ABSTRACT

The catalytic hydrogenation of 2-butyne has been studied in a constant volume static system over nickel, copper, cobalt, iron, homogeneous nickel-copper alloy powders and pumice supported iron.

The orders of the reaction with respect to initial pressures of the reactants, activation energies and frequency factors for various catalysts have been determined. The order of reaction with respect to hydrogen is one and nearly independent of temperature, while the order of reaction with respect to 2-butyne is slightly negative and temperature dependent except for copper where it is zero and temperature independent. The activation energies for nickel, copper and cobalt are 9.13, 6.5 and 33.5 k cal/mol respectively. The activation energy for the alloy catalyst varies from 6.5 to 9.2 k cal/mol.

The catalytic activities of pure metals are

$\mathrm{Ni} \gg \mathrm{Co} > \mathrm{Fe} > \mathrm{Cu}$.

For nickel-copper alloy series, the activity increases with small additions of copper, passes through a maximum for about 10% copper and then decreases on further addition of copper. Correlation has been made between the catalytic activity and holes in the d band of the catalyst.

An extensive study of the product analysis has been made over all catalysts except over supported and unsupported iron. The effect of various variables such as catalyst composition, initial pressure of reactants and reaction temperature on selectivity have been discussed. A possible mechanism has been proposed.

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TABLE OF CONTENTS

LIST OF TABLES

TABLE PAGE

APPENDIX A

APPENDIX B

TABLE PAGE

LIST OF FIGURES

Page

NOMENCLATURE

a	cell dimension ^{0}A
A	frequency factor in Arrhenius equation min^{-1} gm^{-1}
A, B	reactants
E	energy of activation k cal/gm mol
ΔP	total pressure fall mm Hg
k	overall reaction rate constant min^{-1}
$\bar{k}$	overall reaction rate constant min^{-1} gm^{-1}
ks	overall reaction rate constant min^{-1} m^{-2}
m	reaction order with respect to initial 2-butyne pressure
n	reaction order with respect to initial hydrogen pressure
$\bar{n}$	number of runs
% P	percent polymerization
$P_{C_4H_6}$	initial pressure of 2-butyne mm Hg
$P_{1-C_4H_8}$	pressure of 1-butene mm Hg
$P_{C-C_4H_8}$	pressure of cis-2-butene mm Hg
$P_{t-C_4H_8}$	pressure of trans-2-butene mm Hg
$P_{C_4H_{10}}$	pressure of n-butane mm Hg
P_{H_2}	initial pressure of hydrogen mm Hg
R	gas constant cal/mol ^{o}K
r_o	initial reaction rate mm Hg/min
$(r_o)_{m+1}$	initial reaction rate of (m+1)th run mm Hg/min
$(r_o)_{m+n}$	initial reaction rate of(m+n)th run mm Hg/min

$\bar{R}$	initial hydrogen pressure/initial 2-butyne pressure
s	surface area m^2/gm
S	Selectivity
t	reaction time min
T	reaction temperature ^{o}K
Tr	reference temperature ^{o}C

I INTRODUCTION

Wartime industrial investigations yielded a variety of novel catalysts, selected wholly by empirical methods. The published reports revealed the almost total ignorance of the precise role played by the solids in heterogeneous catalysis. A survey of the relevant literature, including patents, in 1943 showed that the kinetic studies for the most part were uncorrelated with the electronic and geometric characteristics of the catalysts.

The kinetics of homogeneous catalysis have been considerably advanced in recent years by the introduction of free radicals and radical ions. Broad analogies, drawn between homogeneous acid catalysed reactions and similar heterogeneous processes at the surface of some oxide insulators containing protons, encourage the view that the same intermediate particles are active in both. Less well defined relations suggest identical species at the surface of metals. Recent publications concerning the catalytic activity of pure metals and alloys in hydrogenation and dehydrogenation reactions and related observations on the adsorption, catalytic activity and other physical properties of the catalyst surface indicate that a definite correlation must exist between the structure of the solids and their catalytic activity. Though considerable work has been done in the last decade, the mechanism of heterogeneous catalysis is not as yet very clearly understood. Recently, kinetic studies have been undertaken on the alloy catalysts with a view to find if any correlation exists between the catalytic activity and geometric and electronic parameters of the catalyst.

The transition metals of the eighth group, in combination with metals of first group form generally solid solutions (binary compounds of varying composition) commonly called alloys. Despite the similarities in the structure of some alloys, a remarkable range of electronic properties are displayed. The electronic properties of these are involved in the basic chemisorption steps which in turn subsequently effect the catalytic activity.

In the last few years, the activity pattern shown by one of the alloy system (nickel-copper) in the hydrogenation reaction has aroused considerable interest, and quite controversial results have been reported. The cause of these discrepancies in the results has not been explored yet.

Though the hydrogenation of the acetylenes (acetylene and methylacetylene) over supported and unsupported metals and their alloys has been studied extensively in the past, very little has been published about the hydrogenation of 2-butyne over supported and unsupported metals. Nothing has been reported about the hydrogenation of 2-butyne over metal powders and their alloys.

The catalytic hydrogenation of 2-butyne (di methylacetylene) was studied in a static constant volume system over unsupported nickel, copper, cobalt, iron and nickel-copper alloys and iron supported on pumice.

The object of the present study of the catalytic hydrogenation of 2-butyne was -

1) to study the kinetics of the reaction over nickel, cobalt, copper, iron and nickel-copper alloys and to evaluate the activation energies, frequency factors and relative activities.
2) to find whether the geometric and electronic structures of these metals are related in any way to their catalytic activities and to correlate, if possible, the results of other investigators over the alloy series.
3) to compare the kinetics of 2-butyne hydrogenation with that of methylacetylene, over the same type of catalysts.
4) to postulate a possible mechanism of the reaction based on the detailed product analysis and,
5) to find the effect of different operating variables, such as, temperature, concentration of reactants, composition of alloys on the course of reaction, selectivity and conversion.

II LITERATURE SURVEY

The literature on the catalytic hydrogenation of hydrocarbons over supported and unsupported metals and their alloys is quite voluminous and is beyond the scope of this review. The first part of this review is devoted mainly to the published literature dealing with the experimental work done on the hydrogenation of hydrocarbons of the acetylene series (acetylene, methylacetylene and ethylacetylene). The second part deals with the preparation of the catalysts and the results obtained from the hydrogenation of hydrocarbons over nickel-copper alloys catalysts and a discussion of different theories suggested to correlate the catalytic activity with several parameters of nickel-copper alloy system. The last part is devoted to a brief review of the results obtained in the catalytic hydrogenation of 2-butyne.

(A) LITERATURE RELATED TO ACETYLENE SERIES: -

In the hydrogenation of acetylene over reduced nickel powder, Sabatier and Senderens (1) observed the formation of higher hydrocarbons in addition to ethane and ethylene. Later investigators (2 to 8) reported varying yields of these products on nickel catalysts. Sheridan (9) reported a zero order reaction with respect to acetylene and a first order with respect to hydrogen. While de Pauw and Jungers (10), using hydrogen in excess, reported a negative order (0.5) with respect to acetylene and first order with respect to hydrogen, Bond (11) reported a two rate expression for nickel-pumice catalyst. Subsequently Bond and Mann (12) confirmed the earlier findings of Bond (11).

Sheridan (13) found an activation energy of about 12 k cal/mol over pumice supported palladium catalyst. Tamaru (14) reported the hydrogenation of acetylene over palladium catalyst to be taking place in two steps. Bond, Dowden and Mackenzie (15) studied the hydrogenation of acetylene over alumina supported palladium catalysts and found that the selectivity ($S = \frac{P_{C_2H_4}}{P_{C_2H_4} + P_{C_2H_6}}$) could be increased to more than 96% by using hydrogen/acetylene ratios greater than two. A selectivity of the order of 0.86 was observed over platinum-alumina catalyst. Sheridan (16) reported a negative order with respect to acetylene over pumice supported platinum catalysts. Sabatier and Senderens (17) found that cobalt was active only at temperatures higher than 180° C and that the main product was ethane. Similar orders of reaction with respect to hydrogen and acetylene were observed as over nickel. Bond and Mann (18) investigated the kinetics of the reaction over supported and unsupported cobalt catalysts. In each case the order with respect to hydrogen and acetylene was one and zero respectively. Using iron-pumice catalysts, Sheridan (13) obtained reaction orders similar to those over nickel. Sheridan and Reid (19) also studied the reaction of acetylene with hydrogen over pumice supported rhodium, ruthenium, iridium and osmium catalysts. They found that the reaction orders were similar to those for nickel pumice catalysts and that iridium showed a poor selectivity. In the hydrogenation of acetylene over nickel-copper and nickel-cobalt alloys, Bond and Mann (18) observed that the catalytic activity for pure nickel was the highest.

Bond and Sheridan (20) studied the hydrogenation of methylacetylene over pumice supported nickel, palladium and platinum catalysts. For hydrogen-methylacetylene ratios 0.4 to 6.0, they found that in case of nickel catalyst the orders of reaction at 91° C were the same as for acetylene hydrogenation at about 60° C. Recently, Mann and Naik (21) have reported the reaction of hydrogen and methylacetylene over supported and unsupported nickel. They observed a zero order reaction with respect to methylacetylene and positive order of more than one with respect to hydrogen. Mann and Khulbe (22) have reported the reaction over unsupported nickel, iron and cobalt and nickel-copper alloys (23). A maximum in the activity composition diagram was observed for the alloy containing 20% copper. Positive orders of reaction (0.45) with respect to methylacetylene have been reported in the case of pure copper and the alloy containing 75% copper.

Meyer and Burwell (24) studied the gas phase reaction between deuterium and ethylacetylene using 0.3% palladium on alumina as catalyst and reported the products to consist of 1-butene (99.1%) cis and trans -2-butene (each .2%) and n-butane (.5%) only. The reaction was highly selective in the sense that very little n-butane was obtained in the product as long as ethylacetylene remained unreacted. Isomerization and further addition of deuterium to 1-butene occurred only after the alkyne was completely removed. Recently Mann and Khulbe (25, 26) have reported the hydrogenation of ethylacetylene over supported and unsupported nickel, cobalt and iron catalysts. They observed that while the order with respect to hydrogen was one and nearly independent of temperature, it was negative with respect to ethylacetylene and temperature dependent. In the case of iron powder, the orders of the reaction could not be determined due to the deactivation of the catalyst slowly.

(B) LITERATURE RELATED TO NICKEL-COPPER ALLOYS

Long, Frazer and Ott (27) demonstrated that nickel-copper alloys could be prepared by coprecipitating the metals as hydroxides from the solution of mixed ions; these were then reduced to metals with hydrogen. The lattice parameters were found to be identical with those of alloys formed by melting the metals together. Subsequent investigations of Best and Russell (28), Hall and Alexander (34) confirmed the earlier findings of Long, Frazer and Ott.

Best and Russell (28) modified the method of Long et al (27) by using ammonium bicarbonate to coprecipitate the nickel-copper ions as carbonate. The dried precipitate was calcined at a temperature of 400° C and reduced in a stream of hydrogen.

Harold et al (29) prepared nickel-copper silica alumina catalyst by impregnating various supports with aqueous solutions of nickel and copper salts to the point of incipient wetness. The catalysts were then oven dried at 115° C for 18 hours and calcined at 500° C for 24 hours.

Granular alloys were prepared by Takeuchi et al (30) by mixing the solutions of nickel and copper in appropriate amounts and evaporating the mixed solutions to dryness and igniting it to metal oxides in a furnace at 500° C. Massive alloys were also prepared by completely melting nickel and copper in a furnace.

Sachtler and Dorgelo (31) prepared nickel copper alloy films in three ways.

1) by evaporating an alloy wire from a supporting tungsten tantalum filament.
2) by simultaneous evaporation of two pieces of pure metals

or of an alloy from a tungsten cup heated by high energy electron bombardment.

3) by successive evaporation of two metals from different sources followed by heat treatment to homogenize the film.

Gharpurey and Emmett (32) deposited thin films of nickel in high vacuum and then superimposed thin films of copper. Sintering the films for few hours in 5 c.m. pressure of hydrogen at 300° C appeared to yield a homogeneous alloy. Campbell and Emmett (33) prepared thin films by evaporating nickel directly from a heated wire and evaporating copper from an electrically heated tungsten support.

Hall and Alexander (34) studied the formation of nickel-copper alloys by the low temperature reduction of mixed oxides with hydrogen. They have shown that even when two oxide phases were present originally, subsequent reductions formed a single metallic phase at the surface of the catalyst. The studies made by Takeuchi et al (35) with an electron diffraction showed that the concentration of nickel at surface of the granular nickel copper alloy differs from that of the internal material.

In the hydrogenation of benzene over nickel-copper and their alloys, Long, Frazer and Ott (27) observed that nickel catalyst had the highest activity and the catalyst containing 28% copper was the least active. The activity rose slightly as the concentration of copper in the catalyst increased from 54% to 79%. Pure copper did not hydrogenate benzene. Emmett and Skau (36) found that the hydrogenation of benzene over nickel free copper powder did not take place even at 200° C but on the addition of as much as 0.001% nickel, small activities were observed. Hall and Emmett (37) have reported specific activities and apparent activation energies for a series of nickel-copper alloys for the hydrogenation of benzene. The maximum activity appeared to be for the catalyst containing 75% nickel. Pure catalyst was as active as the one containing 45% nickel. Recently Condenhead and Masse (38) reported similar trend in the variation of specific activity and the apparent activation energy with the composition of nickel in the nickel-copper alloys as reported by Hall and Emmett (37).

Rienacker and Bommer (39) observed a marked drop in the catalytic activity for the alloy containing between 80.2% and 80.8% copper for ethylene hydrogenation over nickel-copper alloy foil. Best and Russell (28) studied the hydrogenation of ethylene over nickel-copper powder and found maximum activity in the copper rich region (approximately 60 atom percent of copper). Hall and Emmett (40) and Hall and Hassell (41) showed that hydrogen had a poisoning effect on nickel catalyst and a promotional effect on nickel copper alloys. They found two maxima in the activity, one in the nickel rich region and the other in the copper rich region. The work of Gharpurey and Emmett (32) partly supported the work of Hall and Emmett (40). Campbell and Emmett (33) observed that the rate of reaction in the hydrogenation of ethylene over nickel-copper films in the temperature range 0 to 21° C over catalysts containing 5 to 20% nickel was 7 to 15 times greater than that for pure nickel. In the 25-35% nickel region, the activity was nearly the same as that for pure nickel. The reaction was first order with respect to hydrogen and was independent of ethylene pressure for the alloys. The results of Takeuchi et al (30) in the hydrogenation of ethylene over two different series of nickel-copper alloys (massive and granular alloys, prepared by physical and chemical methods respectively) were different from other investigators. The activity of granular pure nickel was highest. Takai et al (42) have reported the liquid phase hydrogenation of acetone, allyl alcohol and maleic acid over nickel copper powder. In all the three cases, the activity for hydrogenation reached a maximum at the catalyst composition of more than 95% nickel and then decreased with the increasing copper concentrations. Takai and Masaki (43) studied in detail the liquid phase hydrogenation of acetone over nickel-copper powders at 60° C. They reported that the specific activities were almost proportional to the specific surface of the catalysts in all cases except for the existence of small maxima for the alloys containing 30 and 70% nickel. No such maximum was observed by Bond and Mann (18) in the acetylene hydrogenation. They found that the activity for nickel was highest and that while at high temperatures d band hole concentration determined the activity, the situation became more complex at low temperatures. The activation energy increased with increasing copper content of the nickel-copper alloys.

Mann and Khulbe (23) have reported the hydrogenation of methylacetylene over nickel copper powders. The order of reaction with respect to hydrogen was one and nearly temperature independent. The order of reaction with respect to methylacetylene over nickel was zero to slightly negative and temperature dependent. The order with respect to methylacetylene was positive (about .5 ± .05) for copper and nickel-copper alloy containing 75% copper. The overall activation energy varied between 9 and 21.2 k cal/mol. The maximum activity was observed in the nickel rich region. The selectivity for propylene production and polymerization effects increased with increasing copper concentrations.

According to Beeck (44), who postulated that a correlation existed between the catalytic activity of the metals and their lattice parameters, the activity of the nickel-copper catalysts would be expected to increase markedly between pure nickel and copper. Hall and Emmett (40), Gharpurey and

Emmett (32) and Lyubarskii et al (45) also observed a marked increase in the catalytic activity in ethylene hydrogenation on nickel being alloyed with small amounts of copper. They attributed this to the hydrogen exercising a poisoning effect on pure nickel and a promotional effect on alloys.

Sachtler and Jongepier (46) have concluded from their studies on ethylene hydrogenation that nickel-copper alloy films at intermediate composition between 3% and 80% copper equilibrates at 200°C and such solid phases were produced in which the phase containing higher copper concentrations was exposed on the surface of the catalyst. The second phase (containing lower percentage of copper) was presumably buried within the catalyst and did not appear on the surface. Sachtler and Dorgelo (31) obtained experimental evidences regarding the consistency in the composition of the surface by work function measurements of the alloys through photoelectric techniques. They concluded that the catalytic activity did not appear to change much over this region. The work of Best and Russell (28), Hall (47), Campbell and Emmett (33) casts doubt on the general validity of this conclusion.

Recently Takeuchi (48) studied a number of nickel-copper alloy catalysts prepared by different methods. They suggest that this activity factor is due to the imperfection of the crystal. Takeuchi et al (54) studied the catalytic activity and electric resistance of evaporated nickel-copper films. The dependence of hydrogenation catalytic activity and electric resistance of nickel-copper films on the composition of the films were investigated. The film was prepared by the evaporation of nickel and copper metals and their alloys into a substrate cooled by liquid oxygen. The maximum activity for the hydrogenation of ethylene was always in the alloy region of the film, irrespective of the order of deposition when the film was treated at 30° C. However, the maximum activity shifted to that of pure nickel when the treatment temperature was about 250° C. The electric resistance of 50% nickel was always maximum.

Tetenyi et al (49) prepared ten samples of nickel by different methods and observed that while their lattice parameters were nearly equal, the specific surface areas were different. The rates for the dehydrogenation of cyclohexane, isopropanol and tertiary butanol were nearly the same. According to Tetenyi et al (49) the method of the catalyst preparation actually influences both the specific surface and the catalytic activity to an appreciable extent. In another paper (50) they have reported that the degree of hydrogen adsorption, heat of adsorption and equilibrium constant of adsorption were also influenced to an appreciable extent by the method of catalyst preparation.

Takeuchi et al (30) have concluded that the amount of hydrogen adsorbed, the heat of adsorption and the catalytic activity for the granular alloy catalyst were related to the concentration of nickel at the surface. The activity of massive alloys may be interpreted on the basis of Dowden's theory (51).

Takai and Yamanaka (42) observed that the ability of nickel metal to adsorb hydrogen increased with increasing amounts of copper with a maximum for an alloy containing 80% of copper.

(C) LITERATURE RELATED TO 2-BUTYNE:

Meyer and Burwell (55) studied the reaction of deuterium and 2-butyne over alumina supported palladium catalyst and observed that the main product was cis-2-butene 2, 3, d_2. They proposed a possible mechanism for the reaction. Phillipson, Wells and Gray (56) have studied the kinetics and reported the product distribution for the gas phase hydrogenation of 2-butyne catalysed by alumina supported iron, cobalt, nickel, copper, rhodium, iridium and platinum at temperatures ranging between 100 and 200° C. The yield of cis-2-butene was always high (more than 75%) and small amounts of trans-2-butene and 1-butene were formed as initial products for all the metals investigated except copper. n-Butane appeared as initial product in minor amounts over noble metals only. While the order of reaction with respect to hydrogen was one for nickel, cobalt and copper, it varied with respect to 2-butyne from zero (cobalt and copper) to slightly negative (-0.3 for nickel). An activation energy of 12 ± 2 k cal/mol was evaluated. Similar kinetic features were observed over the noble metals. Webb and Wells (57) studied the reaction of 2-butyne with hydrogen and deuterium over alumina supported ruthenium and osmium at temperatures varying between 80 and 150° C. The orders of reaction with respect to hydrogen and 2-butyne were one and zero respectively. Activation energies of the order of 10 to 12.5 k cal/mol were obtained.

III EXPERIMENTAL

Experiments were carried out in a static constant volume reactor. The reactor consisted of a pyrex glass vessel, approximately 25 c.c. volume and was connected to a high vacuum system.

A. APPARATUS:

The apparatus consisted of five sections

1) Hydrogen purification and storage
2) 2-butyne purification and storage
3) Reactor and temperature controls
4) Reaction product analysis
5) High vacuum

The experimental apparatus used in the study of the reaction is shown schematically in figure 1.

B. PURIFICATION OF REACTANTS:

1. Hydrogen.

Hydrogen (Linde Co.) was purified by passing it at a rate 20 cc/min through the glass thimble containing palladium asbestos catalysts at a temperature of about 200° C to convert the residual oxygen in the previously evacuated connecting tube and the oxygen present as an impurity in the cylinder hydrogen, to water vapor. Water vapor thus formed was condensed in the liquid nitrogen trap. The purified hydrogen was first rejected

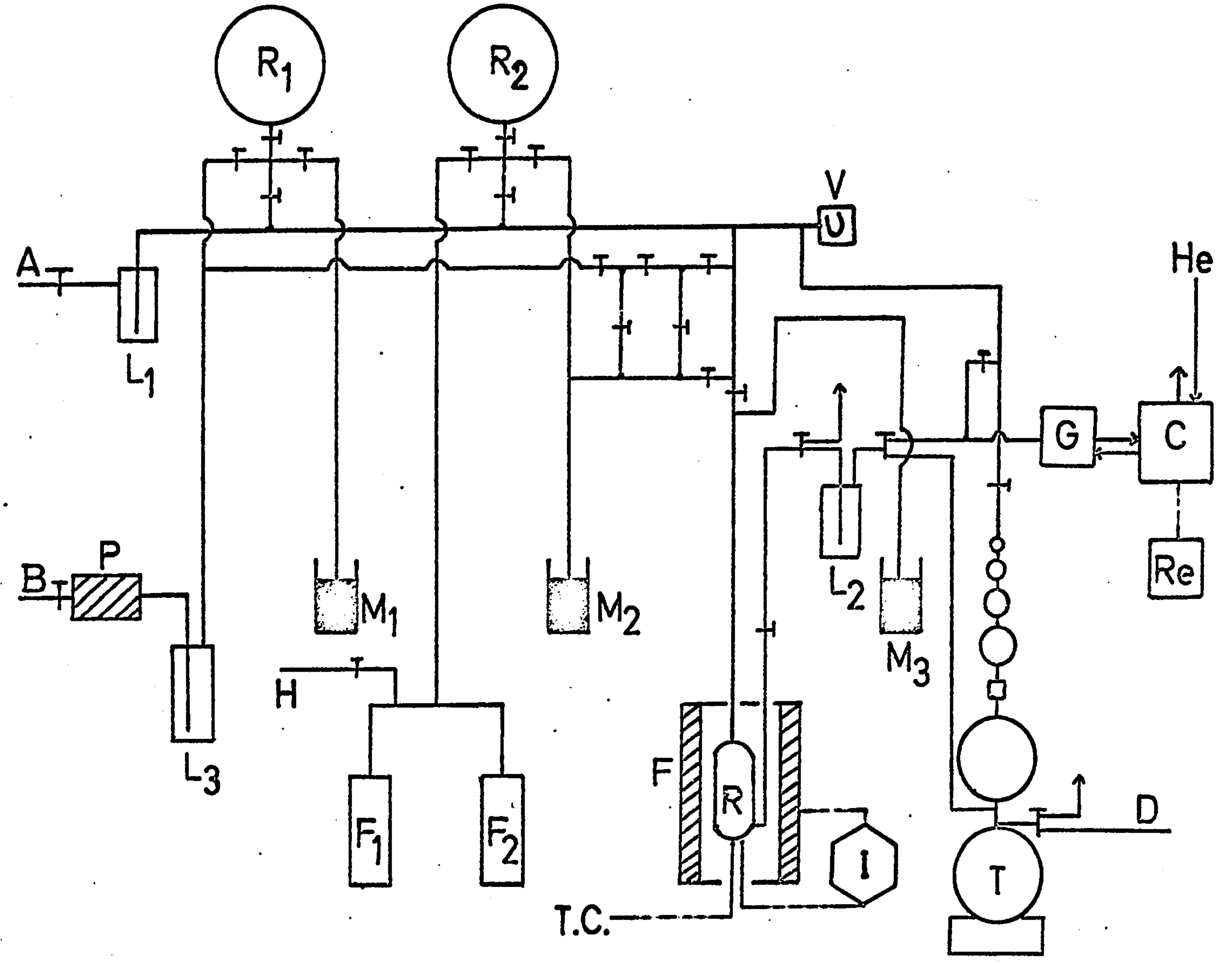


Figure 1 - Schematic diagram of the experimental apparatus

Figure 1

A = To high vacuum system

B = Hydrogen supply

C = Gas chromatograph

D = Vacuum pump

F = Furnace

F_1, F_2 = Fractionation bulbs

G = Glass sampling loop

H = 2-butyne supply

I = Temperature controller

L_1, L_2, L_3 = Liquid N_2 traps

M_1, M_2, M_3 = Manometers

R = Reactor

R_1, R_2 = Reservoirs

R_e = Recorder

T = Teopler pump

T.C. = Thermocouple

V = Vacustat

for ten minutes through the vacuum pump and then stored in the hydrogen storage vessel or used directly for reduction of the catalysts.

2. 2-butyne.

The liquid 2-butyne was filled in the distillation flask after rinsing the flask thoroughly with it. The air left in the distillation flask was removed by connecting it to the vacuum line after solidifying the 2-butyne at liquid nitrogen temperature. 2-butyne was purified by successive distillation, and rejecting the head and tail fractions. It was subsequently stored in the storage vessel.

C. PREPARATION OF THE CATALYST:

(i) Metal powders.

Standard normal nickel and copper nitrate solutions were prepared using analytical reagent grade $Ni(NO_3)_2.6H_2O$ and $Cu(NO_3)_2.3H_2O$. Copper nitrate solution contained some acetic acid to avoid hydrolysis. Nickel nitrate and copper nitrate solutions were mixed in appropriate ratios to yield the required nickel-copper alloys of desired composition. Powdered reagent grade ammonium bicarbonate was added at room temperature to the mixture of the nickel-copper solutions until a permanent turbidity appeared. The solution was stirred while ammonium bicarbonate was added. Subsequently a solution of 17 gm of bicarbonate, dissolved in 100 cc of water was added and stirred for another 10 minutes. The precipitate was allowed to settle over night, washed with hot water to remove the nitrate ions. The precipitate was first dried at 60° C and left over night at 105° C. The basic carbonate thus formed was broken into small lumps and calcinated at a temperature of 600° C in a muffle furnace for approximately 6 hours.

Iron and cobalt powders were similarly prepared from their respective nitrate solutions.

(ii) Supported iron catalyst.

Pumice stones supplied by the Fisher Scientific Co., Ltd. were crushed and 20 to 40 mesh sizes selected for the catalyst support. Pumice granules were first boiled with concentrated hydrochloric acid for about 30 minutes and were then washed with warm distilled water several times until the addition of silver nitrate solution did not show any precipitate. The cleansed pumice granules were then dried over night in an oven at 105° C. The solution containing the required weight of metal was added to the pumice granules. The impregnated material was dried at 105° C and subsequently calcined at 600° C in a muffle furnace for 12 hours.

D. REDUCTION AND STABILIZATION OF CATALYST:

A weighed amount of the catalyst was placed at the bottom of the reaction vessel and the vessel sealed. The reaction vessel containing the catalyst was evacuated until a high vacuum was obtained. The temperature of the vessel was raised to 400° C and a stream of hydrogen (80 ml/min) was passed through the reaction vessel for 24 hours. The stream of hydrogen was stopped and the reaction vessel allowed to cool to room temperature in about 200 mm of hydrogen.

In the present study, the catalyst was aged by hydrogenating 2-butyne over the catalyst for sufficient time at room temperature until the catalyst attained constant activity.

E. EXPERIMENTAL PROCEDURE:

Once the catalyst in the reactor was stabilised, the reactor temperature was adjusted to the required value by means of a Fisher proportional temperature controller. The reactor was evacuated and a hard vacuum obtained. The required amount of hydrogen was introduced into the reactor and the connecting lines evacuated for about three minutes. Soon after the admission of the required amount of the second reactant (2-butyne) into the reactor, the change of pressure with time was measured by the mercury manometer connected to the reaction vessel. In order to make the second and subsequent runs, the reactor was again evacuated for several minutes and the procedure repeated. The runs were made at random to nullify the effect of any change in the activity of the catalyst.

For a particular temperature, a number of runs were taken by changing the hydrogen pressure while keeping 2-butyne pressure constant at 50 mm of Hg. These runs gave the order of reaction with respect to hydrogen. Similar procedure was followed to obtain the order of reaction with respect to 2-butyne by keeping the hydrogen pressure fixed at 50 mm and varying 2-butyne pressures. The change of temperature during the reaction was within ± 0.1° C.

Runs were taken at five different temperatures, usually on five successive days. After completing the runs at a temperature, the catalyst was kept in about 200 mm hydrogen before starting the next series.

F. ANALYSIS OF THE PRODUCTS:

A series of runs was carried out with each catalyst except for supported and unsupported iron.

The gases were analysed by a gas chromatograph (Aerograph Model P-90 A-3). A 20 ft column packed with dimethylsulpholane supported on A/W chromosorp P (60-80 mesh) was used to separate the hydrocarbons at 35° C. Helium was used as the carrier gas and flowed through the column at a flow rate of 80 ml/min. Hydrogen was measured with the help of the Toepler pump. Hydrogen was transferred to a series of calibrated bulbs at different pressures.

After the pressure had fallen to the desired extent, the reactor was connected to the glass trap kept in liquid nitrogen and the condensable products condensed. The non-condensable hydrogen was transferred to the bulbs with the help of the Toepler pump and the pressure of unreacted hydrogen measured. The glass trap was disconnected from the reactor and Toepler pump and the condensed products transferred to the sampling glass loop maintained at room temperature. A definite volume (5 ml) was injected into the chromatograph and the product composition determined. The product distribution was obtained for different temperatures, pressure drops and initial reactant pressures.

IV RESULTS

The experimental results obtained in the course of the study of the reaction of 2-butyne with hydrogen over nickel, copper, cobalt, iron and nickel copper alloy catalysts can be divided for convenience into (1) Kinetics of the reaction, and (2) Distribution of the products and selectivity.

1. KINETICS:

The kinetic studies of the hydrogenation reactions usually involve the determination of the following:

a) Shape of pressure fall-time curves.

b) Orders of reaction with respect to the reactants.

c) Activation energy.

a) Shape of pressure fall-time curve.

Bond (11) studied the pressure fall-time curves obtained in the hydrogenation of acetylene over several nickel catalysts. He classified the observed pressure fall-time curves as follows:

Type I. Zero order reaction, the rate being constant up to a pressure fall nearly equal to the initial pressure of acetylene. Such curves were obtained when acetylene was first admitted into the reaction vessel and the initial hydrogen/acetylene ratios were greater than two (figure 2).

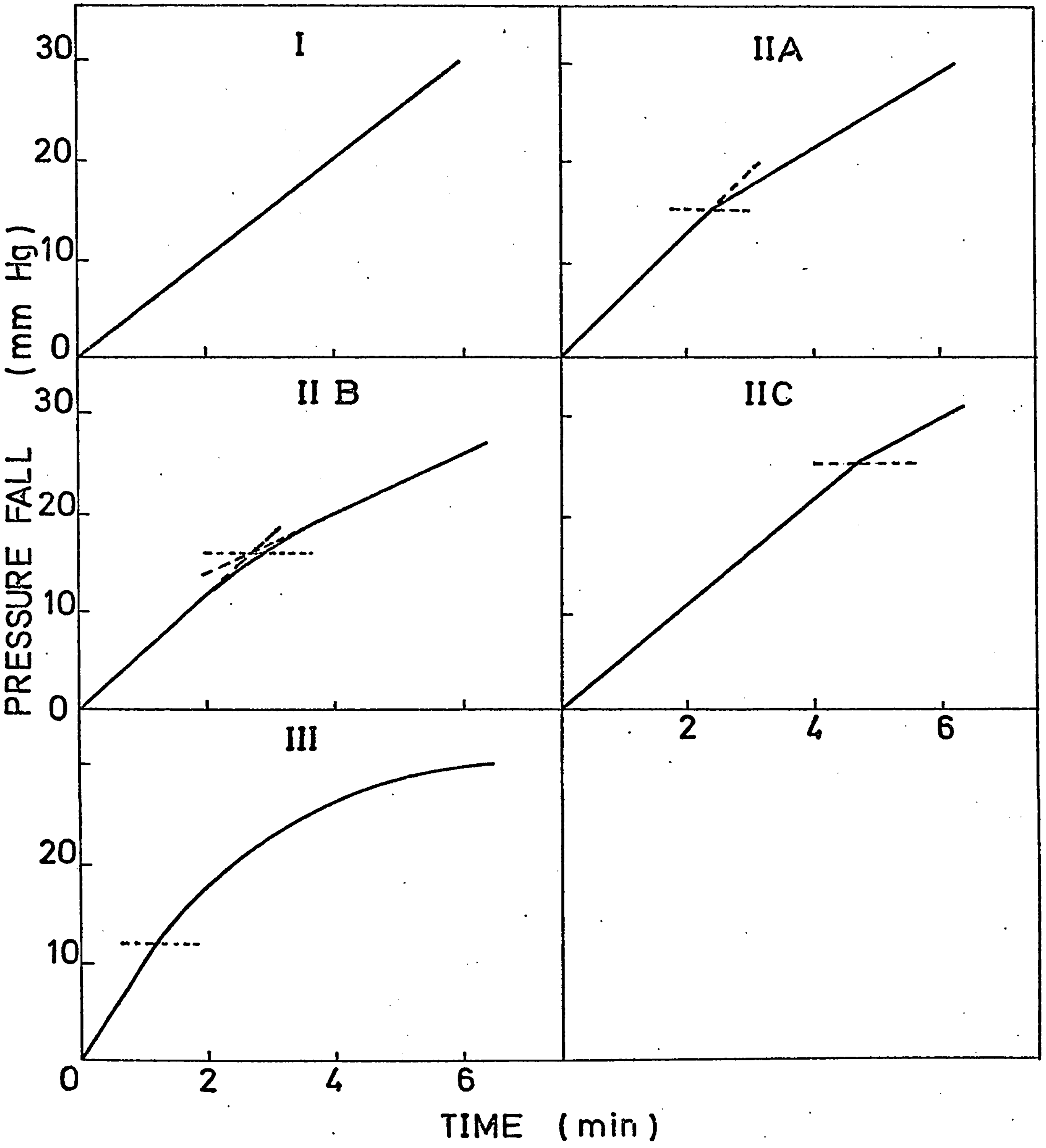


Figure 2 - Various types of pressure-time curves.

Type II A. A broken curve consisting of two linear portions of different rates. The inflection occurred after a pressure fall equal to one half of the initial acetylene pressure. Such curves were observed when the hydrogen/acetylene ratios were greater than two and the reactants were premixed (figure 2).

Type II B. A broken curve consisting of a curved portion followed by a linear portion. Such curves were observed when hydrogen/acetylene ratios were greater than two and hydrogen was admitted first into the reaction vessel. The break occurred after the pressure had fallen by an amount equal to one half of the initial pressure of acetylene (figure 2).

Type II C. Similar to type II A, but the inflection occurring after a pressure fall equal to about five-sixths of the initial acetylene pressure. This type of curve was observed when the premixed reactants were added to acetylene pretreated catalyst (figure 2).

Type III. First order reaction in hydrogen. Such curves were obtained when hydrogen/acetylene ratios were less than two, and acetylene was admitted first into the reaction vessel (figure 2).

The kinetic form of these curves depend on the hydrogen/acetylene ratios, the order of reactants, if added separately, the pretreatment of the catalysts, if the reactants are added together and the type of the catalysts.

b) Order of reaction.

A surface reaction between two substances involves interaction between two adsorbed molecules, the adsorption occurring on neighbouring sites. For the reaction occurring between reactants A and B whose initial pressures are P_A and P_B respectively, the overall initial rate (r_o) equation could be written as

$$r_o = k\ (P_A)^n\ (P_B)^m \quad \ldots\ldots\ldots \quad (1)$$

where n and m are reaction orders with respect to A and B respectively and k the specific reaction rate constant.

For hydrogenation of 2-butyne the initial rate equation (r_o) could be written as

$$r_o = k\ (P_{H_2})^n\ (P_{C_4H_6})^m \ \ldots\ldots\ldots \quad (2)$$

Rewriting the equation (2),

$$\log r_o = \log k + n \log P_{H_2} + m \log P_{C_4H_6} \ \ldots\ldots \quad (3)$$

The orders of reaction n and m can be determined by keeping the initial pressure of one of the reactants constant and varying the other. Series of experiments were performed to determine the order of reaction, n and m by the initial rate method. The reaction order with respect to hydrogen was obtained by using a fixed initial 2-butyne pressure (50 mm) and varying initial hydrogen pressures at several temperatures.

Similarly reaction order with respect to 2-butyne was obtained by using a constant initial hydrogen pressure (50 mm) and varying the pressure of 2-butyne. Such orders of reactions were obtained for all the catalysts.

c) Activation energy.

An increase in the reaction temperature frequently causes a marked increase in the rate of reaction. The most satisfactory method for expressing the influence of temperature on reaction velocity is the one used by Arrhenius following Vant Hoff's equation:

$$k = A \exp(-E/RT) \qquad (4)$$

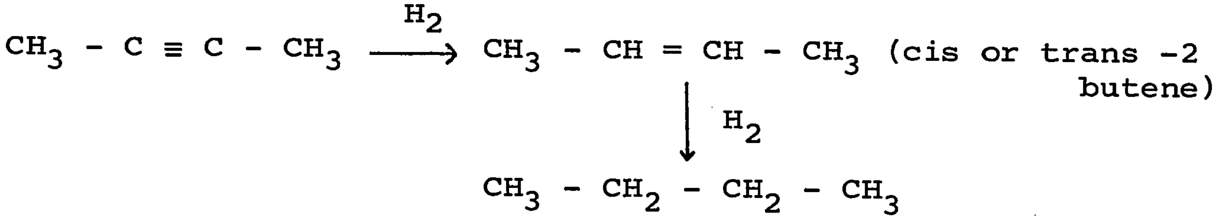
where k = the rate constant at $T^{o}A$, A = the frequency factor and E = the energy of activation. When the reaction occurs between A and B, an equilibrium exists between A + B and the activated complex. The energy difference between the adsorbed molecule and the activated complex is known as apparent energy of activation. There may be several activated complexes in existence at a given time in the reaction system, but only those with the energy E are capable of forming products directly.

A, the frequency factor for the reaction, is defined as the product of a true collision number (Z) and the probability factor. The factor exp (-E/RT) is recognized as the Boltzman factor for the fraction of system having energy in excess of the value E.

A plot of $\log_{10}k$ or ln k against the reciprocal of the absolute temperature T gives usually a straight line. The energy of activation for various catalysts were obtained from the slope of these lines.

2. PRODUCT DISTRIBUTION AND SELECTIVITY :

The hydrogenation of 2-butyne usually takes place according to the following sequence.



$$\begin{tikzcd} CH_3 - C \equiv C - CH_3 \arrow[r, "H_2"] & CH_3 - CH = CH - CH_3 \text{ (cis or trans -2 butene)} \arrow[d, "H_2"] \\ & CH_3 - CH_2 - CH_2 - CH_3 \end{tikzcd}$$

Several products, besides cis or trans-2-butene and n-butane could form during the reaction depending on the nature of the catalysts used and other operating conditions prevailing. However, in the present study over different catalysts only 1-butene was formed in addition to the normally formed 2-butene and butane.

Selectivity is defined as

$$S = \frac{P_{cis\text{-}C_4H_8}}{\sum P_{butene} + P_{butane}}$$

where $P_{cis\text{-}butene}$ = pressure of cis-2-butene, mm Hg. P_{butane} = $P_{C_4H_{10}}$ = pressure of n butane, mm Hg. $\sum P_{butene} = P_{cis\ C_4H_8} + P_{trans\ C_4H_8} + P_{1\text{-}C_4H_8}$. $P_{1\text{-}C_4H_8}$ = pressure of 1-butene mm Hg. $P_{trans\text{-}C_4H_8}$ = pressure of trans-2-butene mm Hg.

3. REACTION OVER NICKEL POWDER:

(a) KINETICS

The experimental data obtained for the hydrogenation of 2-butyne over nickel powder (.075 gm as oxide) are given in Table 1.

The rate of reaction over fresh catalyst was quite fast in the beginning at room temperature but it got deactivated with each successive run. The catalyst was stabilized only after about 30 runs. The reaction had a measurable rate at 40° C. The pressure-fall time curve at 40° C for various initial reactant ratios $({}^{P}H_{2}/{}^{P}C_{4}H_{6} = \bar{R})$ are shown in figure (3A). In the initial stages pressure decreased linearly with reaction time. The initial rate r_o was obtained from the slope of such lines. A Type III pressure time curve similar to those obtained by Bond (11) for acetylene hydrogenation over nickel pumice were obtained.

The dependence of initial rates on the initial hydrogen and 2-butyne pressures at different temperatures is shown in figures (4,5A & B). The order of reaction with respect to hydrogen was always one and temperature independent (figure 5A). Though the order of reaction with respect to 2-butyne was zero at lower temperatures, it became gradually slightly negative with increasing temperatures (figure 5B). The results are consistent with the results of most of the investigators for the hydrogenation of methylacetylene over nickel (22, 23) and of 1-butyne over nickel powder (25, 26). Phillipson et al (56) observed a negative order of reaction (-0.3) with respect to 2-butyne in the hydrogenation of 2-butyne over alumina supported nickel. The overall reaction rate can be expressed as

$$r_o = k\ (P_{H_2})^1\ (P_{C_4H_6})^{-.15\ \pm\ .15}$$

Plots of $\log_{10}$ of specific rates (Table 1) obtained from figure 4 against the reciprocal of absolute temperatures was good straight line over a wide range of temperatures (figure 6) satisfying the Arrhenius equation. An apparent activation energy of 9.13 k cal/gm mol and frequency factor 2.98 x 10^{+5} min^{-1}/gm were obtained.

(b) SELECTIVITY

The reaction products were analysed for different reactant ratios ($\bar{R}$) at various pressure falls at several temperatures. Experimental results are given in Table 1. Special attention was paid to the manner in which the observed yield of cis-2-butene depended on the operating variables.

All the three butenes (cis-2-butene, trans-2-butene and 1-butene) and n-butane were observed as initial products of the reaction under all operating conditions. Cis-2-butene was always the major product.

(i) The course of reaction:-

The course of the reaction was followed by analyzing the products of the reaction after various pressure falls for hydrogen -2-butyne ratio of 1 and 2.4. The results are given in Table (1). The distribution of products and the selectivity during the course of reaction are shown in figure 7A and 8.

(ii) Dependence of selectivity on pressure fall:-

For hydrogen -2-butyne ratio of 1 (50 mm of each reactant) the selectivity was nearly independent of pressure fall. In the case of hydrogen -2-butyne ratio 2.4 (120 mm of hydrogen and 50 mm of 2-butyne) the selectivity was independent of pressure fall up to a pressure fall of 35 mm after which it decreased due to the further hydrogenation of cis-2-butene and formation of trans-2-butene. The yield of cis-2-butene was maximum at 35 mm pressure fall.

(iii) Dependence of selectivity on the initial pressure of hydrogen

The dependence of selectivity upon hydrogen pressure was studied at 50° C keeping 2-butyne pressure at 50 mm and varying the hydrogen pressures between 50 mm and 120 mm. The products were analyzed at 20 mm pressure fall in all cases. The selectivity was independent of the initial hydrogen pressure up to 100 mm and then decreased slightly (figure 9A).

(iv) Dependence of selectivity on the initial 2-butyne pressure

The dependence of selectivity upon 2-butyne pressures

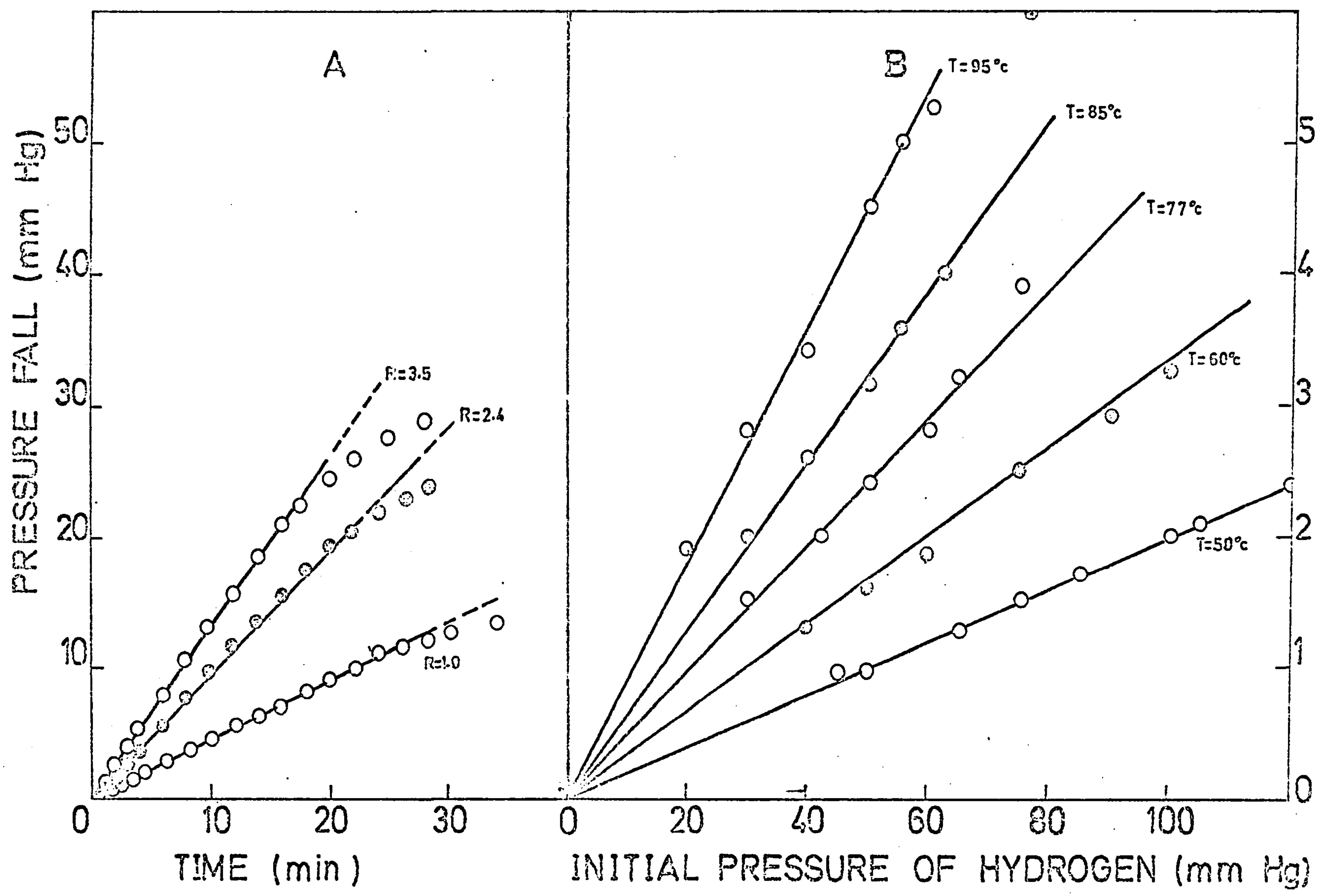


Figure 3 - A - Pressure-time curves, nickel powder
B - Dependence of initial rate upon initial pressure of hydrogen
80% Ni - 20% Cu.

