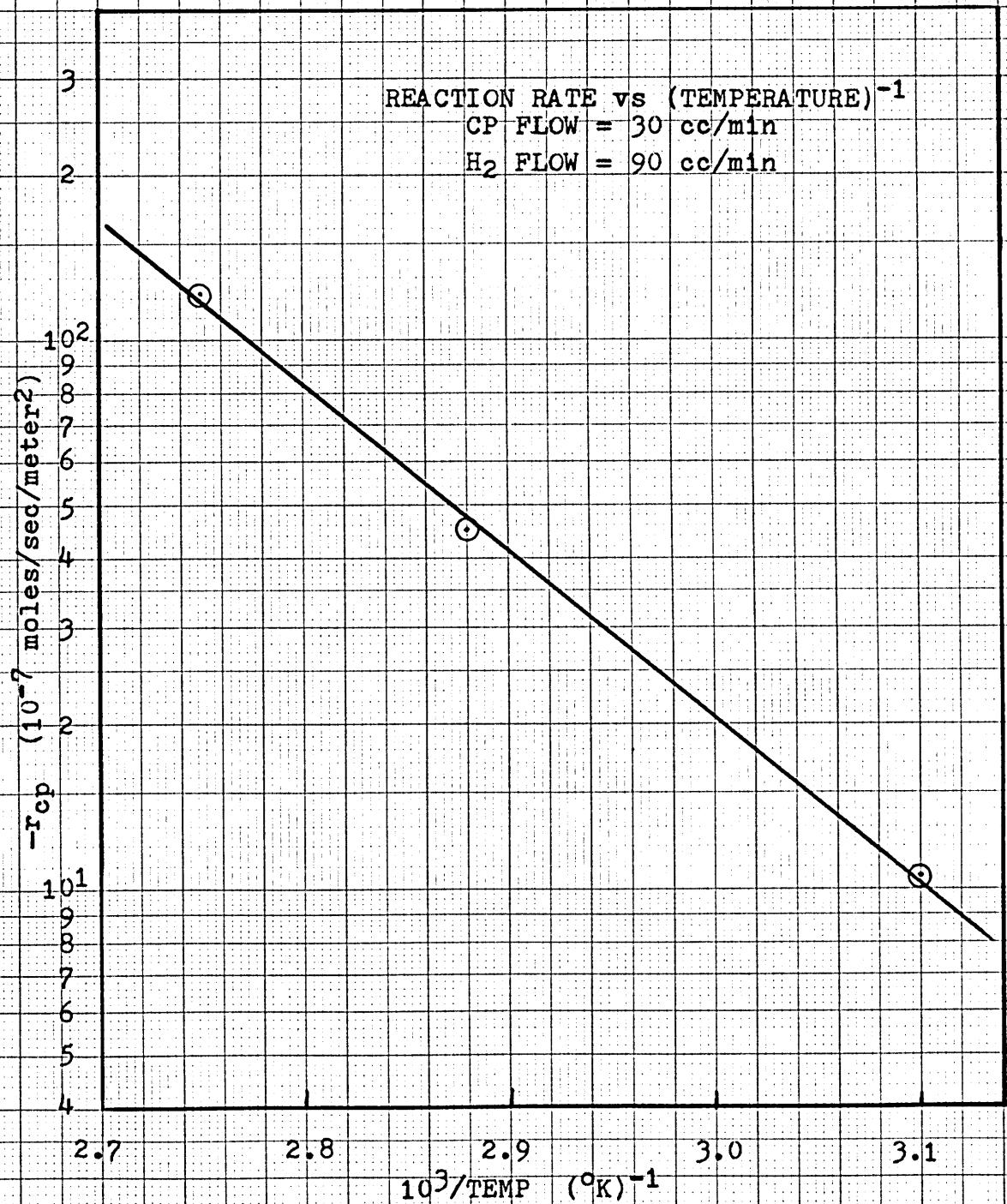
FIGURE 13

made their measurements in a static reactor at a total pressure of 1.2 - 1.5 mm of Hg, whereas in the present investigation, measurements were taken in a flow reactor at a total pressure of 1 atmosphere.

A final comparison with the works of other investigators was made on the reaction order of hydrogen and cyclopropane in the overall rate expression. In general, the reaction orders have been found to go from zero in cyclopropane and minus one in hydrogen at temperatures around 0°C to an order to one in cyclopropane and zero in hydrogen at temperatures above 150°C.

In the present study, the cyclopropane order was 0.4 and the hydrogen order was -0.6 at 65°C. These reaction orders were estimated from figures 8 and 9. These orders are in very good agreement with those previously observed.