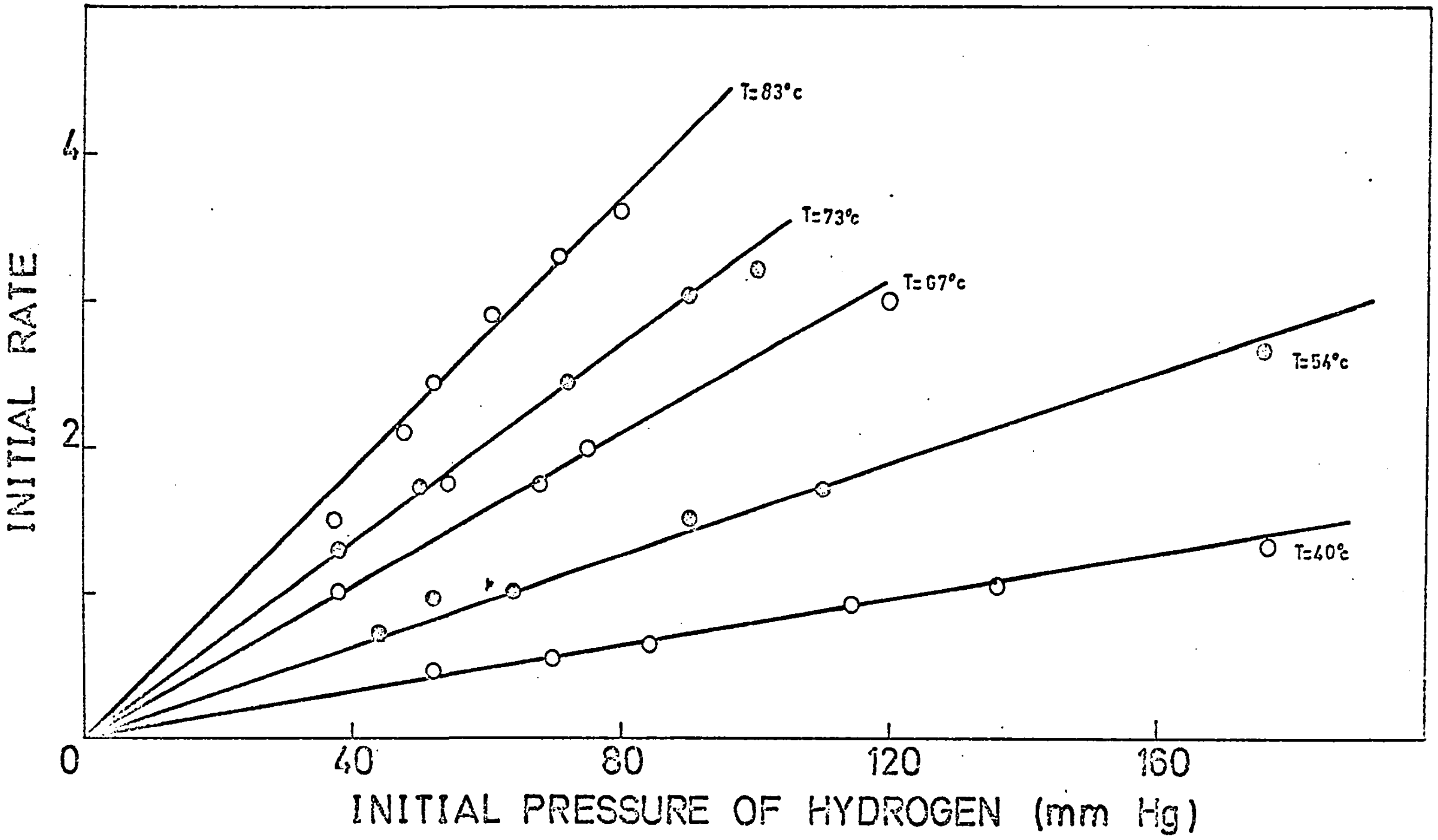


Figure 4 - Dependence of initial rate upon initial pressure of hydrogen nickel powder

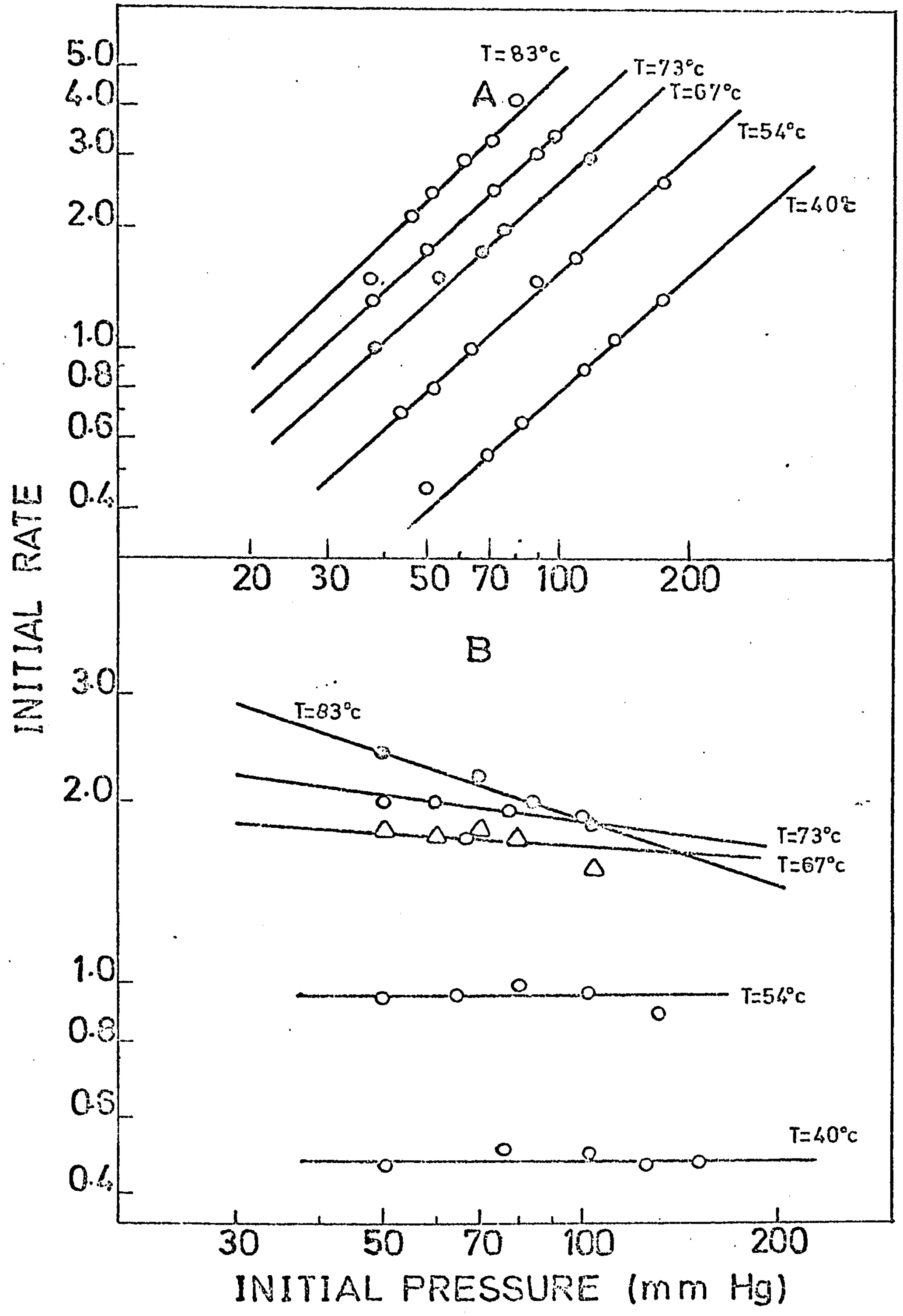


Figure 5 - Dependence order of reaction upon temperature
A-Hydrogen B-2-butyne

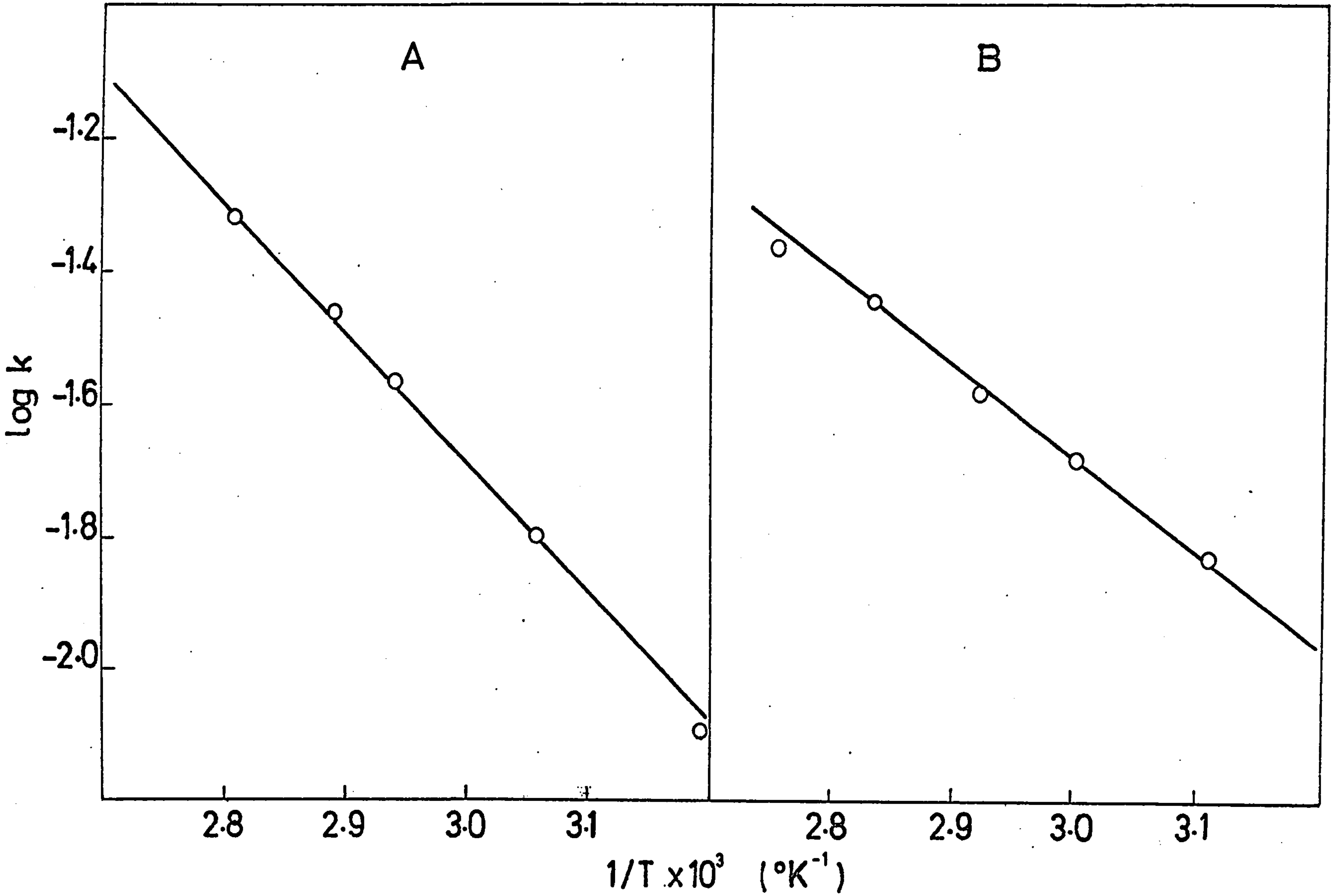


Figure 6 - Arrhenius plot A-nickel powder B-cobalt powder

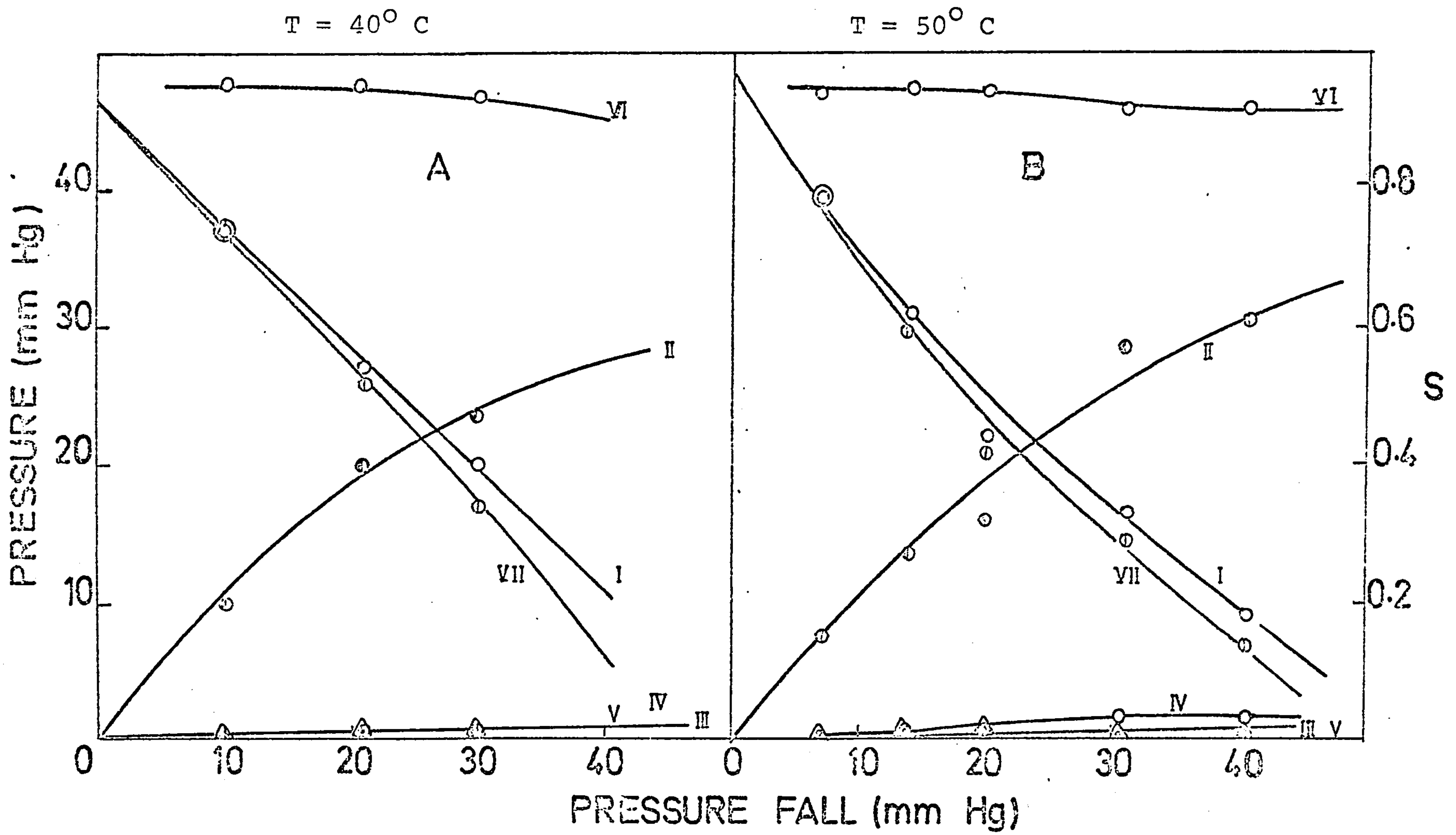


Figure 7 - A - nickel powder B - 90% nickel - 10% copper
P_{H_2} = 50 ± 1 mm Hg $P_{C_4H_6}$ = 50 ± 2 mm Hg
I = C_4H_6 II = C-C_4H_8 III = t-C_4H_8 IV = 1-C_4H_8 V = n-C_4H_{10}
VI = Selectivity VII Hydrogen

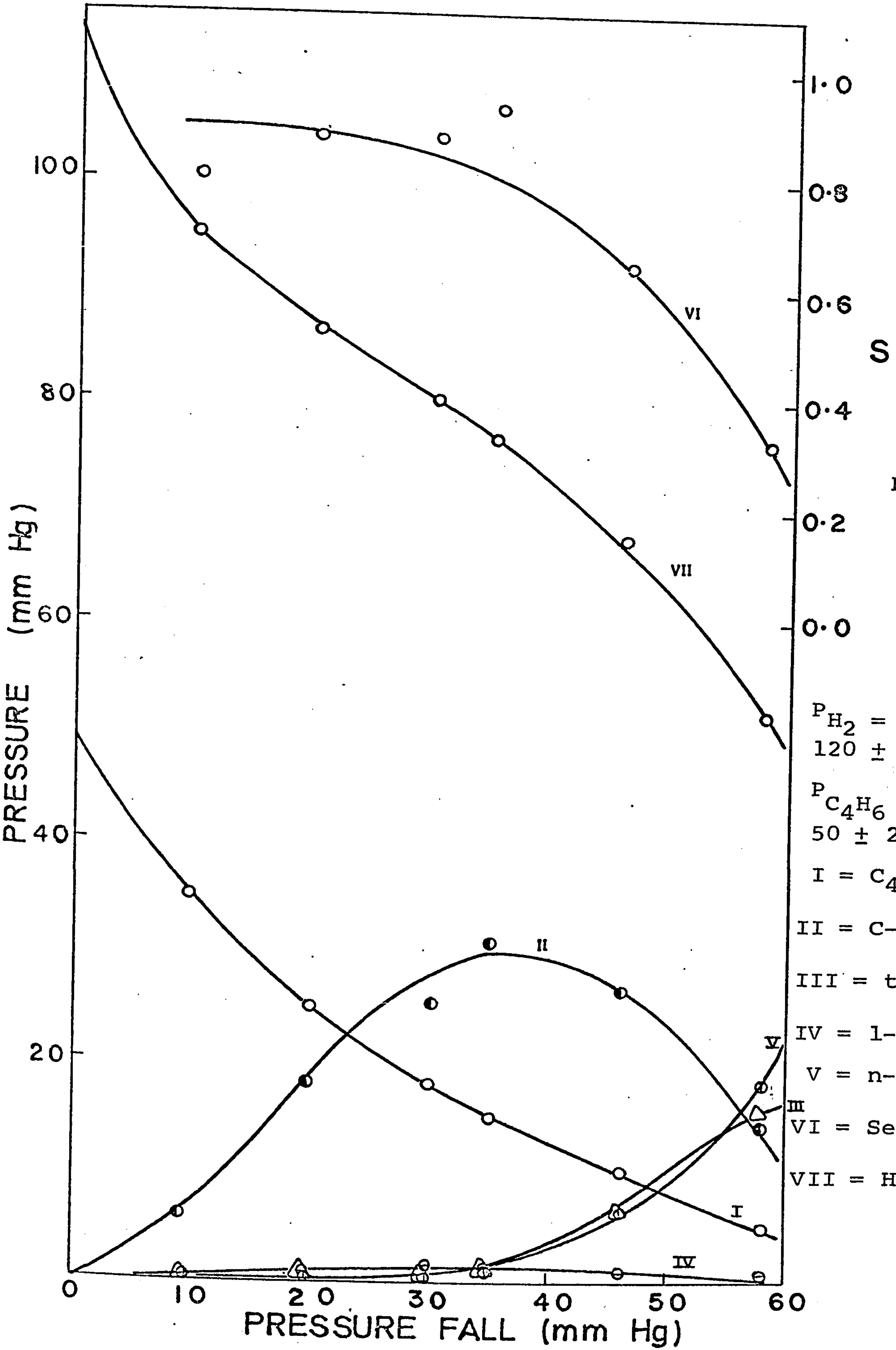


Figure 8

Course
of
Reaction

Nickel
powder

P_{H_2} =
120 ± 1 mm Hg

$P_{C_4H_6}$ =
50 ± 2 mm Hg

I = C_4H_6

II = $C\text{-}C_4H_8$

III = $t\text{-}C_4H_8$

IV = $1\text{-}C_4H_8$

V = $n\text{-}C_4H_{10}$

VI = Selectivity

VII = Hydrogen

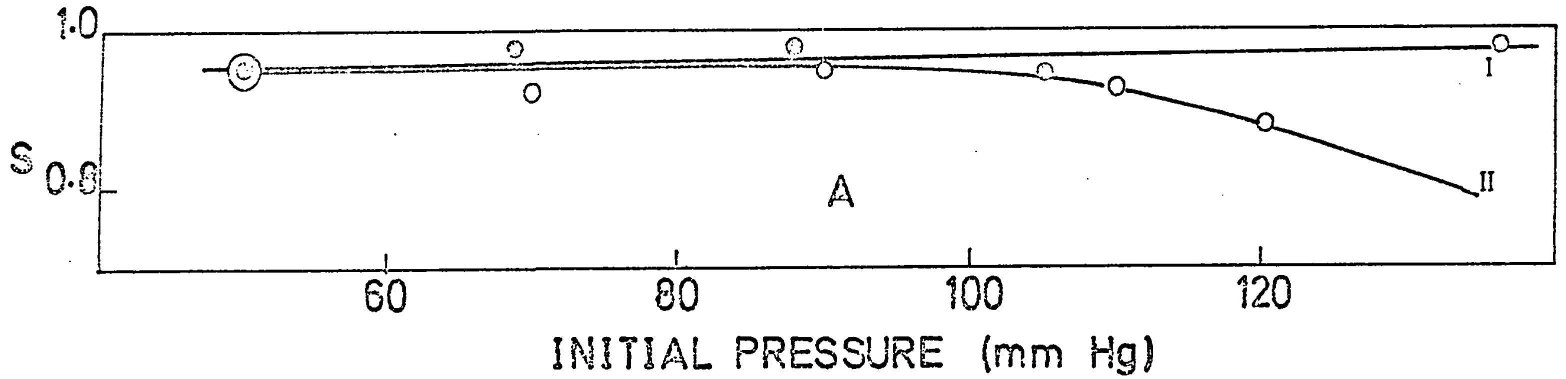


Figure 9A - Dependence of selectivity upon initial reactant pressure
I - With respect to 2-butyne $P_{H_2} = 50 \pm 1$ mm Hg
II - With respect to hydrogen $P_{C_4H_6} = 50 \pm 2$ mm Hg

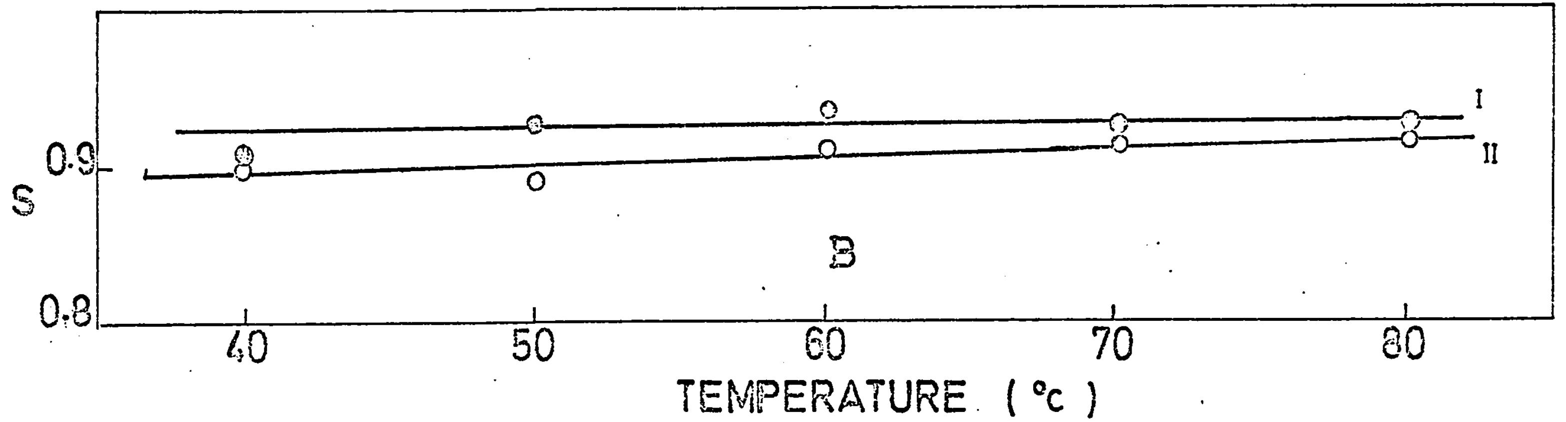


Figure 9B - Dependence of selectivity upon temperature
I = $P_{H_2} = 50 \pm 1$ mm Hg $P_{C_4H_6} = 50 \pm 2$ mm Hg
II = $P_{H_2} = 120 \pm 1$ mm Hg

was studied at 50° C keeping hydrogen pressure constant at 50 mm while varying 2-butyne pressures between 50 mm and 136 mm and analyzing the products at 20 mm pressure fall. The selectivity increased with increasing 2-butyne pressures (figure 9A).

(v) Dependence of selectivity on the temperature:-

The temperature dependence of selectivity was studied at hydrogen -2-butyne ratios of 1 (50 mm of each reactant) and 2.4 (120 mm of hydrogen and 50 mm of 2-butyne) between 40° C and 80° C. The products were analyzed for a 20 mm pressure fall. No significant change in the selectivity with temperature was observed. (figure 9B)

4. REACTION OVER 90% NICKEL AND 10% COPPER ALLOY POWDER:

(a) KINETICS

The experimental data for the hydrogenation of 2-butyne over the alloy powder containing 90% of nickel and 10% of copper (.075 gm as oxide) are given in Table (2). The reaction had a measurable rate at 40° C.

Figure (10A) shows the kinetic form of pressure fall-time curves for various hydrogen/2-butyne ratios at 40° C. The curves consisted of two linear portions. In the first region the order of reaction was one. For hydrogen -2-butyne ratios of less than two; the second rates (decreased rate) were observed when the pressure had fallen by an amount nearly equal to half of the initial 2-butyne pressure. However, for hydrogen -2-butyne ratios greater than two the increase in the second rate were observed at pressure drops nearly equal to half of the initial 2-butyne pressures. These curves (Type I and II) were similar to the curves obtained by Bond (11) in the hydrogenation of acetylene over nickel pumice catalyst.

The dependence of initial rates upon the initial hydrogen pressures at various temperatures is shown in figure (10 B). The order of reaction with respect to hydrogen was one and temperature independent (figure 11A). The order of reaction with respect to 2-butyne was zero but became slightly negative at higher temperatures (figure 11 B). The overall reaction rate can be expressed as

$$r_o = (P_{H_2})^1 \, (P_{C_4H_6})^{-.03 \pm .03}$$

The plot of $\log_{10}$ k against the reciprocal of absolute temperature was a good straight line over a wide range of temperature (figure 12) satisfying the Arrhenius equation. The derived apparent activation energy and frequency factor were 6.5 k cal/gm mol and 1.17×10^4 min^{-1}/gm respectively.

(b) SELECTIVITY

(i) Course of reaction

The course of reacton was followed by analyzing the

the products of the reaction at various pressure drops for hydrogen -2-butyne ratio of 1 (P_{H_2} = $P_{C_4H_6}$ =50mm) and 2.4 (P_{H_2} = 120 mm, $P_{C_4H_6}$ = 50 mm) at 50° C. The results are given in Table 2.

The distribution of products at different pressure falls for a reactant ratio 1 is shown in figure (7B). The major product of the reaction was cis-2-butene but in the initial stages very small amounts of trans-2-butene, 1-butene and n-butane were also formed.

The distribution of products at various pressure falls for hydrogen -2-butyne ratio of 2.4 is shown in figure (13). Though the major product was cis-2-butene, small amounts of trans-2-butene, 1-butene and n-butane were also formed in the initial stages of the reaction. At a pressure fall of nearly 35 mm, while the amount of the cis-2-butene in the product started decreasing, trans-2-butene and n-butane started increasing in the same proportion. The amount of 1-butene in the product increased slightly up to a pressure fall of 35 mm and then decreased with further pressure falls.

(ii) Dependence of selectivity on the pressure fall

For hydrogen/2-butyne ratio of 1 (P_{H_2} = 50 mm, $P_{C_4H_6}$ = 50 mm) the selectivity was nearly independent of pressure fall (figure 7B). For hydrogen/2-butyne ratio of 2.4 though the selectivity was independent of pressure fall up to a pressure fall of 35 mm, it decreased rapidly after this due to the further hydrogenation of cis-2-butene to n-butane and also possibly due to isomerization of cis-2-butene to trans-2-butene (figure 13).

(iii) Dependence of selectivity on the initial hydrogen pressure

The dependence of selectivity on the initial hydrogen pressures was studied by keeping a fixed 2-butyne pressure (50 mm) and varying hydrogen pressures. The products were analyzed at 20 mm pressure fall. Selectivity was constant up to an initial hydrogen pressure of about 100 mm and then decreased slightly (figure 14A).

(iv) Dependence of selectivity on 2-butyne pressure

The dependence of selectivity on the initial pressure of 2-butyne was studied at 50^{o} C by keeping the initial hydrogen pressure fixed at 50 mm and varying initial 2-butyne pressure between 50 mm and 150 mm and analyzing the products for a 20 mm pressure drop. Though the selectivity increased slightly with increased 2-butyne pressures initially, it became independent of initial 2-butyne pressure (figure 14A).

(v) Dependence of selectivity on temperature

The dependence of selectivity on temperature was studied for hydrogen/2-butyne ratios of 1 ($^{P}H_2$ = 50 mm, $^{P}C_4H_6$ = 50 mm) and 2.4 ($^{P}H_2$ = 120 mm, $^{P}C_4H_6$ = 50 mm). The products were analyzed for a pressure fall of 20 mm.

Though selectivity was nearly independent of temperature

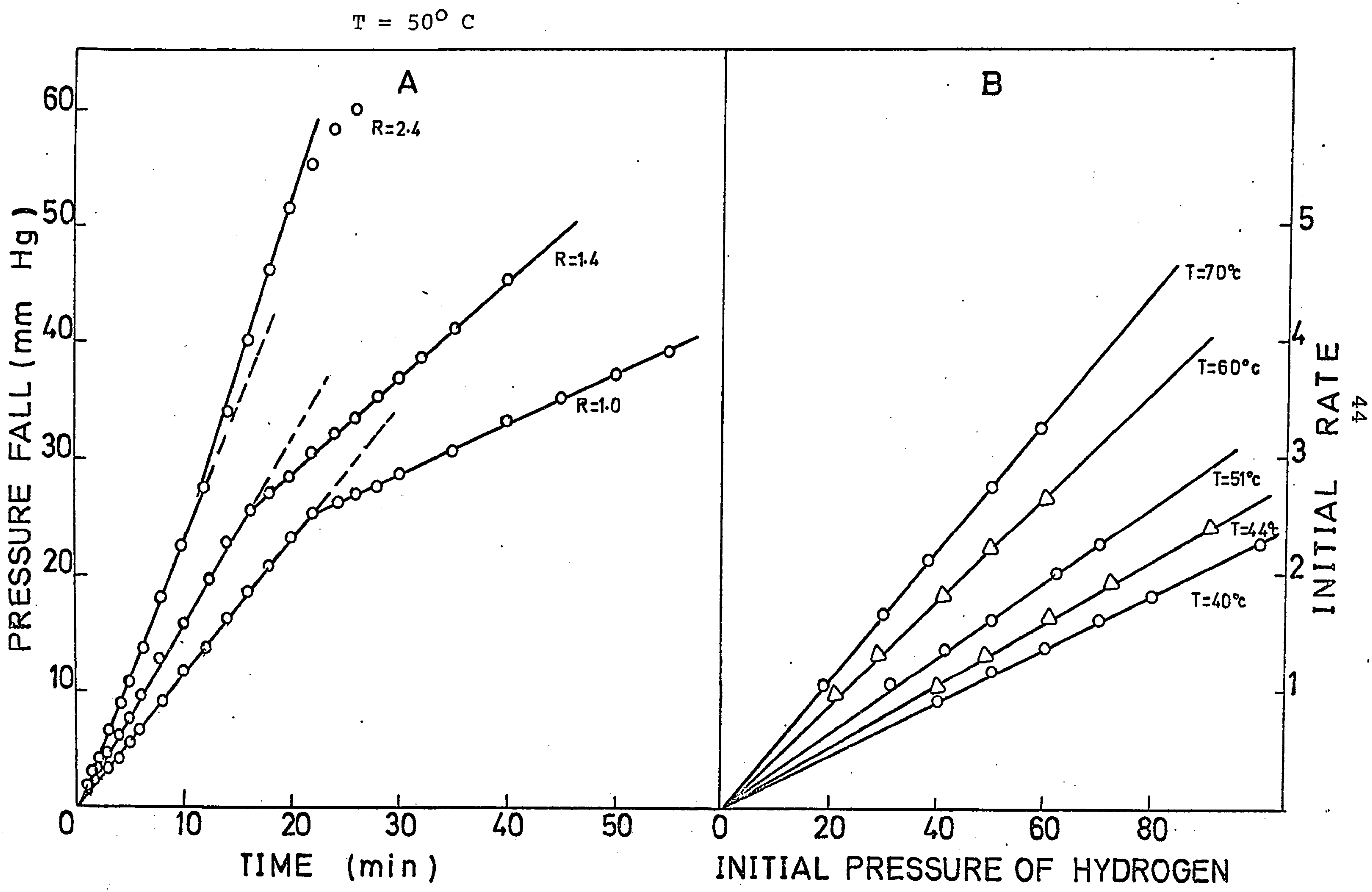


Figure 10 - A - Pressure-time curve 90% Ni - 10% Cu
B - Dependence of initial rate upon initial hydrogen pressure

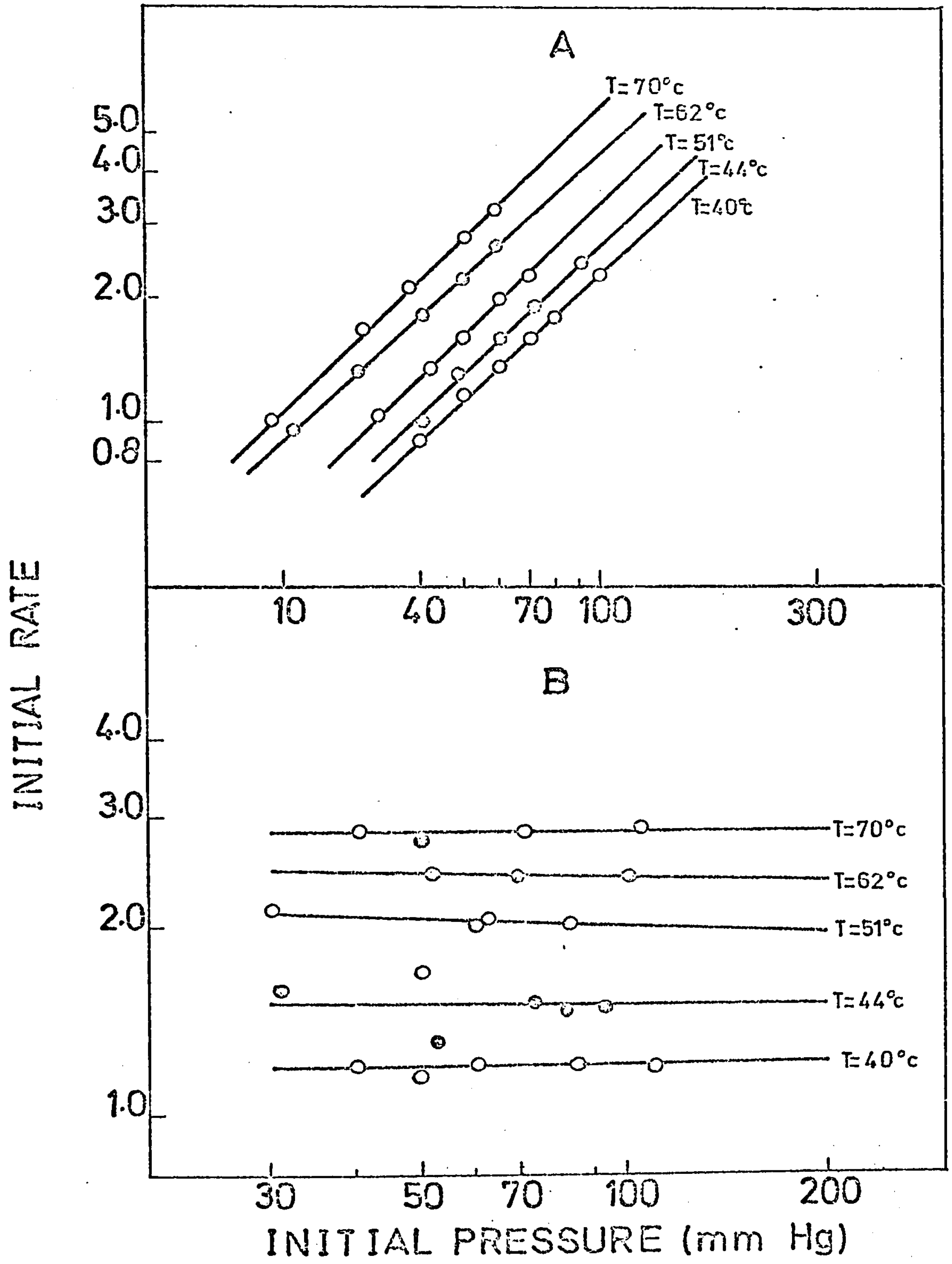


Figure 11 - Dependence of order of reaction upon temperature
A -- Hydrogen B - 2-butyne

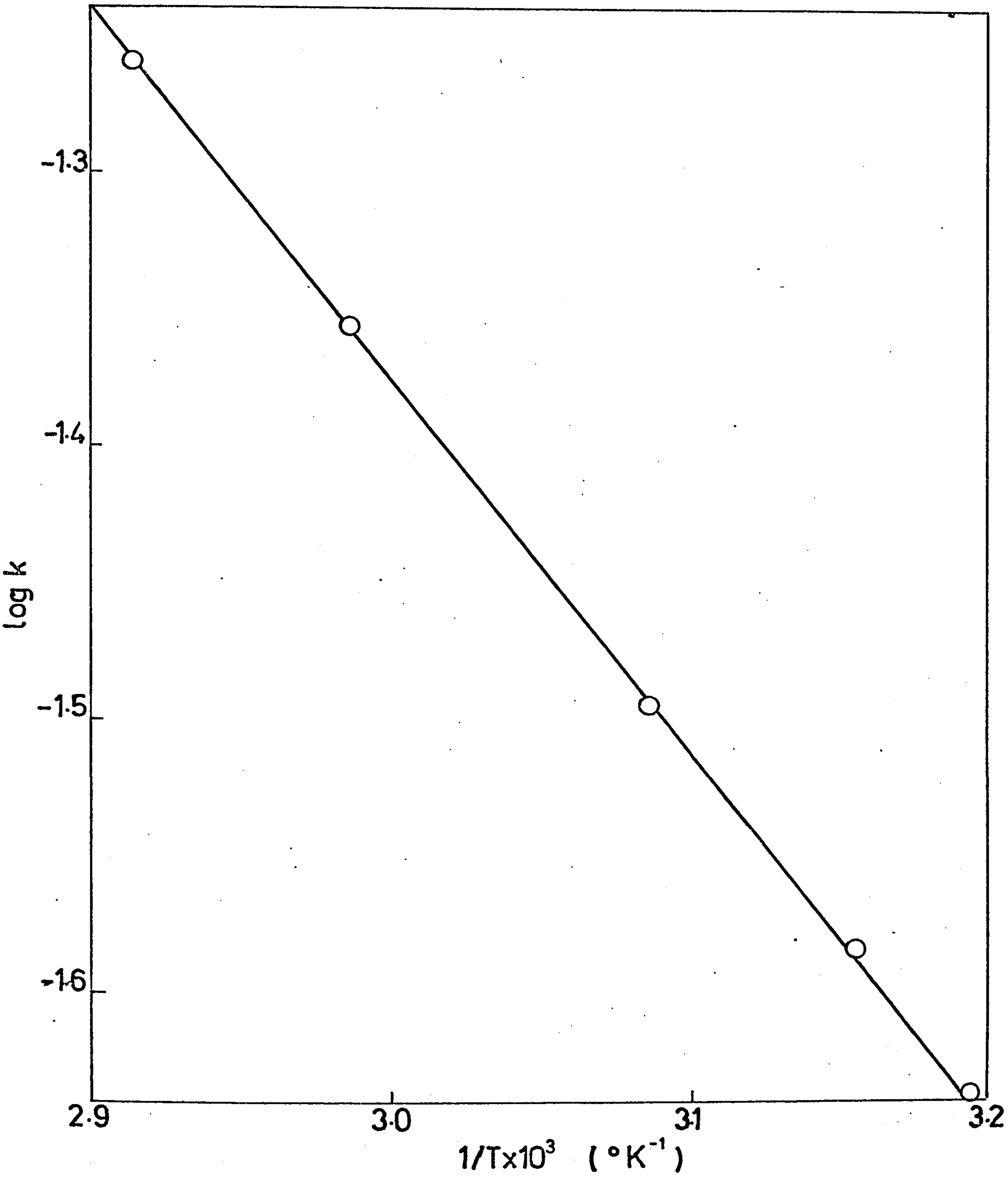


Figure 12 - Arrhenius Plot Ni 90% - Cu 10%

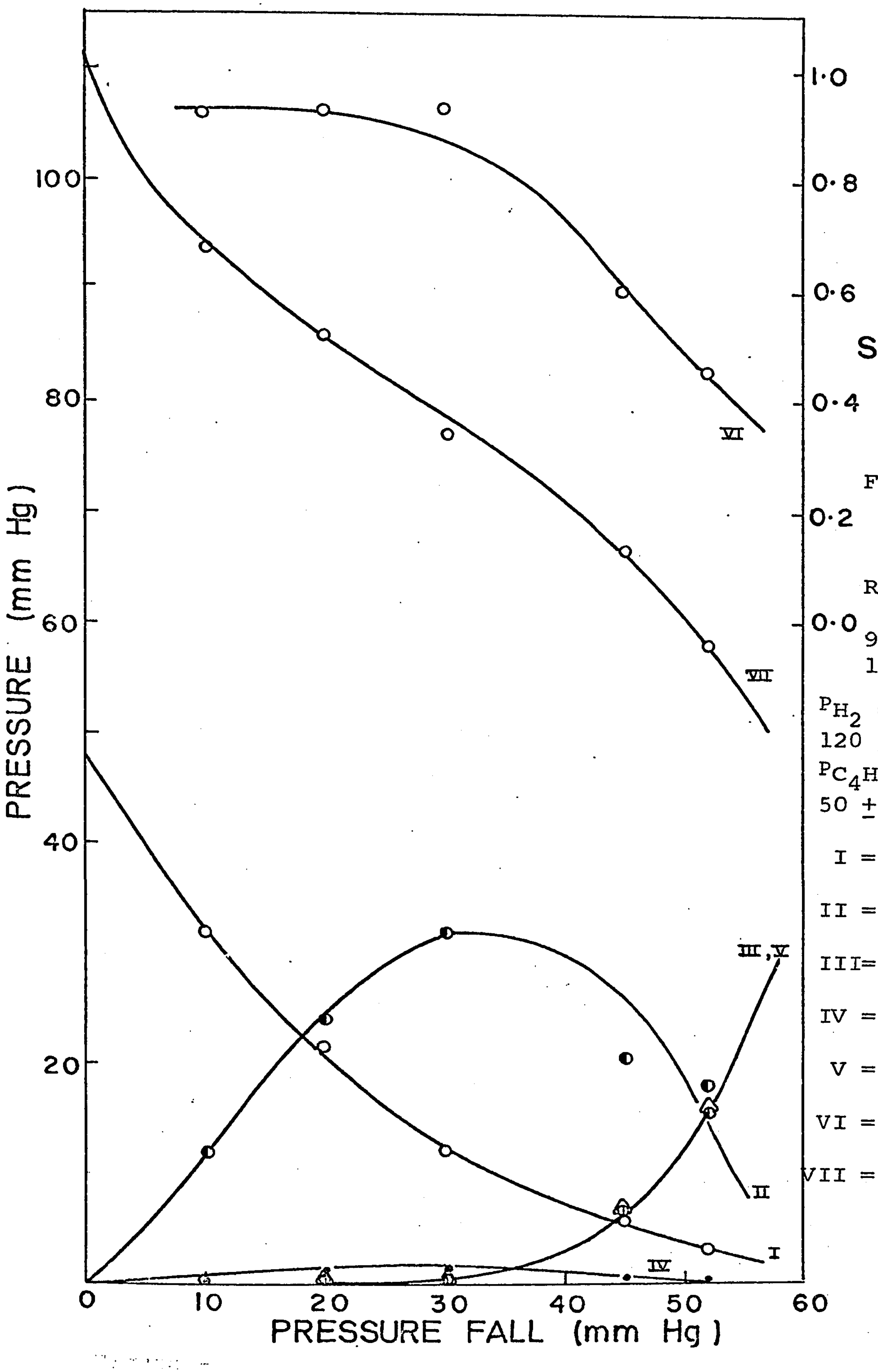


Figure 13

Course of Reaction

90% Ni
10% Cu

P_{H_2} =
120 ± 1 mm Hg
$P_{C_4H_6}$ =
50 ± 2 mm Hg

I = C_4H_6
II = $C-C_4H_8$
III= $t-C_4H_8$
IV = $1-C_4H_8$
V = $n-C_4H_{10}$
VI = S
VII = H_2

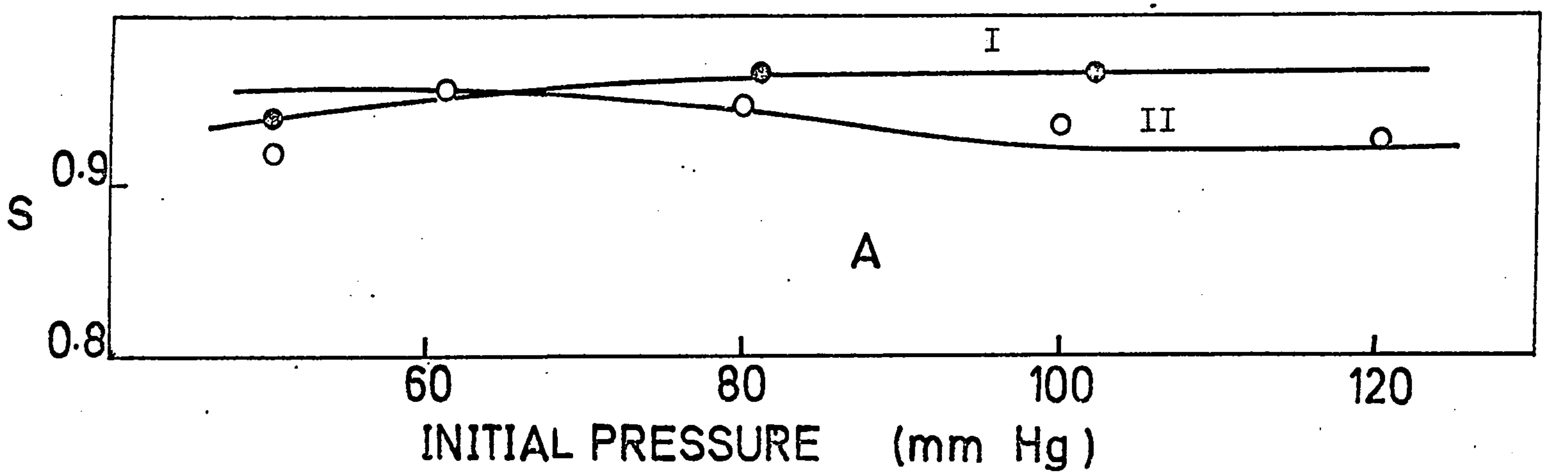


Figure 14A - Dependence of selectivity upon initial reactant pressure

I - with respect to 2-butyne $P_{H_2} = 50 \pm 1$ mm Hg

II - with respect to hydrogen $P_{C_4H_6} = 50 \pm 2$ mm Hg

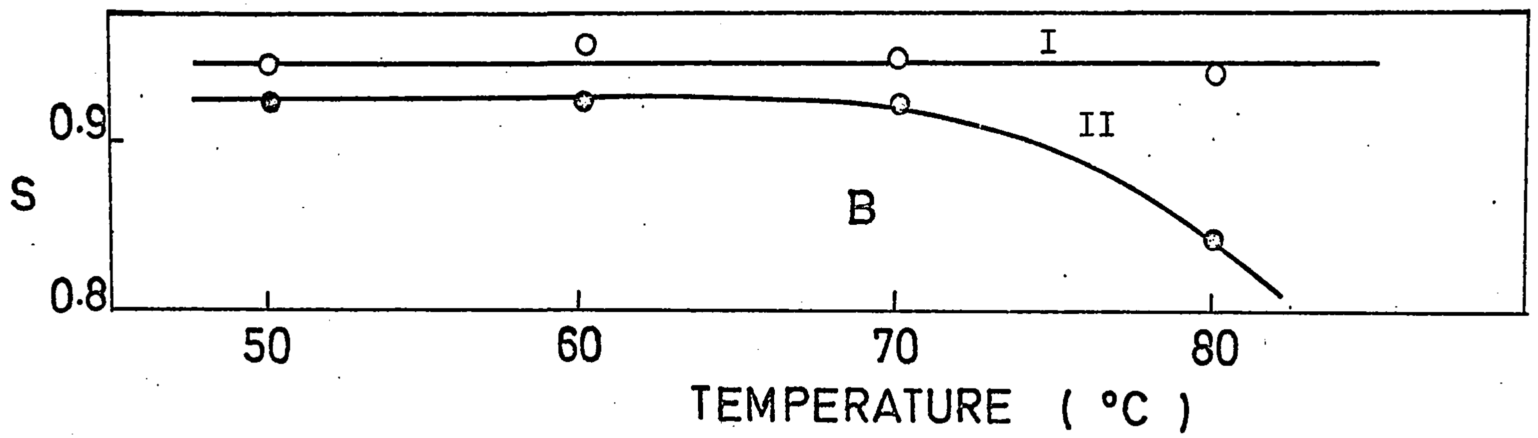


Figure 14B - Dependence of selectivity upon temperature

I = $P_{H_2} = 50 \pm 1$ mm Hg

II = $P_{H_2} = 120 \pm 1$ mm Hg

$P_{C_4H_6} = 50 \pm 2$ mm Hg

for hydrogen/2-butyne ratio of 1 (curve I, figure 14B), for a ratio of 2.4 it decreased rapidly after 70° C (curve II, figure 14B).

5. REACTION OVER 80% NICKEL AND 20% COPPER ALLOY POWDER:

(a) KINETICS

The experimental data obtained for the hydrogenation of 2-butyne over the alloy catalyst containing 80% nickel and 20% copper (.075 gm as oxide) are given in Table (3).

After the activity of the catalyst had stabilized the reaction had a measurable rate at 50° C. The pressure fall-time curves at 60° C are shown in figure (15A). The curves consisted of two linear portions similar to the pressure fall time curves observed in the hydrogenation of 2-butyne over the alloy catalyst containing 90% nickel and 10% copper.

The dependence of the initial rate on the initial hydrogen pressure at various temperatures is shown in figure (3B).

The order of reaction with respect to hydrogen was one and independent of temperature (figure 16A). The order of reaction with respect to 2-butyne was zero and became slightly negative with increasing temperatures (figure 16B). The overall rate equation can be expressed

$$r_o = k\ (P_{H_2})^1\ (P_{C_4H_6})^{-.05 \pm .05}$$

Plots of $\log_{10}$ of specific reaction rates against reciprocal of the absolute temperatures was a good straight line satisfying Arrhenius equation (figure 15B). The derived apparent energy of activation and frequency factor were 7.69 k cal/mol and 4.863×10^4 min^{-1}/gm respectively.

(b) SELECTIVITY:

(1) Course of the reaction:

The distribution of products during the course of reaction for hydrogen/2-butyne ratio of 1 (50 mm of each) is shown in figure (17A). In the initial stages of the reaction trans-2-butene was the main product. The maximum amount of trans-2-butene was found when the pressure had fallen nearly equal to 10 mm after which it decreased (curve III). At this stage, the formation of cis-2-butene started. 1-butene was formed only after a pressure fall of 15 mm.

Figure (18) shows the distribution of the products during the course of the reaction for a hydrogen/2-butyne ratio of 2.4 ($^{P}H_2$ = 120 mm, $^{P}C_4H_6$ = 50 mm). The main product in the initial stage was cis-2-butene which reached a maximum value at about 30 mm pressure fall. In the initial stages, the formation of trans-2-butene was very small but after a pressure drop of 20 mm, it started increasing and reached a maximum value at 55 mm pressure fall (curve III). Though the amount of n-butane was less in the initial stages, it increased with increasing pressure falls (curve V).

(ii) Dependence of selectivity upon pressure fall:

For a hydrogen/2-butyne ratio of 1 ($^{P}H_2$ = 50 mm, $^{P}C_4H_6$ = 50 mm), the selctivity was nearly zero at 10 mm pressure fall due to the trans-2-butene being the main product in the initial stages of the reaction. After 10 mm pressure fall the formation of cis-2-butene increased and the selectivity increased rapidly with increased pressure falls (figure 17A, curve VI).

For hydrogen/2-butyne ratio of 2.4, the selectivity was independent of pressure falls initially, it decreased for pressure falls greater than 30 mm (figure 18, curve VI).

(iii) The dependence of selectivity upon hydrogen pressure:

The dependence of selectivity upon hydrogen pressure at 40° C was studied by keeping 2-butyne pressure fixed (50 mm) and varying hydrogen pressures. The reaction products were analyzed at 20 mm pressure drop. Selectivity increased with increasing hydrogen pressures up to a pressure of 90 mm and then levelled off (figure 19A).

(iv) The dependence of selectivity upon 2-butyne pressure:

The dependence of selectivity upon 2-butyne pressure was studied at 40° C by analyzing the reaction products for a 20 mm pressure falls, keeping initial hydrogen pressure at 50 mm. The selectivity increased with 2-butyne pressures reaching a maximum value at initial 2-butyne pressure of 80 mm, beyond

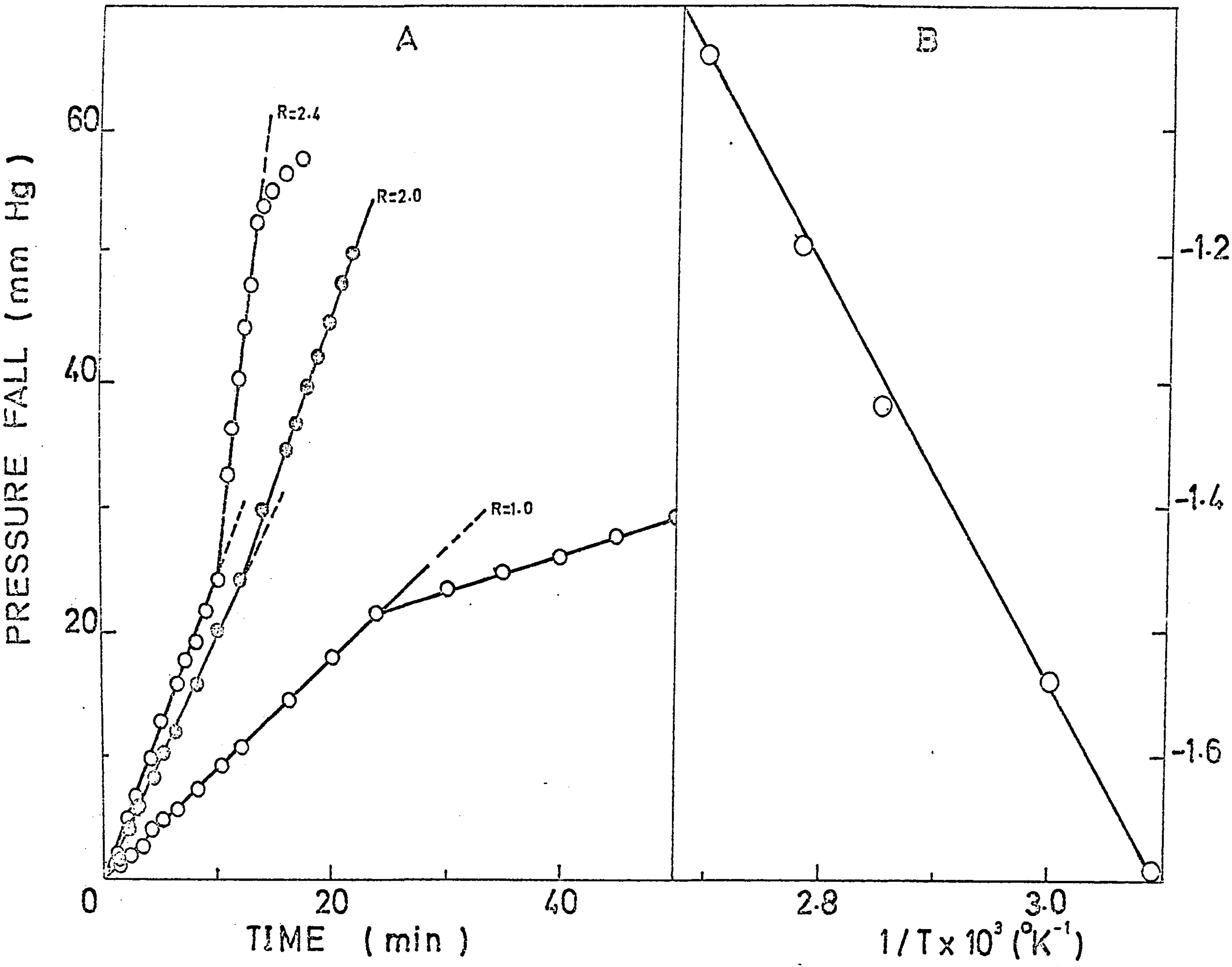


Figure 15A - Pressure time curves   Figure 15B - Arrhenius plot

80% Ni, 20% Cu

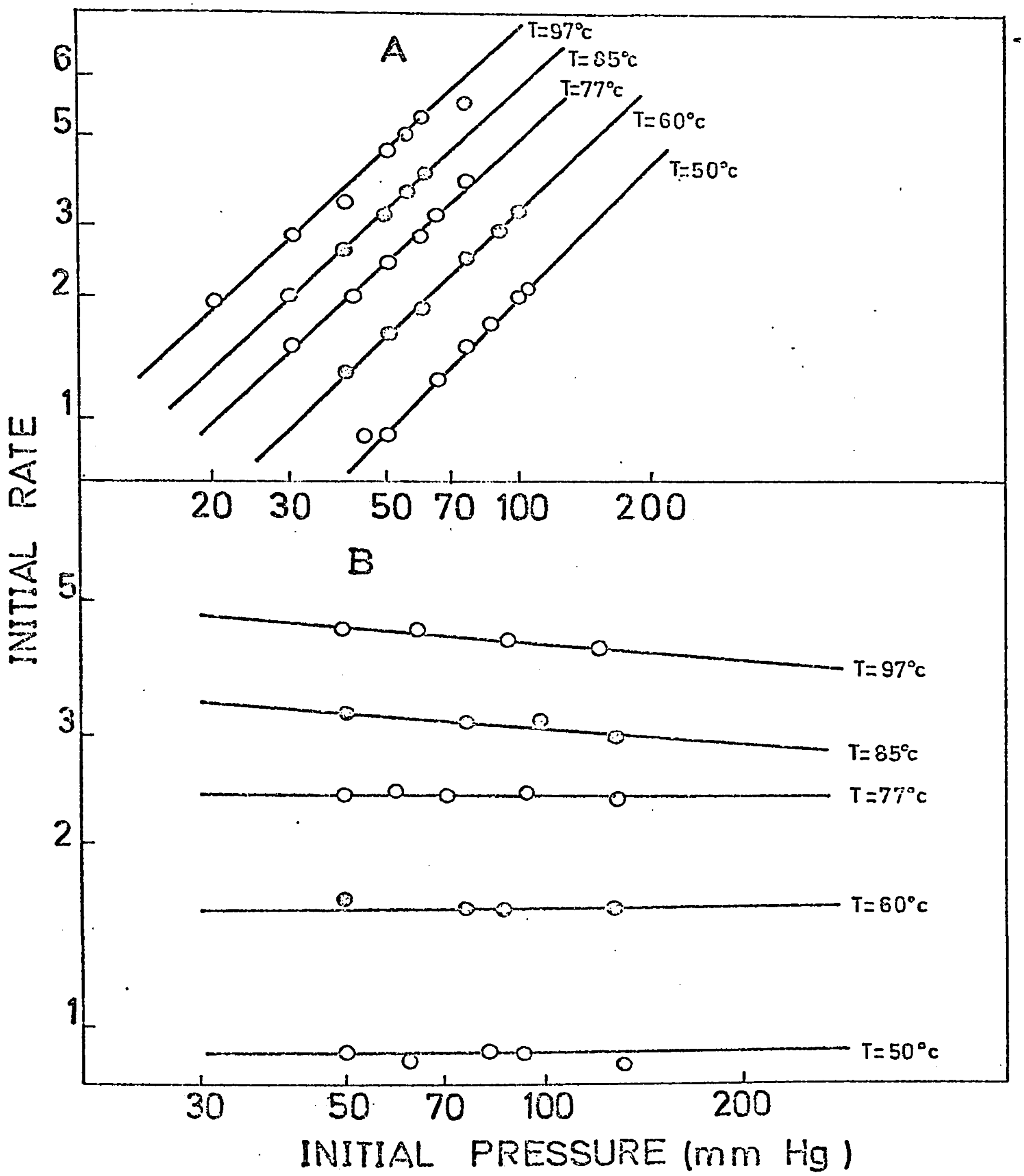


Figure 16 - Dependence order of reaction upon temperature
A - hydrogen B - 2-butyne

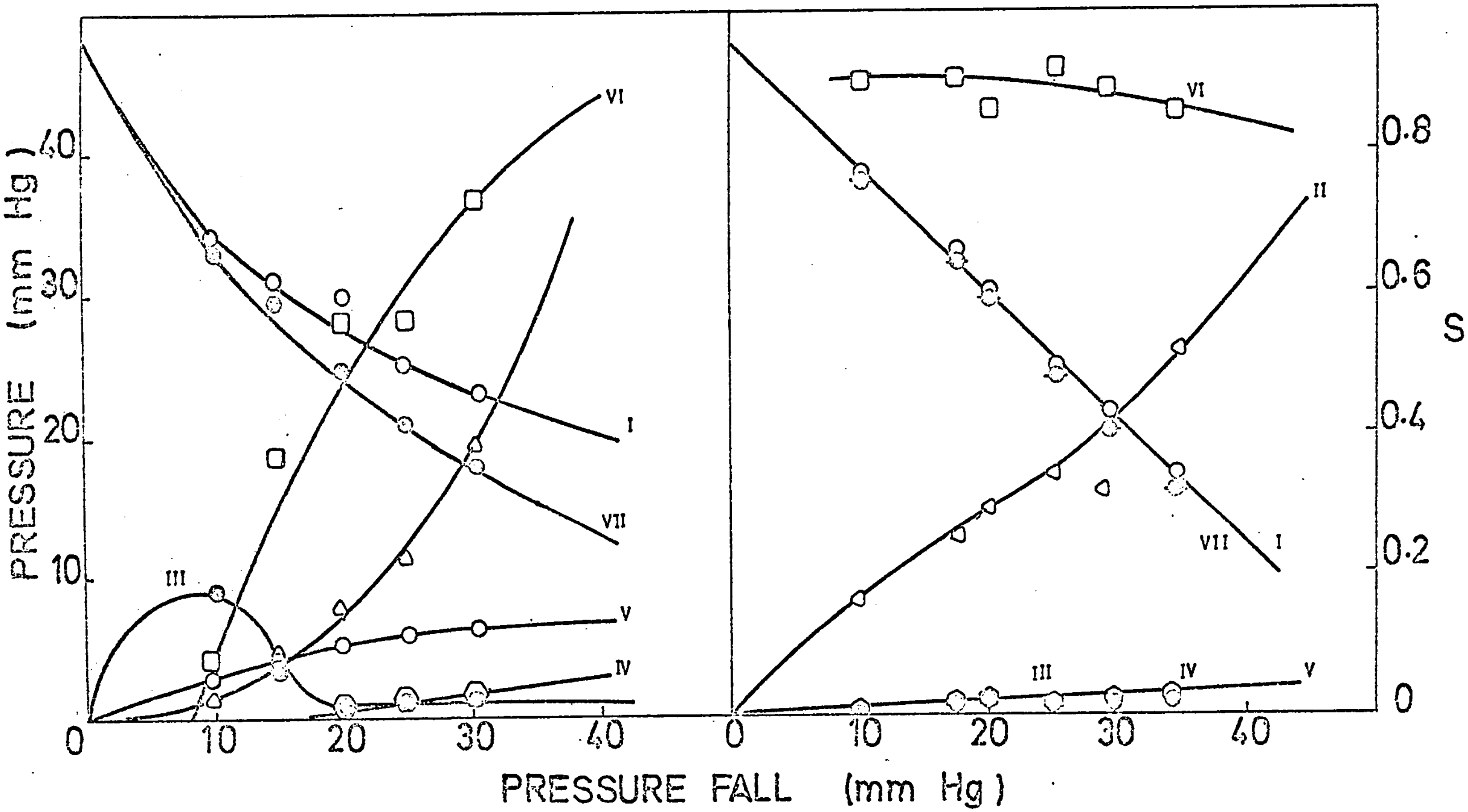


Figure 17 - A - 80% Ni - 20% Cu B - 70% Ni - 30% Cu
P_{H_2} = 50 ± 1 mm Hg $P_{C_4H_6}$ = 50 ± 2 mm Hg
I = C_4H_6 II = C-C_4H_8 III = t-C_4H_8 IV = 1-C_4H_8 V = n-C_4H_{10}
VI = Selectivity VII = Hydrogen

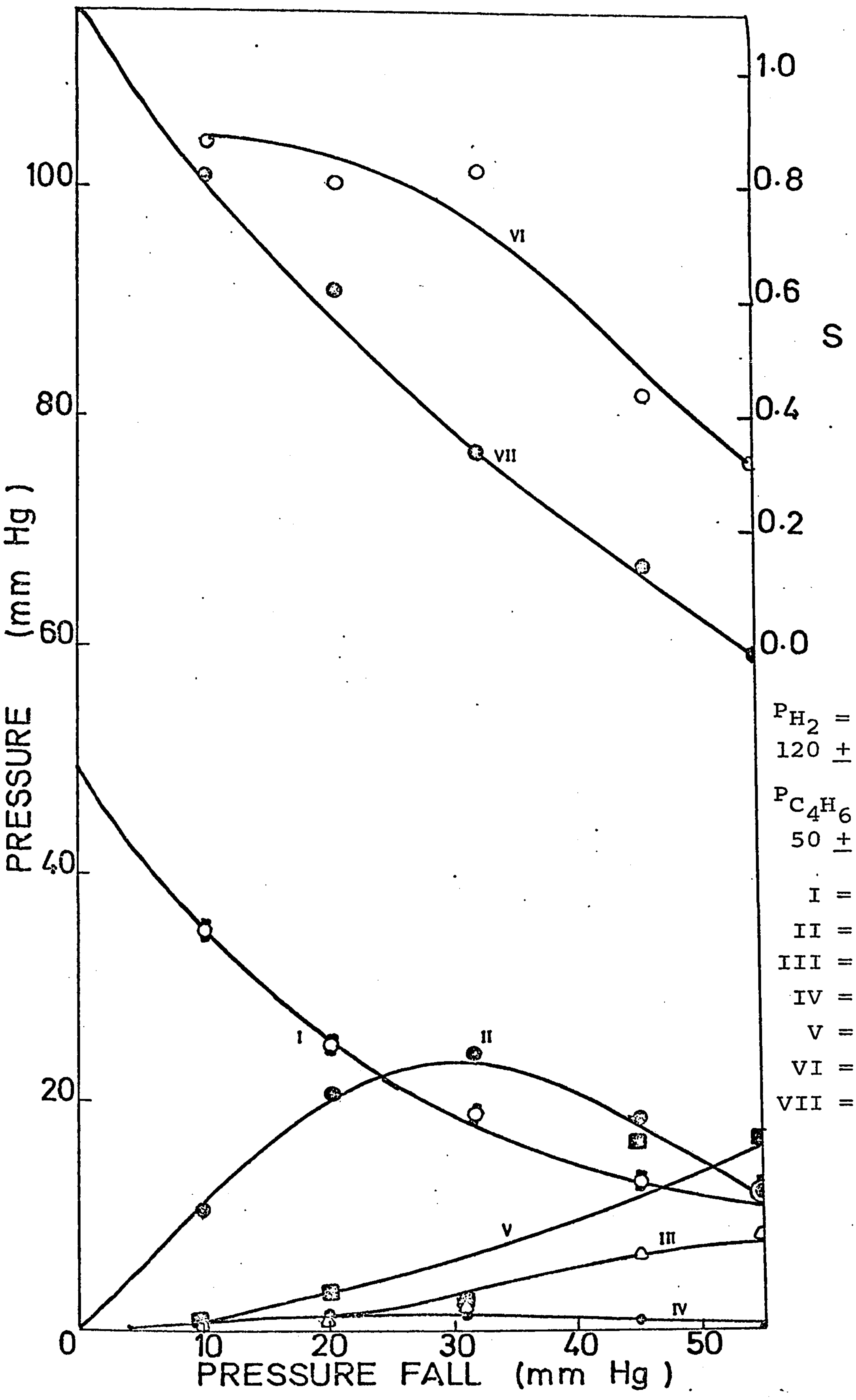


Figure 18

Course of Reaction

80% Ni
20% Cu

P_{H_2} = 120 ± 1 mm Hg

$P_{C_4H_6}$ = 50 ± 1 mm Hg

I = C_4H_6
II = $c\text{-}C_4H_8$
III = $t\text{-}C_4H_8$
IV = $1\text{-}C_4H_8$
V = $n\text{-}C_4H_{10}$
VI = S
VII = H

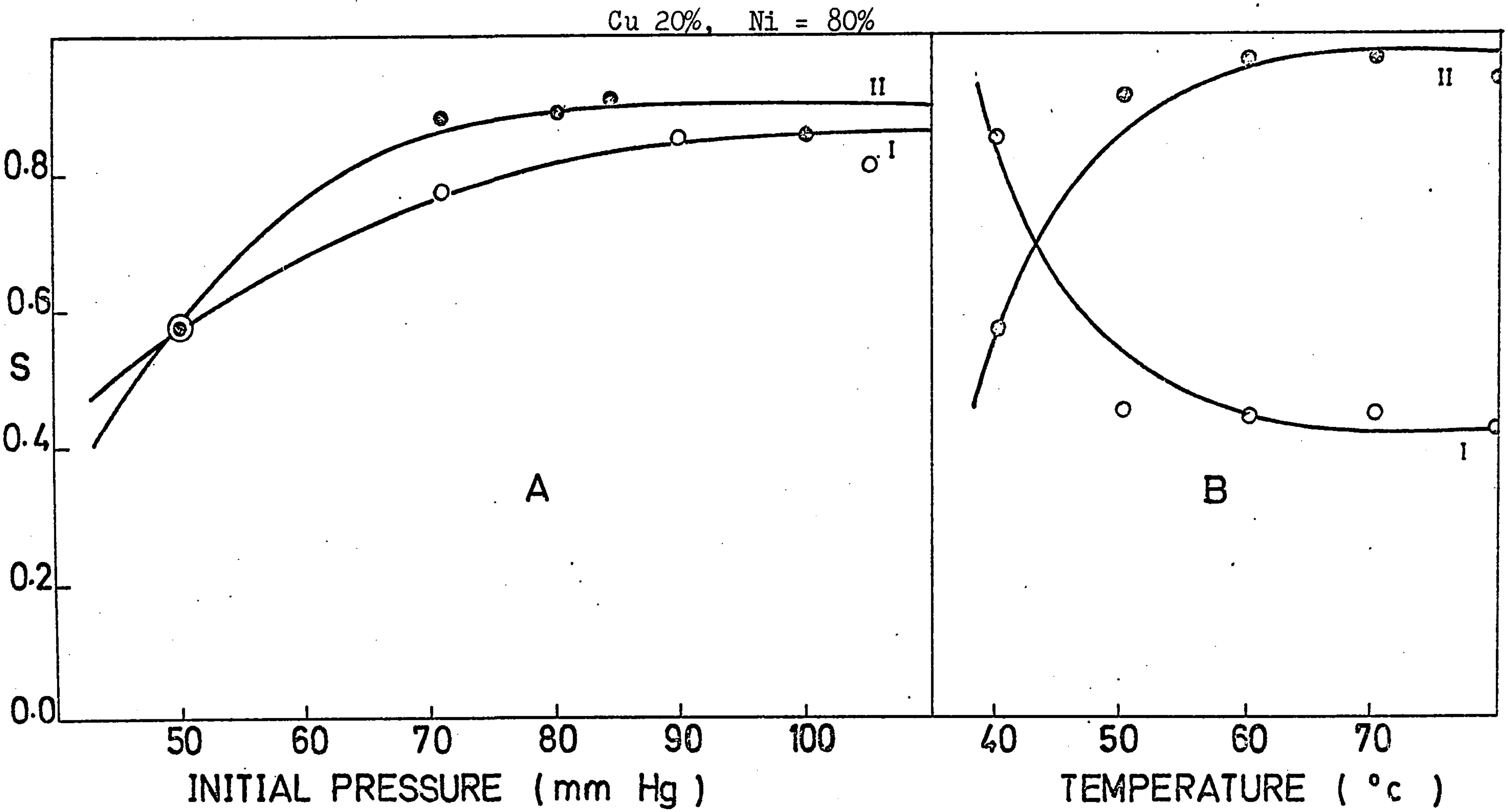


Figure 19A - Dependence of selectivity upon initial reactant pressure

I - With respect to 2-butyne $P_{H_2} = 50 \pm 1$ mm Hg

II - With respect to hydrogen $P_{C_4H_6} = 50 \pm 2$ mm Hg

Figure 19B - Dependence of selectivity upon temperature

I - $P_{H_2} = 50 \pm 1$ mm Hg

II - $P_{H_2} = 120 \pm 1$ mm Hg

$P_{C_4H_6} = 50 \pm 2$ mm Hg

which it was constant (figure 19A, curve II).

(v) The dependence of selectivity upon temperature:

The dependence of selectivity upon temperature was studied by analyzing the products at 20 mm pressure fall, for hydrogen/2-butyne ratios of 1 (50 mm of each reactant and 2.4 (P_{H_2} = 120 mm, $P_{C_4H_6}$)= 50 mm).

For a hydrogen/2-butyne ratio of 1, the selectivity increased initially with increasing temperatures and then it became nearly temperature independent.

For hydrogen/2-butyne ratio of 2.4, the selectivity initially decreased rapidly from .85 to .425 with increasing temperatures and then became independent of temperature (figure 19B, curve I).

6. REACTION OVER 70% NICKEL AND 30% COPPER ALLOY POWDER:

(a) KINETICS:

The kinetics of the hydrogenation of 2-butyne over alloy catalyst containing 70% nickel and 30% copper was studied in the temperature range 50° - 80° C. The experimental data obtained are given in Table (4). The shape of pressure time curve was similar to those obtained over nickel catalyst (figure 20).

The dependence of initial rates on initial hydrogen pressures is shown in figure (21B). The order of reaction with respect to hydrogen was one and was independent of temperature

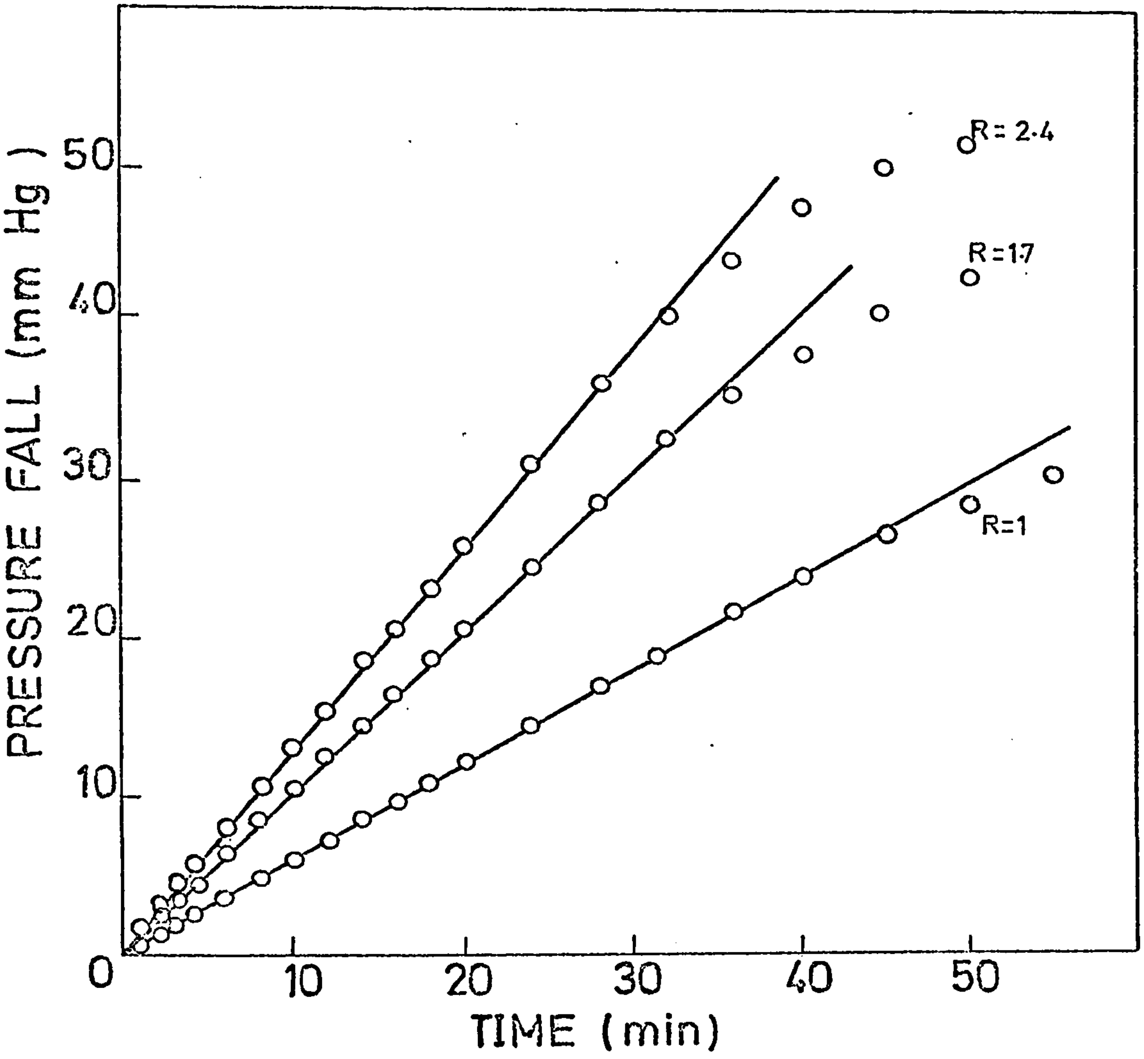
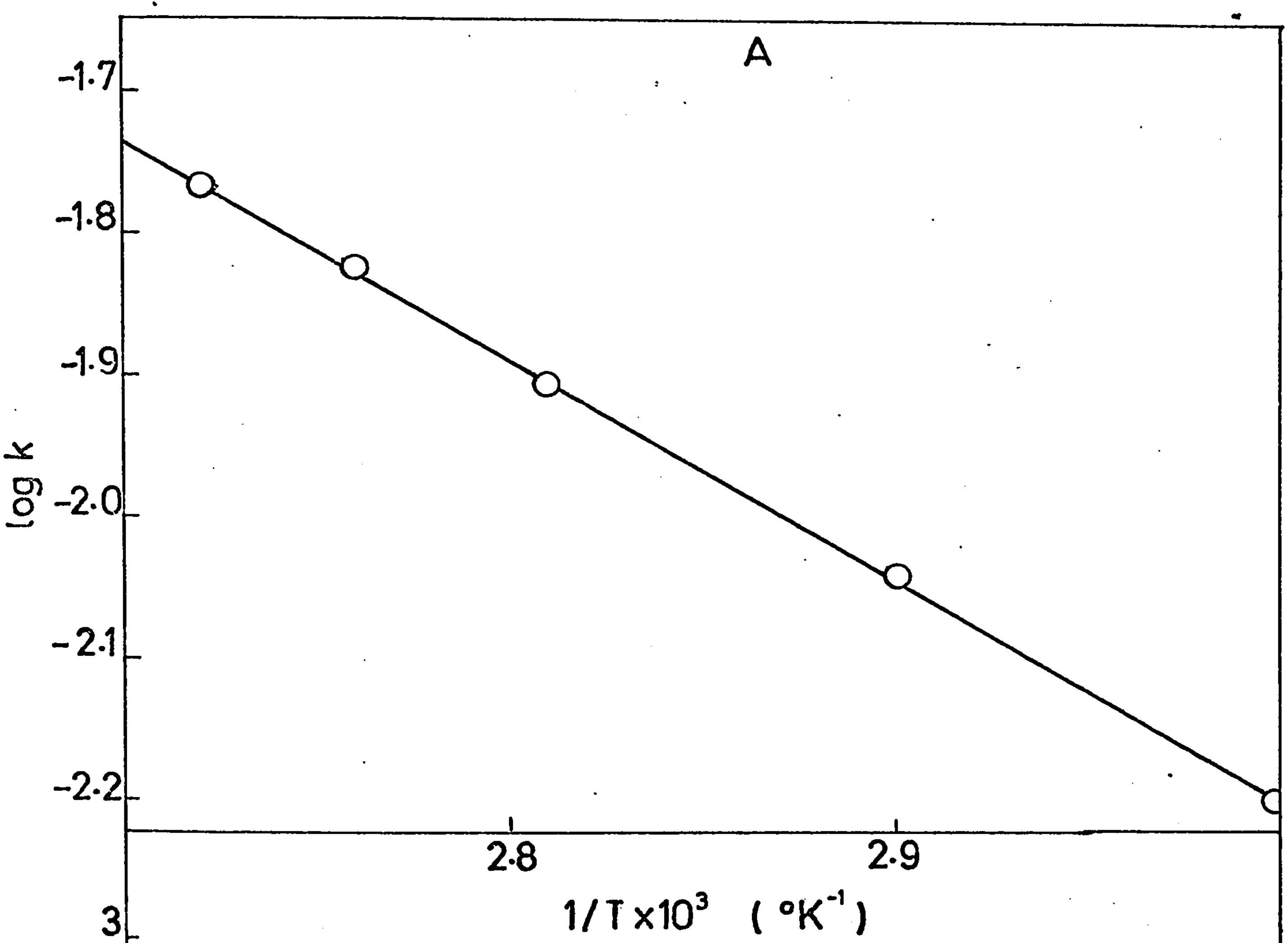


Figure 20 - Pressure-time curves

Figure 21A - Arrhenius plot



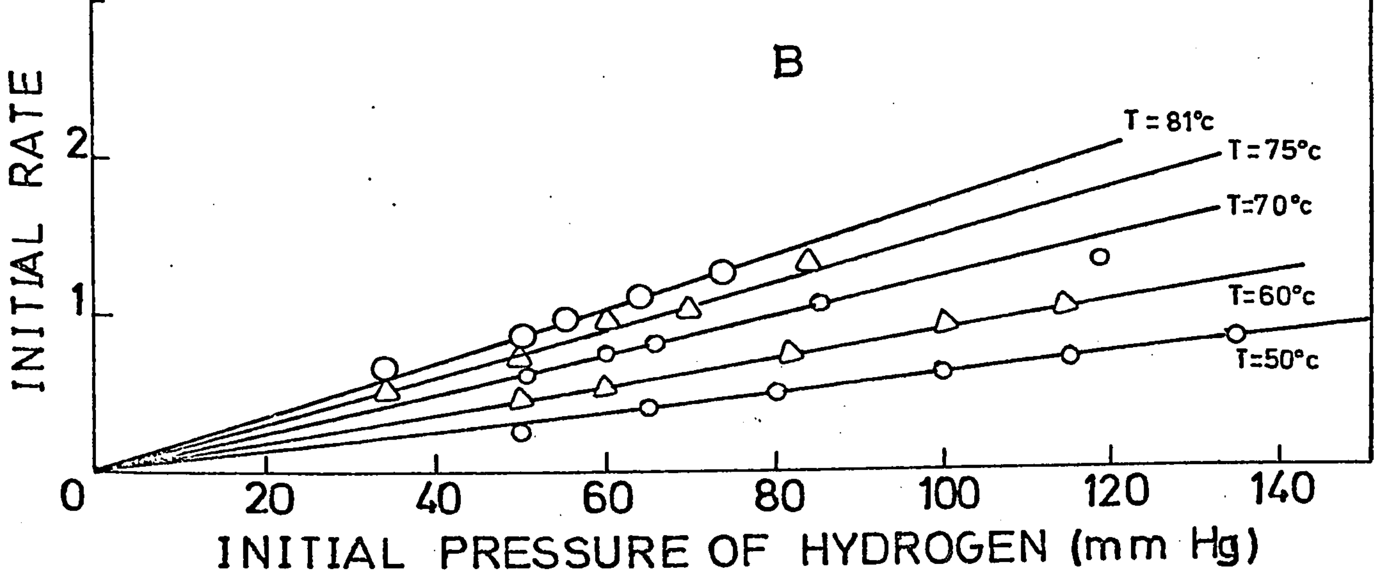


Figure 21B - Dependence of initial rate upon initial hydrogen pressure

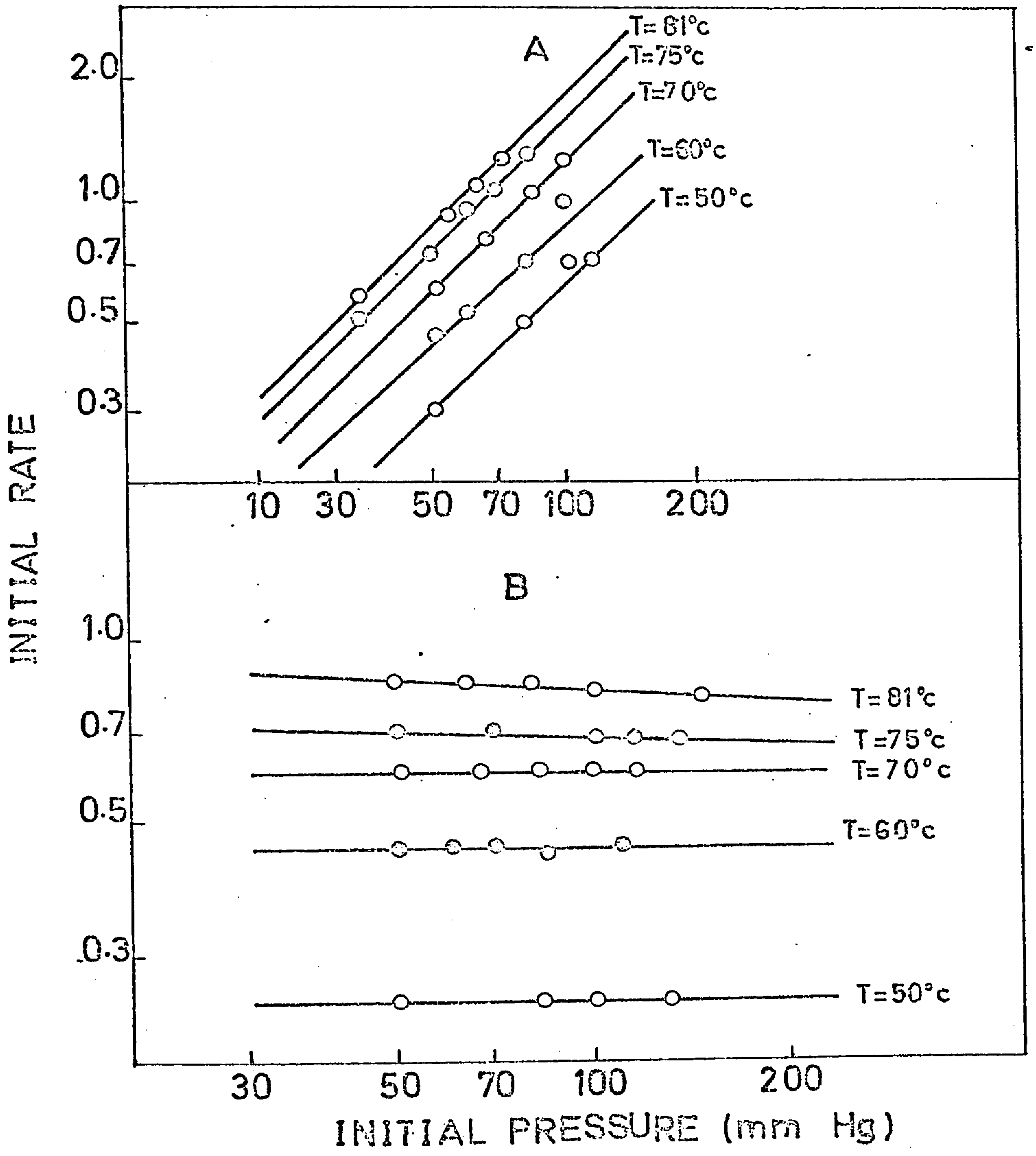


Figure 22 - Dependence order of reaction upon temperature
A - Hydrogen B - 2-butyne

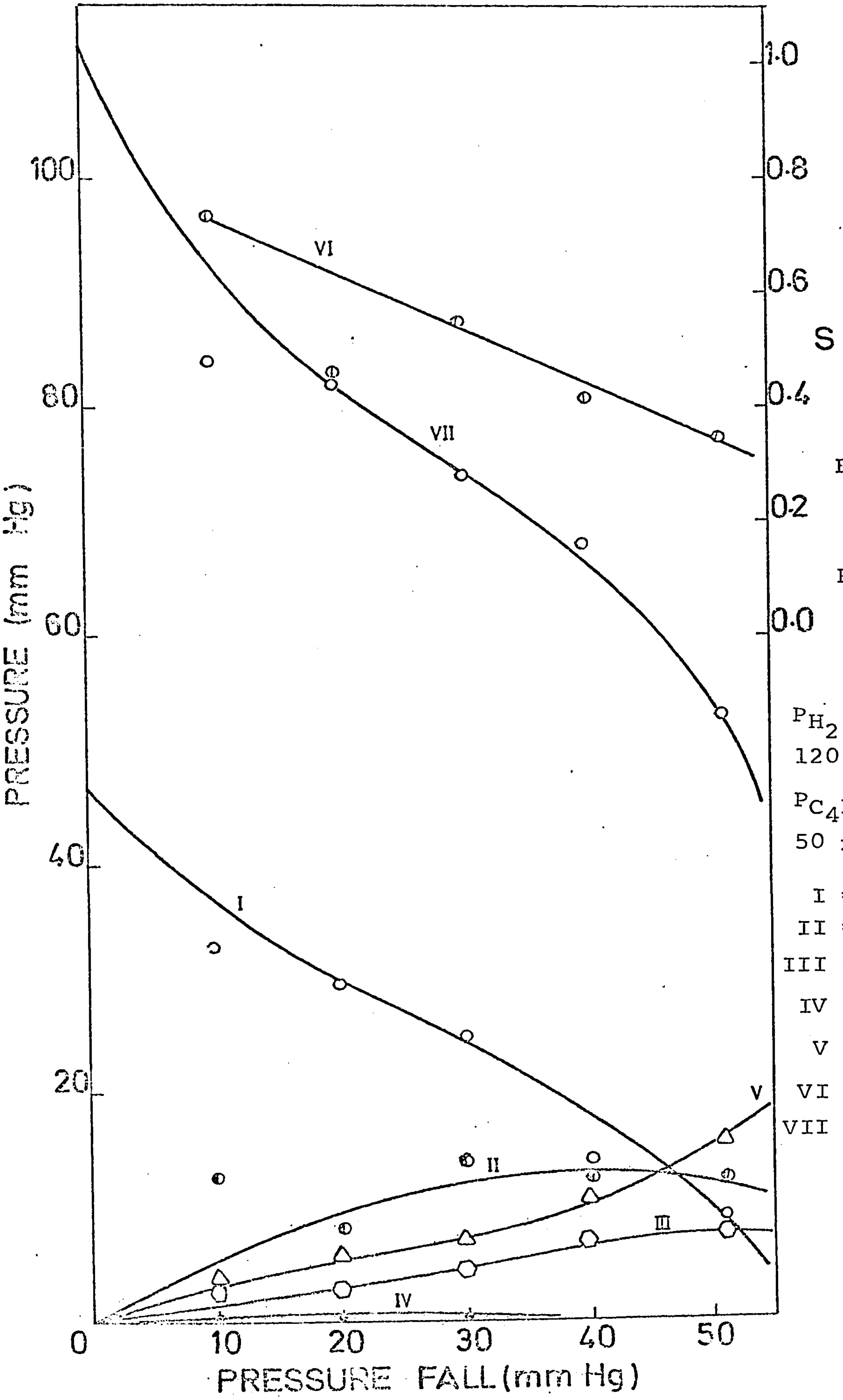


Figure 23

Course
of
Reaction

70% Ni
30% Cu

P_{H_2} =
120 ± 1 mm Hg

$P_{C_4H_6}$ =
50 ± 2 mm Hg

I = C_4H_6
II = $c-C_4H_8$
III = $t-C_4H_8$
IV = $1-C_4H_8$
V = $n-C_4H_{10}$
VI = S
VII = H

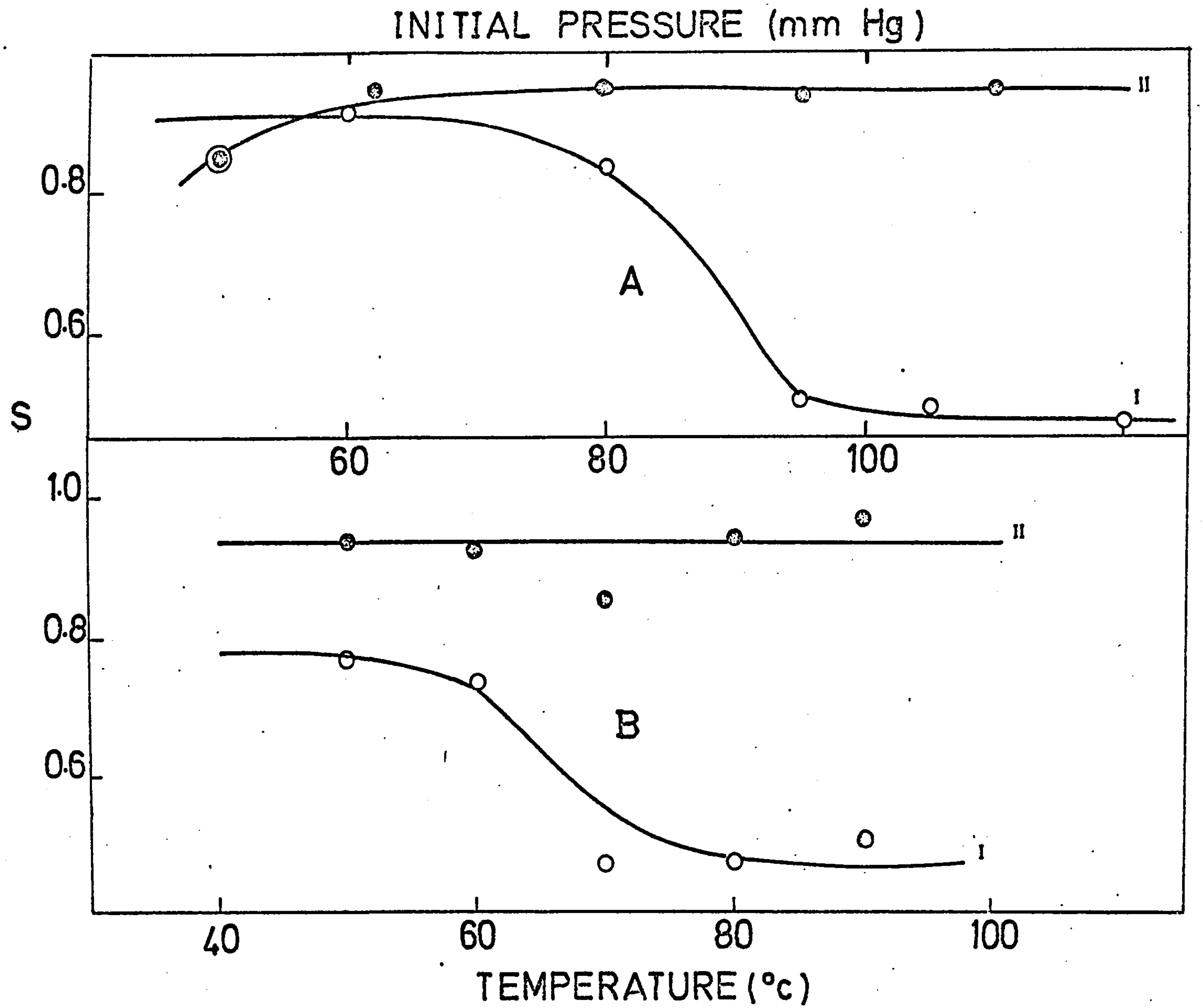


Figure 24A - Dependence of selectivity upon initial reactant pressure
I - 2-butyne   II - Hydrogen

24B - Dependence of selectivity upon temperature
II - P_{H_2} = 50 ± 1 mm Hg   I - P_{H_2} = 120 ± 1 mm Hg

(figure 22A). The order with respect to 2-butyne was zero and became slightly negative at higher temperatures (figure 22B). The overall rate equation was

$$r_o = k\ (P_{H_2})^1\ (P_{C_4H_6})^{-0.03\ \pm\ 0.03}$$

Plot of $\log_{10}$ of specific rate constants against the reciprocal of absolute temperature was a good straight line (figure 21A) over a wide range of temperatures satisfying Arrhenius equation. The derived apparent activation energy and frequency factor were 7.1 k cal/mol and 6.466 x 10^3 min^{-1}/gm respectively.