It is seen that good comparisons with the results of previous investigators were found for cyclopropane hydrogenation kinetics data. Thus, it is concluded that the methods and apparatus used in this investigation work well for this system and that the data obtained are reliable.

B. Deactivation Kinetics

1. Correlation with R

In Fig. 14, the relative rate of deactivation was plotted as a function of R. Also plotted was the R corresponding to a mixture of hydrogen and cyclopropane which would yield no excess reactant. This mixture is defined as the stoichiometric mixture. Since the ratio of hydrogenation to hydrogenolysis varied between 3:1 and 4:1, the stoichiometric mixture fell in a range of 0.80 to 0.83. The runs plotted in Fig. 14 are those found in Figs. 10 and 11. All runs were made at 65°C on a catalyst that had been reactivated at 400°C.

In Fig. 14, the five data points with R's less than the above defined stoichiometric mixture form a straight line of positive slope. Thus as the ratio of cyclopropane to hydrogen increases, the rate of deactivation increases linearly up to the stoichiometric ratio.

The single point corresponding to an R greater than the stoichiometric mixture falls below the line formed by the other data points. It seems probably that the maximum rate of deactivation lies near this concentration, although more data at high R's is needed to confirm this conclusion.

2. Temperature and Pressure Dependences of Deactivation

From Figs. 8, 9, and 12, rates of deactivation were determined for an R of one-third and at reaction temperature of 55°, 65°, 75°, and 90°C. These rates of deactivation, shown in Table I, clearly show a dependence on temperature - the rate of deactivation increases with increasing temperature.

46.

Limiting speed of deactivation of the catalyst vs. the ratio of CP to H_2 in the feed

Reaction Temp. = 65°C.

FIGURE 14
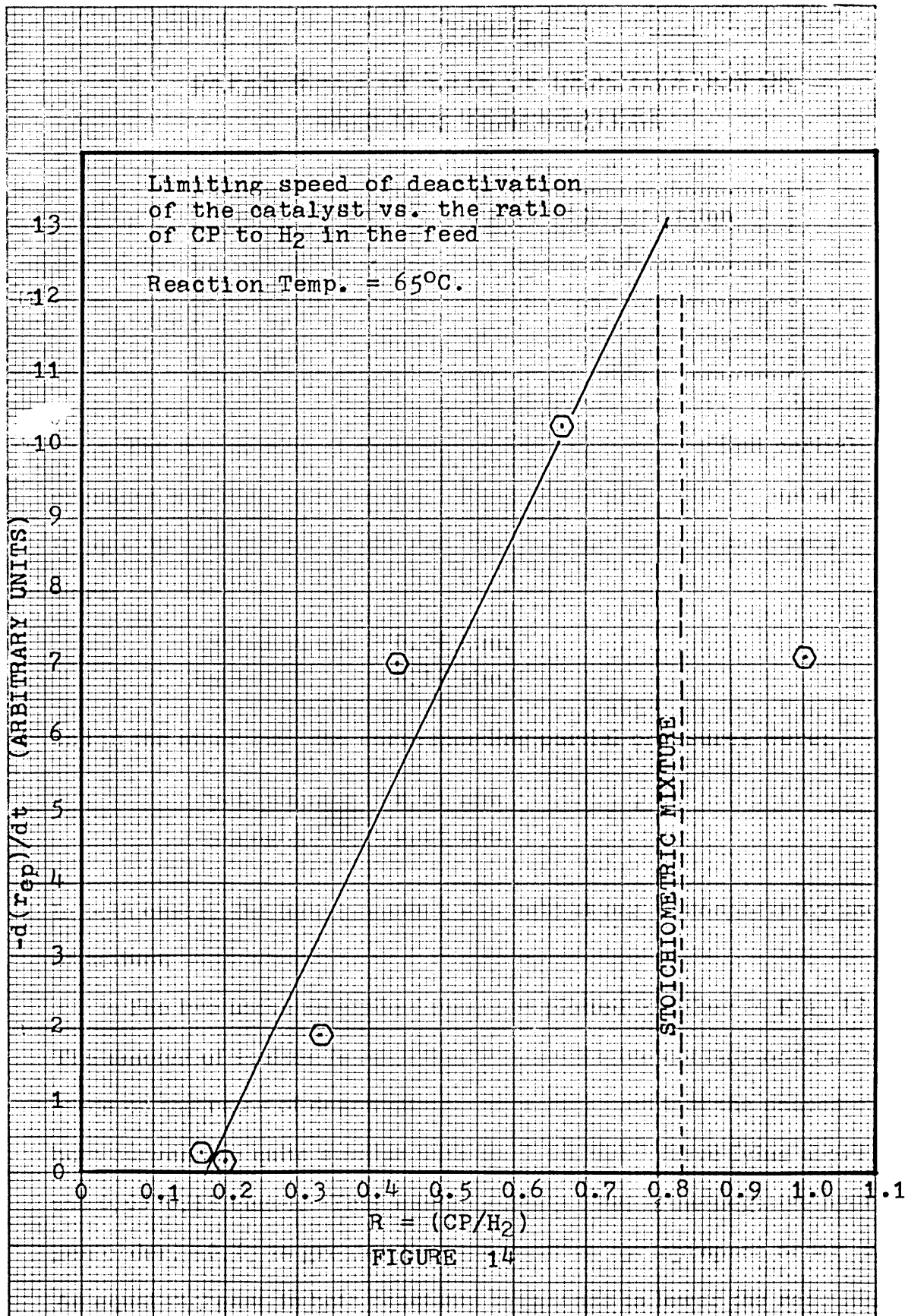
TABLE I

DEPENDENCE OF RATE OF DEACTIVATION ON REACTION TEMPERATURE

Temp. (^{O}C)	Rate of Deactivation
55°	1.1
65°	1.8
75°	2.1
90°	2.8

The dependence of reaction rate on the total reactant partial pressure was also investigated. Runs were made at 65°C and at an R equal to one-third. In one run, the reactant partial pressures were:

cyclopropane = 0.04 atm.
hydrogen = 0.12 atm.

and in the other run, the corresponding partial pressures were:

cyclopropane = 0.05 atm.
hydrogen = 0.15 atm.

In both cases, the total pressure was held at one atmosphere by use of helium.

The two above described runs are plotted together in Fig. 12. The amount of scatter is such that no quantitative conclusions can be made on the rates of deactivation. It is observed that the shapes of both curves are quite similar with the 0.04/0.12 curve lying above the 0.05/0.15 curve. This was as expected since the negative hydrogen order, -0.6, is greater than the positive cyclopropane order, 0.4. An equal increase in both reactants thus tends to lower the reaction rate.

3. Catalyst Break-in Period

It was earlier observed that the catalyst has initially a very low activity, rises steeply through a maximum, and finally begins a linear deactivation. The time required until the catalyst reaches this linear deactivation was called the catalyst break-in period. This period was usually between 40 and 50 minutes long, but was as low as 20 minutes for runs with very slow rates of deactivation. It was not possible to correlate the catalyst break-in period to either temperature or composition. Also the cause of this break-in period was not determined.

4. Mechanism

Griffith and Marsh (11a) have called the type of deactivation observed in this investigation fouling. They apply this term to the formation of carbonaceous deposits on catalysts used for reaction involving organic molecules. Fouling is normally the result of polymerization and is gummy. The characteristic properties of fouling is its reversibility - it can usually be totally removed by combustion.

Since it was found in this work that cleaning the catalyst surface with flowing hydrogen at high temperatures completely restored the catalyst activity, it was concluded that fouling was the cause of deactivation. McKee, who investigated the hydrogen-cyclopropane system over platinum black catalysts, determined the composition of this carbonaceous residue to be approximately $CH_{1.1}$ (15). A similar composition would be expected on the nickel catalyst used in this work.

Since fouling proceeds by covering the surface of the catalyst

with a carbonaceous deposit and thus effectively lowering the amount of active catalyst surface, it was expected that both the rate of coke formation would be inversely proprotional to the coke concentration, C, as found by Voorhies (22a) and others. This can be expressed mathematically as

$$\frac{dC}{dt} = \frac{K}{C} \tag{5}$$

Integrating between C = 0, t = 0 and C = C, t = t yields:

$$C = \sqrt{2Kt} \tag{6}$$

Since the activity for hydrogenation is proportional to the reciprocal of the coke concentration, it follows that the activity for hydrogenation (and hydrogenolysis) is proportional to (time)$^{-1/2}$ - i.e.:

$$-r_{Cp} \; \alpha \; 1/\sqrt{t} \tag{7}$$

The actual results found did not show the relationship predicted from Equation 7. As shown in Figs. 10 and 11, the catalyst activity for hydrogenation and hydrogenolysis was directly proportional to the first power of time for periods of over an hour. The linear deactivation was best described by an equation of the form:

$$-r_{Cp} = -mt + b \tag{8}$$

It was then concluded that only a reaction rate of polymerization, independent of active surface area could account for the observed time dependency of the catalytic activity. This was determined by first noting that at constant reactant concentration, the overall reaction rate, $-r_{Cp}$, was equal to:

$$-r_{Cp} = -\frac{d(Cp)}{dt} = K_1 A \theta \tag{9}$$

where K_1 = a constant (moles/time/area)