(b) SELECTIVITY:

(i) Course of reaction

The distribution of products during the course of reaction for hydrogen/2-butyne ratio of 1 (50 mm of each) at 70° C is shown in figure (17B). The main product of the reaction was cis-2-butene, the amounts of which increased nearly linearly with increasing pressure falls. In addition to cis-2-butene, small amounts of trans-2-butene, 1-butene and n-butane were also formed. The amounts of these increased slightly as the reaction progressed.

The distribution of products for various pressure drops for a hydrogen/2-butyne ratio of 2.4 (P_{H_2} = 120 mm, $P_{C_4H_6}$ = 50 mm) is shown in figure (23). Though the main products were cis-2-butene, trans-2-butene and 1-butene, small amount of n-butane was also formed in the initial stages. The maximum amounts of cis-2-butene and trans-2-butene were formed at pressure falls of about 40 mm and 50 mm respectively (curve II and III).

(ii) Dependence of selectivity upon pressure fall

The reaction products were analyzed at different pressure falls at 70° C for hydrogen/2-butyne ratios of 1 and 2.4. For hydrogen/2-butyne ratio of 1, the selectivity decreased slightly after a pressure fall of 30 mm. For hydrogen/2-butyne ratio of 2.4, the selectivity decreased linearly with pressure fall in the range of 10 - 51 mm pressure fall (fig-23, curve VI).

(iii) Dependence of selectivity upon initial hydrogen pressure:

The dependence of selectivity on the initial hydrogen pressure at 70° C was studied by keeping 2-butyne pressure at 50 mm and varying hydrogen pressures between 50 and 120 mm and analyzing the products at 20 mm pressure fall. The selectivity was observed to be constant up to an initial hydrogen pressure of ~75 mm and then decreased, reaching a constant value at 100 mm (figure 24A).

(iv) Dependence of selectivity upon 2-butyne pressure

The dependence of selectivity at 70° C was studied by having a fixed hydrogen pressure (50 mm) and varying initial 2-butyne pressure between 50 and 120 mm analyzing the products at 20 mm pressure fall. Selectivity increased initially at lower initial 2-butyne pressure and then became constant beyond 60 mm initial 2-butyne pressure (figure 24A, curve II).

(v) Dependence of selectivity upon temperature

The effect of temperature on the selectivity was studied at hydrogen/2-butyne ratios of 1 (P_{H_2} = 50 mm, $P_{C_4H_6}$ = 50 mm) and 2.4 (P_{H_2} = 120 mm, $P_{C_4H_6}$ = 50 mm) over a wide range of temperatures, analyzing the products at 20 mm pressure fall.

While the selectivity was independent of temperature for hydrogen/2-butyne ratio of 1 (figure 24B), for a ratio of 2.4, it decreased between 40 and 70° C beyond which it was nearly constant with temperatures.

7. REACTION OVER 50% NICKEL AND 50% COPPER ALLOY POWDER:

(a) KINETICS

The experimental data obtained for the hydrogenation of 2-butyne over the alloy catalyst containing 50% nickel and 50% copper (.075 gm as oxide) are given in Table (5). The reaction had a measurable rate at 50° C after the catalyst was stabilized. The pressure time curves at 50° C for various reactant ratios were similar to those obtained in the hydrogenation of 2-butyne over nickel powder (figure 25A).

The dependence of initial rate upon initial hydrogen pressure was studied between 50 and 92° C (figure 26B). The order of reaction with hydrogen was one and temperature independent (figure 27A). Figure (27B) shows the dependence of

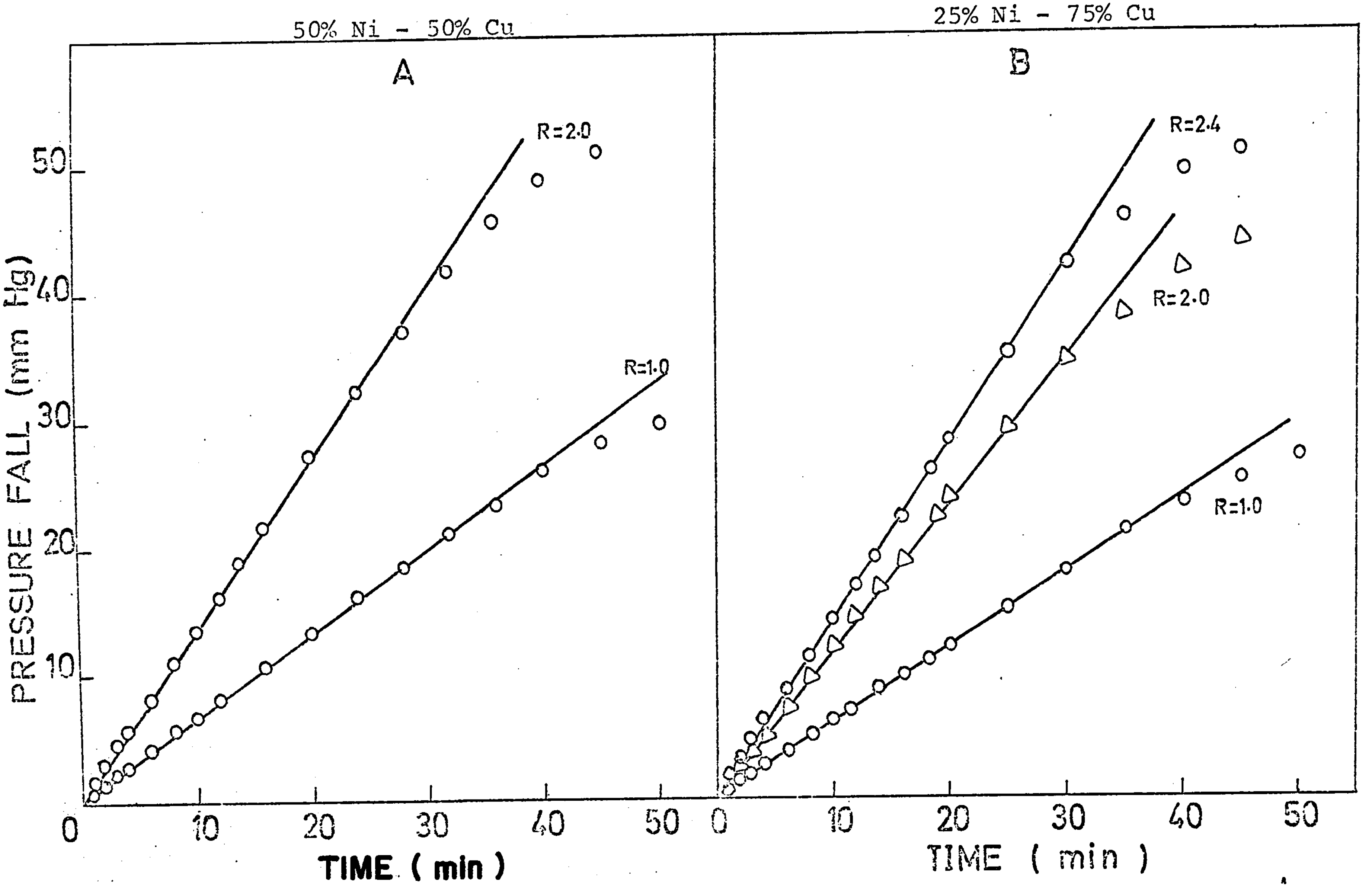


Figure 25 - Pressure-time curves

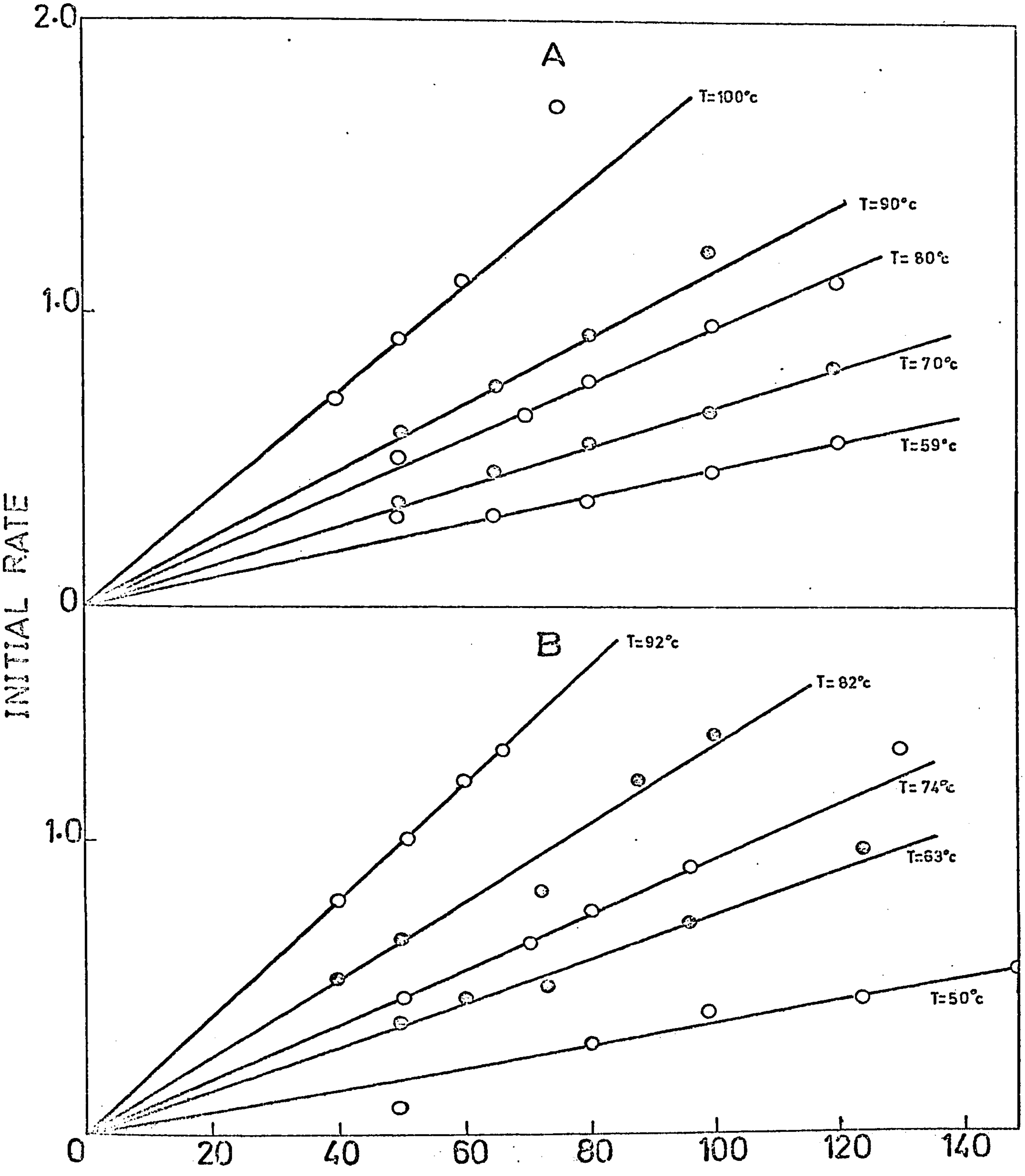


Figure 26 - Dependence of initial rate upon initial hydrogen pressure

A - 25% Ni - 75% Cu   B - 50% Ni - 50% Cu

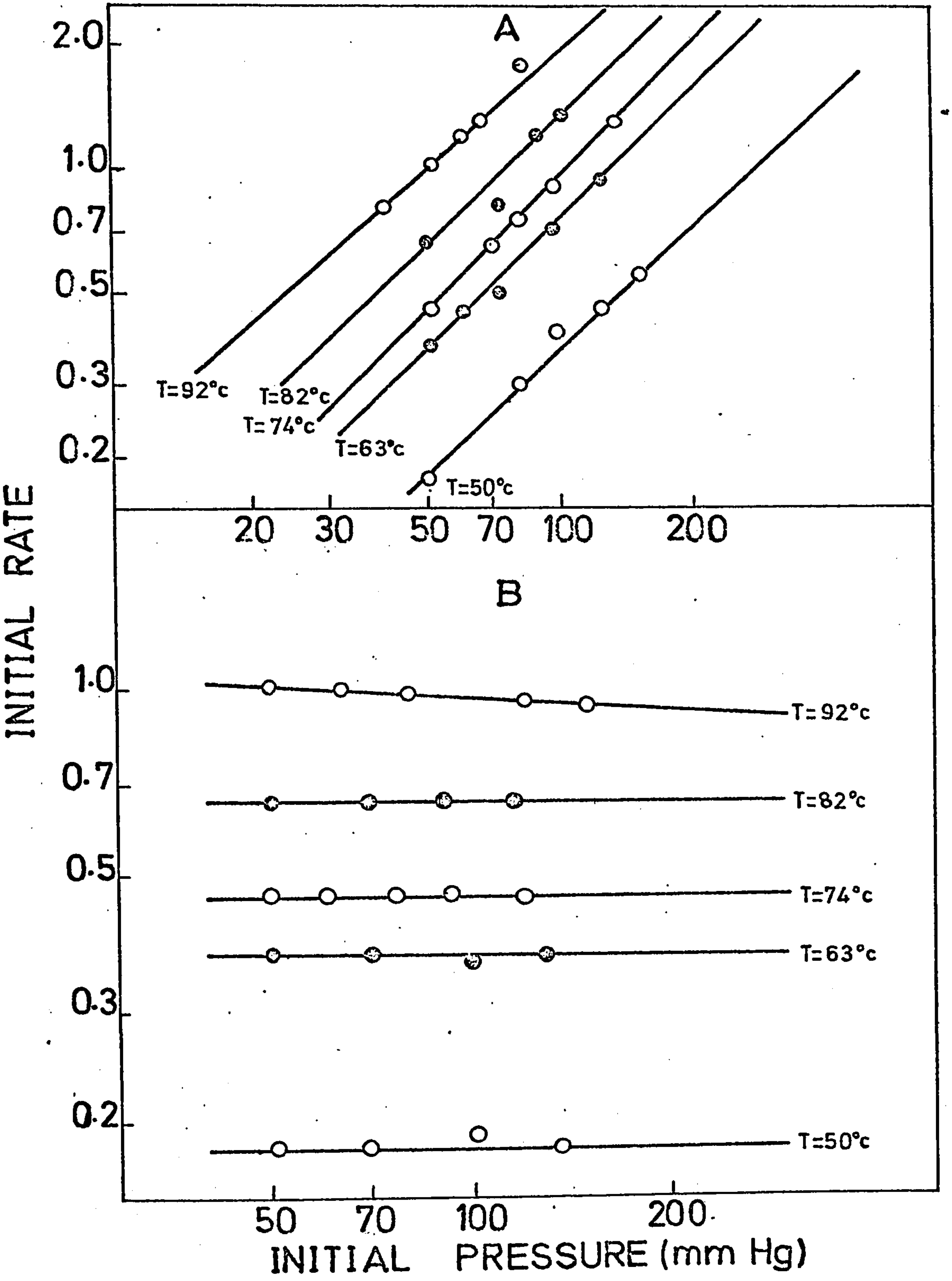


Figure 27 - Dependence order of reaction upon temperature
A - Hydrogen B - 2-butyne

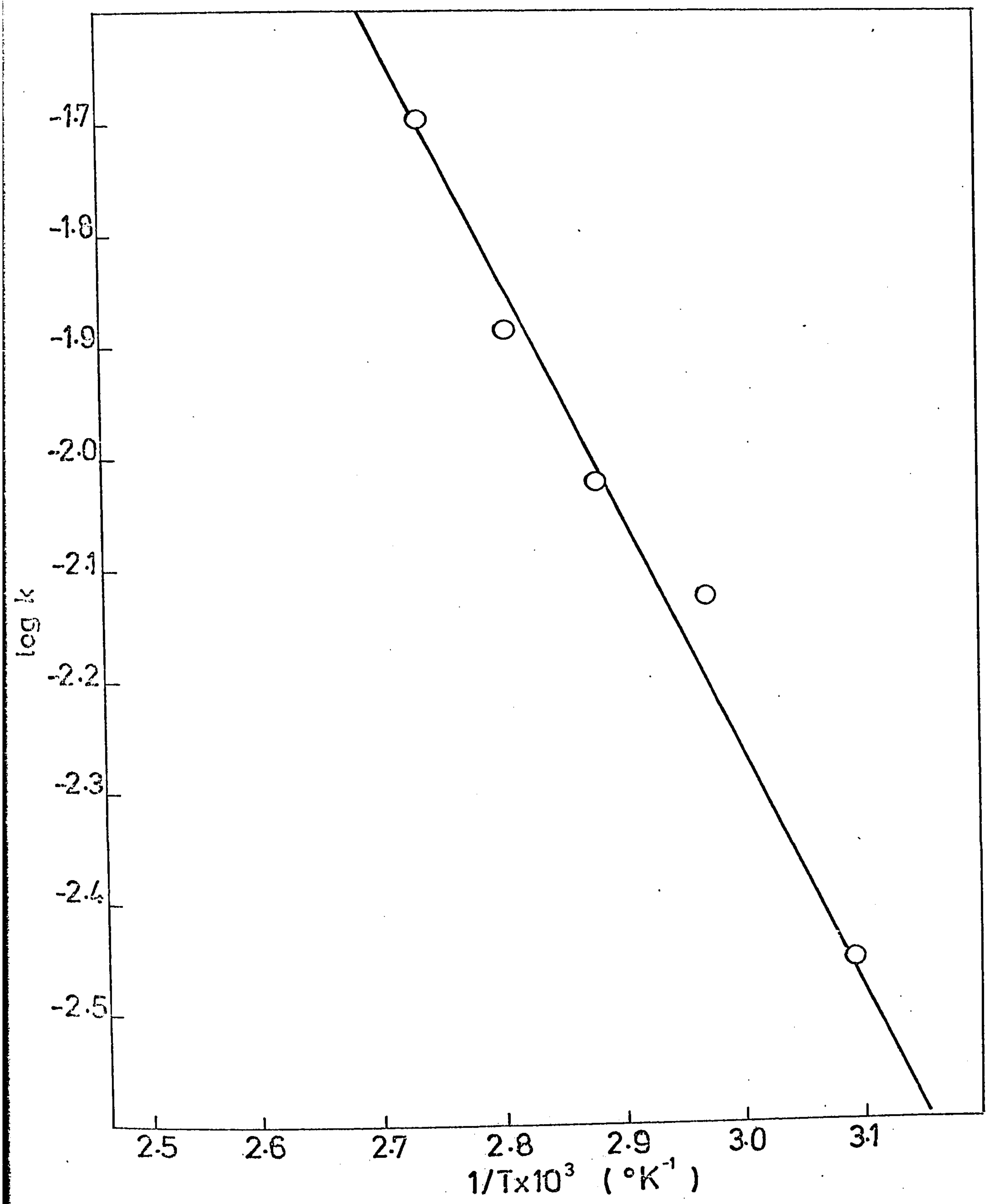


Figure 28 - Arrhenius plot

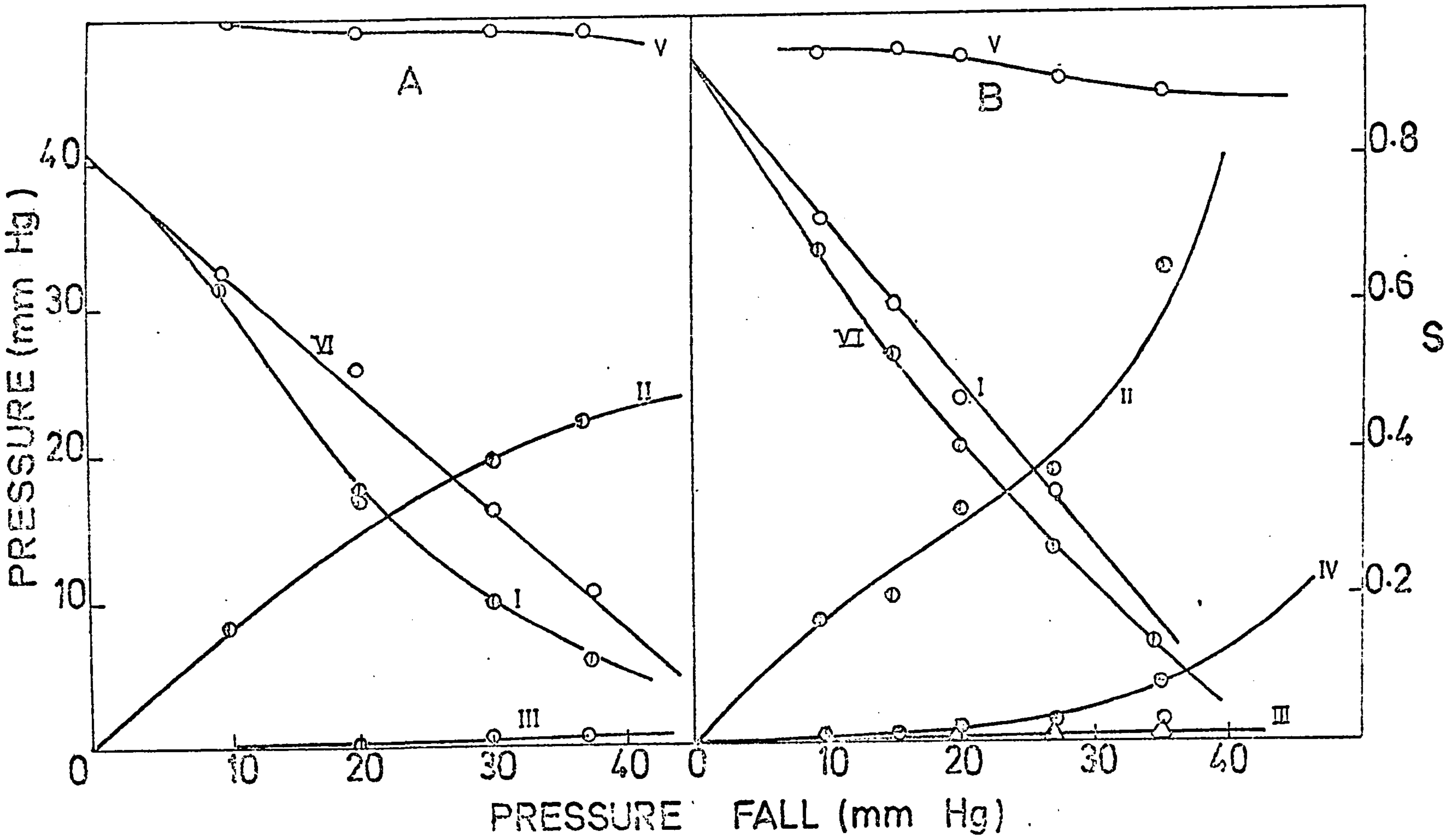


Figure 29 - A - 50% Ni 50% Cu B - 25% Ni 75% Cu
P_{H_2} = 50 ± 1 mm Hg $P_{C_4H_6}$ = 50 ± 2 mm Hg
I = C_4H_6 II = C-C_4H_8 III = t-C_4H_8 IV = 1-C_4H_8
V = Selectivity VI = Hydrogen

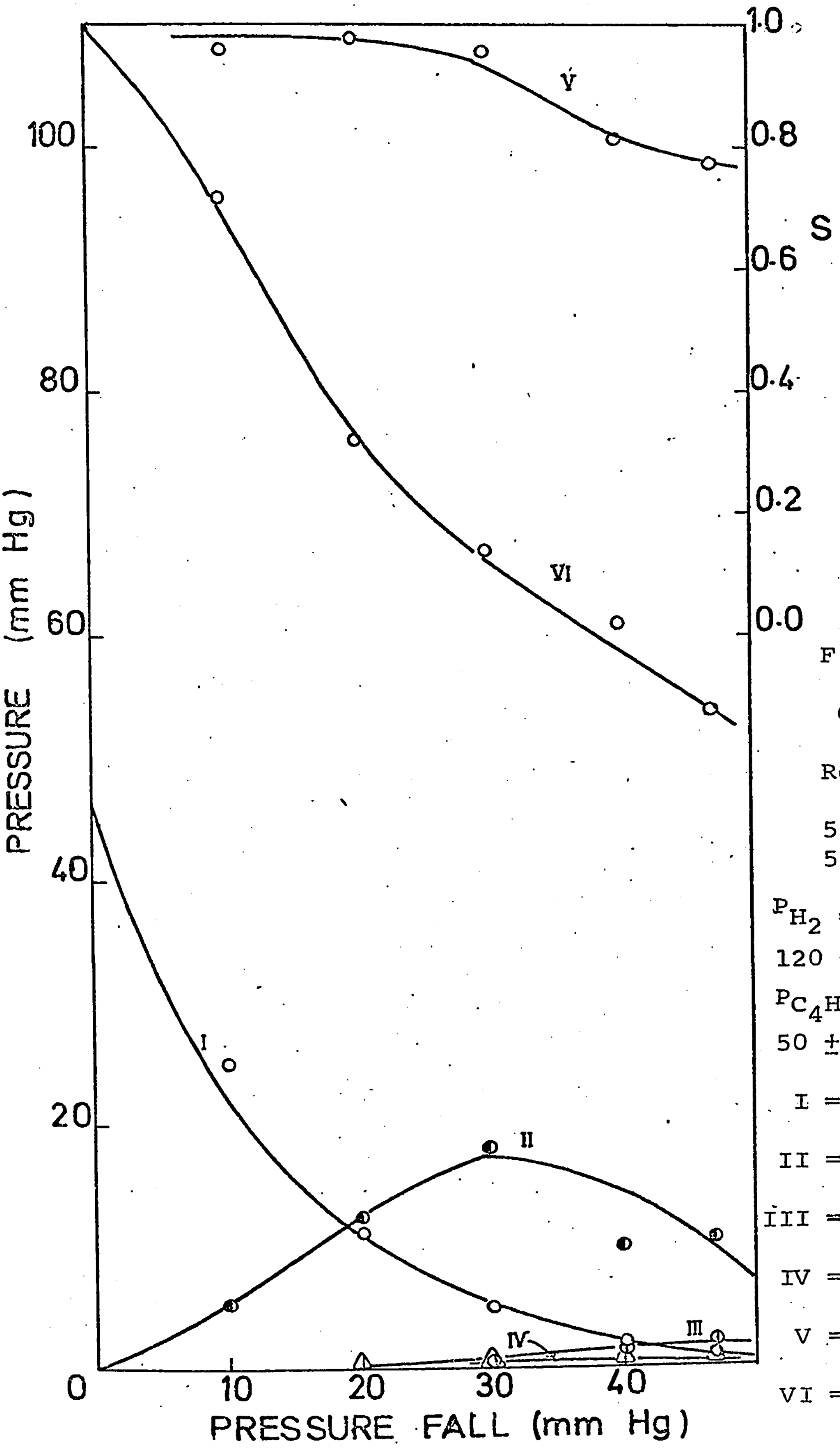


Figure 30

Course
of
Reaction

50% Ni
50% Cu

P_{H_2} =
120 ± 1 mm Hg
$P_{C_4H_6}$ =
50 ± 2 mm Hg

I = C_4H_6
II = $c\text{-}C_4H_8$
III = $t\text{-}C_4H_8$
IV = $1\text{-}C_4H_8$
V = S
VI = H_2

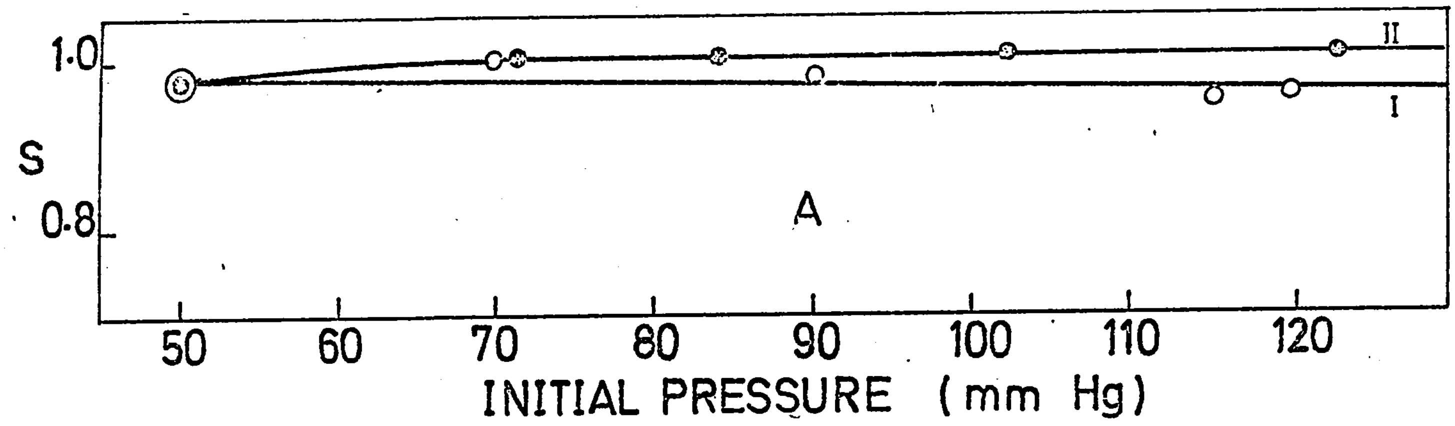


Figure 31A - Dependence of selectivity upon initial reactant pressure
I - With respect to 2-butyne $P_{H_2} = 50 \pm 1$ mm Hg
II - With respect to hydrogen $P_{C_4H_6} = 50 \pm 2$ mm Hg
Temperature = 130° C

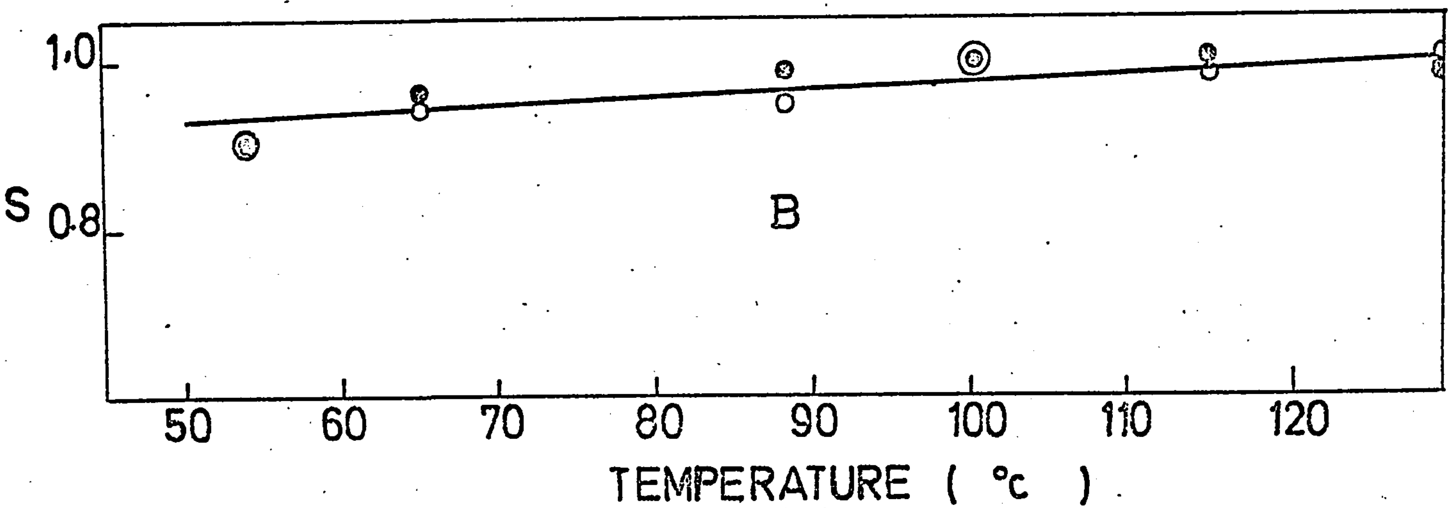


Figure 31B - Dependence of selectivity upon temperature
I - $P_{H_2} = 50 \pm 1$ mm Hg $P_{C_4H_6} = 50 \pm 2$ mm Hg
II - $P_{H_2} = 120 \pm 1$ mm Hg

initial rate on 2-butyne pressure in the temperature range of 50° C to 92° C. Though the order of reaction with respect to 2-butyne was zero at lower temperatures it became slightly negative at higher temperatures. The overall rate equation thus can be written as

$$r_o = k \, (P_{H_2})^1 \, (P_{C_4H_6})^{-0.02 \pm 0.02}$$

Plot of $\log_{10}$ of specific rate against the reciprocal of absolute temperature was a good straight line over a wide range of temperature satisfying Arrhenius equation (figure 28). The derived apparent activation energy and frequency factor were 9.212 k cal/gm mol and 9.38 x 10^4 min^{-1}/ gm respectively.

(b) <u>SELECTIVITY</u>

(i) The course of reaction:

Figure (29A) shows the distribution of products at various pressure falls during the course of the reaction for a hydrogen/2-butyne ratio of 1 (50 mm of each) at 130° C. Cis-2-butene was the main product but a small amount of trans-2-butene and 1-butene were also formed.

Figure (30) shows the distribution of the products during the course of the reaction for a hydrogen/2-butyne ratio of 2.4. Cis-2-butene was the major product. It attained a maximum value at 30 mm pressure drop and then it decreased. The decrease in the pressure of the cis-2-butene was greater than the formation of trans-2-butene, 1-butane, and n-butane, indicating that cis-2-butene was being polymerized at higher pressure falls.

(ii) Dependence of selectivity upon pressure fall:

Though the selectivity was independent of pressure falls for hydrogen/2-butyne ratio of 1 ($P_{H_2} = P_{C_4H_6} = 50$ mm), it was constant up to 30 mm pressure fall and then it decreased slightly for hydrogen/2-butyne ratio of 2.4 at 130° C.

(iii) Dependence of selectivity upon hydrogen pressure:

The dependence of selectivity upon initial hydrogen pressure was studied at 130° C by keeping initial 2-butyne pressure fixed at 50 mm and varying initial hydrogen pressures between 50 mm and 120 mm. The products were analyzed at 20 mm pressure fall. The selectivity was independent of hydrogen pressure (figure 31A, curve I).

(iv) Dependence of selectivity upon initial 2-butyne pressure:

The dependence of the selectivity upon initial 2-butyne pressure was studied at 130° C by keeping initial hydrogen pressure fixed at 50 mm and varying 2-butyne pressures between 50 mm and 130 mm and analyzing the products at 20 mm pressure drop. The selectivity first increased slightly and then became independent of 2-butyne pressures (figure 31A, curve II).

(v) Dependence of selectivity upon temperature:

The dependence of selectivity upon temperature was studied for hydrogen/2-butyne ratio of 1 ($P_{H_2} = P_{C_4H_6} = 50$ mm) and 2.4 between 54° C and 130° C and analyzing the products at 20 mm pressure drop. The selectivity increased slightly with increasing temperatures (figure 31B).

8. REACTION OVER 25% NICKEL AND 75% COPPER ALLOY POWDER:

(a) KINETICS

The experimental data obtained for the hydrogenation of 2-butyne over the alloy catalyst containing 75% copper and 25% nickel are given in Table (6). The shape of pressure time curve was similar to those obtained in the hydrogenation of 2-butyne over nickel powder (figure 25B).

The dependence of initial rates upon initial hydrogen pressures is shown in figure (26A). The order of reaction with respect to hydrogen was found to be one and independent of temperature (figure 32A). The order of reaction with respect to 2-butyne was zero at lower temperatures and became slightly negative at higher temperatures (figure 32B). The overall rate equation can be written as

$$r_o = k\,(P_{H_2})^{1}\,(P_{C_4H_6})^{-0.03 \pm 0.03}$$

Plot of $\log_{10}$ of specific rate against reciprocal of absolute temperature resulted in a good straight line over a wide range of temperature satisfying the Arrhenius equation (figure 33). The observed apparent activation energy and frequency factor were 8.95 k cal/gm mol and 4.242×10^{3} min^{-1}/gm respectively.

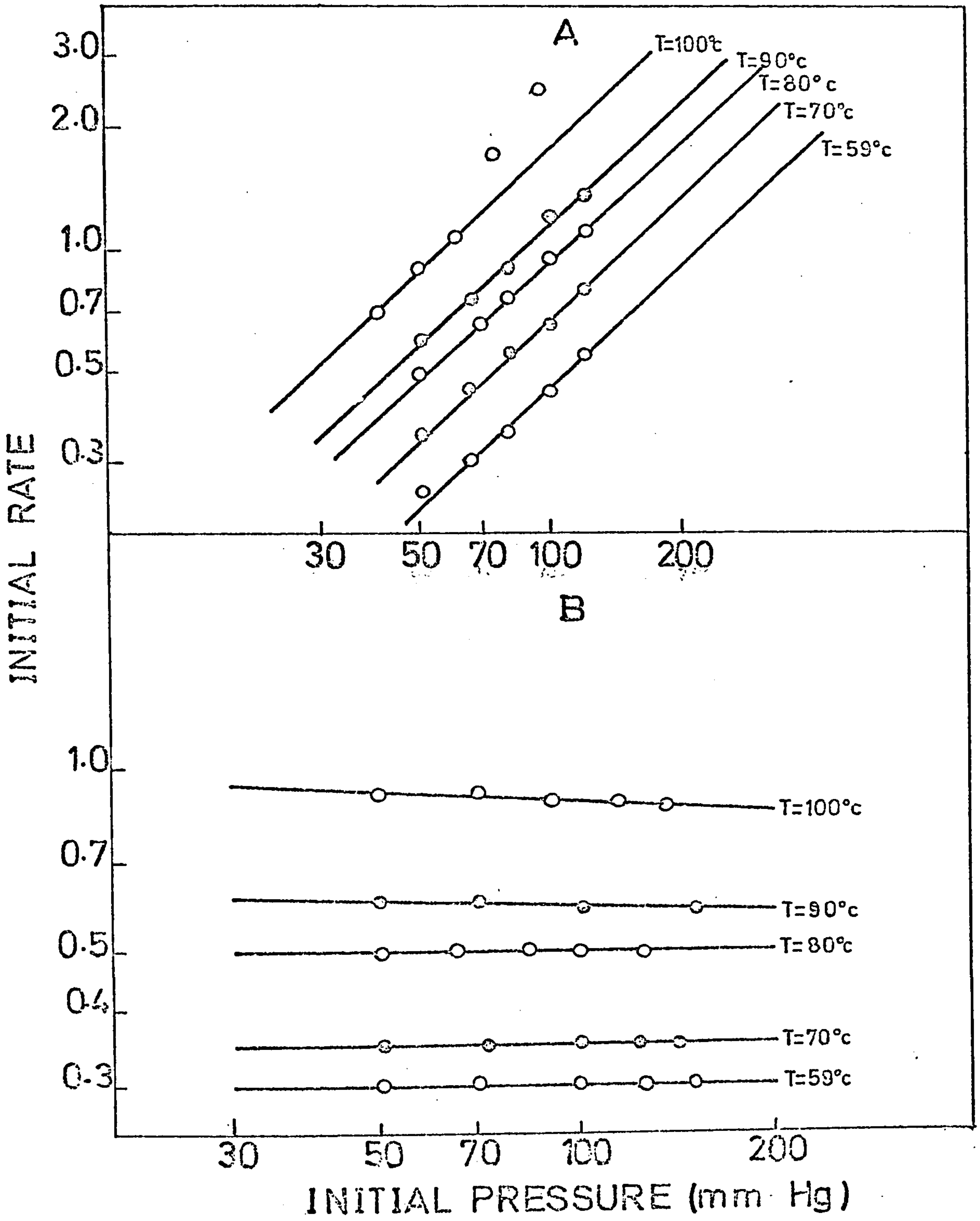


Figure 32 - Dependence order of reaction upon temperature

A - hydrogen B - 2-butyne

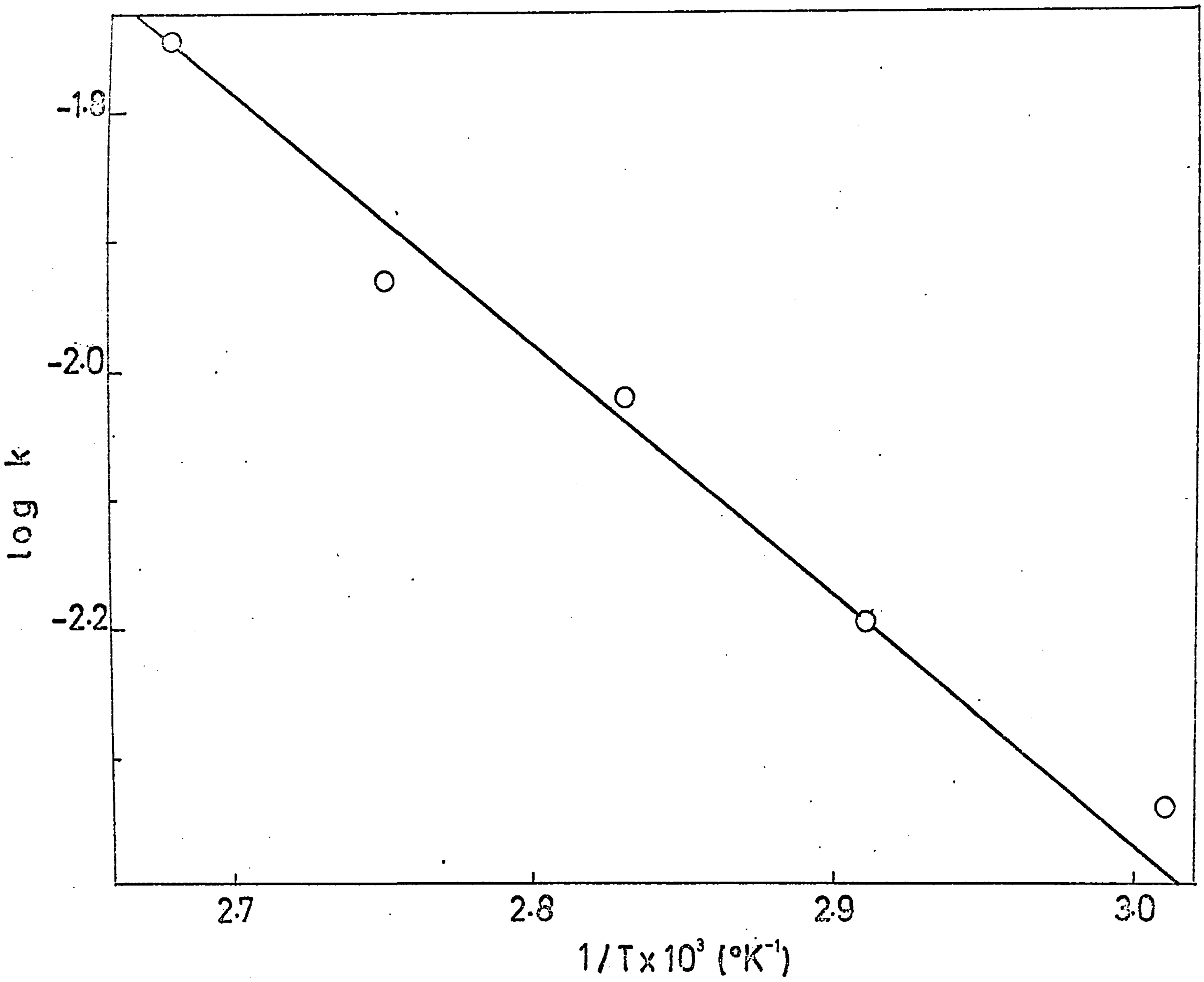


Figure 33 - Arrhenius plot, 25% Ni - 75% Cu

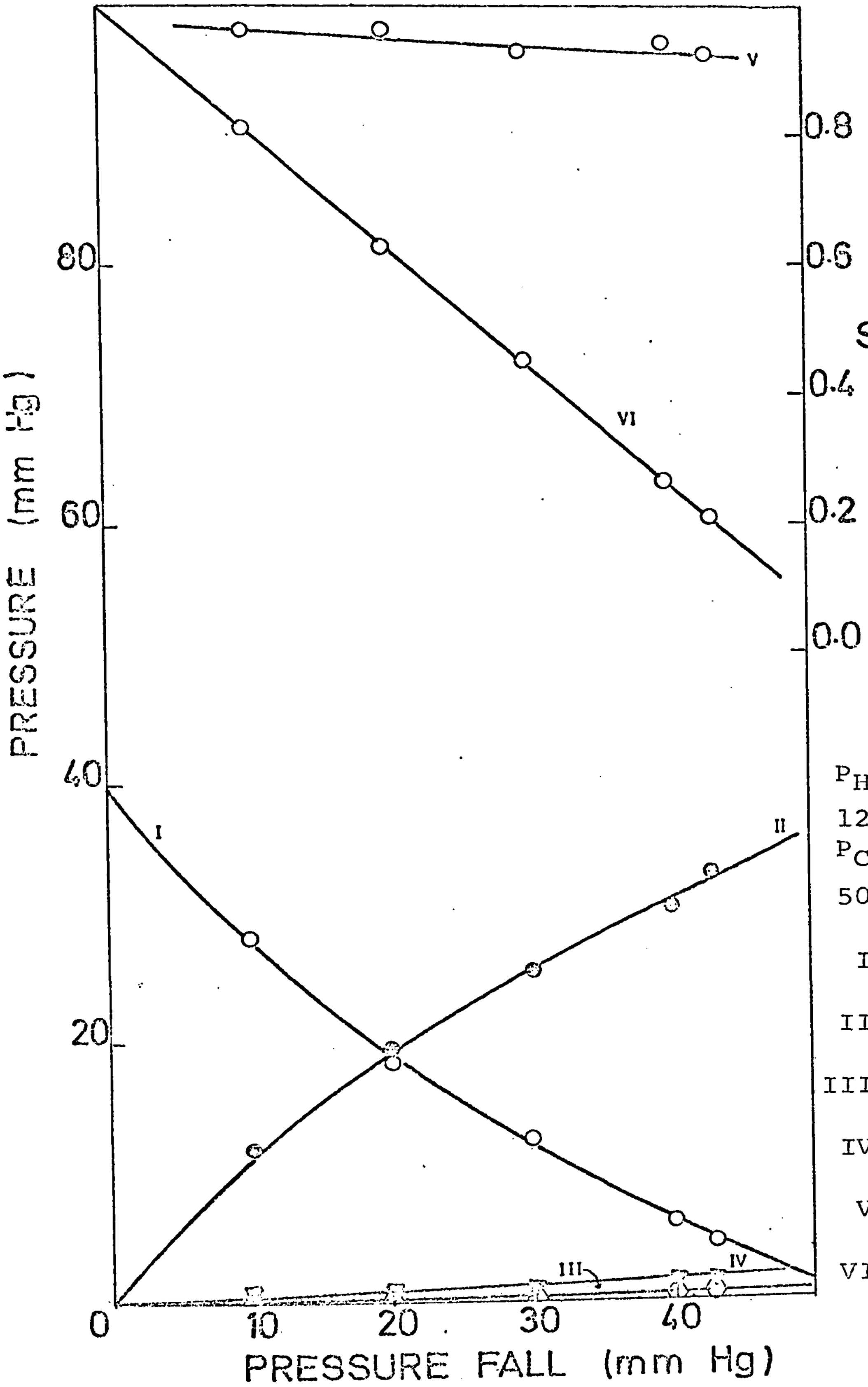


Figure 34

Course
of
Reaction

25% Ni
75% Cu

P_{H_2} =
120 ± 1 mm Hg
$P_{C_4H_6}$ =
50 ± 2 mm Hg

I = C_4H_6

II = $c\text{-}C_4H_8$

III = $t\text{-}C_4H_8$

IV = $1\text{-}C_4H_8$

V = S

VI = H_2

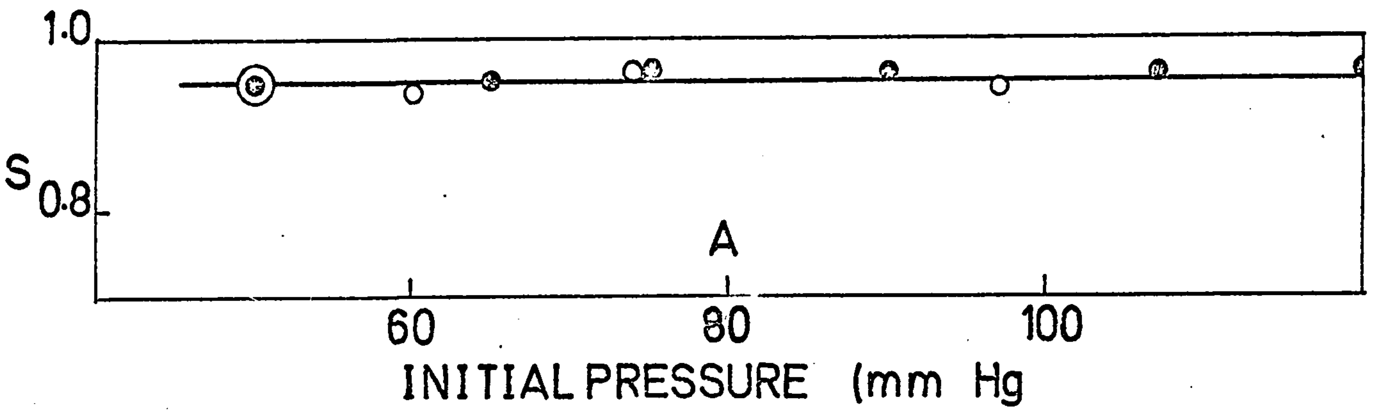


Figure 35A - Dependence of selectivity upon initial reactant pressure

I - With respect to 2-butyne $P_{H_2} = 50 \pm 1$ mm Hg

With respect to hydrogen $P_{C_4H_6} = 50 \pm 2$ mm Hg

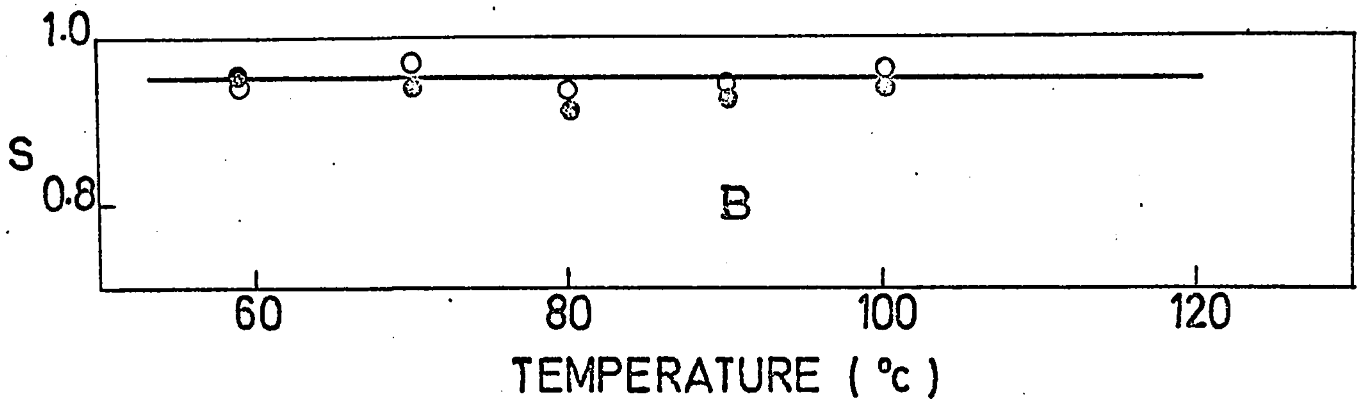


Figure 35B - Dependence of selectivity upon temperature

$P_{H_2} = 50 \pm 1$ mm Hg $P_{C_4H_6} = 50 \pm 2$ mm Hg

$P_{H_2} = 120 \pm 1$ mm Hg

(b) SELECTIVITY:

(i) The course of reaction

Figure (29B) shows the distribution of products at different pressure falls for hydrogen/2-butyne ratio of (50 mm of each) at 100° C. Though the main products was cis-2-butene small amounts of trans-2-butene and 1-butene were also formed. Figure (34) shows the distribution of products for hydrogen/2-butyne ratio of 2.4. In addition to the cis-2-butene, small amounts of trans-2-butene and 1-butene were also formed. The amount of 1-butene formed increased slightly with increased pressure fall.

(ii) Dependence of selectivity upon pressure fall

The dependence of selectivity upon pressure fall was studied at 100° C for hydrogen/2-butyne ratio of 1 (50 mm of each reactant) and 2.4 (P_{H_2} = 120 mm, $P_{C_4H_6}$ = 50 mm) by analyzing the products at different pressure falls. At both reactant ratios the selectivity was found to be independent of pressure fall.

(iii) Dependence of selectivity upon initial hydrogen pressure

The dependence of selectivity upon initial hydrogen pressure was studied at 100° C by keeping the initial 2-butyne pressure fixed (50 mm). The products were analyzed for a 20 mm pressure drop. The selectivity was found to be independent of initial hydrogen pressures (figure 35A).

(iv) Dependence of selectivity upon 2-butyne pressure

The dependence of selectivity upon initial 2-butyne pressure was studied at 100° C by maintaining the initial hydrogen at 50 mm and varying 2-butyne pressure between 50 mm and 100 mm by analyzing the products at 20 mm pressure drop. The selectivity was found to be independent of initial 2-butyne pressure (figure 35A).

(v) Dependence of selectivity upon temperature

The dependence of selectivity upon temperature was studied for hydrogen/2-butyne ratios of 1 and 2.4 for a wide range of temperatures by analyzing the products at a 20 mm pressure drop. In both the cases the selectivity was found to be temperature independent (figure 35B).

9. REACTION OVER COPPER POWDER:

The experimental data obtained for the hydrogenation of 2-butyne over copper powder are given in Table (7). After the catalyst was stabilized, the reaction had a measurable rate at 200° C. The pressure fall time curves were found to be similar to those observed in the hydrogenation of 2-butyne over nickel powder (figure 36)

Figure 37 shows the dependence of initial rates upon the initial hydrogen pressures between 200° C and 250° C. The order of reaction with respect to hydrogen was always one and independent of temperature (figure 38A). The order of reaction

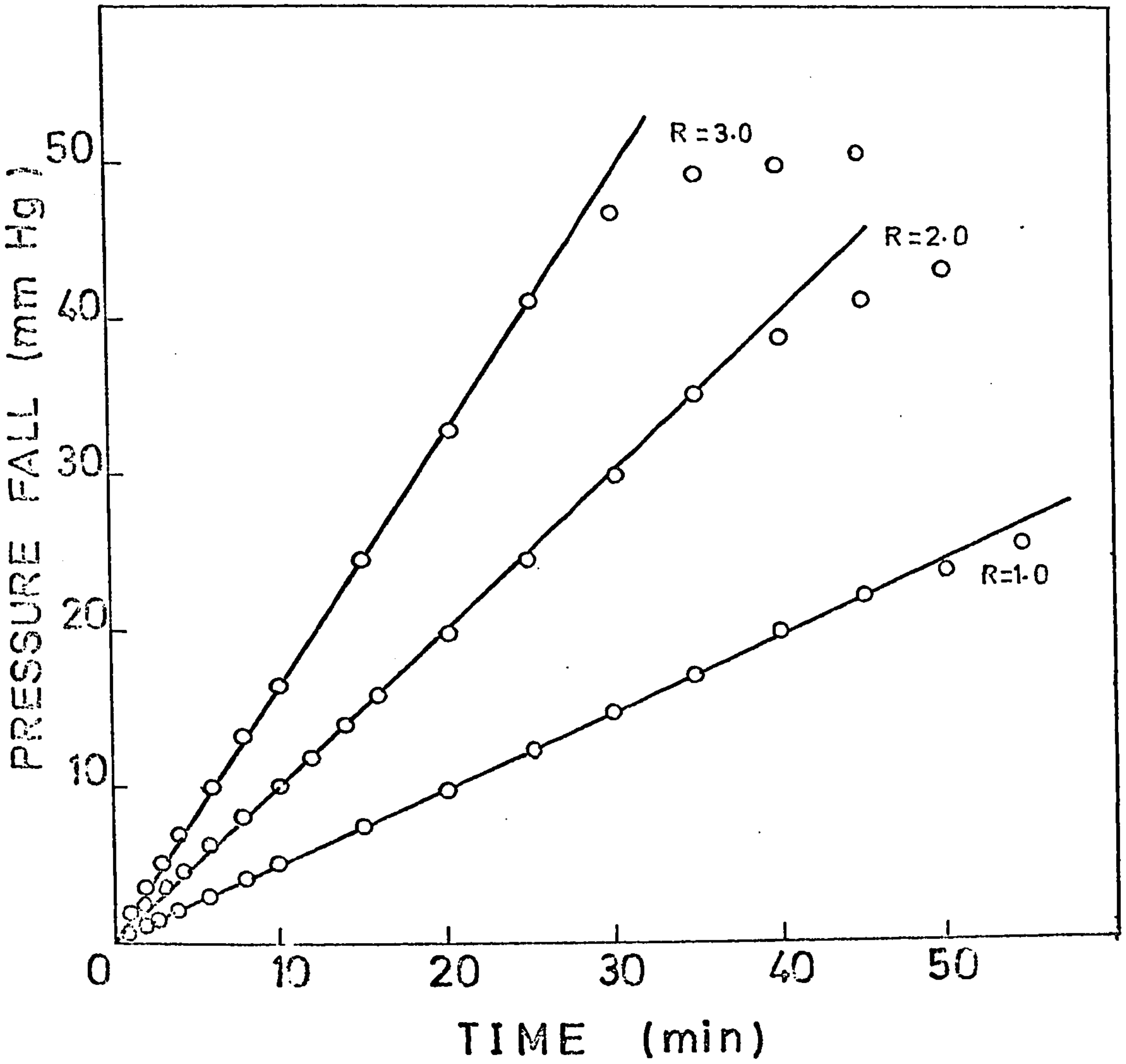


Figure 36 - Pressure-time curves

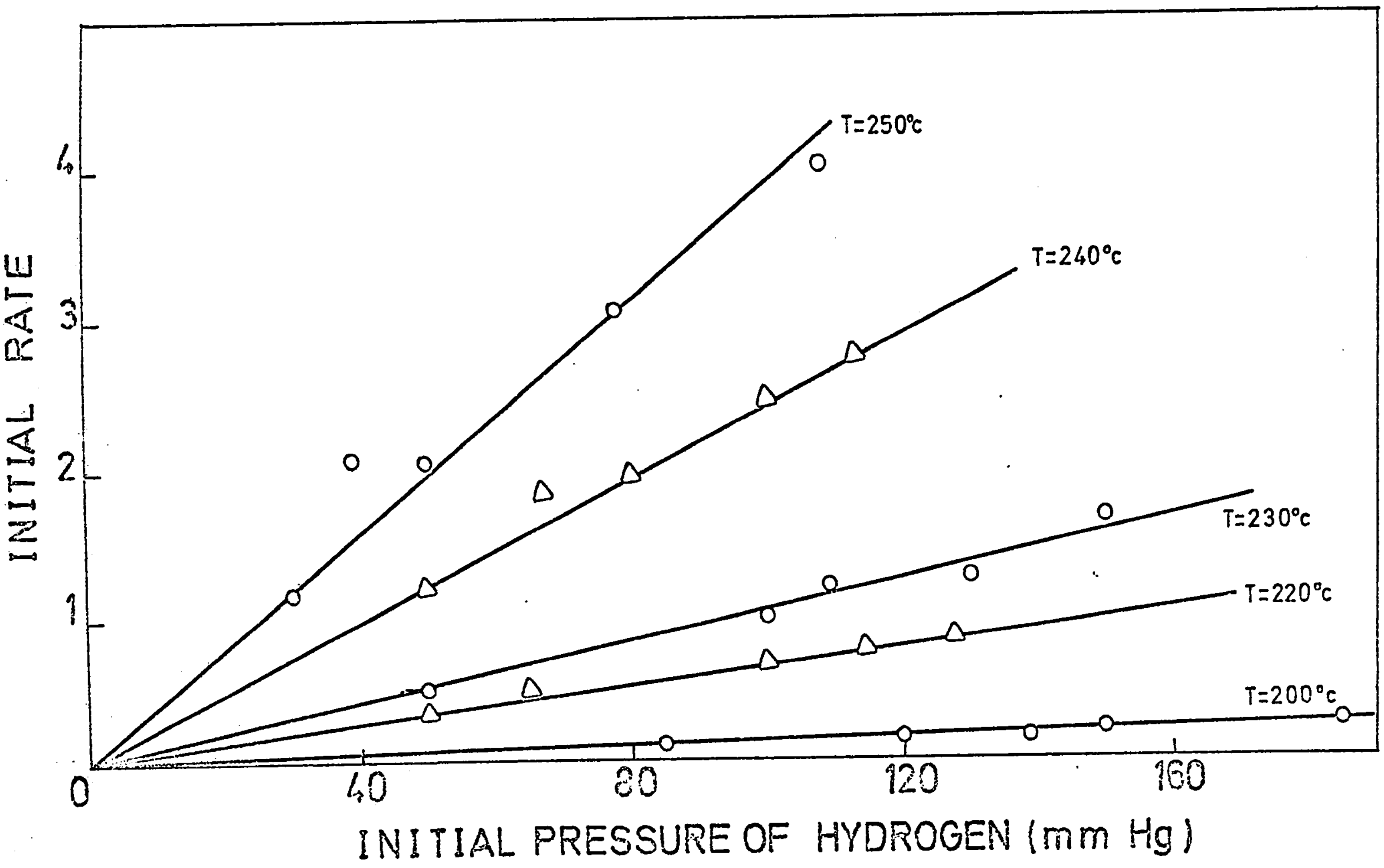
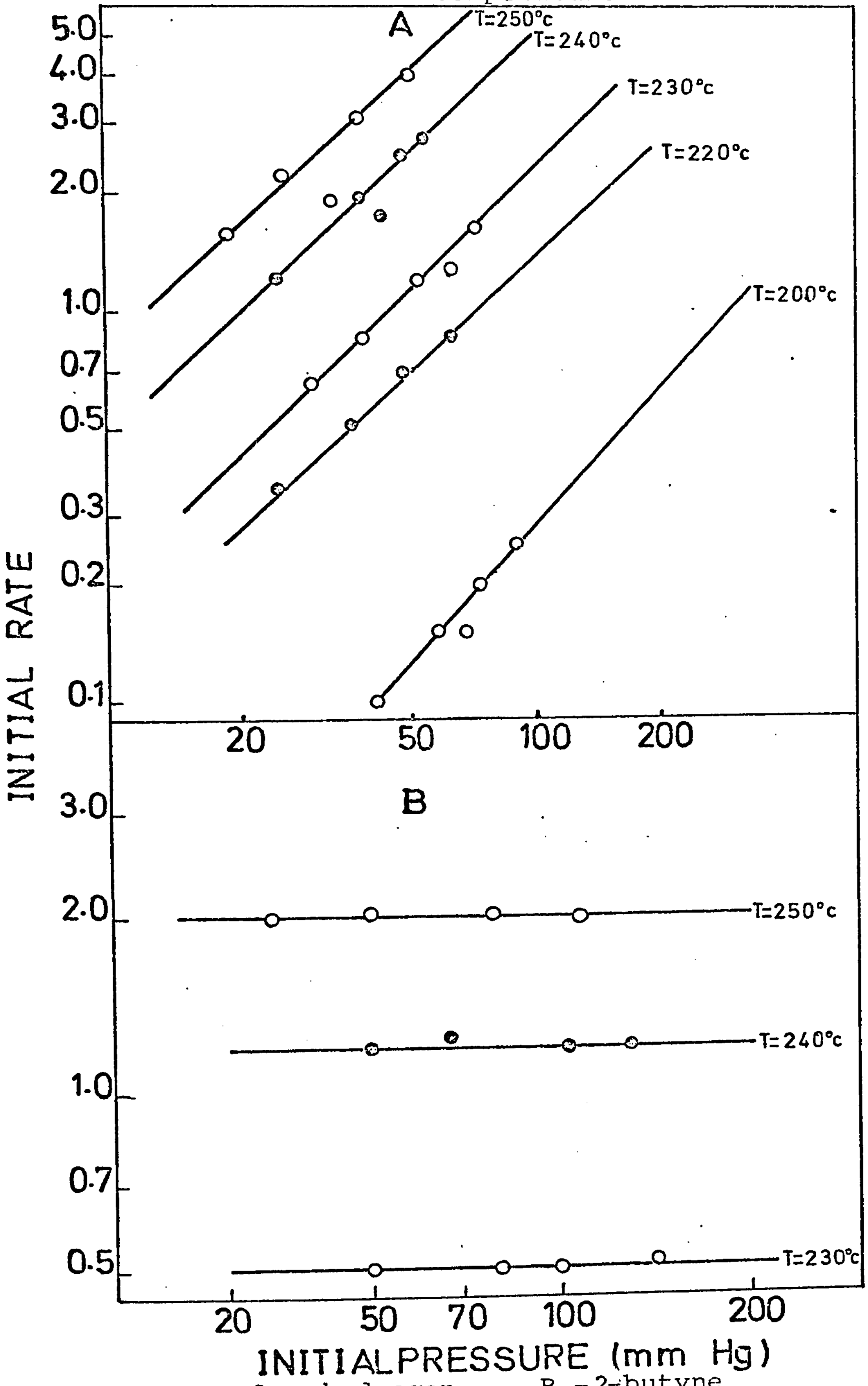


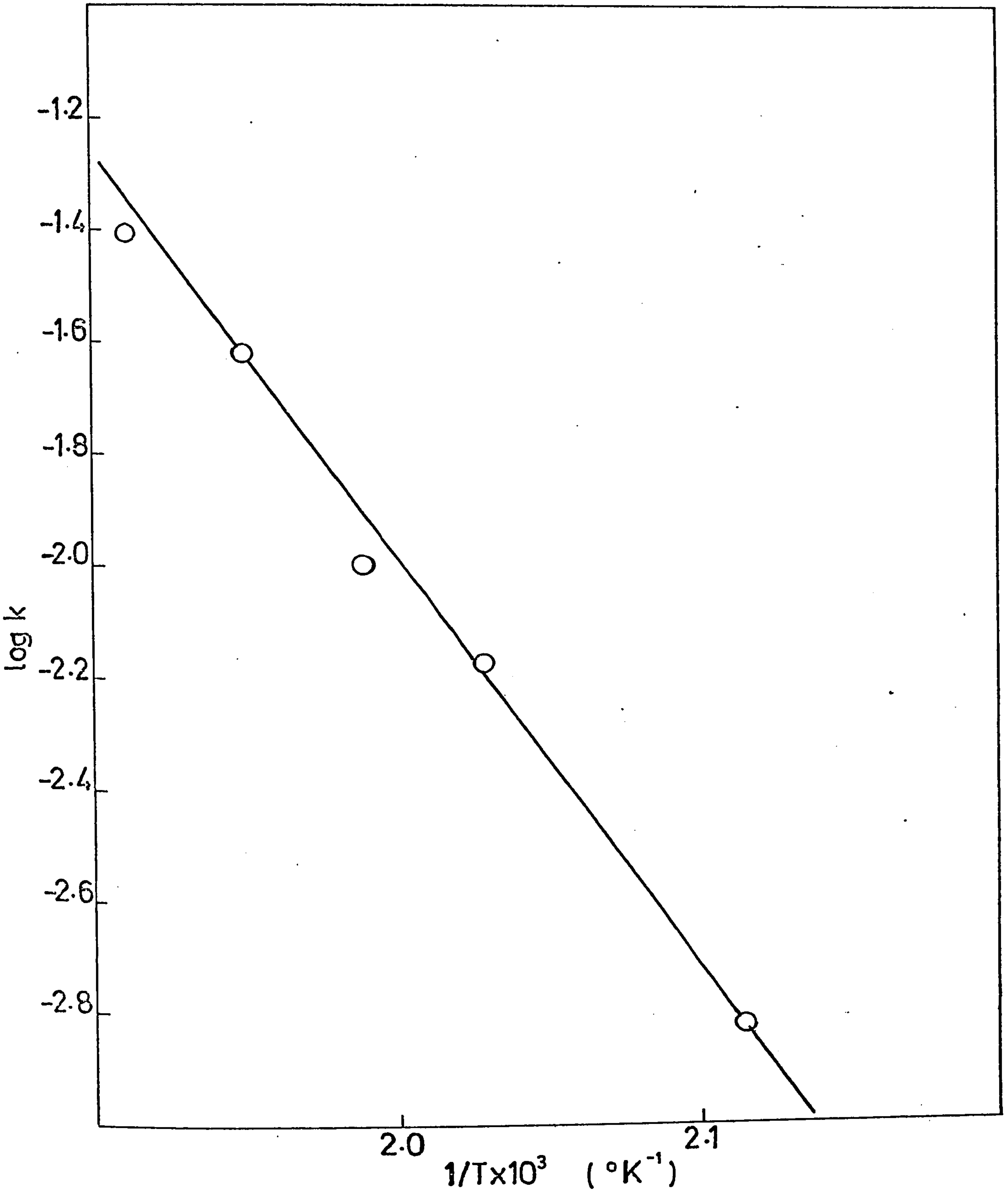
Figure 37 - Dependence of initial rate upon initial hydrogen pressure

Figure 38 - Dependence of order of reaction upon temperature



A - hydrogen B - 2-butyne

Figure 39 - Arrhenius plot, copper powder



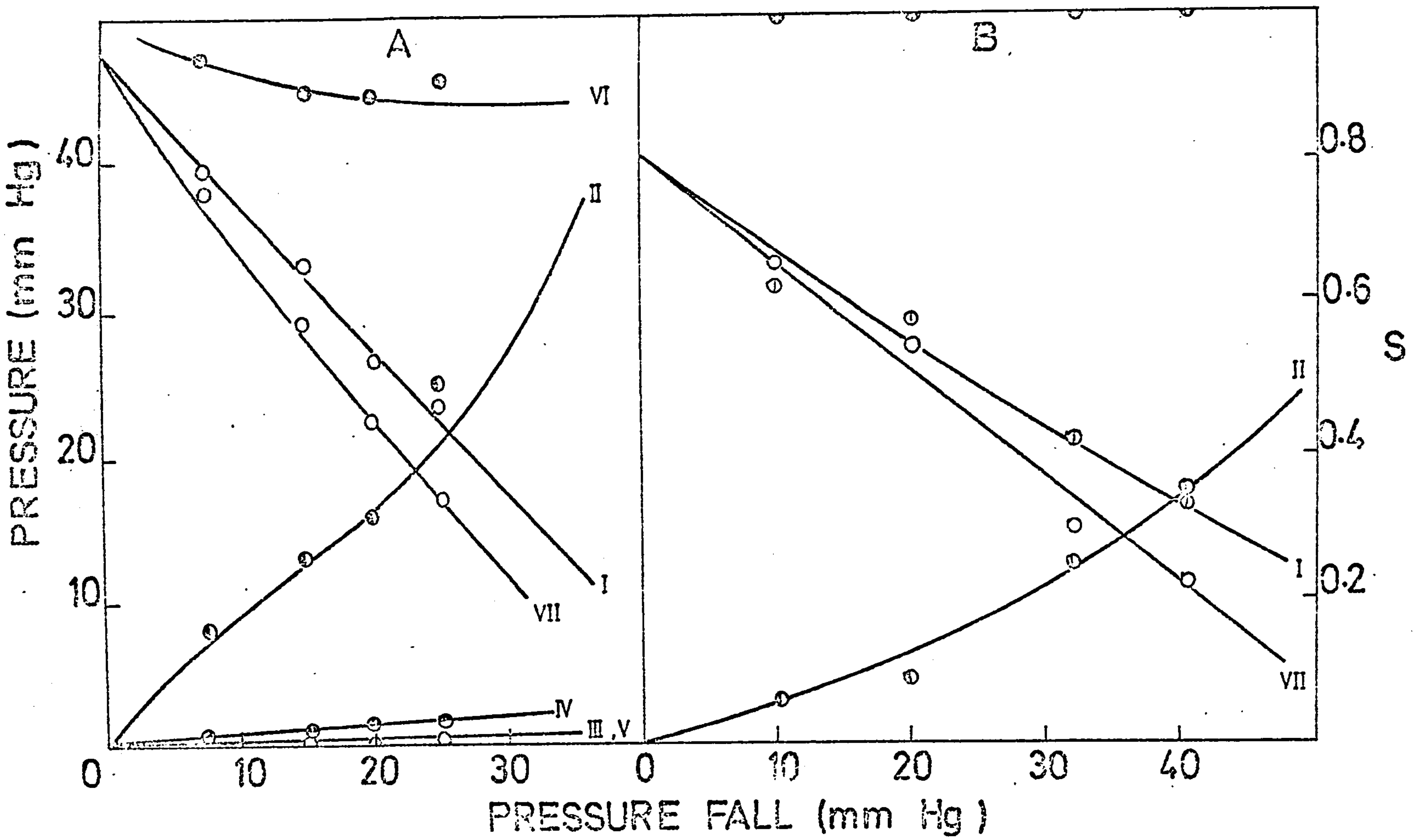


Figure 40 - A - cobalt powder B - copper powder
$P_{H_2} = 50 \pm 1$ mm Hg $P_{C_4H_6} = 50 \pm 2$ mm Hg
I = C_4H_6 II = C-C_4H_8 III = t-C_4H_8 IV = 1-C_4H_8 V = n-C_4H_{10}
VI = Selectivity VII = Hydrogen

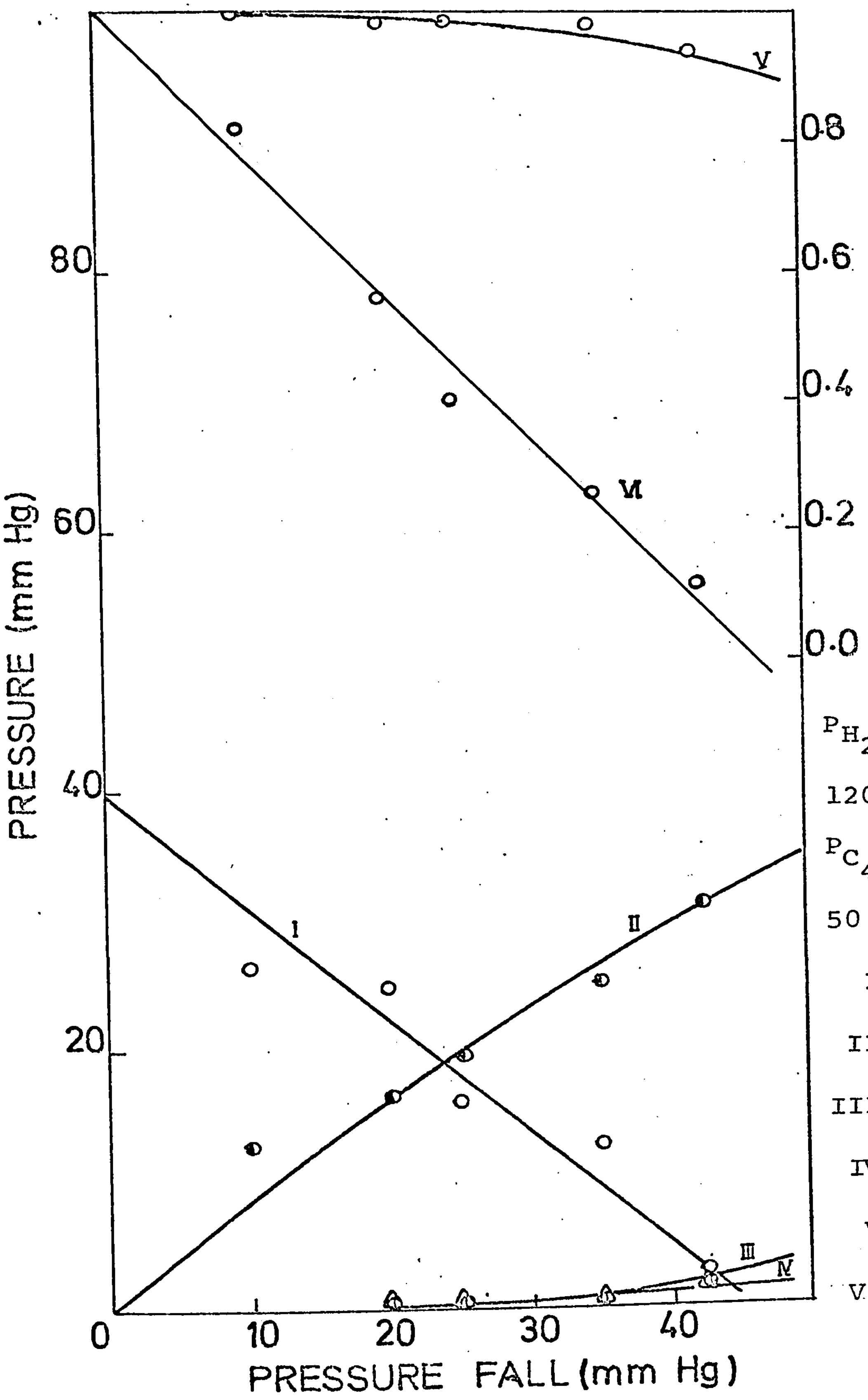


Figure 41

Course
of
Reaction

Copper powder

P_{H_2} =

120 ± 1 mm Hg

$P_{C_4H_6}$ =

50 ± 2 mm Hg

I = C_4H_6

II = $c\text{-}C_4H_8$

III = $t\text{-}C_4H_8$

IV = $1\text{-}C_4H_8$

V = S

VI = H_2

with respect to 2-butyne was always zero and temperature independent (figure 38B).

The overall rate equation can be represented as

$$r_o = k\ ({}^{P}H_2)^{1}\ ({}^{P}C_4H_6)^{0}$$

Plot of $\log_{10}$ of specific reaction rates against reciprocal of absolute temperature was a good straight line over the entire temperature range (figure 39) satisfying the Arrhenius equation. The derived activation energy and the frequency factor were 33.5 k cal/gm mol and 4.515 x 10^{12} min^{-1}/gm respectively.

(b) SELECTIVITY

(i) The course of the reaction:

Figure (40B) shows the distribution of products for hydrogen/2-butyne ratio of 1 (${}^{P}H_2$ = ${}^{P}C_4H_6$ = 50 mm) at 240° C. Only cis-2-butene was obtained in the product. Figure (41) shows the distribution of the products at various pressure falls for hydrogen/2-butyne ratio of 2.4.(${}^{P}H_2$ = 120 mm, ${}^{P}C_4H_6$ = 50 mm). In the initial stages the only product was cis-2-butene but at higher conversion (pressure drop) small amounts of trans-2-butene and 1-butene were also formed.

(ii) The dependence of selectivity upon pressure fall

The dependence of selectivity upon pressure fall was studied at 240° C by analyzing the products at various pressure falls for hydrogen/2-butyne ratios of 1 (50 mm of each reactant) and 2.4 (P_{H_2} = 120 mm, $P_{C_4H_6}$ = 50 mm). The selectivity was independent of pressure fall in both cases.

(iii) Dependence of selectivity upon initial hydrogen pressure

The dependence of selectivity upon hydrogen pressure was studied at 240° C keeping 2-butyne pressure fixed at 50 mm and varying hydrogen pressures. The products were analyzed for a pressure fall of 20 mm. The selectivity was one and independent of initial hydrogen pressure.

(iv) Dependence of selectivity upon initial 2-butyne pressure

The dependence of selectivity upon initial 2-butyne pressure was studied at 240° C keeping hydrogen pressure fixed at 50 mm and varying 2-butyne pressure over a wide range and analyzing the products for 20 mm pressure fall. The selectivity was one and independent of initial 2-butyne pressures.

(v) Dependence of selectivity upon temperature

The dependence of selectivity upon temperature was studied for hydrogen/2-butyne ratios of 1 (P_{H_2} = $P_{C_4H_6}$ = 50 mm) and 2.4 (P_{H_2} = 120 mm, $P_{C_4H_6}$ = 50 mm) between 200° C to 250° C. Selectivity was one and independent of temperature.

10. REACTION OVER COBALT POWDER:

(a) KINETICS

The experimental data for the hydrogenation of 2-butyne over cobalt powder (0.75 gm as oxide) are given in Table (8).

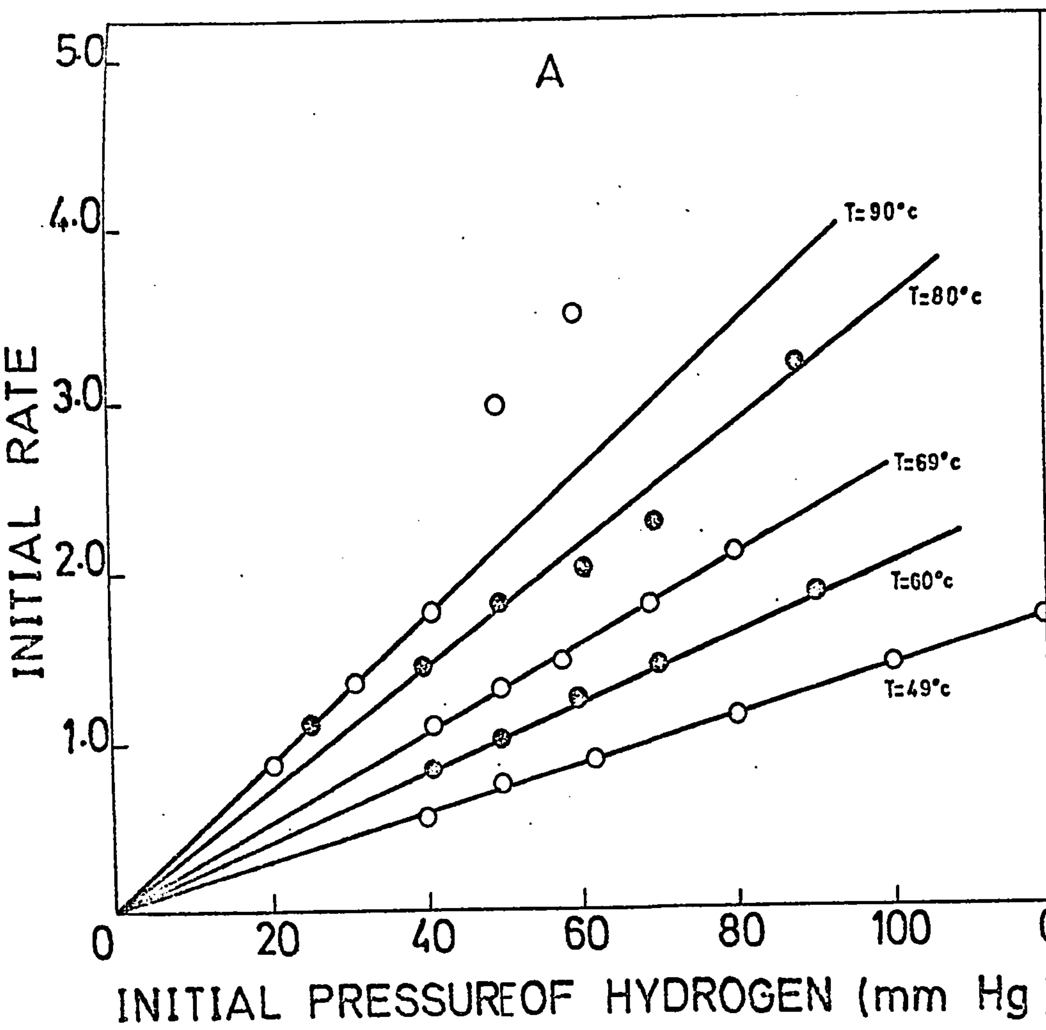


Figure 42A - Dependence of initial rate upon initial hydrogen pressure

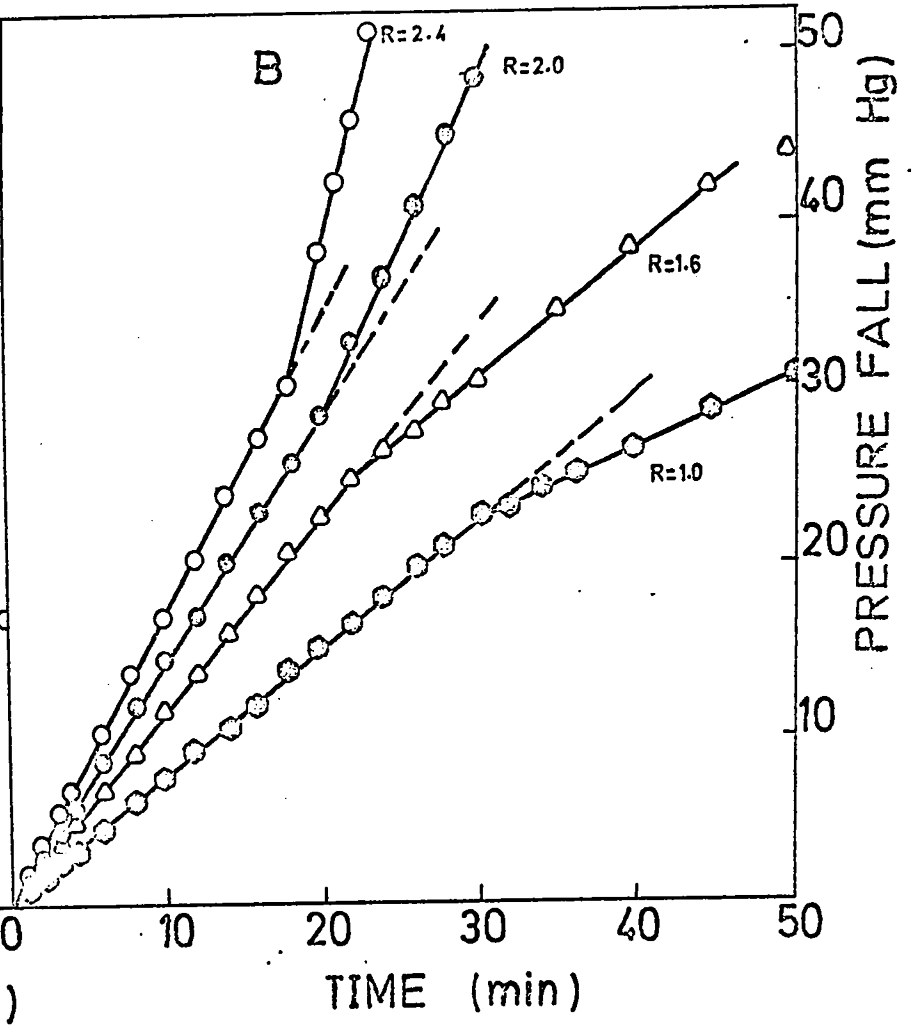


Figure 42B - Pressure-time curves

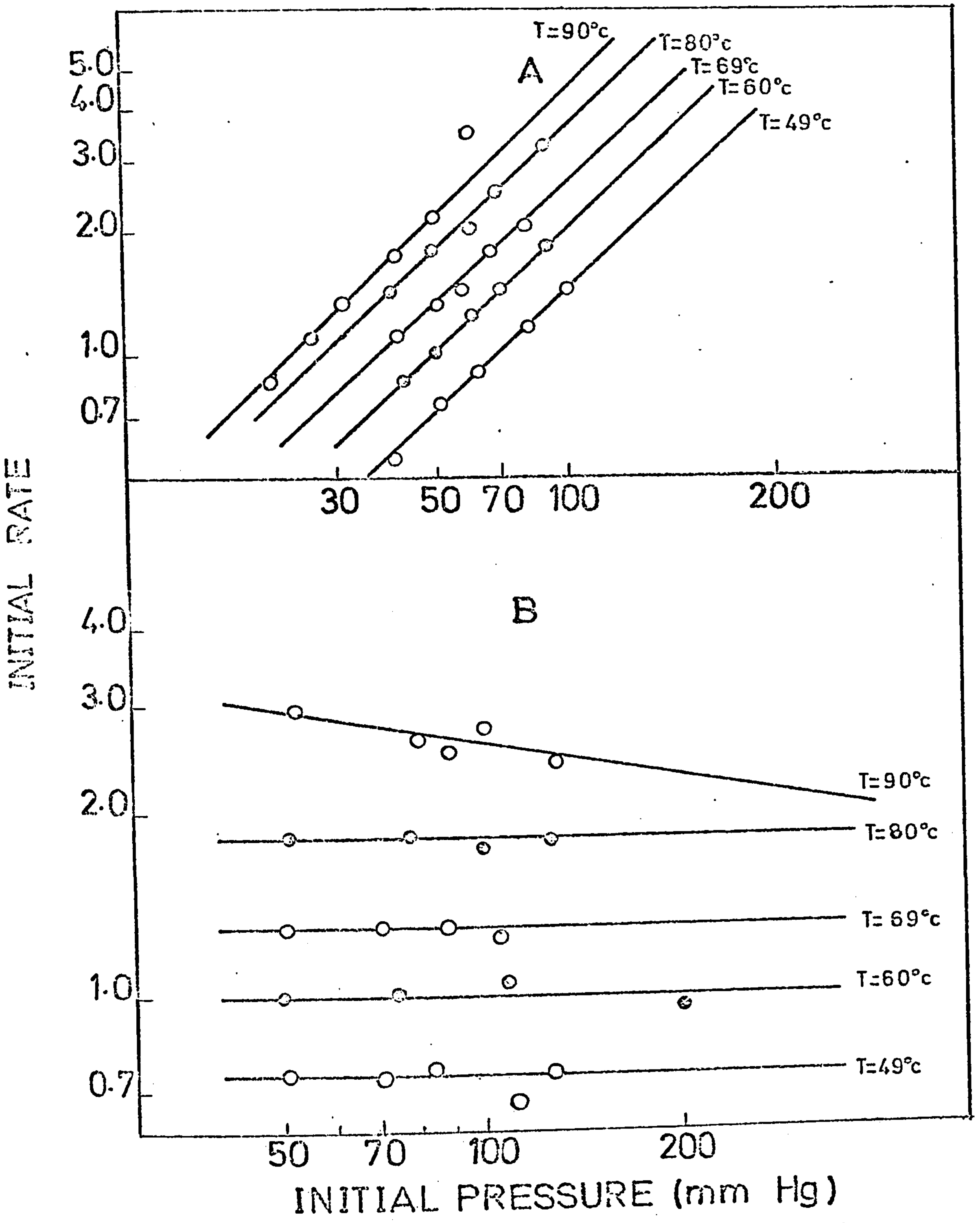


Figure 43 - Dependence of order of reaction upon temperature

A - Hydrogen B - 2-butyne

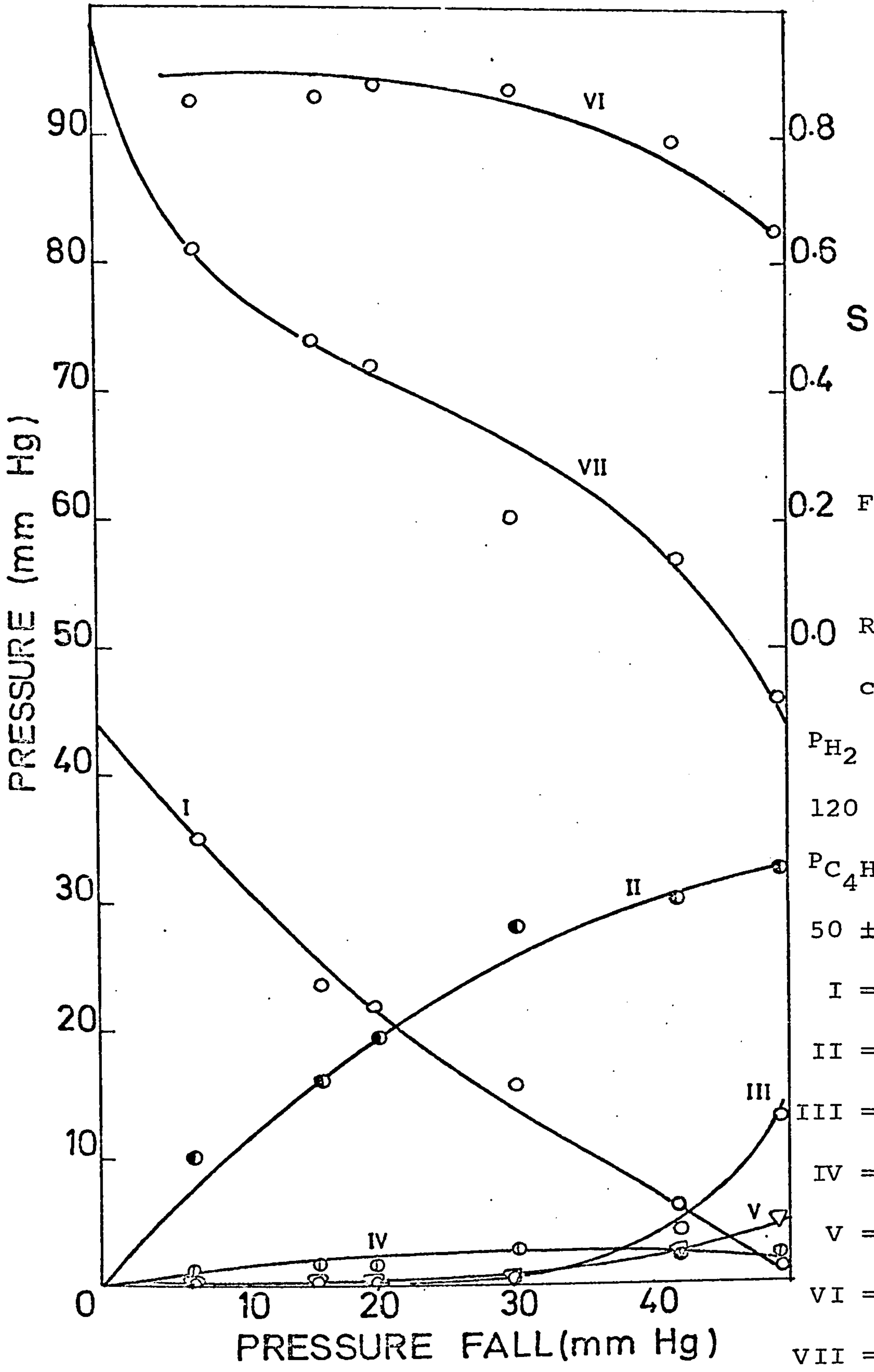


Figure 44

Course
of
Reaction

cobalt powder

P_{H_2} =

120 ± 1 mm Hg

$P_{C_4H_6}$ =

50 ± 2 mm Hg

I = C_4H_6

II = $c\text{-}C_4H_8$

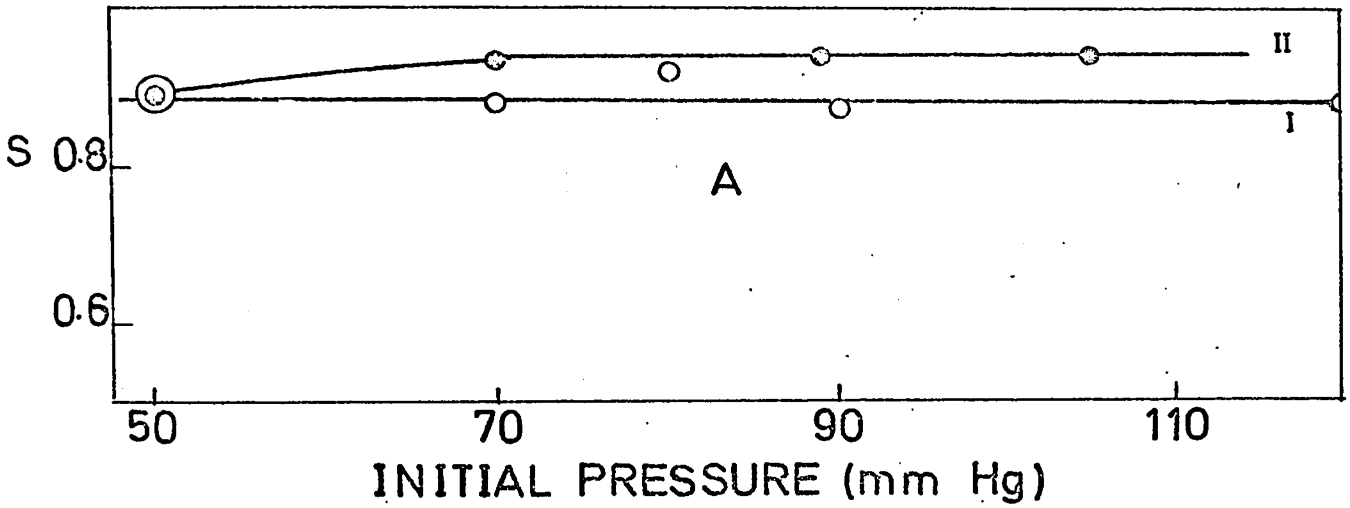
III = $t\text{-}C_4H_8$

IV = $1\text{-}C_4H_8$

V = $n\text{-}C_4H_{10}$

VI = S

VII = H_2



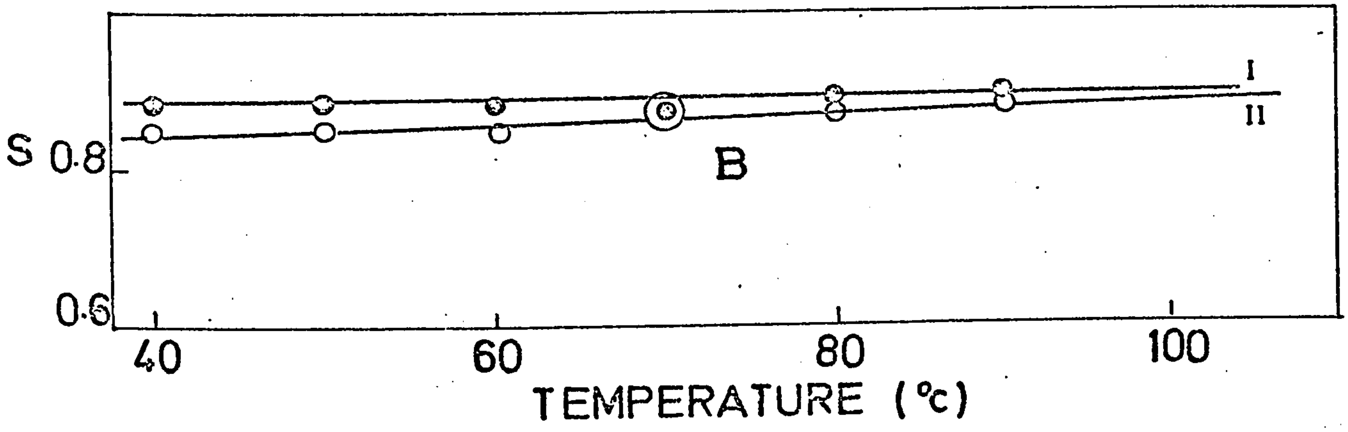


Figure 45A - Dependence of selectivity upon initial reactant pressure

I - With respect to 2-butyne $P_{H_2} = 50 \pm 1$ mmHg

II - With respect to hydrogen $P_{C_4H_6} = 50 \pm 2$ mmHg

Figure 45B - Dependence of selectivity upon temperature

I - $P_{H_2} = 50 \pm 1$ mm Hg $P_{C_4H_6} = 50 \pm 2$ mm Hg

II - $P_{H_2} = 120 \pm 1$ mm Hg

The reaction had a measurable rate at 40° C over the stabilized catalyst. The observed pressure fall-time curves at 49° C were similar to those obtained in the hydrogenation of 2-butyne over the catalyst containing 90% nickel and 10% copper (figure 42B).