A = initial surface area

θ = fraction of the surface available for reaction

Differentiating equation 9 with respect to time yields,

$$\frac{dr_{Cp}}{dt} = -K_1 A \frac{d\theta}{dt} \tag{10}$$

But from the observed results as expressed in Equation 8, it can be seen that:

$$\frac{dr_{Cp}}{dt} = K_2 \tag{11}$$

where K_2 = rate of deactivation. Now combining Equations 10 and 11 gave:

$$\frac{d\theta}{dt} = -\frac{K_2}{K_1 A} \tag{12}$$

Assuming that there exists some constant, b, equal to the area covered per mole of coke, θ was expressed as:

$$\theta = 1 - \frac{bC}{A} \tag{13}$$

Differentiating with respect to time,

$$\frac{d\theta}{dt} = -\frac{b}{A} \frac{dC}{dt} \tag{14}$$

Combining Equations 12 and 14 finally gave the desired results that,

$$\frac{dC}{dt} = +\frac{K_2}{bK_1} \tag{15}$$

$$C = \left(\frac{K_2}{bK_1}\right)t \qquad (16)$$

That is, the amount of carbonaceous deposits increases linearly with time independent of the amount of active surface available.

The one assumption made in this derivation was that the area covered per gram of carbonaceous deposit, b, is a constant. It would be expected that this would hold true as long as the surface was not completely covered with the deposit and that the deposit is of uniform thickness. Since the reaction was always stopped before the reaction rate reached zero or leveled off, the surface could not have been completely covered. Since it is unlikely that the thickness of the deposit is a strong function of θ, the assumption that b is a constant is highly probable.

A completely satisfactory model that would account for the independence of the rate of carbonaceous deposition with respect to θ has not been found. It is thus recommended that further investigation be conducted towards developing such a model.

C. Catalyst Reactivation Kinetics

The deactivation of the catalyst was observed on all runs conducted during the present investigation and has also been observed by previous investigators (3), (5), (15), (18), (19), (20), (21), (24). Benson and Kwon (3) had reported that this deactivation was completely reversible and that by evacuation at reaction temperature and then cleaning with flowing hydrogen at 350°C, the initial activity of the catalyst could be completely restored. One of the purposes of this investigation was to examine this reactivation procedure.

From the results of this investigation, it is concluded that the

deactivation of the catalyst can be completely resotred by proper treatment. This catalyst treatment consists of evacuating the catalyst at a temperature greater than $350^{o}C$ and then flowing hydrogen over the catalyst at the same temperature. Fig. 7 shows that the reaction rates on the catalysts reactivated at 360° and $400^{o}C$ are nearly equal with the former averaging only seven per cent higher than the latter.

The reaction rates on the catalyst reactivated at $310^{o}C$ averaged about 50% below that of the catalyst reactivated at $400^{o}C$. Finally, the catalyst activated at $290^{o}C$. had a reaction rate averaging 75% below that of the catalyst reactivated at $400^{o}C$. This information is summarized below in Table II.

TABLE II

EFFECT OF REACTIVATION TEMPERATURE
ON TIME AVERAGED REACTION RATES

Temperature	rate/(rate at $400^{o}C$)
$400^{o}C$	—
$360^{o}C$	1.07
$310^{o}C$	0.50
$290^{o}C$	0.25

The results of Table II show that if the catalyst is reactivated first under vacuum followed by flowing hydrogen at a temperature above $360^{o}C$, the catalyst can be assumed to be returned to its initial activity. The seven per cent difference between the runs on the catalysts activated at $400^{o}C$ and $360^{o}C$ is probably the limit of experimental precision.

VI. Conclusions

1. The observed catalytic deactivation is completely reversible on treatment of the catalyst with high vacuum followed by flowing hydrogen at temperatures above $360^{\circ}C$.

2. At constant temperature and total pressure, the rate of deactivation increases linearly with increasing ratio of cyclopropane partial pressure to hydrogen partial pressure, up to the ratio at which there are no excess reactants.

3. At a constant ratio of cyclopropane partial pressure to hydrogen partial pressure and at constant total pressure, the rate of deactivation increases exponentially with increasing temperature.

4. The concentration of carbonaceous deposits increases linearly with time, independent of the amount of active surface area.