Figure (42A) shows the dependence of initial rates upon initial hydrogen pressure. Figure (43A) shows that the order of reaction with respect to hydrogen was always one and temperature independent. Figure (43B) shows the dependence of initial rate upon the initial pressure of 2-butyne. The order of reaction with respect to 2-butyne was zero and became slightly negative with increasing temperatures. The overall rate equation can be represented as

$$r_o = k\,(P_{H_2})^1\,(P_{C_4H_6})^{-0.08 \pm 0.08}$$

Plot of $\log_{10}$ of specific rate constant against reciprocal of the absolute temperature was a good straight line satisfying Arrhenius equation (figure 6B). The derived apparent activation energy and frequency factor were 6.5 k cal/mol and 6.608 $\times 10^3$ min^{-1}/gm respectively.

(b) SELECTIVITY:

(i) The course of the reaction

Figure (40A) shows the distribution of the products with pressure fall for hydrogen/2-butyne ratio of 1 (50 mm of each) at 90° C. In addition to cis-2-butene, small amounts of trans-2-butene, 1-butene and n-butane were also formed in the initial stages of the reaction. The amount of 1-butene in the product was greater than either n-butane or trans-2-butene. Figure (44) shows the distribution of the products with pressure fall for a hydrogen/2-butyne ratio of 2.4 (P_{H_2} = 120 mm, $P_{C_4H_6}$ = 50 mm. Cis-2-butene was the major product of the reaction. In addition to cis-2-butene, small amounts of trans-2-butene, 1-butene and n-butane were also formed.

(ii) Dependence of selectivity upon pressure fall

The dependence of selectivity upon pressure fall was studied at 90° C by analyzing the products at different pressure falls for hydrogen/2-butyne ratios of 1 and 2.4. While for hydrogen/2-butyne ratio of 1 the selectivity decreased slightly with pressure fall, for hydrogen/2-butyne ratio of 2.4, it was constant till a pressure fall of 30 mm and thereafter decreased.

(iii) Dependence of selectivity upon initial hydrogen pressure

The dependence of selectivity upon initial hydrogen pressure was studied at 90° C keeping 2-butyne pressure constant at 50 mm and varying initial hydrogen pressures and analyzing the products at 20 mm pressure drop. Selectivity was independent of hydrogen pressure (figure 45A, curve I).

(iv) Dependence of selectivity upon initial 2-butyne pressure

The dependence of selectivity upon initial 2-butyne pressure was studied at 90° C by using a fixed hydrogen pressure and a wide range of 2-butyne pressures. The products were analyzed at a pressure fall of 20 mm. The selectivity initially increased slightly with pressure fall and then became constant (figure 45A, curve II).

(iv) Dependence of selectivity upon temperature

The dependence of selectivity upon temperature was studied for hydrogen/2-butyne ratio of 1 (50 mm of each reactant) and 2.4 (P_{H_2} = 120 mm, $P_{C_4H_6}$ = 50 mm) and analyzing the products at 20 mm pressure drop. Selectivity was independent of temperature (figure 45B).

11. REACTION OVER IRON POWDER:

About 0.2 gm of iron oxide was reduced in the reactor. It was observed that the iron catalyst lost its activity in successive reactions. The continuous deactivation of the catalyst made the study of the reaction almost impossible. The catalyst regained 90% of its activity by being left over night in about 200 mms of hydrogen.

Bond and Wells (60) observed that the mercury vapors present in the system deactivated the palladium catalyst in the hydrogenation of acetylene and ethylene. Also Mann and Khulbe (26) in the study of 1-butyne hydrogenation over iron powder observed that the reaction started at 130° C. However, they could not make any kinetic study due to the deactivation of the catalyst.

In order to observe the effect of temperature on poisoning, a series of runs were carried out. It was observed that the curves obtained on plotting $\log_{10} \frac{(r_o)_{m+n}}{(r_o)_{m+1}}$ against the $\log_{10}$ of number of runs were parallel but the rate of deactivation decreased with increasing temperature (figure 46), where m is the number of runs taken before the particular set started and n is the number of runs taken in that set.

12. REACTION OVER PUMICE SUPPORTED IRON:

The hydrogenation of 2-butyne was studied on 0.5 gm of pumice supported iron catalyst (5% Fe). Though at room temperature the catalyst was very active, it deactivated rapidly from run to run. In general behaviour, it was similar to unsupported iron.

On plotting $\log_{10} \frac{(r_o)_{m+n}}{(r_o)_{m+1}}$ against $\log_{10}$ of run number, it was observed that the rate of deactivation decreased with increasing hydrogen/2-butyne ratios (figure 47A). Also the rate of deactivation decreased with increasing temperatures for hydrogen/2-butyne ratio of 1 (figure 47B).

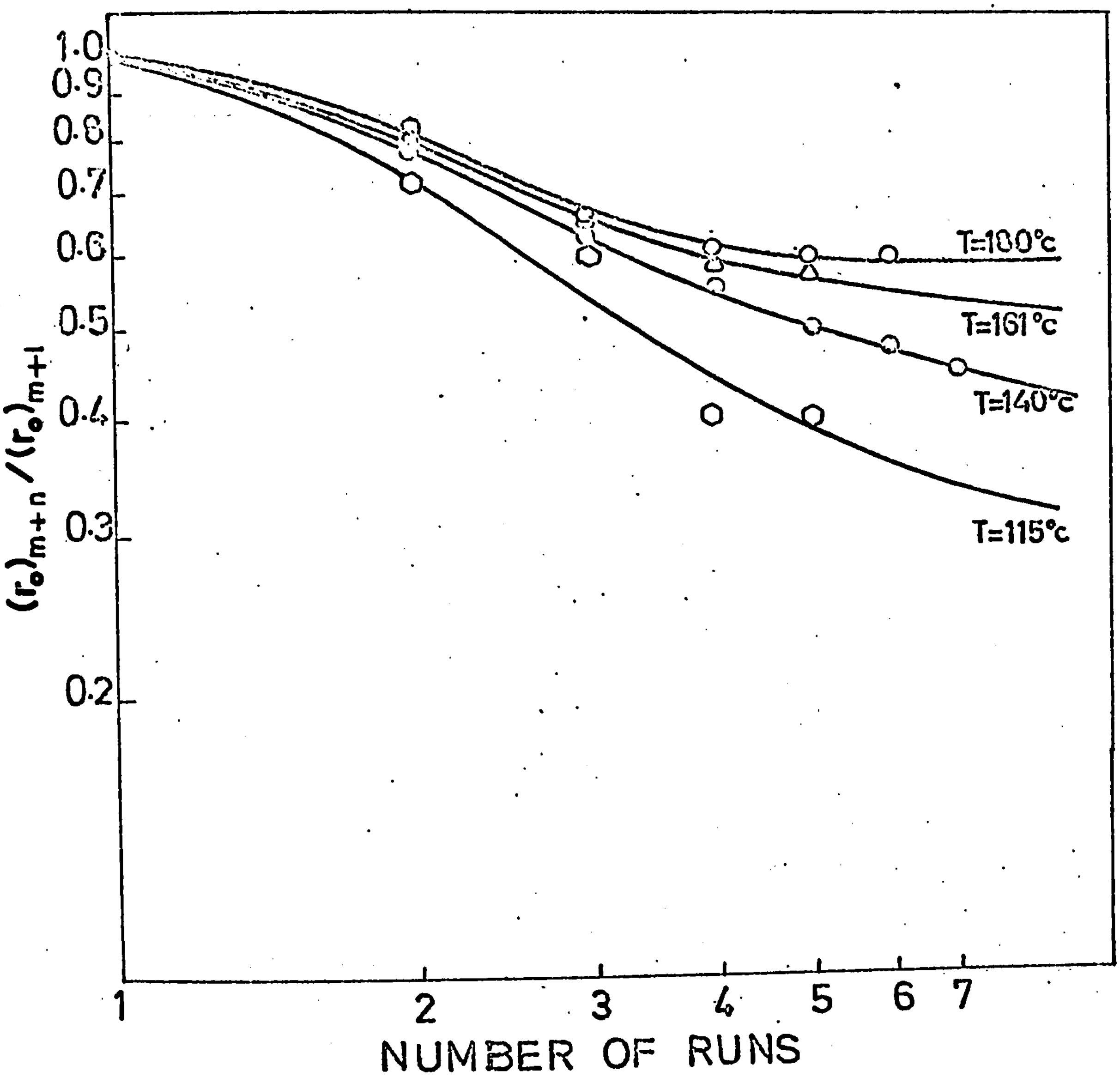


Figure 46 - Effect of temperature on poisoning, iron powder

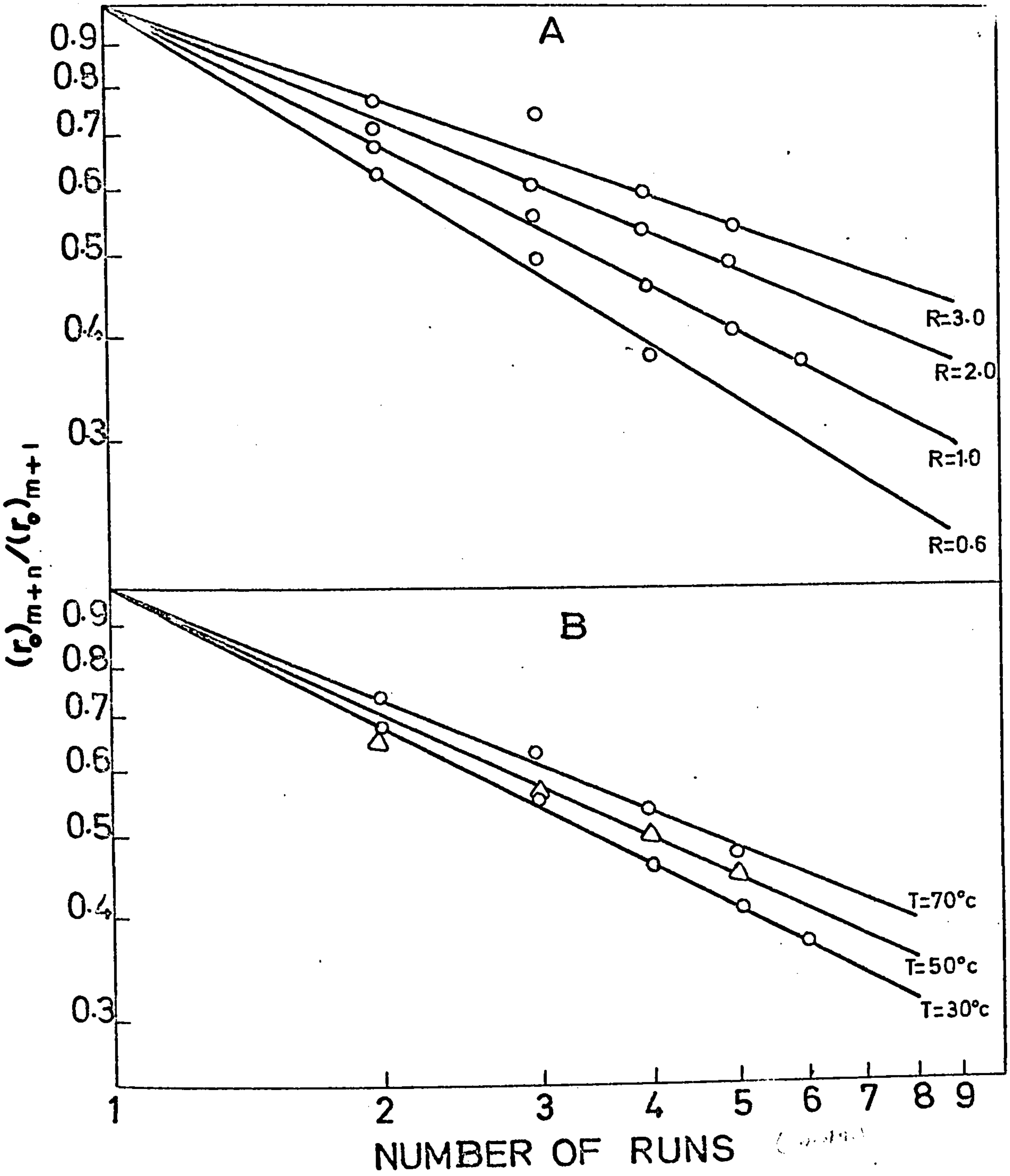


Figure 47A - Effect of reactant ratio on poisoning

Figure 47B - Effect of temperature on poisoning

iron - pumice

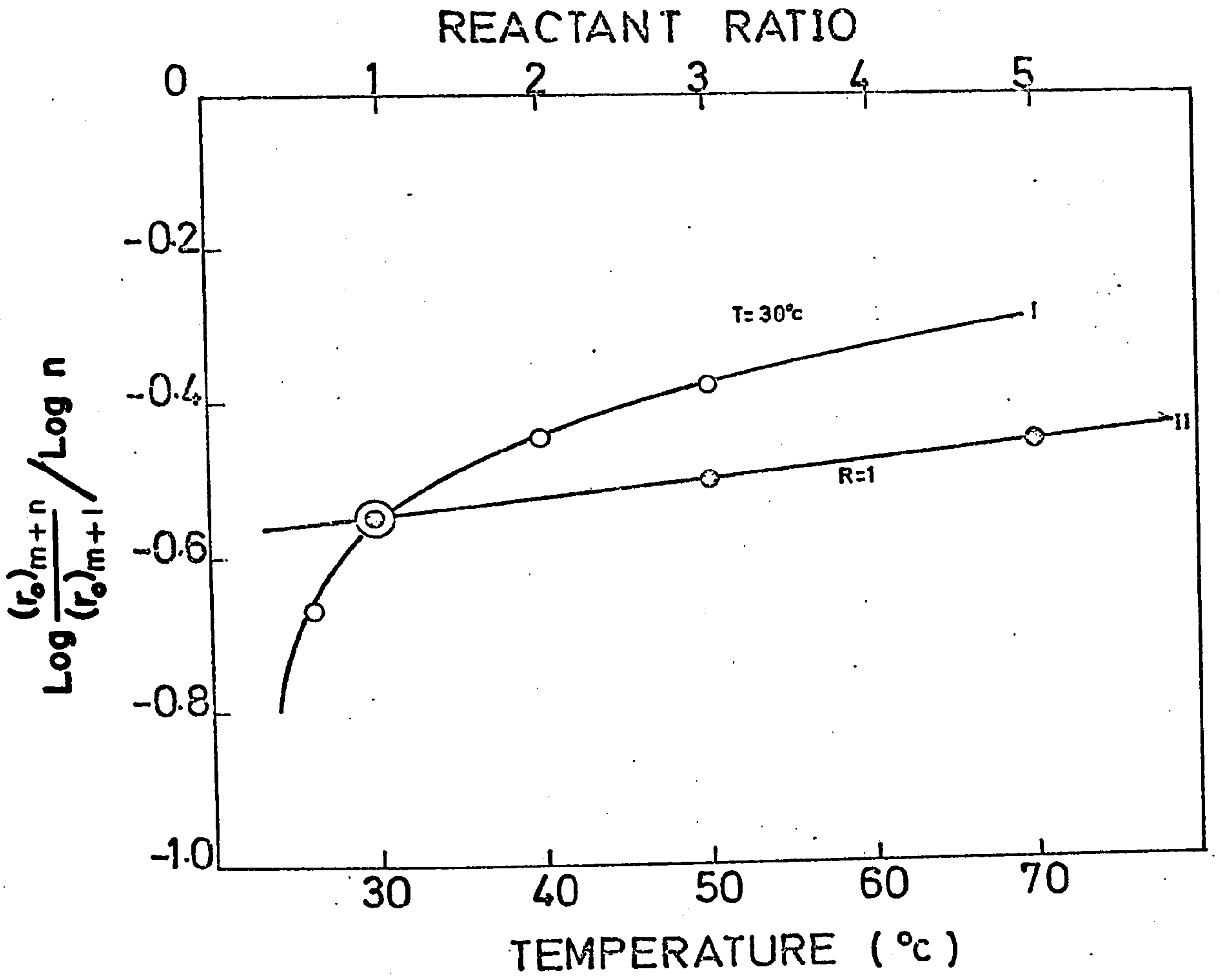


Figure 48 - Dependence of poisoning

I - upon reactant ratio
II - upon temperature

iron - pumice

V DISCUSSION

The different types of curves obtained in the present study over different catalysts are given in Table (11) and are also shown in figure (49).

In the hydrogenation of 2-butyne over cobalt and nickel-copper alloys containing 10% and 20% copper the observed pressure fall-time curves consisted of two linear portions (Curve ADE and Curve AFG) of different rates for hydrogen/2-butyne ratio of less than two and greater than two, at all temperatures. In the first region (AD and AF) the order of reaction was always one. For hydrogen/2-butyne ratios of less than two, the rate of pressure fall (region DE) started decreasing after the pressure had fallen by an amount to half of the initial 2-butyne pressure. This decrease in the rate is possibly due to the pretreatment of the catalyst with hydrogen.

For hydrogen/2-butyne ratios greater than two, the rate of pressure fall accelerated (FG) after the pressure had fallen by an amount equal to about half of the initial 2-butyne pressure. In the region (AF) the main product was cis-2-butene with very small amounts of trans-2-butene, 1-butene and n-butane, whereas after rapid acceleration, region FG, the main process was the further hydrogenation of cis-2-butene to n-butane. This is also supported by the fact that at a pressure drop of 30 mm (at reactant ratio 2.4) the amount of cis-2-butene formed was

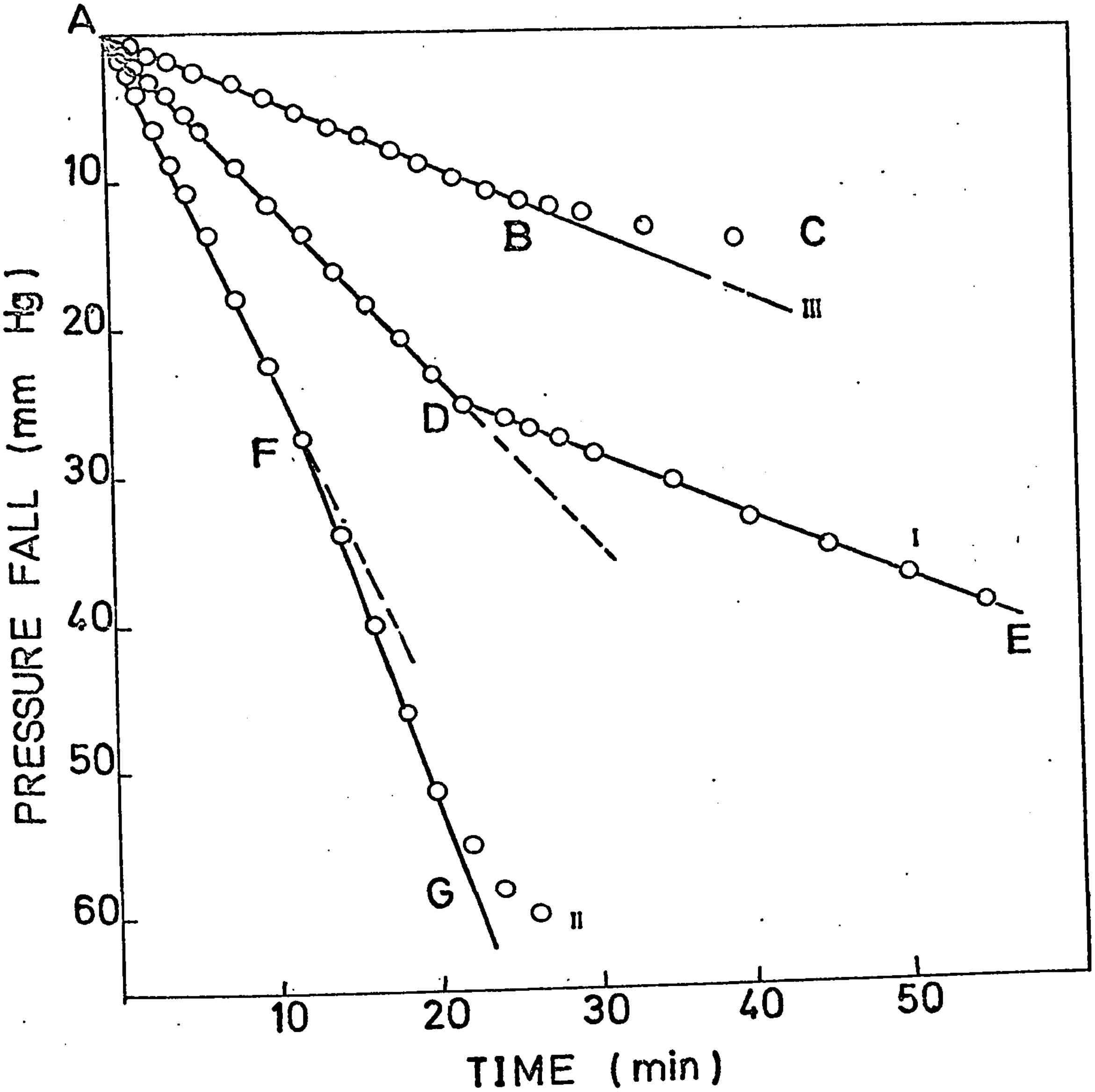


Figure 49 - Pressure-time curves
$P_{C_4H_6} = 50 \pm 2$ mm Hg

I - 90% Ni - 10% Cu $P_{H_2} = 50$ mm Hg
II - 90% Ni - 10% Cu $P_{H_2} = 120$ mm Hg
III - Nickel powder $P_{H_2} = 50$ mm Hg

maximum and then declined due to the further hydrogenation.

Similar type of curves were observed by Mann and Khulbe in the hydrogenation of methylacetylene (23) over nickel-copper alloys and in the hydrogenation of 1-butyne over supported and unsupported nickel cobalt and iron (26). Bond and Wells (59) also observed similar type of curves while investigating the kinetics of acetylene hydrogenation over platinum catalyst.

Bond (11) has classified the observed pressure-time curves into different categories based on his studies on the hydrogenation of acetylene over nickel pumice. Recently Mann and Naik (21) and Mann and Khulbe (22,23) studied the hydrogenation of methylacetylene and 1-butyne over group eight metals and discussed in detail the various factors effecting the kinetic form of these curves. No such pressure-time curve studies are reported for 2-butyne hydrogenation. Hence, no direct comparison of the pressure time curves obtained in this work can be made with any published work.

The kinetic form of the pressure fall time curve depends on the nature and more significantly on the concentration of species in the reactive layer on the surface of the catalyst. when the massive reaction begins. It also depends on the order of admission of the reactants into the reaction vessel, pretreatment and method of preparation of the catalyst.

The order of reaction with respect to hydrogen was always one and was independent of temperature. This is in agreement with the findings of several investigators.

The order of reaction with respect to 2-butyne was slightly negative and dependent on temperature for all catalysts except copper for which it was zero and independent of temperature. The negativity of the order of reaction with respect to 2-butyne increased with increasing temperatures. Similar behavior was observed by Mann and Khulbe (23) in the hydrogenation of methylacetylene over nickel powder and in the hydrogenation of ethylacetylene over supported and unsupported nickel, cobalt and iron (26). Phillipson et al (56) also observed a negative order (-0.3) in the hydrogenation of 2-butyne over nickel and zero order over copper and cobalt. However, no mention has been made regarding the temperature dependency of the order of reaction.

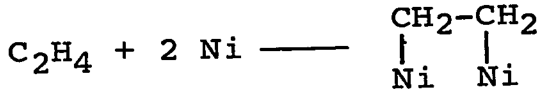
The zero to slightly negative order with respect to 2-butyne and a positive order with respect to hydrogen indicate that the former was strongly adsorbed on the surface of the catalyst and its surface coverage was extensive whereas hydrogen was weakly adsorbed by comparison and its surface coverage was correspondingly low.

An increase in temperature decreases the concentration of reactants in the reactive layer. Since 2-butyne was more strongly adsorbed on the surface than hydrogen it is possible that with increasing temperatures the desorption of the former would be less than the latter, resulting in decreased hydrogen/2-butyne ratios on the surface. Hence, the order with respect to 2-butyne would become more negative with increasing temperatures.

In the chemisorption of ethylene over nickel surface, Jenkins and Rideal (62) observed that when ethylene was first admitted into the reaction vessel over the fresh catalyst, it was easily adsorbed on the surface. However, very little amount of ethylene was adsorbed after repeated evacuations.

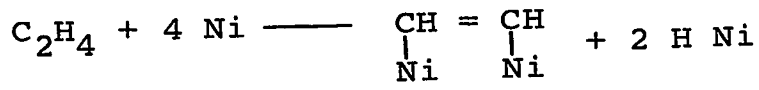
Catalyst	Adsorption (initially)	Adsorption after first evacuation	Adsorption after successive evacuations
A_1	65	2.0	0.5
B_1	110	1.0	nil

The adsorption of ethylene could be as follows



$$C_2H_4 + 2\ Ni \longrightarrow \underset{Ni}{\underset{|}{CH_2}}-\underset{Ni}{\underset{|}{CH_2}}$$

or



$$C_2H_4 + 4\ Ni \longrightarrow \underset{Ni}{\underset{|}{CH}}=\underset{Ni}{\underset{|}{CH}} + 2\ H\,Ni$$

From the above Table, it is clear that on the admission of ethylene, a part of the surface became covered with some acetylenic or ethylenic residue, and hence, no further adsorption even after repeated evacuations. On studying the chemisorption of hydrogen over these catalysts (pretreated with ethylene) it was observed that 80% of the surface was covered with the acetylinic residue.

In the hydrogenation of ethylene over nickel and copper catalysts, Tuul and Fransworth (61) observed that the catalysts were deactivated slightly during the reaction, However, a marked increase in the activity was observed the following day.

Similar behaviour was observed in the present study. It is clear from figure (48) that the rate of deactivation was very fast at hydrogen/2-butyne ratios of less than one and it decreased with increasing reactant ratios indicating that the greater is the formation of the complex residue, greater the amount of 2-butyne in the reaction mixture. At higher temperatures the rate of desorption of 2-butyne increased resulting in a certain decrease in the rate of formation of the complex residue.

It can be concluded from the foregoing discussions that 2-butyne was adsorbed on the surface of the catalyst resulting in the formation of some type of complex residue. This could not be removed even by repeated evacuations and was responsible for marked decrease in the activity of the catalyst. Since the overnight treatment of the catalyst in about 200 mm hydrogen reactivates it, there is a further reason to believe that some type of complex residue exists. The complex was hydrogenated during the overnight treatment of the catalyst in hydrogen.

The rate of reaction expressed in mm Hg per unit time, per unit weight of the metal can be used in correlating the activity of the metals provided that all the catalysts are prepared in the same manner. Since the rate of reaction is dependent on reactant pressure, temperature and composition, it is not suitable to correlate the catalytic activity. However, the overall rate constant (specific reaction rate) which depends on temperature only can be taken as the parameter to correlate the activity. Since the overall rate constant depends on temperature, it is necessary to use a reference temperature T_r for all the catalysts. Such overall rate constants per unit weight or per unit surface area can be calculated at a particular reference temperature from Arrhenius plots.

Considering the overall rate constants $\bar{k}$ as a measure of the catalytic activity, the order of the catalytic activities for pure metals was in the following sequence

$Ni \geqslant Co > Fe > Cu$.

Iron was compared on the basis of its initial rate only as systematic investigation over iron could not be carried out due to its rapid deactivation with each run and its regaining most of its activity on overnight exposure to about 200 mm of hydrogen in the reaction vessel.

In the case of nickel-copper catalysts, the activity increased rapidly with small percentage increase of copper in the alloy reaching a maximum at nearly 10% copper. Further addition of copper decreased the activity progressively. The activity of catalyst containing 60% copper was nearly the same as that of pure copper powder (figure 50).

Chemical, geometric and electronic factors play an important role in establishing the activity of a particular catalyst. Sabatier (63) suggested that the mechanism for the metal catalysts like nickel might involve a chemical factor namely the nickel hydride. At present it has become customary to speak of the reactants as chemisorbed intermediates and not specifically as metallic hydrides. Sachtler and Fahrenfort (64) in the catalytic decomposition of formic acid found that if the heat of the formation of various metal formates was plotted against the temperature at which some particular reaction could be observed, a volcanic shaped curve was obtained.

Taylor (65) introduced the idea of active points which were later known as the different faces of the catalysts. Balandin (66) suggested that the activity of catalysts depended to a large measure on the presence of correctly spaced groups of atoms to accomodate the various reactant molecules. He proposed that for the hydrogenation of benzene, properly spaced face centered cubic metals which hydrogenate benzene should not be active catalysts for hydrogenating 5 and 7 membered rings. Long et al (27) found that only those bimetallic alloys of nickel, cobalt and iron which have a face centered cubic structure

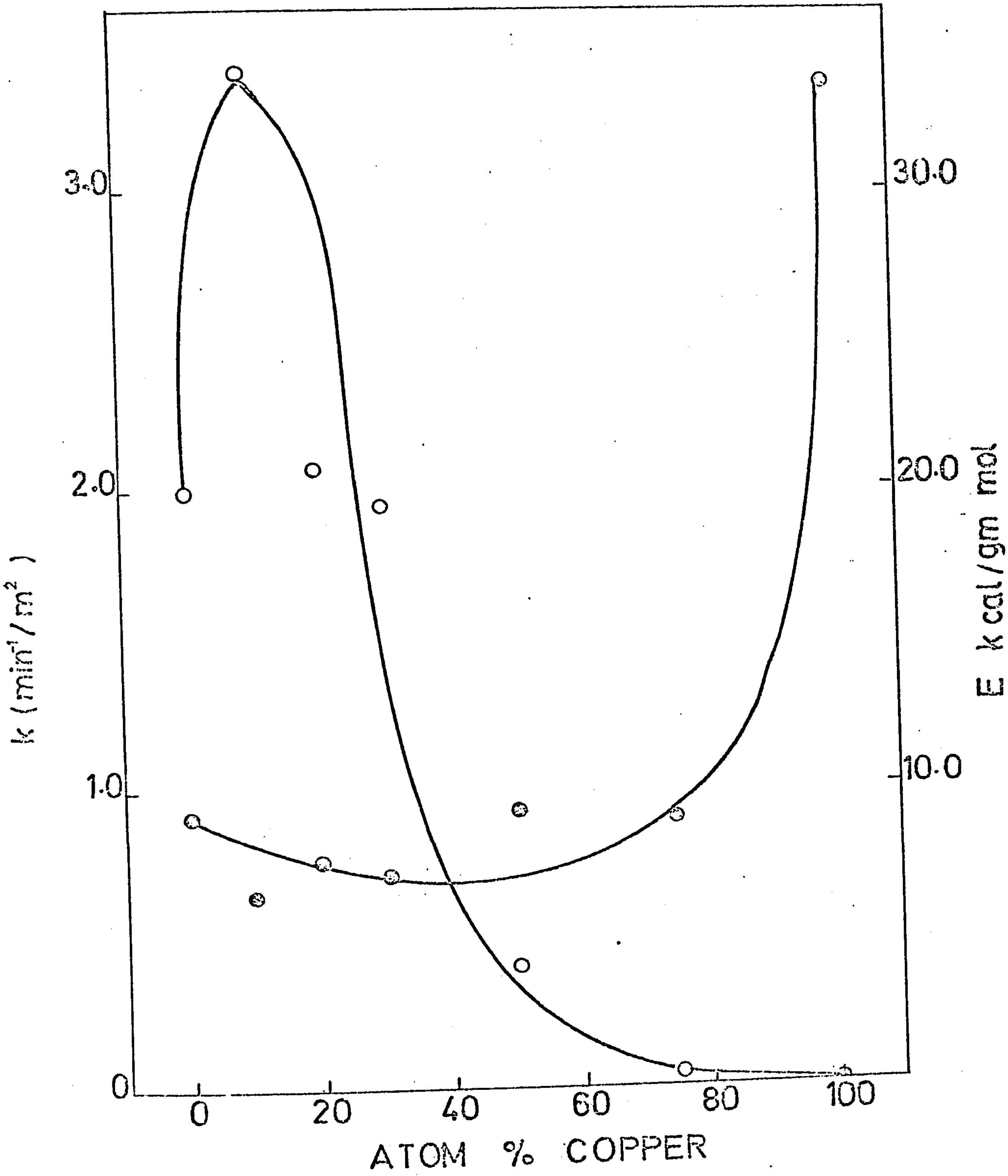


Figure 50 - Effect of copper composition
on activity
on energy of activation
Ni - Cu alloys

were actually capable of causing the conversion of benzene to cyclohexane at temperatures below 200° C.

In the present study while copper catalyst (1 gm) having a face centered cubic structure was active only over 200° C, nickel and cobalt (.0075 gm) both having face centered cubic structure, were very active even at room temperatures. Iron having a body centered cubic structure (.2 gm) was much more active than copper.

Beeck (44) made a systematic study of ethylene hydrogenation on evaporated metals and related the activities of the catalyst to their crystal parameters (figure 51A). Based on the postulation of Beeck, the activity of copper ($a = 3.61^{\circ}$A) should be much higher than nickel ($a = 3.528^{\circ}$ A) and the activity of the alloy series should increase markedly with increasing copper composition. The results of the present investigations are contrary to this.

Boudart (67) suggested that the variation of the activity of metals for the hydrogenation of ethylene could be correlated with Pauling's (52) percentage d-character. Schuit (70) suggested an even better correlation by taking into account the valency of the metals on the Pauling theory. Considering Beeck's suggestion of the activity of metals being a function of either parameter, the activity of copper would be greater than nickel and lesser than rhodium. However, if we considere the suggestion that the activity is a function of percentage d-character, the activity of copper would be lower than that of nickel (figure 51B). Also the activity of nickel-copper alloys should decrease with decrease in percentage d-character (Table I). For pure metals the activity should be in the following sequence

$$\mathrm{Ni}(40) \geqslant \mathrm{Fe}\ (39.7) \geqslant \mathrm{Co}\ (39.5) > \mathrm{Cu}(35.7)$$

where as in the present study the activity was found to be in the following order

$$\mathrm{Ni} \geqslant \mathrm{Co} > \mathrm{Fe} > \mathrm{Cu}.$$

The activities of nickel and cobalt were more or less equal but iron was active at higher temperatures.

Dowden on the basis of the d-band theory concluded that the activity of the transition metals is due to the holes in the d-band. According to this, the activity pattern of these metals should be

$$\mathrm{Fe}\ (hd = 2.2) > \mathrm{Co}\ (hd = 1.7) > \mathrm{Ni}\ (0.6) > \mathrm{Cu}\ (hd = 0.0)$$

According to Dowden (51), when a transition metal having holes in d-band (eg. nickel) is alloyed with another which can donate electrons (eg. copper) at a certain composition, the holes in the d band are completely filled. The catalytic activity of such alloys should drop to a negligible value.

Dowden and Reynolds (53) in their experimental work on the hydrogenation of benzene and styrene observed that the ac-

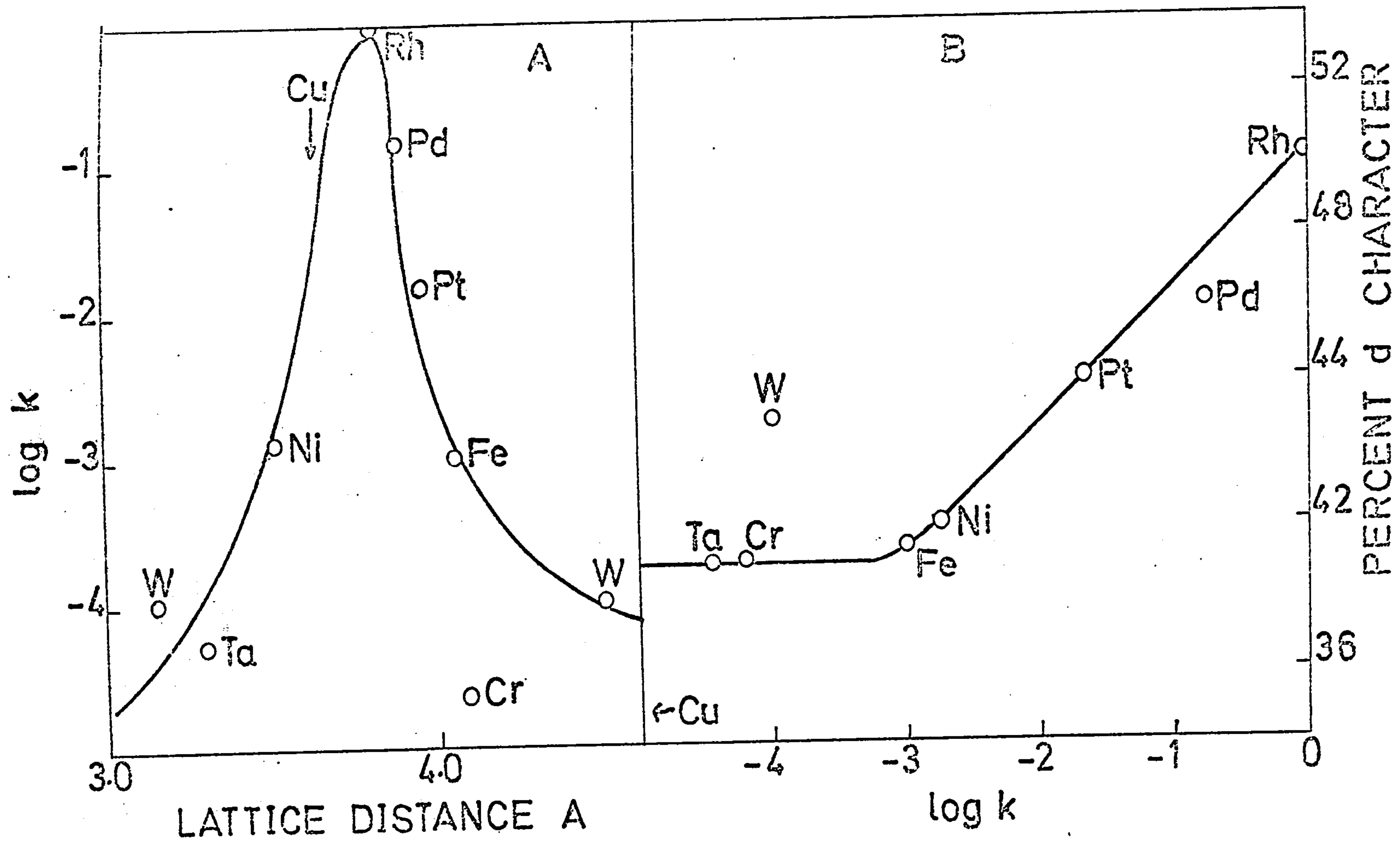


Figure 51A - Dependence of activity upon lattice distance

51B - Dependence of activity upon percent d character

(reference 44)

tivity of the alloy catalyst decreased regularly with increasing copper content to a negligible value at about 40% copper (figure 53). Reynolds (68) also observed that in the hydrogenation of benzene, decomposition of formic acid and methanol over nickel copper, the specific activities of the catalysts decreased with increasing copper content. Best and Russell (28) in the hydrogenation of ethylene found that the addition of copper to nickel increased the activity of nickel catalyst by a factor of 10 or more. The differences in the results are due to the fact that the results of Best and Russell (28) were obtained for the metals prepared with the reduction of homogeneous solutions of the metal oxides whereas those of Dowden and Reynolds were for metal foils prepared from homogeneous alloys. Hall and Emmett (40) in the hydrogenation of ethylene observed that the activity of nickel copper alloys cooled in helium could be correlated with the percentage d-character whereas the activity of nickel catalysts pretreated with hydrogen increased with slight addition of copper. Addition of more than 80% copper caused a rapid decrease in the activity. They suggested that hydrogen has a poisoning effect on pure nickel. Results obtained by Gharpury and Emmett (32) in the hydrogenation of ethylene on evaporated alloy films were in agreement with the work of Hall and Emmett. These results cast doubt on the general validity of Dowden's theory.

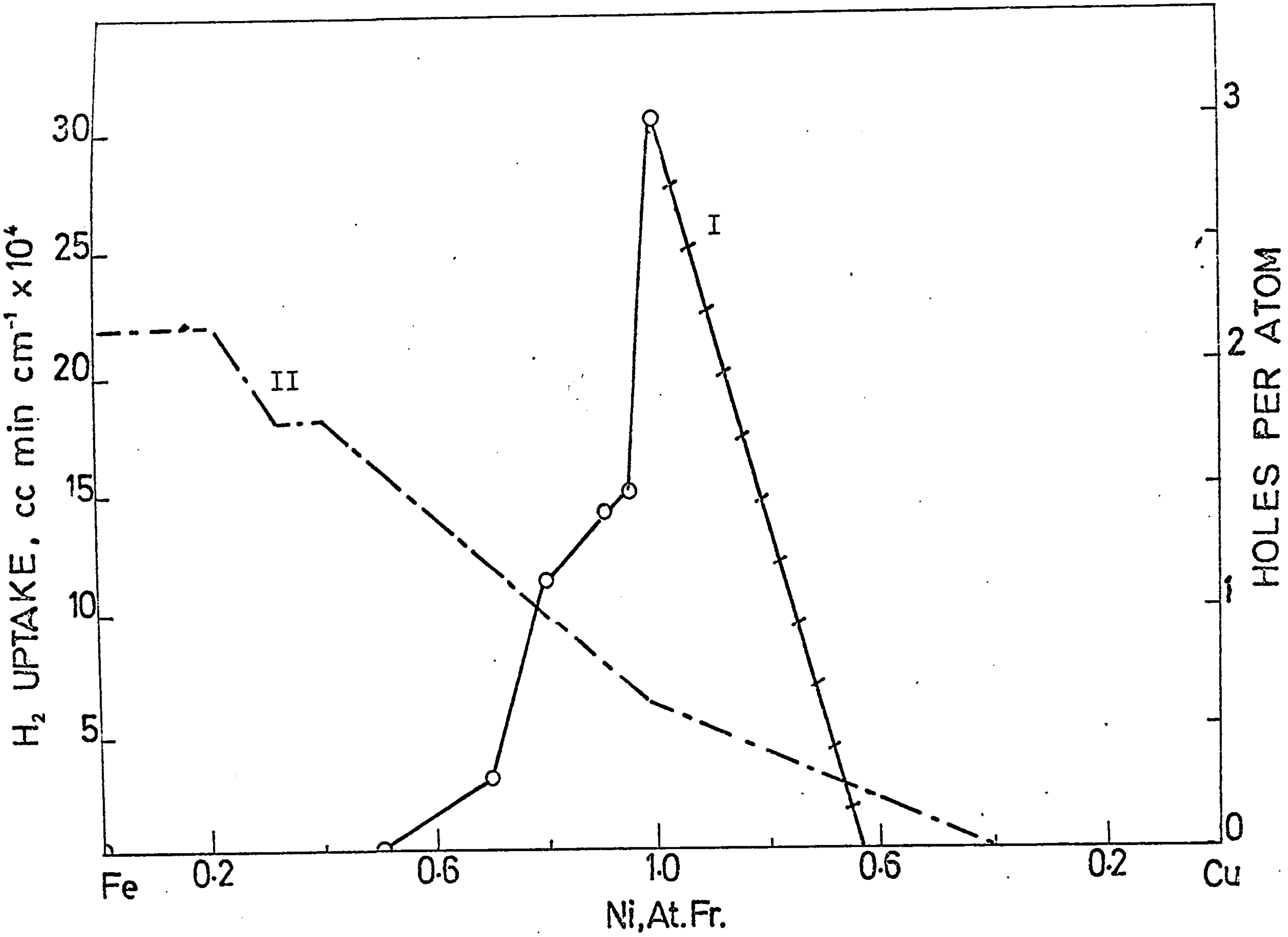


Figure 52 - Dependence of activity upon d holes
I - activity
II - d holes
(reference 53)

Takai and Yamanaka (42) in the liquid phase hydrogenation of maleic acid, acetone and allyl alcohol over nickel-copper alloys observed an increase in the activity on addition of small amounts of copper. The activity pattern for the catalysts containing 5-60% copper could be interpreted on the basis of Dowden's theory. They also observed that the ability for the adsorption of hydrogen was maximum for the alloy containing 80% copper. On addition of further amounts of copper to nickel, the adsorption capacity decreased rapidly. The activity pattern observed by Takai and Yamanaka is similar generally to the one observed in the present investigations.

Takeuchi (48) in the hydrogenation of ethylene and benzene observed that though the activity pattern observed over massive nickel-copper alloy was similar to the one predicted by Dowden, it was quite complicated over granular alloys. On studying the structure of granular alloys with the help of an electron microscope, it was observed that the surface composition of these alloys was different from the interior. They concluded that the amount of hydrogen adsorbed, the heat of adsorption and the catalytic activity of granular alloys were related to the concentration of nickel at the surface.

Recently Takeuchi et al (54) studied the catalytic activity for the hydrogenation of ethylene and electrical resistance of nickel copper film prepared by evaporation of metals.

They observed that the catalytic activity was maximum in the alloy region at about 50% Cu in the alloy irrespective of the order of deposition of the two metals. When the treatment temperature was 250° C, the maximum activity shifted to that of nickel. The electrical resistance of 50% copper alloy was always maximum. The increase in the treatment temperature always resulted in a marked decrease in the electrical resistance. They have suggested that while considering the activity of the metals, due consideration should be given for the lattice imperfections of the film.