5. The methods and apparatus used in this investigation are well suited for analyzing kinetic data for cyclopropane hydrogenation.

VII. Recommendations

1. Additional work should be performed to test the dependency of rate of deactivation upon temperature and upon the ratio of cyclopropane partial pressure to hydrogen partial pressures at and above that ratio which gives no excess reactants.

2. Investigations leading to a satisfactory model of the deactivation should be carried out in order to increase the understanding of this effect. A first step would be to determine if the rate of deactivation continues to be linear down to zero activity.

3. Suggested reaction conditions for conversions in the range of one per cent and for a low rate of deactivation are a reaction temperature around $65^{o}C$ and a ratio of cyclopropane partial pressure to hydrogen partial pressure equal to or less that 0.20.

55.

VIII. Appendix

A. Supplementary Details

1. Standardized Gas Mixture

a. The Matheson Company, Inc.
P. O. Box 136
Morrow, Georgia   30260

Date: July 25, 1967

Analyst: John Oliver

Cylinder No. RR-23657

Cyclopropane	4.71%
Propane	4.88%
Propylene	5.14%
Methane	5.41%
Ethane	5.24%
Helium	Balance

b. Boston Gas Company
144 McBride
Boston, Massachusetts

Date: July 20, 1967

Analyst: Mr. Churchill

Methane	94.02%
Ethane	3.33%
Propane	0.58%
Carbon Monoxide	1.16%
Nitrogen	0.63%
Butanes and Pentanes	Traces

2. Principles of Operation of Model 700 Electrometer

The electrometer consists of an electrometer tube, a series of high input range resistors, zero and balancing network, an attenuator and two battery voltage sources to provide bias for the Flame Ionization

Detector. Batteries also supply power to the plate and filament of the electrometer so that no A. C. line power is required. The current from the detector is permitted to flow through the high input resistors and the zero network. The voltage so developed provides the input signal to the electrometer tube. The zero network provides a voltage which compensates for the voltage due to detector background current by inserting a series voltage of equal magnitude and opposite polarity. The output is taken across a bridge type network in the cathode of the electrometer tube which allows the system to have a "live" zero and also aids in stability. Initially, the electrometer is balanced by means of the coarse and fine potentiometers with the input shorted. An input signal (change in detector current) to the tube causes an unbalance across the bridge output terminals and the resulting voltage is applied to the input terminals of a recorder to provide a permanent record. Various instrument sensitivities are available through the selection of range and attenuation.

3. Description of Gas Sampling Valve

A stainless steel spool rides inside a stainless steel cylinder on silicone rubber O-rings. In the "load" position the spool is pushed in, and the sample flows through the sample inlet port, through the center of the spool, around the sample loop, to the sample vent. In this position the carrier gas flow directly into the chromatograph.

To inject the sample, the spool is pulled out. This causes carrier gas to sweep the sample that is contained in the sample loop into the column; while the sample stream is diverted directly to the vent. By use of double seals, leakage is prevented when the spool is moved from the load to inject position. It also allows the use of larger

holes to reduce pressure drop across the valve.

The silicone rubber O-rings were replaced during the data taking period (F & M part # 6303) and the entire valve was cleaned and regreased with a high grade silicone grease.

4. Theory of Flame Ionization Detectors

In a hydrogen flame ionization detector, the column effluent is mixed with hydrogen fuel and burned at the tip of the metal jet in an excess of air. To reduce spurious noise, the hydrogen and air streams are filtered to remove particulate alkali salts and carbon compounds which produce ion avalanches as they pass through the flame. Hydrogen burning at the jet produces a very low background, of the order of 10^{-14} amperes, depending on flow rate and impurity content, which can be electrically compensated. The ions are collected at the electrodes, the jets being negative and the positive electrode, the electrode collector, a metal ring placed just above the tip of the flame. The phenomena producing ions in the flame have not been fully established. Whatever the actual mechanism, both electrons and positive ions are produced, the latter having the lower transport velocity in any given field because of their larger mass. After the ionization event, recombination occurs to a degree that is determined by the electrode voltage and ion concentrations. The electrode voltage is adjusted to obtain the saturation current for optimum performance. This voltage is a function of the electrode spacing but is independent of electrode size.

B. Sample Calculations

1. Normalized Standardization Factors

$$f_p = \frac{hcp}{hp} \times \frac{\%p_s}{\%CP_s}$$

For average of runs S-12 through S-15 (8/22)

height of CP peak	hcp	$= 3.9 \pm 0.1$ cm
height of propane peak	hp	$= 5.1 \pm 0.1$ cm
% propane in sample gas	$\%p_s$	$= 4.88 \pm 0.01\%$
% CP in sample gas	$\%CP_s$	$= 4.71 \pm 0.01\%$

$$f_p = \frac{3.9 \pm 0.1}{5.1 \pm 0.1} \times \frac{4.88 \pm 0.01}{4.71 \pm 0.01}$$

$$f_p = 0.79 \pm 0.015 \text{ unitless}$$

TABLE III

NORMALIZED STANDARDIZATION FACTORS

f_i	8/22/67	9/1/67	9/12/67
f_{Me}	1.48	1.26	1.78
f_{Et}	0.965	0.923	1.03
f_p	0.79	0.82	0.784
$f_{C_3H_6}$	0.96	0.90	0.874

2. **Per cent Propane in Effluent Stream**

$$\% P = \frac{h_p}{h_{cp}} \times \frac{f_p}{} \times 100\% - \%(C_3H_6)_B$$

For run 13-8 (8/31)

height of propane peak	h_p	$= 6.2 \pm 0.1$ cm
height of CP peak	h_{cp}	$= 16.8 \pm 0.1$ cm
attenuation factor	a	$= 20.$

normalization factor for propane $f_p = 0.79 \pm 0.015$

per cent propylene in the blank $\%(C_3H_6)_B = 0.22 \pm 0.005\%$

$$\%P = \frac{6.2 \pm 0.1}{16.8 \pm 0.1} \times \frac{0.79 \pm 0.015}{20} \times 100\% - 0.22 \pm 0.005\%$$

$\%P = 1.46 \pm 0.01\% - 0.22 \pm 0.005\%$

$\%P = 1.24 \pm 0.015$ unitless

3. Per cent Conversion of Cyclopropane

$$\% \text{ conversion} = \frac{\%P + \frac{2}{3}(\% ET) + \frac{1}{3}(\%M)}{\%CP + \%P + \frac{2}{3}(\% ET) + \frac{1}{3}(\%M)}$$

For Run 13-8 (8/31)

per cent propane in effluent $\% P$ = $1.24 \pm 0.015\%$

per cent ethane in effluent $\% ET$ 0.42 ± 0.010

per cent methane in effluent $\% M$ 0.35 ± 0.008

per cent CP in effluent $\% CP$ 97.99 ± 0.03

% conversion

$$= \frac{(1.24 \pm 0.015) + \frac{2}{3}(0.42 \pm 0.01) + \frac{1}{3}(0.35 \pm 0.008)}{(97.99 \pm 0.03) + (1.24 \pm 0.015) + \frac{2}{3}(0.42 \pm 0.01) + \frac{1}{3}(0.35 \pm 0.008)}$$

% conversion = $1.64 \pm 0.10\%$

4. Reaction Rate

$$-r_{cp} = \frac{F_{cp} \ (\% \text{ conversion})}{A \ (100\%)}$$

For Run 13-8 (8/31)

molal flow rate of CP entering the reactor $\quad F_{cp} = (3.00 \pm 0.15) \times 10^{-5}$ moles/sec

% conversion of CP $\quad$ % conversion $= 1.64 \pm 0.10\%$

BET surface area of the catalyst $\quad A = 1.64 \pm 0.12$

$$-r_{cp} = \frac{(3.00 \pm 0.15) \times 10^{-5} \text{ mole/sec} \times (1.64 \pm 0.01)\%}{1.64 \pm 0.12 \text{ m}^2 \times 100\%}$$

$$-r_{cp} = (3.0 \pm 0.2) \times 10^{-7} \text{ moles/sec/m}^2$$

5. Concentration Ratio

$$R = \frac{F_{cp}}{F_{H_2}}$$

For Run 13

cyclopropane flow rate $\quad F_{cp} = 40 \pm 2 \text{ ml/min}$

hydrogen flow rate $\quad F_{H_2} = 120 \pm 2 \text{ ml/min}$

$$R = \frac{(40 \pm 2)}{(120 \pm 2)}$$

$$R = 0.333 \pm 0.006$$

6. Activation Energy

$$\Delta E_{ACT} = -R \left[\frac{d \ln(-r_{cp})}{d(1/T)} \right]$$

For Runs 8, 10, and 12

Gas Law Constant $\quad = 1.987 \text{ cal/g mole } {}^{\circ}K$

Slope of Figure 13 $\quad = 6.93 \pm 0.10 \times 10^3 \; ({}^{\circ}K)$

$$\Delta E_{ACT} = -1.987(6.93 \pm 0.10) \times 10^3$$

$$\Delta E_{ACT} = 13.8 \pm 0.2 \text{ kcal/g mole}$$

7. Reaction Rate at $0^{\circ}C$

$$-r_o = (-r_T) \exp \left[-\frac{\Delta E_{ACT}}{R} \left(\frac{1}{T} - \frac{1}{273.1} \right) \right]$$