The work of Takeuchi et al (35) and Tetenyi et al (50) indicates that the method of the preparation of the catalyst and treatment temperature influences both the specific surface and the catalytic activity.

However, if the homogeneous alloy catalysts are prepared in the same manner on the basis of holes in the d-band, according to Bond and Mann (18) there can be three activity patterns (figure 53). In case of 'A', there is a progressive decrease in the activity as the concentration of holes in the d-band falls until it becomes zero at 60% of copper. Hydrogenation of styrene on nickel copper foils by Dowden and Reynolds (53) and hydrogenation of ethylene and benzene on massive nickel-copper alloys (prepared by completely melting the metals) by Takeuchi et al (35) confirms this pattern. In case of 'B', it is sug-

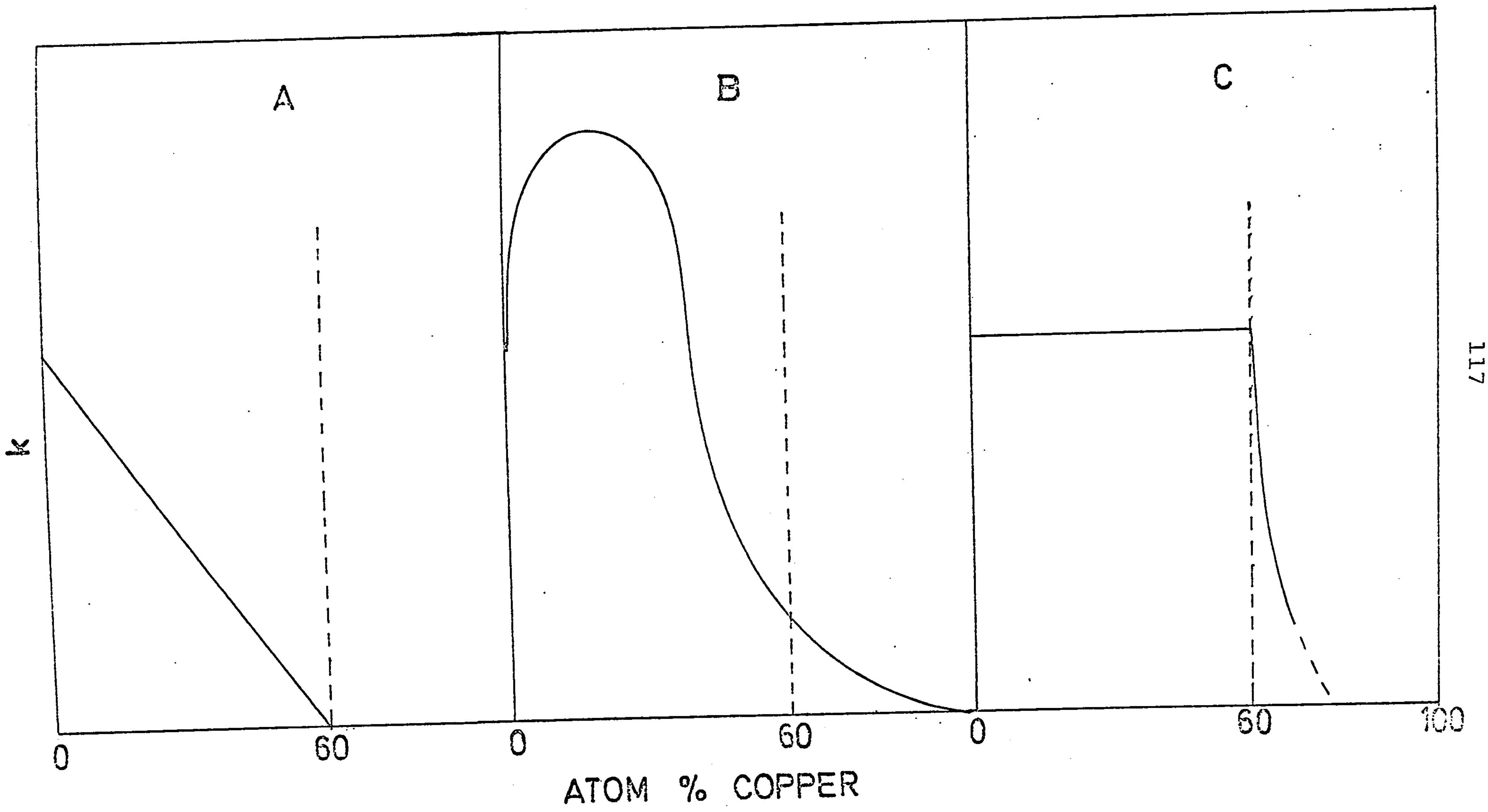


Figure 53 - Idealized forms of activity pattern

gested that as d-band is filled, the binding strength decreases and the activity increases reaching a maximum before the d-band is completely filled. This type of pattern has been confirmed by Couper and Eley (69) in the para hydrogen conversion over palladium-gold alloys, Hall and Emmett (37) in the hydrogenation of benzene, Takai and Yamanaka (42) in the liquid phase hydrogenation of maleic acid, acetone and allyl alcoholaand Mann and Khulbe (23) in the hydrogenation of methylacetylene and the present study over nickel-copper alloys prepared by the reduction of the homogeneous oxides. However, the maximum activity was observed in each case at a different composition of the alloy indicating that the molecular structure of the reactants may also play some important role in the activity of the catalyst. In case of 'C', the activity of the catalysts is independent of the concentration of holes in d-band so long as there are some holes in the d-band. The result of Rienacker and Bommer (39) for the hydrogenation of ethylene on nickel copper foils at 500° C confirms this pattern.

On the basis of pattern 'B' (figure 53), the activity of pure metals in the present study can also be explained. As the number of holes in the d-band decreases, the activity increases and at no holes the activity suddenly decreases to zero. According to this view the activity of these metals should be in the following sequence

Ni $>$ Co $>$ Fe $>$ Cu

which is in agreement to the activity pattern observed in the present study.

Due to the unstable nature of iron catalyst, its energy of activation could not be calculated. In the case of copper-nickel alloys, the activation energy first decreased from 9.1 k cal/mol (for nickel) to 6.5 k cal/mol (for 10% copper alloy) and then increased slightly initially with increasing amounts of copper. For nickel copper alloys containing more than 75% copper, the activation energy increases very rapidly with increasing concentration of copper (figure 50). Similar trend has been observed by Mann and Khulbe (23) in the hydrogenation of methylacetylene over nickel-copper alloys catalysts. The activation energy for cobalt was 6.5 k cal/mol. It appears that there is no simple relationship between the energy of activation and other parameters.

Appendix (A) shows the values of frequency factor, $\log_{10} A$ with lattice parameter, percent d-character and d holes. It appears that there is no simple relationship between the frequency factor and other parameters.

The selectivity and the amount of polymerization for the catalyst were found to depend on temperature initial pressure of the reactants and pressure fall. In order to visualize the effect of the copper composition on the selectivity and polymerization on a comparable basis, these have been calculated for a temperature of 80° C. The results are given in Table (12, 13) and figure (54).

The selectivity decreased slightly with the increasing amounts of copper reaching a minimum for 30% copper (figure 54). For amounts greater than 30%, the selectivity increased with increasing copper concentrations. Mann and Khulbe (23) in the hydrogenation of methylacetylene over nickel-copper alloys observed that the selectivity always increased with increasing amounts of copper.

While the percentage of 1-butene formed in the products increased with increasing amounts of copper, the amounts of cis-2-butene decreased slightly with increasing copper composition. No 1-butene was formed over copper. The effect of the copper concentration in the alloy on the formation of n-butane and trans-2-butene was barely noticeable.

The extent of polymerization increased with copper concentration. Similar behaviour was observed by Mann and Khulbe (23) in methylacetylene hydrogenation.

A study of the kinetics of the reaction and the product analysis of the hydrogenation of 2-butyne over nickel copper, cobalt and nickel copper alloys shows a close similarity between each other. Hence, it is possible that reaction takes place by a similar mechanism over all the catalysts. The results obtained largely confirm that there

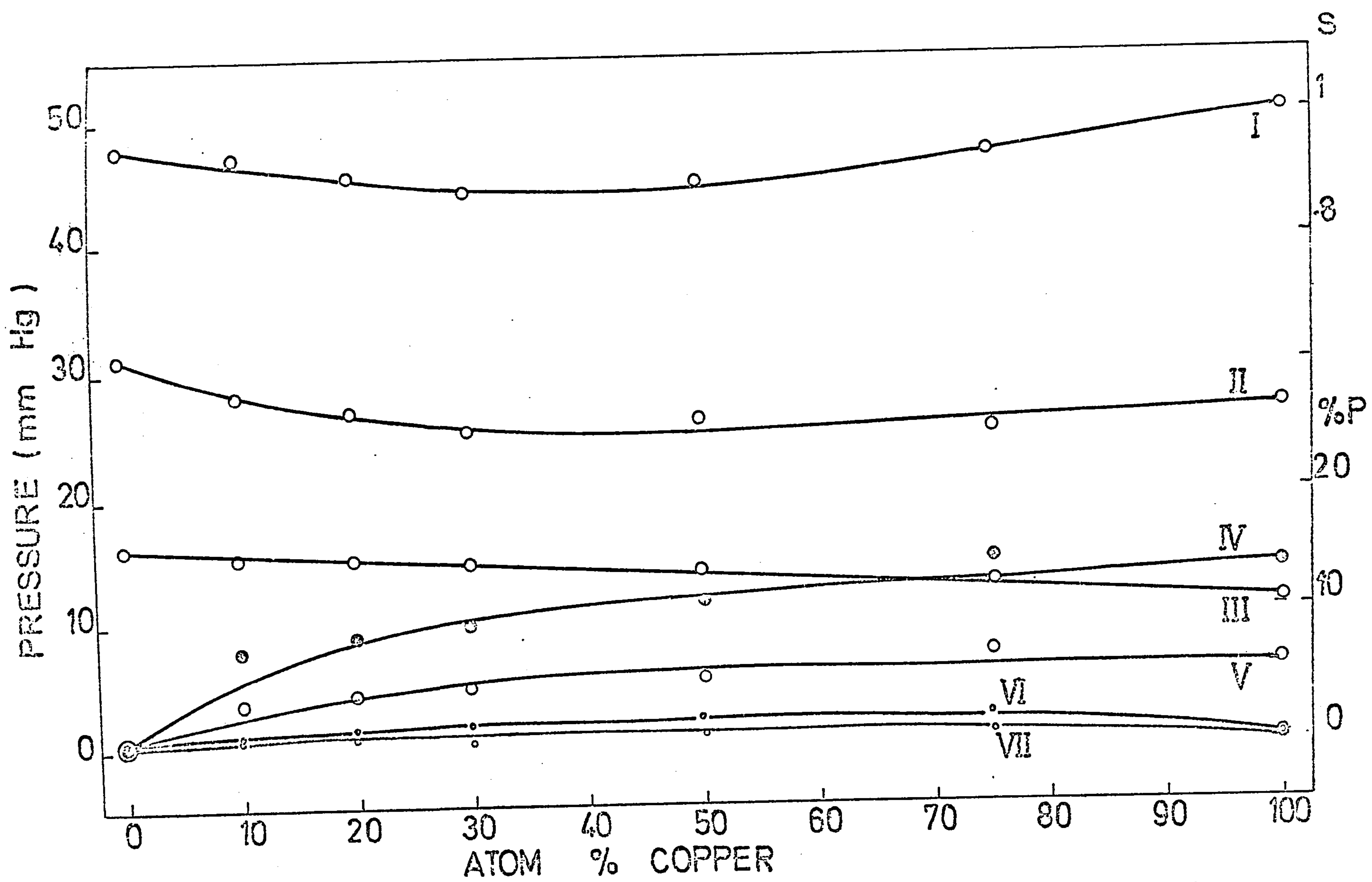
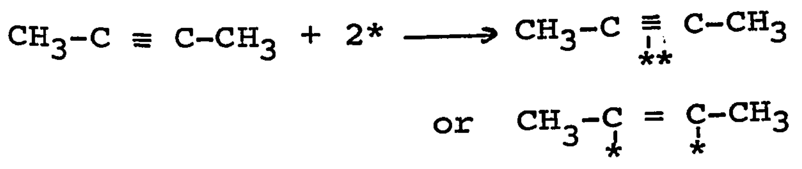


Figure 54 - Effect of copper composition on product distribution, selectivity and polymerization
P_{H_2} = 50 ± 1 mm Hg $P_{C_4H_6}$ = 50 ± 2 mm Hg   P = 20 mm Hg

is much similarity in the reaction of hydrogen with 2-butyne and methylacetylene in most of the aspects except for the formation of some isomeric butenes in case of 2-butyne hydrogenation.

In the present study, with few exceptions, the major product was cis-2-butene over all the catalysts. However, in the initial stages of the reaction, very small amounts of trans-2-butene, 1-butene and n-butane were also formed. Meyer and Burwell (55) studied the addition of deuterium to 2-butyne on alumina supported palladium catalysts. They observed that the exchange reaction gave exclusively cis-2-butene 2, 3 d_2. Phillipson et al (56) also observed the four products in the hydrogenation of 2-butyne over alumina supported cobalt, nickel, iron and copper catalysts.

The stronger adsorption of 2-butyne on the surface of the catalyst as compared to the corresponding butenes is of much importance in determining the nature of the mechanism. Yates and Lucchesi (71) suggest that the molecule of 2-butyne is generally strongly adsorbed on alumina catalyst parallel to the surface. The adsorption of 2-butyne molecule on the surface of the catalyst can be represented as:



$$CH_3\text{-}C \equiv C\text{-}CH_3 + 2^* \longrightarrow CH_3\text{-}C \underset{**}{\overset{\equiv}{|}} C\text{-}CH_3 \qquad \text{I} \qquad \text{(A)}$$

$$\text{or} \quad CH_3\text{-}\underset{*}{\overset{}{\underset{|}{C}}} = \underset{*}{\underset{|}{C}}\text{-}CH_3 \qquad \text{II}$$

In the present study in addition to cis-2-butene, small amounts of trans-2-butene and 1-butene were also observed. The formation of isomeric butenes may be attributed to the following reactions.

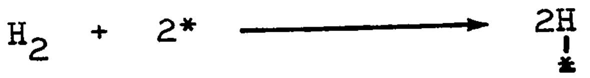
a) The direct addition of atomic or molecular hydrogen to the reactant molecule followed by immediate desorption of alkenes.

b) Isomerization of the reactant.

c) Isomerization of alkenes between the initial formation of alkenes and its desorption.

d) Addition of atomic or molecular hydrogen.

Hydrogen is adsorbed on the two active sites with dissociation as follows:

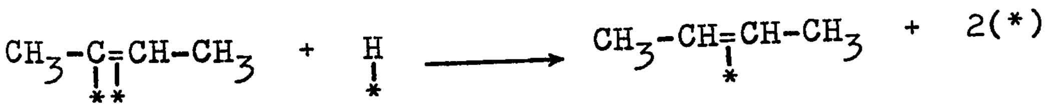


$$\mathrm{H_2} + 2{*} \longrightarrow \underset{\overset{|}{*}}{2\mathrm{H}} \qquad \text{(B)}$$

The adsorbed hydrogen then reacts with adsorbed 2-butyne forming the half hydrogenated state;

$$\mathrm{CH_3{-}\underset{\overset{|}{**}}{C}{\equiv}C{-}CH_3} + \underset{\overset{|}{*}}{\mathrm{H}} \longrightarrow \mathrm{CH_3{-}\underset{\overset{|||}{**H}}{C{=}C}{-}CH_3} + ({*}) \qquad \text{(C)}$$

The half hydrogenated state may react with an adsorbed hydrogen atom to form cis-2-butene.



$$\mathrm{CH_3{-}\underset{\overset{||}{**}}{C}{=}CH{-}CH_3} + \underset{\overset{|}{*}}{\mathrm{H}} \longrightarrow \mathrm{CH_3{-}CH{=}\underset{\overset{|}{*}}{CH}{-}CH_3} + 2({*}) \qquad \text{(D)}$$

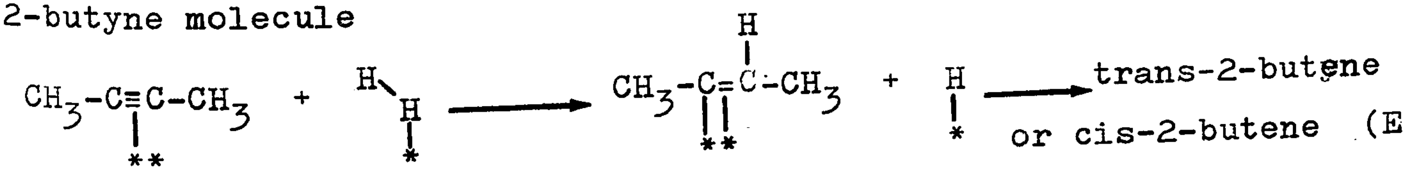
Equation (A) and (B) describes the adsorption of the reactants at a pair of adjacent sites. Such adsorption takes place for a given pair of sites. When the surface is extensively covered with the adsorbate requiring two adsorption sites, single sites will remain vacant. Hydrogen adsorption may take place non-competitively at such sites.

In the catalytic hydrogenation of ethylene on the surface of nickel catalyst, Jenkins and Rideal (62), while discussing chemisorption on the surface, have shown the following picture of a catalyst surface in the presence of a hydrogen ethylene mixture.

Sites occupied by C_2H_4 complex	occupied by hydrogen as pair	unoccupied
242	24	24
83.4%	8.3%	8.3%

By taking 100 sites surrounded by a guard ring to eliminate the end effects, they found that the percentage of the sites occupied by C_2H_4 complex, hydrogen as pair and single were 78, 13 and 9% respectively.

These single sites are capable of activating a molecule of hydrogen. Bond and Wells (59) have considered this type of mechanism in the hydrogenation of acetylene over platinum catalyst. The adsorbed hydrogen molecule then reacts with an adsorbed 2-butyne molecule

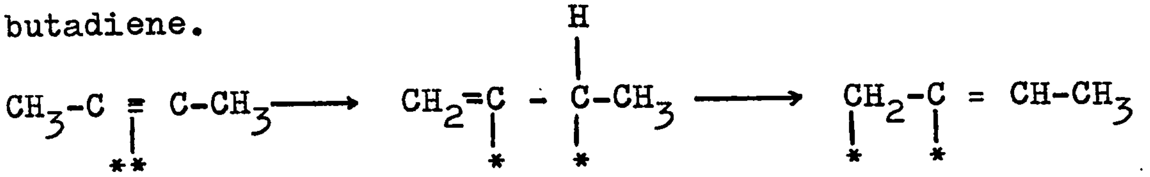


$$\underset{**}{CH_3-C\equiv C-CH_3} + \underset{*}{H-H} \longrightarrow \underset{**}{CH_3-C=\overset{H}{C}-CH_3} + \underset{*}{H} \longrightarrow \text{trans-2-butene or cis-2-butene} \qquad (E)$$

1-butene could not be produced by this direct route.

b) Isomerization of the reactant:

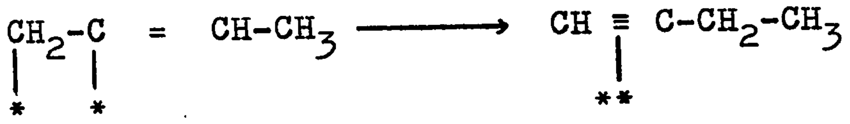
The adsorbed 2-butyne either could isomerize to 1-2, butadiene.



$$CH_3-C\underset{|\atop **}{\equiv}C-CH_3 \longrightarrow CH_2=\underset{|\atop *}{C}-\overset{H\atop |}{\underset{|\atop *}{C}}-CH_3 \longrightarrow \underset{|\atop *}{CH_2}-\underset{|\atop *}{C}=CH-CH_3$$

(F)

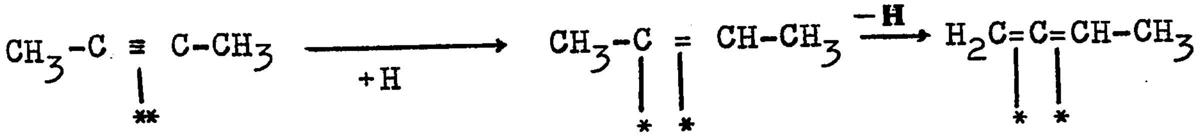
or to 1-butyne



$$\underset{|\atop *}{CH_2}-\underset{|\atop *}{C}=CH-CH_3 \longrightarrow CH\underset{|\atop **}{\equiv}C-CH_2-CH_3$$

(G)

or to 1-2butadiene through indirect route



$$CH_3-C\underset{|\atop **}{\equiv}C-CH_3 \xrightarrow[+H]{} CH_3-\underset{|\atop *}{C}=\underset{|\atop *}{C}H-CH_3 \xrightarrow{-H} H_2C=\underset{|\atop *}{C}=\underset{|\atop *}{C}H-CH_3$$

(H)

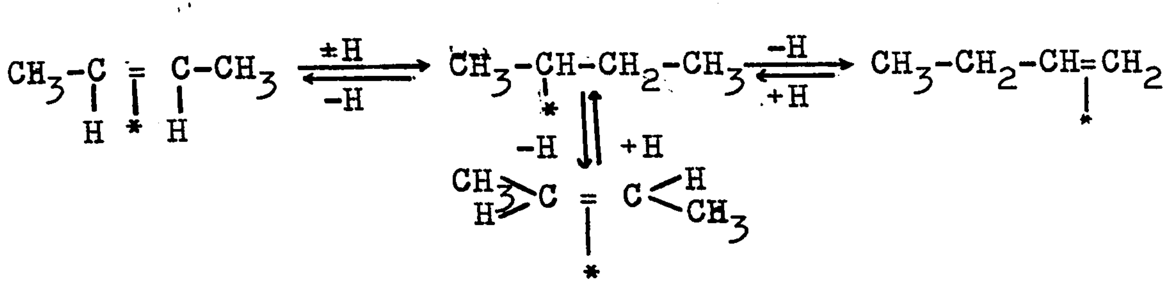
The further hydrogenation of these products could produce 1-butene. If the mechanism postulated above is true, then 1-2butadiene and 1-butyne should be present in the product. However, no other products besides n-butane, cis and trans-2-butene and 1-butene were observed.

Other investigators (56,57) have also observed the formation of cis and trans-2-butene, n-butane and 1-butene in the hydrogenation of 2-butyne over alumina supported cobalt, iron, nickel and copper. Phillipson et.al.(56) observed a further product in addition to n-butenes and n-butane over rhodium and iridium catalyzed reactions. Though the concentration of this was about 2 to 3% in the product, yet it could not be completely identified. The hydrocarbon appeared to give a parent ion at m/e = 54 in the mass spectrometer, indicating that it was an isomer of the reactant. However, gas chromatography showed that it was neither 1-butyne nor 1-3butadiene. They assumed that it was probably 1-2butadiene. They concluded that this molecule must have been present in the adsorbed state on the surface. Its non-appearance in the product for the reaction over Fe, Co, Ni, Cu and Pt catalyst involves the assumption that its desorption rate over the metals was too slow for it to be produced in detectable quantities.

Mann and Khulbe (26) in the hydrogenation of 1-butyne over supported and unsupported Ni, Co and Fe observed only four products (three butenes and n-butane). In the hydrogenation of acetylene (19), methylacetylene (72) and ethylacetylene (73), iridium shows a poor selectivity for ethylene, propylene and butenes. They suggested that the mechanism over iridium catalyst may be different from other catalyst.

c) Isomerization of butene

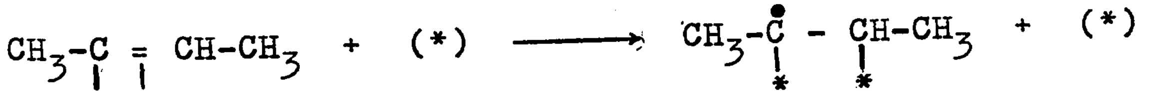
Bond, Webb and Wells (74) have studied the hydrogenation of n-butenes catalyzed by alumina supported ruthenium and osmium. They have proposed the following mechanism for isomerization of butenes.



$$CH_3-\underset{H}{C}\underset{*}{=}\underset{H}{C}-CH_3 \underset{-H}{\overset{\pm H}{\rightleftharpoons}} CH_3-\underset{*}{CH}-CH_2-CH_3 \underset{+H}{\overset{-H}{\rightleftharpoons}} CH_3-CH_2-CH\underset{*}{=}CH_2$$

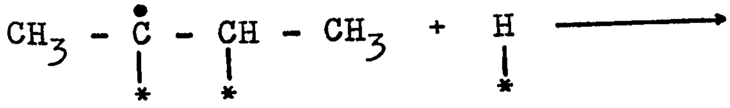
$$CH_3-\underset{*}{CH}-CH_2-CH_3 \underset{+H}{\overset{-H}{\rightleftharpoons}} \begin{matrix}CH_3\\H\end{matrix}\!\!>C\underset{*}{=}C<\!\!\begin{matrix}H\\CH_3\end{matrix}$$

With the few exceptions, it was observed (Table 4) that when tans-2-butene was formed, n-butane appeared as a product which provide some evidence for the alkyl mechanism. From the other studies of the hydro-isomerization of butene (34), one would except trans-2-butene/1-butene ratios greater than one in the product but in the present study, trans-2-butene/1-butene ratios were less than one. It appears therefore that butene isomers were obtained by some other mechanism. It is possible that the half hydrogenated state converts into a radical before it could react with another atom of hydrogen.

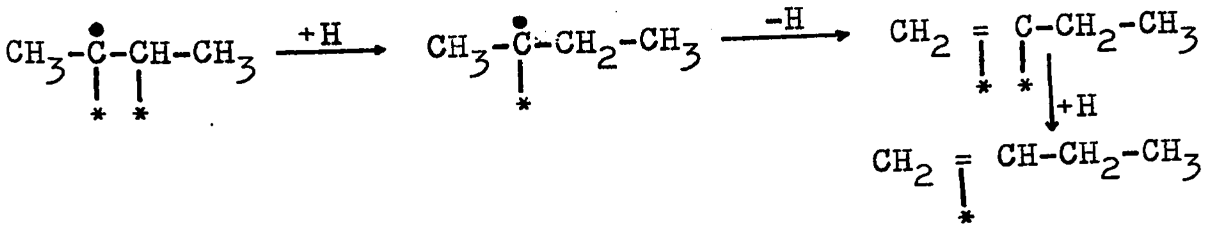


$$CH_3-\underset{*}{C}=\underset{*}{CH}-CH_3 + (*) \longrightarrow CH_3-\underset{*}{\overset{\bullet}{C}}-\underset{*}{CH}-CH_3 + (*) \qquad (i)$$

which on further hydrogenation gives butenes as follows

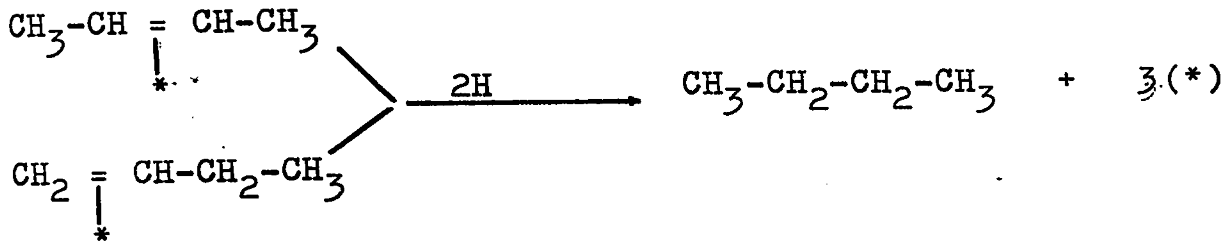


$$CH_3-\underset{*}{\overset{\bullet}{C}}-\underset{*}{CH}-CH_3 + \underset{*}{H} \longrightarrow \text{cis or trans-2-butene} \qquad (j)$$



$$CH_3-\underset{*}{\overset{\bullet}{C}}-\underset{*}{CH}-CH_3 \xrightarrow{+H} CH_3-\underset{*}{\overset{\bullet}{C}}-CH_2-CH_3 \xrightarrow{-H} \underset{*}{CH_2}=\underset{*}{C}-CH_2-CH_3 \xrightarrow{+H} CH_2\underset{*}{=}CH-CH_2-CH_3 \qquad (k)$$

In the early stages of 2-butyne hydrogenation, small amounts of n-butane were observed. This would have come from the further hydrogenation of butenes



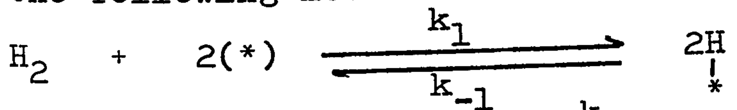
$$\left.\begin{array}{l} CH_3-\underset{|\,*}{CH}=CH-CH_3 \\ CH_2\underset{|\,*}{=}CH-CH_2-CH_3 \end{array}\right\rangle \xrightarrow{2H} CH_3-CH_2-CH_2-CH_3 + 3(*)$$

(L)

The result obtained in the deuterium exchange reaction of 2-butyne over rhodium, supports this mechanism. The deuterium distribution was as follows at 25% removal of the reactant.

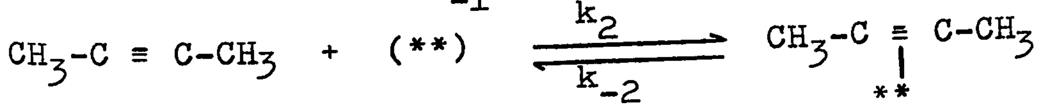
	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
cis-2-butene	1.3	23.7	73.1	1.7	0.2	0.0	0.0	0.0	0.0
trans-2-butene	2.2	24.1	60.5	8.1	3.2	1.8	0.1	0.0	0.0
1-butene	2.0	10.7	43.8	36.1	5.1	2.1	0.2	0.0	0.0

Similar distribution was obtained by Webb and Wells (57) over ruthenium and osmium. The addition of deuterium or hydrogen in step (K) should be nearly equal resulting in a nearly equal percentage of d_2 and d_3 products of 1-butene. Considering that 2-butyne was strongly adsorbed, its surface coverage was high and that of weakly adsorbed hydrogen to be correspondingly low, the following mechanism is proposed:



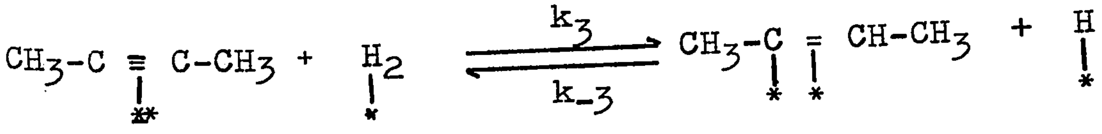
$$H_2 + 2(*) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{|\,*}{2H}$$

(1)



$$CH_3-C\equiv C-CH_3 + (**) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_3-C\underset{|\,**}{\equiv}C-CH_3$$

(2)



$$CH_3-C\underset{|\,**}{\equiv}C-CH_3 + \underset{|\,*}{H_2} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CH_3-\underset{|\,*}{C}\underset{|\,*}{=}CH-CH_3 + \underset{|\,*}{H}$$

(3)

Assuming that $k_1 \gg k_{-1}$ and $k_3 \gg k_{-3}$ as suggested by Bond and Wells (59), from equations (1) and (3), rate of adsorption of hydrogen

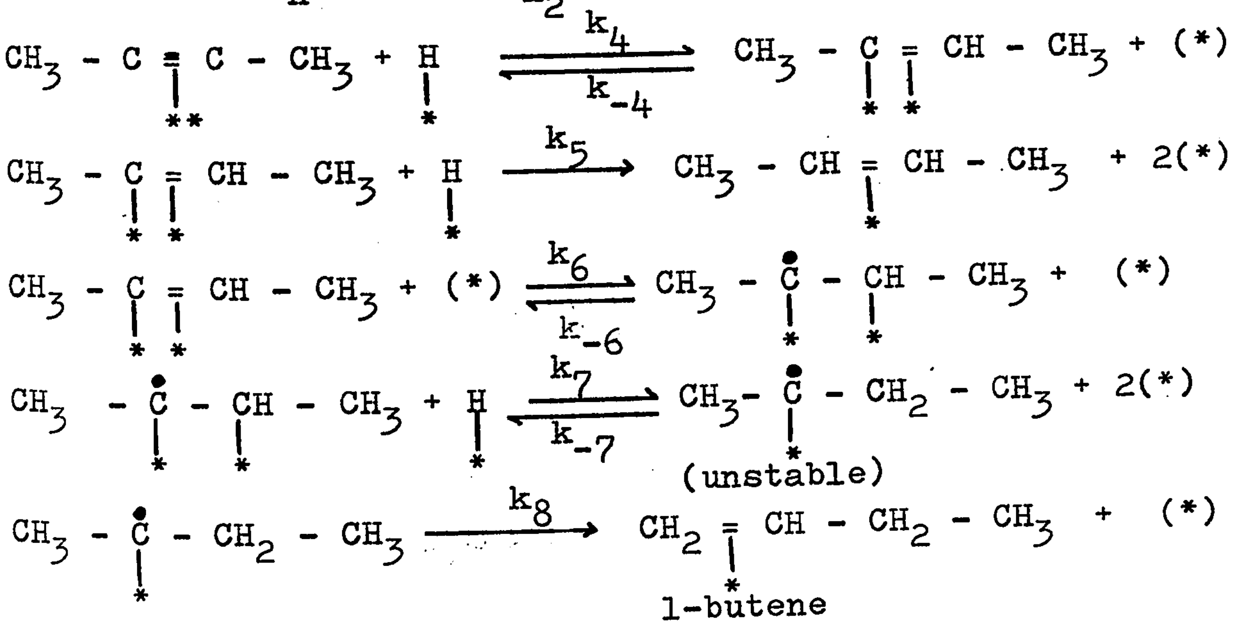
$$= k_1 P_{H_2}(**) \quad + \quad k_3 P_{H_2} \theta_{C_4H_6}$$

where $O_{C_4H_6}$ is fraction of surface covered by C_4H_6.

Since $\theta_{C_4H_6} \longrightarrow 1$, due to strong adsorption of 2-butyne and the concentration of single and pair of sites remaining constant for a certain pressure of 2-butyne at a particular temperature, the rate of adsorption of hydrogen would be proportional to the fraction of the surface covered by hydrogen (O_H)

$$\text{as } \theta_H = \left[k_1(**) + k_3 \right] P_{H_2}$$

$$\theta_H \propto P_{H_2}$$



$$CH_3 - \underset{**}{C} \equiv C - CH_3 + \underset{*}{H} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} CH_3 - \underset{*}{C} \underset{*}{=} CH - CH_3 + (*) \qquad (4)$$

$$CH_3 - \underset{*}{C} \underset{*}{=} CH - CH_3 + \underset{*}{H} \xrightarrow{k_5} CH_3 - CH \underset{*}{=} CH - CH_3 + 2(*) \qquad (5)$$

$$CH_3 - \underset{*}{C} \underset{*}{=} CH - CH_3 + (*) \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} CH_3 - \underset{*}{\overset{\bullet}{C}} - \underset{*}{CH} - CH_3 + (*) \qquad (6)$$

$$CH_3 - \underset{*}{\overset{\bullet}{C}} - \underset{*}{CH} - CH_3 + \underset{*}{H} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} CH_3 - \underset{*}{\overset{\bullet}{C}} - CH_2 - CH_3 + 2(*) \qquad (7)$$

(unstable)

$$CH_3 - \underset{*}{\overset{\bullet}{C}} - CH_2 - CH_3 \xrightarrow{k_8} CH_2 \underset{*}{=} CH - CH_2 - CH_3 + (*) \qquad (8)$$

1-butene

Step (5) and (8) are not shown reversible as (1) butene formed in these steps was desorbed and was replaced by 2-butyne and (2) adsorbed butene so formed was further hydrogenated to n-butane.

Rate of formation of C_4H_8 from equations (5) and (8)

$$= k_5 \, \theta_{C_4H_7} \, \theta_H + k_8 \, \theta_{C_4\dot{H}_8} \qquad (9)$$

where $\theta_{C_4H_7}$ and $\theta_{C_4\dot{H}_8}$ are surface covered by C_4H_7 and $C_4\dot{H}_8$ respectively. Applying steady state assumption for C_4H_7, $C_4\dot{H}_7$ and C_4H_8 :

$$k_3 \, \theta_{C_4H_6} \, P_{H_2} + k_4 \, \theta_{C_4H_6} \, \theta_H = k_{-3} \, \theta_{C_4H_7} \, \theta_H + k_{-4} \, \theta_{C_4\dot{H}_7} [*]$$
$$+ k_5 \, \theta_{C_4H_7} \, \theta_H + k_6 \, \theta_{C_4H_7} [*] - k_{-6} \, \theta_{C_4\dot{H}_7} [*] \qquad (10)$$

From equations (6) and (7)

$$k_6 \, \theta_{C_4H_7} [*] + k_{-7} \, \theta_{C_4\dot{H}_8} [*]^2 = k_{-6} \, \theta_{C_4\dot{H}_7} [*] + k_7 \, \theta_{C_4\dot{H}_7} \theta_H$$
$$\text{-----} \quad (11)$$

$$k_7 \, \theta_{C_4\dot{H}_7} \, \theta_H - k_{-7} \, \theta_{C_4\dot{H}_8} [*]^2 = k_8 \, \theta_{C_4\dot{H}_8} \qquad (12)$$

Combining equations (11) and (12) with (10) the rate of formation of C_4H_8

$$= k_5 \, \theta_{C_4H_7} \, \theta_H + k_8 \theta_{C_4\dot{H}_8} = k_3 \, \theta_{C_4H_6} P_{H_2}$$
$$- k_{-3} \, \theta_{C_4H_7} \, \theta_H + k_4 \, \theta_{C_4H_6} \, \theta_H - k_{-4} \, \theta_{C_4H_7} [*]$$
$$\text{---} \ (13)$$

If $k_3 \, \theta_{C_4H_6} P_{H_2} \gg k_{-3} \, \theta_{C_4H_7} \, \theta_H$

and $k_4 \, \theta_{C_4H_6} \, \theta_H \gg k_{-4} \, \theta_{C_4H_7}$ [*]

$$\text{The rate of reaction} = k_3 \, \theta_{C_4H_6} P_{H_2} + k_4 \theta_{C_4H_6} \theta_H$$

$$= \left[k_3 P_{H_2} + k_4 \theta_H \right] \theta_{C_4H_6}$$

$$\approx P_{H_2}, \text{ as } \theta_{C_4H_6} \longrightarrow 1.$$

The order of reaction reduces to first order, which is in agreement with the experimentally obtained order (Table 3).

The observed negative order in 2-butyne may be due to the fact that at high pressures, the molecules form a more ordered array on the surface, thus reducing the number of vacant sites, alternatively an increase in 2-butyne pressure may enable it to compete more effectively with hydrogen for the surface.

VI CONCLUSIONS

A detailed kinetic study and the product analysis of the hydrogenation of 2-butyne over nickel copper, cobalt, supported and unsupported iron and nickel-copper alloy catalysts was carried out in a static system over a wide range of temperatures and reactants ratios.

The observed pressure time curve in the hydrogenation of 2-butyne over nickel, copper, cobalt and nickel copper alloys were similar to those observed by Mann and Khulbe (23) in methylacetylene hydrogenation over nickel copper alloy catalysts.

The observed order with respect to hydrogen was always one and independent of temperature. Though the order with respect to 2-butyne was zero and became slightly negative with increasing temperatures, for copper it was independent of temperature.

The energy of activation for nickel copper alloys was between 6.5 and 33.5 k cal/mol. No direct relationship between the energy of activation and the copper composition in the alloy was observed.

The relative activities of the metals were in the following sequence

$$Ni \gg Co > Fe > Cu$$

The activity increased on the addition of small amounts of copper to nickel increasing to a maximum for the catalyst containing 10% copper; on further additions of copper, the activity decreased. The activity pattern in the nickel-copper alloys could be explained on the basis of holes in d band.

The products obtained in the hydrogenation of 2-butyne were only cis-2-butene, trans-2-butene, 1-butene and n-butane. The main product was cis-2-butene. No direct relationship between the selectivity and the composition of copper in the nickel copper alloys existed. The following sequence was observed for the selectivity of cis-2-butene over metals

$$\text{Cu} > \text{Fe} > \text{Ni} > \text{Co}$$

VII RECOMMENDATIONS

Though the detailed study of the 2-butyne hydrogenation over nickel, iron, cobalt, copper and nickel copper alloys confirms the earlier suggestions of a direct relationship between the catalytic activity and d holes in the catalysts, the method of the preparation of the catalyst and the molecular structure of the reactants play an important role in governing the activity of a particular reaction over the various catalysts. In order to obtain a better correlation for the catalytic activity and explain the reaction mechanism more clearly, it is suggested that the following further information should be collected.

(1) The hydrogenation of 2-butyne should also be studied over cobalt, nickel, iron, copper and nickel-copper alloys prepared by various other methods. This would explain the variation of the catalytic activity with the method of the preparation of the catalysts.

(2) The hydrogenation of 1-butyne, 1:2 butadiene and 1:3 butadiene (isomers of 2-butyne) should be studied over the same catalysts to determine the effect of the structure of the reactant on the catalytic activity.

(3) A study should be made over platinum-copper alloys to find out clearly the role played by d-band holes in catalysis.

(4) The reaction of deuterium with 2-butyne should be studied over the catalysts in order to obtain further information re-

garding the reaction mechanism.

(5) The nature of adsorbed 2-butyne species should be determined by infrared and N.M.R spectroscopy.

(6) The nature of the polymers should be determined if possible.

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APPENDIX A

Properties of the catalysts used

Table 1

Catalyst	Composition	Lattice Structure	Lattice parameter	% d character	d holes
Ni powder	100% Ni	f.c.c.	3.521	40.0	0.6
Ni-Cu alloy	90% Ni	f.c.c.	3.530	39.9	-
Ni-Cu alloy	80% Ni	f.c.c.	3.538	39.5	-
Ni-Cu alloy	70% Ni	f.c.c.	3.543	39.2	-
Ni-Cu alloy	50% Ni	f.c.c.	3.570	38.6	-
Ni-Cu alloy	25% Ni	f.c.c.	3.590	37.3	0.0
Cu powder	100% Cu	f.c.c.	3.610	35.7	0.0
Co powder	100% Co	f.c.c. c.p.h.	3.537 2.502/4.061	39.5	1.7
Fe powder	100% Fe	b.c.c.	2.477	39.7	2.2
Fe pumice	5% Fe			39.7	2.2

f.c.c. face centred cubic   b.c.c. body centred cubic   c.p.h. - closed packed hexagon

APPENDIX A

Properties of the catalysts used

Table 2

Catalyst	Composition	Surface area m^2/gm	Energy of activation k cal/mol.	A min^{-1}/gm	k $min^{-1}/sq\ m$
Ni powder	100% Ni	1.70	9.13	$2.98x10^5$	.1996
Ni-Cu alloy	90% Ni	2.00	6.5	$1.17x10^4$	.3387
Ni-Cu alloy	80% Ni	3.29	7.7	$4.86x10^4$	.2071
Ni-Cu alloy	70% Ni	0.78	7.1	$6.47x10^3$	.1947
Ni-Cu alloy	50% Ni	2.29	9.2	$9.38x10^4$	.0404
Ni-Cu alloy	25% Ni	1.45	8.95	$4.24x10^3$	.0043
Cu powder	100% Cu	0.40	33.5	$4.516x10^{12}$	.000
Co powder	100% Co	-	6.58	$6.61x10^3$	.3389*
Fe powder	100% Fe	-			
Fe pumice	5% Fe	-			

$*min^{-1}/gm.$

APPENDIX B

Table 1. Results for nickel powder catalysts

Weight of the catalyst = 0.0750 gm.
Equivalent weight of metal = 0.05895 gm.

1) Dependence of initial rate (r_o, mm Hg/min) upon initial reactant pressure

$P_{C_4H_6} = 50 \pm 2$ mm

Run No	T°C	P_{H_2}	r_o
1	40.0	52.0	0.45
2		70.0	0.55
3		114.0	0.90
4		136.0	1.05
5		84.0	0.65
6		176.0	1.30
12	54.0	52.0	0.95
13		176.0	2.65
14		90.0	1.50
15		44.0	0.70
16		64.0	1.00
17		110.0	1.70
23	67.0	54.0	1.75
24		120.0	3.00
25		75.0	2.00
26		68.0	1.75
27		38.0	1.00
33	73.0	50.0	1.75
34		72.0	2.45
35		100.0	3.20
36		90.5	3.05
37		30.0	1.30
43	83.0	52.0	2.40
44		61.0	2.90
45		48.0	2.10
46		80.0	3.60
47		71.0	3.30

$P_{H_2} = 50 \pm 1$ mm

Run No	T°C	$P_{C_4H_6}$	r_o
7	40.0	50.0	0.50
8		150.0	0.50
9		105.0	0.52
10		76.0	0.52
11		125.0	0.50
18	54.0	50.0	0.95
19		105.0	0.95
20		130.0	0.88
21		80.0	0.98
22		65.0	0.95
28	67.0	50.0	1.75
29		80.0	1.70
30		105.5	1.55
31		70.0	1.80
32		60.0	1.75
38	73.0	50.0	2.00
39		100.0	1.85
40		78.0	1.95
41		68.0	1.75
42		60.0	2.00
48	83.0	50.0	2.40
49		105.0	1.80
50		85.0	2.00
51		70.0	2.20

Table 1. (cont.)

2) Summary of results

Temp° C	1/T x 10^3 K^{-1}	n	m	k x 10^2 (min^{-1}/gm)	log k
40	3.1948	0.99	0.00	0.80	-2.0969
54	3.0581	0.99	0.00	1.60	-1.7959
67	2.9412	1.00	-0.06	2.70	-1.5686
73	2.8900	0.99	-0.16	3.40	-1.4685
83	2.8085	0.97	-0.31	4.80	-1.3187

E = 9.13 k cal/mol

A = 2.98 x 10^5 min^{-1}/gm

Table 1. (cont.)

3) Product distribution during the course of the reaction

$P_{H_2} = 50 \pm 1$ mm $P_{C_4H_{10}} = 50 \pm 2$ mm   T = 50° C

Run No.	ΔP mmHg	H_2	Pressure of the product stream (mm Hg)				C_4H_6	S
			C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$		
52	30.0	17.0	0.50	0.75	0.50	23.5	20.0	0.930
53	21.0	26.0	0.25	0.50	0.25	20.0	27.0	0.951
54	10.0	37.0	0.00	0.25	0.25	10.0	37.0	0.952

$P_{H_2} = 120 \pm 1$ mm $P_{C_4H_6} = 50 \pm 2$ mm   T = 50° C

Run No.	ΔP mmHg	H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
55	10.0	95.0	0.5	0.5	0.5	6.0	35.0	0.800
56	30.0	80.0	1.5	1.5	0.5	25.5	18.0	0.879
57	46.0	67.5	6.5	1.0	7.0	26.5	10.0	0.646
58	58.0	52.0	18.0	0.5	10.5	14.2	5.0	0.329
59	35.0	77.0	1.0	1.0	1.0	30.8	15.0	0.935
60	20.0	86.~~6~~0	1.0	1.0	0.5	18.0	25.0	0.878

Table 1. (cont.)

4) Effect of initial reactant pressure upon product distribution

$P_{C_4H_6} = 50 \pm 2$ mm Hg $\Delta P = 20$ mm $T = 50^\circ$ C

Run No.	P_{H_2}	H_2	Pressure of the product stream (mm Hg)				C_4H_6	S
			C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$		
61	70.0	45.0	0.75	0.50	0.25	16.5	32.0	.917
62	90.0	60.0	0.25	0.25	0.25	13.5	20.0	.946
63	105.0	73.0	0.50	0.50	0.50	17.5	23.0	.921

$P_{H_2} = 50 \pm 1$ mm Hg $\Delta P = 20$ mm $T = 50^\circ$ C

Run No.	$P_{C_4H_6}$	H_2	Pressure of the product stream (mm Hg)				C_4H_6	S
			C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$		
64	50.0	24.5	0.00	0.50	0.25	17.5	30.0	.948
65	69.0	24.5	0.00	0.50	0.00	16.6	48.0	.985
66	136.0	26.0	0.00	0.25	0.00	13.6	109.0	.982
67	105.0	25.0	0.25	0.50	0.25	17.5	79.0	.945
68	88.0	25.5	0.25	0.25	0.25	16.0	65.5	.985

Table 1 (cont.)