For Run 13-8 (8/31)

Reaction rate at $T = 50^{\circ}C$ $-r_T = 3.0 \pm 0.2 \times 10^{-7} \text{ moles/sec/m}^2$

Activation Energy $\Delta E_{ACT} = 13.8 \pm 0.2 \text{ kcal/g mole}$

Gas Law Constant $R = 1.987 \text{ cal/g mole } ^{\circ}K$

Reference temperature $T = 323.0 \pm 1 \ ^{\circ}K$

$$-r_o = (3.0 \pm 0.2) \times 10^{-7} \exp \left[\frac{13.8 \pm 0.2)}{1.987} \times 10^3 \left(\frac{1}{323 \pm 1} - \frac{1}{273.1} \right) \right]$$

$$-r_o = 6 \pm 1.2 \times 10^{-9} \text{ moles/sec/m}^2$$

8. Catalyst Porosity

$$P = (1 - \rho_P/\rho_S) \times 100\%$$

For catalyst sample A   (9/13/67)

actual density of nickel powder $\rho_P = 1.35 \pm 0.01 \text{ gm/cm}^3$

density of pure solid nickel $\rho_S = 8.90 \text{ gm/cm}^3$

$$P = \left(1 - \frac{1.35 \pm 0.01}{8.90}\right) \times 100\%$$

$$P = 84.2 \pm 0.1\%$$

C. Location of Original Data and Detailed Calculations

The original data and detailed calculations are in the custody of the author. Permanent copies of all of this material are held by Professor Max C. Deibert, Department of Chemical Engineering, MIT, Room 12-148.

D. Summary of Data and Calculated Values

Run	Cp Flow ml/min	H_2 Flow ml/min	Reaction Temperature $^{\circ}C$	Regeneration Temperature $^{\circ}C$	Rate of Deactivation moles/sec/m^2/min
8	30	90	55	409	1.1×10^{-9}
9	30	91	65	300	——
10	30	90	90	420	2.8×10^{-9}
13	40	120	65	360	1.8×10^{-9}
14	50	150	65	390	——
15	40	120	65	400	——
16	40	120	65	300	——
17	30	90	75	400	2.1×10^{-9}
18	40	120	65	310	——
19	40	120	65	490	1.86×10^{-9}
20	40	90	65	407	6.95×10^{-9}
21	15	90	65	390	0.29×10^{-9}
22	40	200	65	390	0.19×10^{-9}
23	60	90	65	408	10.2×10^{-9}
24	40	40	65	396	7.1×10^{-9}

E. Nomenclature

Symbol	Definition
A	Surface area - meter^2
a	Attenuation factor for the electrometer
b	Specific area - m^2/gm
C	Concentration of carbonaceous deposits on the surface - moles/cm^2
CP	Cyclopropane
E	Energy - kcal/gm mole
Et	Ethane
F	Molar flow rate - moles/sec
f	Normalized Standardization Factor
g	Gaseous state
h	Height of chromatograph peak - cm
K	Arbitrary constants
k	Rate constants - specific rate units
M	Micrometer valve
Me	Methane
P	Propane
p	Porosity
R	Gas law constant - 1.987 cal/gm mole $^\circ K$
R	Ratio of the partial pressure of Cp to the partial pressure of H_2
r	Reaction rate - $\text{moles}/\text{sec}/\text{meter}^2$
T	Temperature - $^\circ C$ or $^\circ K$
t	Time - minutes
Δ	The final state - the initial state

Symbol	Definition
ρ	Density - gm/cm^3
θ	Fraction of the surface available for reaction

Subscripts

Symbol	Definition
A	Actually measured
ACT	Activation (apparent)
B	Blank
Cp	Cyclopropane
Et	Ethane
i	Pertaining to substance i
Me	Methane
0	Referenced to $0^{o}C$
P	Propane
R	Reactivation
s	Pure solid substance
s	Pertaining to standardized sample
1	First arbitrary constant
2	Second arbitrary constant

F. Bibliography

1. Addy, J., and G. C. Bond, Trans. Fara. Soc., 53, 368-376 (1957) and 53, 383-392 (1957).

2. Baddour, R. F. and M. C. Deibert, J. Phys. Chem., 70, 2173 (1966).

3. Benson, J.E., and Takaokwan, "Kinetics and Mechanism of the Hydrogenation of Cyclopropane Over a Nickel-Silica-Alumina Catalyst," The Journal of Physical Chemistry, 60, 1601 (1957).

4. Bond, G. C., and J. Newham, "Catalysis on Metals of Group VIII, Part 5 - The Kinetics of the Hydrogenation of Cyclopropane and of Methylcyclopropane," Trans. Fara. Soc., 56, 1501-1514 (1960).

5. Bond, G. C., and J. Sheridan, "Studies in Heterogeneous Catalysis, Part 4." Trans. Fara. Soc., 48, 713-715 (1962).

6. Bond, G. C., and John Turkevich, "The Reaction of Cyclopropanes with Deuterium over a Platinum Catalyst," Faraday Society Transactions, 50, 1335 (1954).

7. Boudart, M., A. Aldag, J. E. Benson, N. A. Dougharty, and C. Girvin Hawkins, "On the Specific Activity of Platinum Catalysts," Journal of Catalysis, 6, 92-99 (1966).

8. Campbell, K. C., and S. J. Thomson, "The Investigation of Chemisorption and Catalyst Poisons by Radiochemical Techniques, Part 2 - Selective Catalysts Poisoning in the Hydrogenation of Cyclopropane and Propylene," Trans. Fara. Soc. 55, 985-991 (1959).

9. Dal Nogare, S. and R. S. Juvet, Jr., Gas-Liquid Chromatography, pp. 214-221, Interscience Publishers, New York, (1962).

10. Deibert, M. C., "The Interaction Between a Catalyst and its Support," Sc.D. Thesis in Chem. Eng., MIT, Cambridge, Mass. (1964).

11. Fieser, L. F., and Mary Fieser, "Organic Chemistry," D. C. Heath and Company, Boston (1956).

11a. Griffith, R. H. and J. D. F. Marsh, Contact Catalysis, pp. 192-211, Oxford University Press, London (1957).

12. Kline, R. W., "The Promoting Effect of Electronic Interaction Between Catalyst and Support in the Hydrogenation of Cyclopropane," Thesis Proposal, MIT, Cambridge, Mass. (1967).

13. Knor, Z., V. Ponec, Z. Herman, Z. Dolejseki, and S. Cerng, "Chemisorption and Hydrogenation of Cyclopropane on Nickel," Journal of Catalysis, 2, 299-309 (1963).

14. Krell, E., "Handbook of Laboratory Distillation," Elsevier Publishing Co., New York (1963), translated by C. G. Verver, pp. 264-273.

15. McKee, D. W., "Catalytic Activity and Sintering of Platinum Black, Part II-Demethylization and Hydrogenolysis of Cyclopropane," J. Phys. Chem., 67, 1336-1340 (1963).

16. Podbielniak, W. J., "Apparatus and Methods for Precise Fractional-Distillation Analysis," Industrial Eng. Chem. Anal. Ed., Part I, 3, 177 (1931), and Part II, 5, 119 (1933).

17. Roginski, S. Z., and F. H. Rathman, "Analysis of Propylene and Cyclopropane in Mixtures Containing Both," J. Amer. Chem. Soc., 55, 2800 (1933).

18. Schuit, G. C. A., and L. L. van Reijen, Advanced Catalysis, 10, 242 (1958).

19. Sinfelt, J. H., "Hydrogenolysis of Ethane over Supported Platinum," J. of Phys. Chem., 68, 344 (1964).

20. Sinfelt, J. H., D. J. C. Yates, and W. F. Taylor, "Kinetics of the Reaction of Cyclopropane with Hydrogen over a Series of Silica-supported Metals, " J. Phys. Chem, 69, 1877-1882 (1965).

21. Taylor, W. F., D. J. C. Yates, and J. H. Sinfelt, "Catalytic Reaction of Cyclopropane with Hydrogen over Supported Nickel," J. of Catalysis, 4, 374-379 (1965).

22. Veillard, A., and G. Del Re, Theor, Chim. Acta., 2, 55-62 (1964).

22a. Voorhies, Industr. Eng. Chem. 37, 318 (1945).

23. Walsh, A. D., "The Structure of Ethylene Oxide, Cyclopropane, and Related Molecules," Trans. of Fara. Soc., 45, 179 (1949).

24. Yates, D. J. C., W. F. Taylor, and J. H. Sinfelt, "Catalyst Over Supported Metals, Part I," J. Am. Chem. Soc., 86, 2996 (1964).