5) Effect of temperature on product distribution

$P_{H_2} = P_{C_4H_6} = 50 \pm 2$ mm $\Delta P = 20$ mm

Run No.	T° C	Pressure of the product stream (mm Hg)					C_4H_6	S
		H_2	C_4H_{10}	1-C_4H_8	t-C_4H_8	C-C_4H_8		
69	50.0	25.0	0.5	1.00	0.75	22.2	25.0	.910
70	60.0	27.5	0.0	0.25	0.00	11.2	26.5	.968
71	80.0	27.0	0.0	0.50	0.25	16.0	31.0	.955

$P_{H_2} = 120 \pm 1$ mm $P_{C_4H_6} = 50 \pm 2$ mm $\Delta P = 20$ mm

Run No.	T° C	H_2	C_4H_{10}	1-C_4H_8	t-C_4H_8	C-C_4H_8	C_4H_6	S
72	50.0	89.0	0.75	1.00	0.75	19.5	30.5	.900
73	60.0	85.0	0.50	0.75	0.25	18.5	31.5	.925
74	70.0	84.0	0.50	0.50	0.50	18.0	27.0	.924
75	80.0	79.0	0.75	0.75	0.75	20.3	23.5	.932

Table 2. Results for 90% Ni, 10% Cu alloy catalyst

Weight of the catalyst = 0.0750 gm.
Equivalent weight of metal = 0.05904 gm.

1) Dependence of initial rate (r_o, mm Hg/min) upon initial reactant pressure

$P_{C_4H_6} = 50 \pm 2$ mm

Run No	T^{o} C	P_{H_2}	r_o
76	40.0	50.0	1.15
77		70.0	1.60
78		100.0	2.25
79		80.0	1.80
80		60.0	1.35
81		40.0	0.90
87	44.0	50.0	1.30
88		91.0	2.40
89		71.0	1.90
90		40.0	1.00
91		61.0	1.60
97	51.0	51.0	1.70
98		70.0	2.25
99		31.0	1.05
100		62.0	2.00
101		41.0	1.35
106	62.0	51.0	2.45
107		29.0	1.38
108		60.0	2.65
109		41.0	1.80
110		21.0	0.95
113	70.0	49.0	2.75
114		59.0	3.25
115	70.0	38.0	2.10
116		30.0	1.65
117		19.0	1.00

$P_{H_2} = 50 \pm 1$ mm

Run No	T^{o}C	$P_{C_4H_6}$	r_o
82	40.0	50.0	1.15
83		40.0	1.20
84		60.0	1.20
85		85.0	1.20
86		120.0	1.20
92	44.0	52.0	1.30
93		75.0	1.50
94		81.0	1.45
95		95.0	1.50
96		31.0	1.55
97	51.0	50.0	1.70
102		30.0	2.10
103		60.0	2.00
104		63.0	2.05
105		84.0	2.00
106	62.0	50.0	2.45
111		70.0	2.45
112		103.0	2.40
113	70.0	50	2.75
118		40	2.85
119	70.0	71.0	2.85
120		105.0	2.85

Table 2. (cont.)

2) Summary of the results

Temp° C	$1/T \times 10^3$ K^{-1}	n	m	$k \times 10^2$ (min^{-1}/gm)	log k
40	3.195	1.00	0.00	2.3	-1.6383
44	3.155	1.01	0.00	2.6	-1.5856
51	3.086	1.04	-0.05	3.2	-1.4948
62	2.986	0.97	-0.04	4.4	-1.3565
70	2.915	1.03	0.00	5.5	-1.2595

$E = 6.5$ k cal/mol

$A = 1.17 \times 10^4$ min^{-1}/gm

Table 2. (cont.)

3) Product distribution during the course of the reaction

P_{H_2} = 50 ± 1 mm $P_{C_4H_6}$ = 50 ± 2 mm T = 50° C

Run No.	ΔP mmHg	Pressure of the product stream (mm Hg) H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
118	40.5	8.5	0.70	1.75	0.50	30.5	9.0	.918
119	31.0	15.5	0.50	1.50	0.50	28.5	16.5	.919
120	20.0	21.0	0.25	0.50	0.25	16.0	22.0	.942
121	14.0	30.5	0.25	0.50	0.00	13.5	31.0	.949
122	7.0	39.5	0.25	0.25	0.00	7.5	39.5	.940
	P_{H_2} = 120 ± 1 mm		$P_{C_4H_6}$ = 50 ± 2 mm			T = 50° C		
123	20.0	86.0	0.50	1.00	0.50	24.0	21.5	.923
124	45.0	66.5	6.50	0.50	6.50	20.5	6.0	.604
125	52.0	58.0	11.00	0.25	10.50	18.0	3.0	.454
126	10.0	94.0	0.50	0.25	0.25	12.0	32.0	.925
127	30.0	77.0	0.50	1.50	0.50	32.0	12.0	.935

Table 2. (cont.)

4) Effect of initial reactant pressure on product distribution

$P_{C_4H_6} = 50 \pm 2$ mm Hg $\Delta P = 20$ mm Hg $T = 50^\circ$ C

Run No.	P_{H_2}	Pressure of the product stream (mm Hg)						
		H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
128	61.0	32.0	0.25	0.50	0.00	16.3	25.0	.956
129	80.0	53.0	0.00	0.75	0.00	16.5	25.0	.945
130	100.0	75.0	0.50	0.75	0.25	21.0	23.0	.935

$P_{H_2} = 50 \pm 1$ mm Hg $\Delta P = 20$ mm Hg $T = 50^\circ$ C

Run No.	$P_{C_4H_6}$	Pressure of the product stream (mm Hg)						
		H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
131	50.0	24.0	0.25	0.50	0.25	15.2	28.0	.938
132	81.0	24.5	0.25	0.25	0.00	13.0	55.0	.963
133	107.0	24.0	0.25	0.25	0.00	13.0	78.0	.963
134	130.0	24.0	0.00	0.25	0.25	11.5	105.0	.960

Table 2. (cont.)

5) Effect of temperature on product distribution

$P_{H_2} = P_{C_4H_6} = 50 \pm 2$ mm Hg $\Delta P = 20$ mm Hg

Run No.	T° C		Pressure of the product stream (mm Hg)					S
		H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	
135	60	24.0	0.25	0.50	0.00	16.0	26.5	.955
136	70	24.0	0.25	0.25	0.25	16.5	28.0	.943
137	80	23.5	0.25	0.50	0.25	15.2	28.0	.938
	$P_{H_2} = 120 \pm 1$ mm Hg			$P_{C_4H_6} = 50 \pm 2$ mm Hg		$\Delta P = 20$ mm Hg		
138	60	93.0	0.50	0.50	0.25	19.0	24.0	.925
139	70	87.0	0.50	0.50	0.50	18.0	22.0	.923
140	80	84.0	1.00	0.50	1.25	14.5	25.0	.840

Table 3. Results for 80% Ni, 20% Cu alloy catalyst

Weight of the catalyst = 0.0750 gm.
Equivalent weight of metal = 0.05914 gm.

1) Dependence of initial rate (r_o, mm Hg/min) upon initial reactant pressure (mm Hg)

$P_{C_4H_6}$ = 50 ± 2 mm Hg

Run No	T° C	P_{H_2}	r_o
141	50.0	45.0	0.90
142		50.0	0.90
143		105.0	2.10
144		85.0	1.70
145		65.0	1.25
146		100.0	2.00
147		75.0	1.50
148		120.0	2.40
153	60.0	50.0	1.60
154		60.0	1.85
155		100.0	3.25
156		90.0	2.90
157		75.0	2.50
158		40.0	1.30
162	77.0	50.0	2.40
163		60.0	2.80
164		65.0	3.20
165		30.0	1.50
166		42.0	2.00
167		75.0	3.90
172	85.0	30.0	2.00
173		50.0	3.15
174		62.0	4.00
175		76.0	6.00
176	85.0	40.0	2.60
177		55.0	3.60
181	95.0	50.0	4.50
182		60.0	5.50
183		20.0	1.90
184		30.0	2.80
185		40.0	3.40
186		55.0	5.00

P_{H_2} = 50 ± 1 mm Hg

Run No	T°C	$P_{C_4H_6}$	r_o
141	50.0	50.0	0.90
149		92.0	0.90
150		130.0	0.85
151		81.0	0.90
152		62.0	0.85
153	60.0	50.0	1.60
159		76.0	1.55
160		125.0	1.55
161		88.0	1.55
162	77.0	50.0	2.40
168		60.0	2.40
169		70.0	2.45
170		94.0	2.40
171		130.0	2.40
173	85.0	50.0	3.15
178		125.0	3.00
179		75.0	3.10
180		98.0	3.10
181	95.0	50.0	4.50
187		64.0	4.50
188		120.0	4.20
189		88.0	4.30

Table 3. (cont.)

2) Summary of the results

Temp° C	1/T x 10^3 K^{-1}	n	m	k x 10^2 (min^{-1}/gm)	log k
50	3.09	1.10	0.00	2.0	-1.696
60	3.00	1.02	0.00	2.9	-1.538
77	2.85	1.00	0.00	4.8	-1.319
85	2.79	1.00	-0.08	6.45	-1.191
95	2.70	1.02	-0.10	9.0	-1.041

E = 7.69 k cal/mol

A = 4.863 x 10^4 min^{-1}/gm

Table 3. (cont.)

3) Product distribution during the course of the reaction

Run No.	ΔP		Pressure of the product stream (mm Hg)					
	mmHg	H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
	P_{H_2} = 50 ± 1 mm Hg			P_{H_2} = 50 ± 2 mm Hg		T = 40° C		
190	25.0	21.0	5.75	1.50	1.50	11.25	25.0	.563
191	15.0	29.0	4.00	0.00	3.50	4.50	31.0	.375
192	20.0	24.5	5.00	0.50	0.50	8.00	30.0	.572
193	10.0	33.0	3.00	0.00	9.00	1.25	34.0	.094
194	30.5	16.0	0.00	1.00	0.75	19.50	23.0	.715
	P_{H_2} = 120 ± 1 mm Hg			$P_{C_4H_6}$ = 50 ± 2 mm Hg		T = 40° C		
195	69.5	48.0	25.5	0.00	6.00	6.50	8.50	.171
196	55.0	59.0	17.0	0.00	8.50	12.00	12.0	.320
197	20.0	91.0	3.0	1.50	1.00	20.50	25.0	.800
198	45.0	67.0	16.2	0.50	6.50	18.50	13.0	.434
199	31.5	77.0	2.5	1.00	2.00	24.0	19.0	.813
200	10.0	101.0	0.5	0.50	0.50	10.5	35.0	.875

Table 3. (cont.)

4) Effect of initial reactant pressure (mm Hg) on product distribution

$P_{C_4H_6} = 50 \pm 2$ mm Hg $\Delta P = 20$ mm Hg $T = 50^{\circ}$ C

Run No.	P_{H_2}		Pressure of the product stream (mm Hg)					
		H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
201	71	44.0	1.25	0.50	1.00	9.50	33.5	.775
202	90	65.5	2.00	0.00	0.00	11.00	32.0	.852
203	105	83.0	2.50	0.00	0.50	13.00	31.0	.812

$P_{H_2} = 50 \pm 1$ mm Hg $\Delta P = 20$ mm Hg $T = 50^{\circ}$ C

Run No.	$P_{C_4H_6}$		Pressure of the product stream (mm Hg)					
		H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
204	71	33.0	0.50	0.50	0.50	10.5	45.00	.875
205	80	30.5	0.50	1.00	0.50	15.0	55.95	.880
206	99	31.0	0.50	1.00	0.50	12.0	69.00	.855
207	84	25.0	0.5	1.00	0.50	20.0	61.00	.908

Table 3. (cont.)

5) Effect of temperature on product distribution

P_{H_2} = 50 ± 1 mm $P_{C_4H_6}$ = 50 ± 2 mm ΔP = 20 mm Hg

Run No.	T° C	Pressure of the product stream (mm Hg)						
		H_2	C_4H_{10}	1-C_4H_8	t-C_4H_8	C-C_4H_8	C_4H_6	S
208	50.0	30.0	0.00	1.00	0.50	14.0	27.0	.905
209	60.0	31.0	0.00	0.50	0.00	13.0	26.5	.965
210	70.0	30.0	0.00	0.50	0.00	1.45	31.0	.965
211	80.0	29.0	0.50	1.00	0.0	15.0	26.5	.909

P_{H_2} = 120 ± 1 mm Hg $P_{C_4H_6}$ = 50 ± 2 mm Hg ΔP = 20

Run No.	T° C	H_2	C_4H_{10}	1-C_4H_8	t-C_4H_8	C-C_4H_8	C_4H_6	S
212	50.0	90.0	8.5	0.00	3.50	9.00	26.5	.425
213	60.0	92.5	7.0	0.00	3.00	8.00	30.0	.445
214	70.0	92.0	5.0	0.50	2.50	6.50	26.5	.446
215	80.0	91.5	5.0	0.00	3.00	6.00	25.0	.428

Table 4. Results for 70% Ni, 30% Cu alloy powder

Weight of the catalysts = 0.0750 gm.
Equivalent weight of the metal = 0.05924 gm.

1) Dependence of initial rate (mm Hg/min) upon initial reactant pressure

$P_{C_4H_6}$= 50 ± 2 mm Hg

Run No	T^o C	P_{H_2}	r_o
216	50.0	50.0	0.25
217		80.0	0.50
218		115.0	0.70
219		100.0	0.60
220		65.0	0.40
221		135.0	0.80
226	60.0	50.0	0.45
227		115.0	1.00
228		60.0	0.50
229		82.0	0.70
230		100.0	0.90
236	70.0	51.0	0.60
237		85.0	1.05
238		119.0	1.30
239		66.0	0.80
240		60.0	0.75
246	75.0	50.0	0.70
247		70.0	1.00
248		84.0	1.30
249		60.0	0.95
250		34.0	0.50
255	81.0	74.0	1.25
256		50.0	0.85
257		34.0	0.65
258	81.0	55.0	0.95
259		64.0	1.10

P_{H_2} = 50 ± 1 mm Hg

Run No	T^o C	$P_{C_4H_6}$	r_o
222	50.0	50.0	0.25
223		82.0	0.25
224		130.0	0.25
225		100.0	0.25
231	60.0	50.0	0.45
232		110.0	0.45
233		85.0	0.40
234		70.0	0.45
235		60.0	0.45
241	70.0	50.0	0.60
242		98.0	0.60
243		115.0	0.60
244		66.0	0.60
245		82.0	0.60
246	75.0	50.0	0.70
251		100.0	0.65
252		115.0	0.65
253		135.0	0.65
254		70.0	0.70
255	81.0	50.0	0.85
260		100.0	0.82
261		145.0	0.80
262	81.0	80.0	0.84
263		64.0	0.84

Table 4. (cont.)

2) Summary of results

Temp° C	$1/T \times 10^3$ K^{-1}	n	m	$k \times 10^2$ (min^{-1}/gm)	log k
50.0	3.09	0.96	0.00	0.63	-2.201
60.0	3.00	1.00	0.00	0.90	-2.046
70.0	2.91	0.98	0.00	1.25	-1.903
75.0	2.88	1.00	-0.03	1.50	-1.824
81.0	2.82	1.00	-0.06	1.70	-1.769

E = 7.1 k cal/mol

$A = 6.47 \times 10^3\ min^{-1}/gm$

Table 4. (cont.)

3) Product distribution during the course of the reaction

P_{H_2} = 50 ± 1 mm Hg $P_{C_4H_6}$ = 50 ± 2 mm Hg T = 70° C

Run No.	ΔP mmHg	H_2	Pressure of the product stream (mm Hg) C_4H_{10}	$1-C_4H_8$	$t-C_4H_8$	$C-C_4H_8$	C_4H_6	S
264	34.5	15.0	1.50	1.00	1.50	26.0	17.0	.865
265	20.0	29.0	1.00	1.00	1.00	14.5	30.0	.850
266	10.0	38.0	1.00	0.25	0.25	8.0	38.0	.894
267	29.0	20.0	0.50	1.00	0.50	16.0	21.5	.889
268	17.5	32.5	0.50	0.50	0.25	12.5	33.0	.909
269	25.0	23.5	0.50	1.00	0.25	17.0	24.5	.878
	P_{H_2} = 120 ± 2 mm		$P_{C_4H_6}$ = 50 ± 1 mm			T = 70° C		
270	20.0	82.0	6.0	0.25	3.0	8.0	29.5	.470
271	51.0	53.0	16.5	0.00	7.5	12.5	9.0	.343
272	40.0	68.0	10.5	0.00	7.0	12.5	14.0	.416
273	30.0	74.0	7.0	0.25	4.5	14.0	25.0	.550
274	10.0	84.0	4.0	0.25	2.5	12.5	33.0	.735

Table 4. (cont.)

4) Effect of initial reactant pressure upon product distribution

$P_{C_4H_6} = 50 \pm 2$ mm Hg $\Delta P = 20$ mm $T = 70^{\circ}$ C

Run No.	P_{H_2}	Pressure of the product stream (mm Hg)						
		H_2	C_4H_{10}	1-C_4H_8	t-C_4H_8	C-C_4H_8	C_4H_6	S
275	60	44.0	0.75	0.50	0.25	13.0	32.5	.914
276	80	61.0	1.50	0.75	0.50	14.0	31.0	.833
277	95	60.0	8.0	0.25	5.00	13.0	18.0	.500
278	105	80.0	5.0	0.25	3.00	8.0	28.0	.492

$P_{H_2} = 50 \pm 1$ mm Hg $\Delta P = 20$ mm $T = 70^{\circ}$ C

Run No.	$P_{C_4H_6}$	Pressure of the product stream (mm Hg)						
		H_2	C_4H_{10}	1-C_4H_8	t-C_4H_8	C-C_4H_8	C_4H_6	S
279	79.5	32.0	0.0	.75	0.0	14.5	55.0	.950
280	62.0	32.5	0.25	0.50	0.25	14.5	39.0	.950
281	135.5	25.0	0.25	1.00	0.25	22.0	95.0	.938
282	95.0	31.5	0.25	0.50	0.25	14.5	70.0	.95
283	110.0	32.0	0.25	0.50	0.25	14.5	85.5	.95

Table 4. (cont.)

5) Effect of temperature on product distribution

P_{H_2} = 50 ± 1 mm $P_{C_4H_6}$ = 50 ± 2 mm ΔP = 20 mm

Run No.	T° C	Pressure of the product stream (mm Hg)					C_4H_6	S
		H_2	C_4H_{10}	1-C_4H_8	t-C_4H_8	C-C_4H_8		
284	50.0	30.0	0.25	0.25	0.25	8.0	25.0	.935
285	60.0	25.0	0.25	1.00	0.25	17.5	22.0	.920
286	80.0	23.0	0.25	1.50	0.25	14.5	25.0	.878
287	90.0	22.5	0.00	0.50	0.00	17.5	22.0	.97
	P_{H_2} = 120 ± 1 mm		$P_{C_4H_6}$ = 50 ± 2 mm		ΔP = 20 mm			
288	50.0	88.5	3.0	0.00	2.0	10.0	24.5	.770
289	60.0	80.0	4.5	0.00	0.25	15.0	22.5	.733
290	80.0	85.5	4.0	0.25	1.50	6.5	25.5	.475
291	90.0	82.5	4.5	0.25	1.50	6.5	20.0	.500

Table 5. Results for 50% Ni, 50% Cu alloy catalyst

Weight of the catalyst = 0.075 gm.
Equivalent weight of the metal = 0.05944 gm.

1) Dependence of initial rate (r_o, mm Hg/min) upon initial reactant pressure

$P_{C_4H_6}$ = 50 ± 2 mm

Run No	T^o C	P_{H_2}	r_o
292	50.0	50.0	0.18
293		124.0	0.45
294		149.0	0.55
295		80.0	0.30
296		99.0	0.40
300	63.0	50.0	0.37
301		124.0	0.95
302		96.0	0.70
303		74.0	0.50
304		60.0	0.45
308	74.0	50.0	0.46
309		130.0	1.30
310		70.0	0.65
311		96.0	0.90
312		80.0	0.75
317	82.0	50.0	0.65
318		89.0	1.20
319		100.0	1.35
320		72.0	0.80
321		40.0	0.52
325	92.0	40.0	0.80
326		51.0	1.00
327		66.0	1.30
328		82.0	1.80
329		60.0	1.20

P_{H_2} = 50 ± 1 mm Hg

Run No	T^o C	$P_{C_4H_6}$	r_o
292	50.0	50.0	0.18
297		70.0	0.18
298		135.0	0.18
299		100.0	0.18
300	63.0	50.0	0.37
305		70.0	0.37
306		130.0	0.37
307		100.0	0.35
308	74.0	50.0	0.46
313		94.0	0.46
314		120.0	0.46
315		76.0	0.46
316		60.0	0.46
317	82.0	50.0	0.65
322		70.0	0.65
323		115.0	0.65
324		90.0	0.65
325	92.0	50.0	1.00
330		150.0	0.94
331		80.0	0.98
332		64.0	1.00
333		120.0	0.96

Table 5 (cont.)

2) Summary of the results

Temp° C	$1/T \times 10^3$ K^{-1}	n	m	$k \times 10^2$ (min^{-1}/gm)	log k
50.0	3.09	1.00	0.00	0.35	-2.455
63.0	2.97	1.04	0.00	0.75	-2.125
74.0	2.88	1.06	0.00	0.95	-2.023
82.0	2.81	1.02	0.00	1.30	-1.886
92.0	2.74	0.96	-0.05	2.00	-1.696

$E = 9.12$ k cal/mol

$A = 9.38 \times 10^4\ min^{-1}/gm$

Table 5. (cont.)

3) Product distribution during the course of the reaction

Run No.	ΔP mmHg	H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
	$P_{H_2} = 50 \pm 1$ mm		$P_{C_4H_6} = 50 \pm 2$ mm Hg			$T = 130^\circ$ C		
			Pressure of the product stream (mm Hg)					
334	10.0	31.5	0.0	0.0	0.0	8.0	3.3	1.000
335	20.0	26.0	0.0	0.25	0.0	17.0	18.5	0.985
336	37.0	10.5	0.0	0.50	0.0	22.5	6.0	0.980
337	30.0	16.0	0.0	0.50	0.0	19.5	10.0	0.975
	$P_{H_2} = 120 \pm 1$ mm		$P_{C_4H_6} = 50 \pm 2$ mm			$T = 130^\circ$ C		
338	20.0	76.0	0.00	0.25	0.0	12.5	11.0	.980
339	40.0	61.0	0.25	0.75	1.5	10.5	2.0	.808
340	47.0	54.0	0.25	0.75	2.0	10.5	1.0	.785
341	30.0	67.0	0.00	0.50	0.25	18.0	5.0	.956
342	10.0	96.0	0.00	0.25	0.00	5.0	25.0	.952

Table 5. (cont.)

4) Effect of initial reactant pressure (mm Hg) upon product distribution

$P_{C_4H_6} = 50 \pm 2$ mm Hg $\Delta P = 20$ mm $T = 130^\circ C$

Run No.	P_{H_2}	Pressure of the product stream (mm Hg)						S
		H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	
343	70.0	36.0	0.0	0.0	0.0	25.0	14.0	1.00
344	90.0	53.0	0.0	0.50	0.0	25.0	12.0	0.980
345	11.5	70.0	0.0	0.25	0.0	10.0	15.0	0.975

$P_{H_2} = 50 \pm 1$ mm Hg $\Delta P = 20$ mm $T = 130^\circ C$

Run No.	$P_{C_4H_6}$	Pressure of the product stream (mm Hg)						S
		H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	
346	71.0	25.0	0.0	0.0	0.0	20.5	3.00	1.0
347	84.0	24.0	0.0	0.0	0.0	17.5	39.9	1.0
348	102.0	24.5	0.0	0.0	0.0	17.5	76.0	1.0
349	123.0	24.5	0.0	0.0	0.0	17.5	90.0	1.0

Table 5. (cont.)

5) Effect of temperature on product distribution

P_{H_2} = 50 ± 1 mm $P_{C_4H_6}$ = 50 ± 2 mm ΔP = 20 mm

Run No.	T° C	Pressure of the product stream (mm Hg)						
		H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
350	54.0	24.0	0.5	1.25	0.25	19.5	20.0	.905
351	65.0	26.0	0.25	0.50	0.25	16.0	26.5	.942
352	88.0	26.5	0.25	1.50	0.00	14.0	26.0	.889
353	100.0	22.0	0.00	0.00	0.00	24.0	7.5	1.00
354	115.0	26.5	0.00	0.00	0.00	13.5	30.0	1.00
	P_{H_2} = 120 ± 1 mm		$P_{C_4H_6}$ = 50 ± 2 mm		ΔP = 20 mm			
355	54.0	86.0	0.50	1.25	0.25	19.5	23.0	.905
356	65.0	85.5	0.25	0.50	0.00	17.5	26.5	.958
357	80.0	87.0	0.00	0.50	0.00	13.2	23.5	.964
358	100.0	84.0	0.00	0.25	0.00	16.5	26.5	.985
359	115.0	85.0	0.00	0.25	0.00	17.0	23.0	.985

Table 6. Results for 25% Ni, 75% Cu alloy catalyst

Weight of the catalyst = 0.2250 gm.
Equivalent weight of the metal = 0.17904 gm.

1) Dependence of initial rate (r_o, mm Hg/min) upon initial reactant pressure

$P_{C_4H_6}$ = 50 ± 2 mm Hg

Run No	T^o C	P_{H_2}	r_o
360	59.0	50.0	0.30
361		120.0	0.55
362		80.0	0.35
363		100.0	0.45
364		65.0	0.30
368	70.0	50.0	0.35
369		100.0	0.65
370		120.0	0.80
371		80.0	0.55
372		65.0	0.45
376	80.0	50.0	0.50
377		100.0	0.95
378		80.0	0.75
379		70.0	0.65
380		120.0	1.10
384	90.0	50.0	0.60
385		120.0	1.35
386		100.0	1.20
387		80.0	0.90
388		65.0	0.75
392	100.0	60.0	1.10
394		50.0	0.90
395		75.0	1.70
396		97.0	2.50
397		40.0	0.70

P_{H_2} = 50 ± 1 mm Hg

Run No	T^o C	$P_{C_4H_6}$	r_o
360	59.0	50.0	0.30
365		150.0	0.30
366		100.0	0.30
367		70.0	0.30
368	70.0	50.0	0.35
373		100.0	0.35
374		70.0	0.35
375		140.0	0.35
376	80.0	50.0	0.50
381		100.0	0.49
382		120.0	0.50
383		84.0	0.50
384	90.0	50.0	0.60
389		70.0	0.60
390		100.0	0.59
391		150.0	0.58
392	100.0	50.0	0.90
398		70.0	0.90
399		90.0	0.88
400		115.0	0.88
401		135.0	0.86

Table 6. (cont.)

2) Summary of the results

Temp^{o} C	1/T x 10^3 K^{-1}	n	m	k x 10^2 (min^{-1}/gm)
59.0	3.012	1.01	0.00	0.45
70.0	2.910	1.01	0.00	0.65
80.0	2.83	0.98	0.00	0.95
90.0	2.75	1.00	-0.02	1.15
100.0	2.68	1.02	-0.06	1.80

E = 8.95 k cal/mol

A = 4.24 x 10^3 min^{-1}/gm

Table 6. (cont.)

3) Product distribution during the course of the reaction

P_{H_2} = 50 ± 1 mm Hg $P_{C_4H_6}$ = 50 ± 2 mm Hg T = 100° C

Run No.	ΔP mmHg	H_2	Pressure of the product stream (mm Hg)				C_4H_6	S
			C_4H_{10}	1-C_4H_8	t-C_4H_8	C-C_4H_8		
402	9.5	38.0	0.0	0.5	0.00	8.5	41.0	.945
403	35.0	6.5	0.0	4.0	0.25	32.5	1.5	.885
404	27.0	13.0	0.0	1.5	0.25	18.5	17.0	.905
405	15.0	27.0	0.0	0.5	0.00	10.0	30.0	.952
406	20.0	20.0	0.0	1.0	0.00	16.0	23.5	.940
	P_{H_2} = 120 ± 1 mm Hg			$P_{C_4H_6}$ = 50 ± 2 mm Hg		T = 100° C		
407	43.0	60.5	0.25	1.50	0.50	33.0	4.50	.925
408	40.0	63.0	0.00	1.50	0.25	30.5	6.0	.940
409	30.0	72.5	0.00	1.00	0.25	25.5	12.5	.925
410	20.0	81.5	0.00	0.50	0.25	19.5	18.5	.960
411	10.0	90.5	0.00	0.50	0.00	12.0	28.0	.96

Table 6. (cont.)

4) Effect of the initial reactant pressure (mm Hg) upon product distribution

$P_{C_4H_6} = 50 \pm 2$ mm Hg $\Delta P = 20$ mm Hg   T = 100° C

Run No.	P_{H_2}	Pressure of the product stream (mm Hg)						S
		H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$c\text{-}C_4H_8$	C_4H_6	
412	60	34.5	0.0	1.0	0.0	15.0	26.5	.935
413	75	51.5	0.0	0.5	0.0	14.5	23.5	.965
414	97	72.0	0.0	0.75	0.25	17.0	18.5	.940

$P_{H_2} = 50 \pm 1$ mm Hg $\Delta P = 20$ mm Hg   T = 100°C

Run No.	$P_{C_4H_6}$	Pressure of the product stream (mm Hg)						S
		H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$c\text{-}C_4H_8$	C_4H_6	
415	65	25.5	0.0	0.5	0.00	12.0	45.0	.96
416	75	24.0	0.0	0.5	0.00	12.0	54.5	.96
417	90	24.5	0.0	0.25	0.25	12.0	69.5	.96
418	107	25.0	0.0	0.50	0.00	12.0	75.5	.96
419	120	25.0	0.0	0.50	0.00	12.5	94.5	.96

Table 6. (cont.)

5) Effect of temperature on product distribution

P_{H_2} = 50 ± 1 mm Hg $P_{C_4H_6}$ = 50 ± 2 mm Hg ΔP = 20 mm

Run No.	T° C	Pressure of the product stream (mm Hg)						
		H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
420	59.0	23.5	0.0	1.0	0.0	18.5	28.0	.95
421	70.0	22.5	0.0	0.5	0.0	18.5	32.5	.97
422	80.0	22.0	0.0	2.0	0.50	13.0	25.0	.935
423	90.0	22.5	0.0	1.0	0.00	1.30	28.0	.93
	P_{H_2} = 120 ± 1 mm			$P_{C_4H_6}$ = 50 ± 2 mm		ΔP = 20 mm		
424	59.0	95.5	0.25	0.75	0.25	19.5	28.0	.94
425	70.0	97.0	0.00	0.50	0.00	18.5	33.0	.97
426	80.0	93.5	0.00	1.00	0.00	14.0	22.0	.935
427	90.0	96.5	0.00	1.00	0.00	17.5	25.0	.935

Table 7. Results for copper powder catalysts

Weight of the catalyst = 1.0000 gm.
Equivalent weight of the metal = 0.7990 gm.

1) Dependence of initial rate (r_o, mm Hg/min) upon initial reactant pressure

$P_{C_4H_6}$ = 50 ± 2 mm Hg

Run No.	T° C	P_{H_2}	r_o	Run No.	T° C	P_{H_2}	r_o
428	200.0	85.0	0.10	433	220.0	50.0	0.35
429		120.0	0.15	434		128.0	0.85
430		150.0	0.20	435		100.0	0.67
431		185.0	0.25	436		65.0	0.50
432		138.0	0.15	437		115.0	0.75
					P_{H_2} = 50 ± 1 mm		
						$P_{C_4H_6}$	
438	230.0	50.0	0.50	438	230.0	50.0	0.50
439		100.0	1.00	443		80.0	0.50
440		150.0	1.65	444		140.0	0.50
441		130.0	1.25	445		100.0	0.50
442		109.0	1.20				
446	240.0	50.0	1.20	446	240.0	50.0	1.20
447		113.0	2.75	451		105.0	1.20
448		100.0	2.45	452		130.0	1.20
449		80.0	1.95	453		67.0	1.25
450		68.0	1.85				
454	250.0	39.0	2.05	455	250.0	50.0	2.05
455		50.0	2.05	459		35.0	2.00
456		108.0	4.00	460		78.0	2.05
457		78.0	3.05	461		107.0	2.05
458		30.0	1.15				

Table 7. (cont.)

2) Summary of the results

Temp^{o}C	1/T x 10^{3} K^{-1}	n	m	k x 10^{2} (min^{-1}/gm)	log k
200.0	2.1141	1.10	-	0.15	-2.8239
220.0	2.0284	0.98	-	0.67	-2.2174
230.0	2.9881	1.01	0.0	1.00	-2.0000
240.0	1.9493	1.00	0.0	2.40	-1.6198
250.0	1.9120	1.00	0.0	3.90	-1.4089

E = 33.5 k cal/mol

A = 4.51 x 10^{12} min^{-1}/gm

Table 7. (cont.)

3) Product distribution during the course of the reaction

P_{H_2} = 50 ± 1 mm Hg $P_{C_4H_6}$ = 50 ± 2 mm Hg T = 240° C

Run No.	ΔP mmHg		Pressure of the product stream (mm Hg)					
		H_2	C_4H_8	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
462	20.0	29.0	0.0	0.0	0.0	4.5	27.5	1.0
463	40.5	15.5	0.0	0.0	0.0	17.5	11.0	1.0
464	10.0	31.5	0.0	0.0	0.0	3.0	33.0	1.0
465	32.0	21.0	0.0	0.0	0.0	12.5	15.0	1.0
	P_{H_2} = 120 ± 1 mm Hg			$P_{C_4H_6}$ = 50 ± 2 mm Hg		T = 240° C		
466	42.5	56.0	0.0	0.50	1.5	31.0	2.5	0.94
467	35.0	63.0	0.0	0.25	0.25	25.0	12.5	0.98
468	25.0	70.0	0.0	0.25	0.00	19.5	16.0	0.987
469	20.0	78.0	0.0	0.25	0.00	16.5	25.0	0.985
470	10.0	91.0	0.0	0.00	0.00	12.5	26.5	1.00

Table 7. (cont.)

4) Effect of initial reactant pressure on product distribution

$P_{C_4H_6} = 50 \pm 2$ mm Hg $\Delta P = 20$ mm Hg $T = 240^\circ$ C

Run No.	P_{H_2}	Pressure of the product stream (mm Hg) H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
471	63.0	38.0	0.0	0.0	0.0	11.0	25.0	1.0
472	83.0	65.5	0.0	0.0	0.0	18.5	22.0	1.0
473	102.0	76.5	0.0	0.0	0.0	14.0	23.0	1.0

$P_{H_2} = 50 \pm 1$ mm Hg $\Delta P = 20$ mm Hg $T = 240^\circ$ C

Run No.	$P_{C_4H_6}$	Pressure of the product stream (mm Hg) H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
474	67.0	17.0	0.0	0.0	0.0	15.5	40.0	1.0
475	88.0	17.5	0.0	0.0	0.0	15.5	54.0	1.0
476	108.0	17.0	0.0	0.0	0.0	15.5	60.0	1.0
477	144.0	18.0	0.0	0.0	0.0	14.5	86.0	1.0

Table 7. (cont.)

5) Effect of temperature on product distribution

$P_{H_2} = 50 \pm 1$ mm $P_{C_4H_6} = 50 \pm 2$ mm $\Delta P = 20$ mm

Run No.	T° C	Pressure of the product stream (mm Hg)						
		H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
478	185	22.0	0.0	0.0	0.0	11.0	26.5	1.0
479	200	21.5	0.0	0.0	0.0	10.0	26.5	1.0
480	230	22.5	0.0	0.0	0.0	11.0	26.5	1.0
481	250	21.5	0.0	0.0	0.0	10.5	21.5	1.0
482	220	20.0	0.0	0.0	0.0	12.5	21.5	1.0
	$P_{H_2} = 120 \pm 1$ mm		$P_{C_4H_6} = 50 \pm 2$ mm			$\Delta P = 20$ mm		
483	185	80.5	0.0	0.0	0.0	10.0	25.0	1.0
484	200	77.0	0.0	0.0	0.0	14.5	21.5	1.0
485	230	81.0	0.0	0.0	0.0	10.0	25.0	1.0
486	250	79.0	0.0	0.0	0.0	12.5	23.0	1.0
487	220	75.5	0.0	0.0	0.0	20.0	20.0	1.0

Table 8. Results for cobalt powder catalyst

Weight of the catalyst = .0750 gm.
Equivalent weight of the catalyst = .0590 gm.

1) Dependence of initial rate (mm Hg/min) upon initial reactant pressure

$P_{C_4H_6}$ = 50 ± 2 mm

Run No	T^oC	P_{H_2}	r_o
487	49.0	50.0	0.75
488		100.0	1.45
489		80.0	1.15
490		62.0	0.90
491		40.0	0.55
492		120.0	1.70
497	60.0	50.0	1.00
498		90.0	1.85
499		70.0	1.45
500		60.0	1.25
501		41.0	0.85
506	69.0	50.0	1.30
507		41.0	1.10
508		58.0	1.45
509		69.0	1.80
510		80.0	2.10
514	80.0	50.0	1.80
515		61.0	2.00
516		70.0	2.50
517		88.0	3.20
518		26.0	1.10
519		40.0	1.45
523	90.0	50.0	2.95
524		60.0	3.50
525	90.0	41.0	1.75
526		31.0	1.35
527		21.0	0.85

P_{H_2} = 50 ± 1 mm

Run No	T^o C	$P_{C_4H_6}$	r_o
487	49.0	50.0	0.75
493		70.0	0.74
494		110.0	0.68
495		125.0	0.75
496		84.0	0.76
497	60.0	50.0	1.00
502		110.0	1.10
503		200.0	0.98
504		75.0	1.00
505		225.0	1.00
506	69.0	50.0	1.30
511		105.0	1.25
512		70.0	1.30
513		88.0	1.30
514	80.0	50.0	1.80
520		78.0	1.80
521		130.0	1.80
522		100.0	1.75
523	90.0	50.0	2.95
528		130.0	2.40
529	90.0	100.0	2.80
530		90.0	2.50
531		80.0	2.60

Table 8. (cont.)

2) Summary of the results

Temp°C	$1/T \times 10^3$ K^{-1}	n	m	$k \times 10^2$ (min^{-1}/gm)	log k
49.0	3.1056	1.00	0.00	1.45	-1.8386
60.0	3.0003	1.00	0.00	2.05	-1.6882
69.0	2.9232	0.97	0.00	2.60	-1.5850
80.0	2.8328	1.00	0.00	3.60	-1.4437
90.0	2.7548	1.01	-0.16	4.30	-1.3665

E = 6.6 k cal/mol

A = 6.608 min^{-1}/gm

Table 8. (cont.)

3) Product distribution during the course of the reaction

	P_{H_2} = 50 ± 1 mm		$P_{C_4H_6}$ = 50 ± 1		T = 90°C			
Run No.	ΔP		Pressure of the product stream (mm Hg)					
	mmHg	H_2	C_4H_{10}	1-C_4H_8	t-C_4H_8	C-C_4H_8	C_4H_6	S
528	20.0	22.5	0.25	1.50	0.25	16.0	26.5	.889
529	15.0	29.0	0.25	1.00	0.25	13.0	33.0	.897
530	7.5	38.0	0.00	0.50	0.00	0.0	39.5	.941
531	25.0	17.0	0.25	1.50	0.25	20.0	23.5	.909
	P_{H_2} = 120 ± 1 mm		$P_{C_4H_6}$ = 50 ± 2 mm		T = 90° C			
532	20.0	72.0	0.50	1.75	0.25	19.5	22.0	.886
533	49.5	46.0	4.50	2.00	13.00	32.5	1.0	.625
534	42.0	57.0	2.00	2.00	4.00	30.0	6.0	.789
535	7.0	81.0	0.50	1.00	0.25	10.0	35.0	.851
536	16.0	74.0	0.75	1.50	0.50	16.0	23.5	.853
537	30.0	60.0	0.75	2.75	0.50	28.0	15.5	.875

Table 8. (cont.)

4) Effect of initial reactant pressure on product distribution

$P_{C_4H_6} = 50 \pm 2$ mm Hg $\Delta P = 20$ mm Hg $T = 90^{\circ}$ C

Run No.	P_{H_2}	Pressure of the product stream (mm Hg)						
		H_2	C_4H_{10}	1-C_4H_8	t-C_4H_8	C-C_4H_8	C_4H_6	S
538	90	56.5	0.50	2.0	0.25	18.5	24.5	.870
539	80	45.0	0.25	0.75	0.00	11.0	26.0	.916
540	70	43.0	0.50	1.50	0.25	16.0	25.0	.877

$P_{H_2} = 50 \pm 1$ mm Hg $\Delta P = 20$ mm Hg $T = 90^{\circ}$ C

Run No.	$P_{C_4H_6}$	Pressure of the product stream (mm Hg)						
		H_2	C_4H_{10}	1-C_4H_8	t-C_4H_8	C-C_4H_8	C_4H_6	S
541	89.0	30.0	0.25	1.50	0.25	16.0	72.0	.935
542	70.0	29.5	0.25	0.75	0.25	12.5	60.0	.935
543	115.0	29.0	0.25	1.50	0.25	16.0	93.5	.935

Table 8. (cont.)

5) Effect of temperature on product distribution

Run No.	T^o C	Pressure of the product stream (mm Hg)						
		H_2	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
	$P_{H_2} = 50 \pm 1$ mm		$P_{C_4H_6} = 50 \pm 2$ mm		$\Delta P = 20$ mm			
544	40.0	30.5	0.25	1.75	0.25	17.5	28.5	.886
545	50.0	30.5	0.25	1.75	0.25	17.5	28.0	.886
546	60.0	29.0	0.25	2.00	0.25	18.5	27.0	.881
547	70.0	29.5	0.50	1.25	0.25	17.5	26.5	.875
548	80.0	28.0	0.50	1.50	0.25	18.5	21.5	.891
	$P_{H_2} = 120 \pm 1$ mm		$P_{C_4H_6} = 50 \pm 2$ mm		$\Delta P = 20$ mm			
549	40.0	92.0	0.75	2.0	0.25	17.0	27.0	.85
550	50.0	90.0	0.75	2.0	0.25	17.0	26.5	.85
551	60.0	86.5	0.75	2.0	0.75	17.0	25.0	.85
552	70.0	80.0	0.50	2.00	0.25	19.5	22.0	.876
553	80.0	76.0	0.75	2.00	0.25	20.0	21.5	.870

Table 9. Results for iron powder catalyst

Weight of the catalyst = 0.200 gm
Equivalent weight of the metal = .13989 gm

1) Dependence of initial rate (r_o, mm Hg/min) upon number of runs (n^1) at R (H_2/C_4H_6) = 1.0

Temperature = 115° C

Run No.	n	r_o	$(r_o)_n/(r_o)_1$	Run No.*	n	r_o	$(r_o)_n/(r_o)_1$
554	1	1.40	1.0	558	1	1.25	1.00
555	2	1.05	0.75	559	2	0.90	0.72
556	3	0.85	0.60	560	3	0.75	0.60
557	4	0.60	0.40	561	4	0.50	0.40
				562	5	0.50	0.40

Temperature = 140° C

Run No.	n	r_o	$(r_o)_n/(r_o)_1$
563	1	2.90	1.00
564	2	2.30	0.79
565	3	1.80	0.62
566	4	1.60	0.55
567	5	1.45	0.50
568	6	1.40	0.48
569	7	1.30	0.45

Temperature = 161° C

Run No.	n	r_o	$(r_o)_n/(r_o)_1$
570	1	4.00	1.00
571	2	3.10	0.775
572	3	2.65	0.662
573	4	2.35	0.587
574	5	2.30	0.575

Temperature = 180° C

Run No.	n	r_o	$(r_o)_n/(r_o)_1$
575	1	3.80	1.0
576	2	3.15	0.83
577	3	2.50	0.66
578	4	2.70	0.71
579	5	2.25	0.59
580	6	2.30	0.60

2) Product distribution at 140° C

P_{H_2} = 50 mm $P_{C_4H_6}$ = 50 mm ΔP = 20 mm

Run No.	Pressure of the product stream (mm Hg)						
	H_2	C_4H_6	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S
581	20.0	0.25	0.25	0.25	19.50	20.50	0.963
582	20.0	0.25	0.25	0.25	19.50	20.50	0.963
583	20.0	0.25	0.25	0.25	19.00	21.00	0.962

* Runs were taken on next day.

Table 10. Results for iron-pumice (5%) catalyst

Weight of the catalyst = .2 gm
Equivalent weight of the metal = .00699 gm

1) Dependence of initial rate (r_o, mm Hg/min) upon number of runs (n^1) at 30° C

$R = (P_{H_2}/P_{C_4H_6} = \frac{30}{50}) = .60$

Run No.	n	r_o	$(r_o)_n/(r_o)_1$
584	1	0.8	1.00
585	2	0.5	0.62
586	3	0.4	0.50
587	4	0.3	0.38

R = (50/50) = 1.0

Run No.	n	r_o	$(r_o)_n/(r_o)_1$
588	1	2.95	1.000
589	2	2.00	0.678
590	3	1.65	0.559
591	4	1.35	0.458
592	5	1.20	0.407
593	6	1.10	0.373

R = (100/50) = 2.0

Run No.	n	r_o	$(r_o)_n/(r_o)_1$
594	1	3.05	1.000
595	2	2.15	0.705
596	3	1.85	0.607
597	4	1.65	0.541
598	5	1.50	0.492

R = (150/50) = 3.0

Run No.	n	r_o	$(r_o)_n/(r_o)_1$
599	1	3.40	1.000
600	2	2.60	0.765
601	3	2.50	0.735
602	4	2.05	0.603
603	5	1.85	0.544

2) Dependence of initial rate (mm Hg/min) upon number of runs (n^1) at R = 1

Temperature = 50° C

Run No.	n	r_o	$(r_o)_n/(r_o)_1$
604	1	2.60	1.000
605	2	1.70	0.654
606	3	1.45	0.558
607	4	1.30	0.500
608	5	1.11	0.423

Temperature = 70° C

Run No.	n	r_o	$(r_o)_n/(r_o)_1$
609	1	7.4	1.000
610	2	5.5	0.74
611	3	4.7	0.635
612	4	4.0	0.540
613	5	3.5	0.473

Table 11. <u>Pressure-time curves obtained over different catalysts</u>

Catalyst	$P_{H_2}/P_{C_4H_6} < 2$	$P_{H_2}/P_{C_4H_6} > 2$
Ni powder	III	III
10% Cu alloy	I	II
20% Cu alloy	I	II
30% Cu alloy	III	III
50% Cu alloy	III	III
75% Cu alloy	III	III
Copper powder	III	III
Cobalt powder	I	II

Table 12. Effect of catalyst composition on reactant recovered, products and polymerization

catalyst composition	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	S	C_4H_6 lost	% P
0	0.0	0.5	0.25	16.0	31.0	.955	0.0	0.0
10	0.25	0.5	0.25	15.2	28.0	.938	3.55	7.17
20	0.5	1.0	0.00	15.0	26.5	.909	4.0	8.51
30	0.25	1.50	0.25	14.5	25.0	.878	4.5	9.57
50	0.25	7.50	0.0	14.0	26.0	.889	5.25	11.41
75	0.0	2.0	0.5	13.0	25.0	.935	7.00	14.89
*100	0.0	0.0	0.0	11.0	26.5	1.000	6.00	13.793
Co	0.5	1.5	.25	18.5	21.5	.891	3.50	7.61
Fe**	0.25	0.25	0.25	19.5	20.5	.963	0.00	0.00

$H_2 = 50 \pm 2 = 46$ mm at room temperature

T = 80° C

$\Delta P = 20$ mms.

* T = 185° C

$C_4H_6 = 50 \pm 2 = 46 \pm 2$ mm at room temperature

** T = 140° C

Table 13. <u>Effect of catalyst composition of reactant recovered products and polymerization</u>

T = 80° C ΔP = 20 mm, H_2 = 120 ± 2 mm, C_4H_6 = 50 ± 5 mm = 46 ± 4.5 at room temperature

catalyst composition	C_4H_{10}	$1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$C\text{-}C_4H_8$	C_4H_6	Selectivity	C_4H_6 lost	% P
0	.75	.75	.75	20.3	23.5	.932	0.0	0.0
10	1.00	.50	1.25	14.5	25.0	.840	3.75	8.1521
20	5.00	0.0	3.0	6.0	25.0	.428	7.00	15.21
30	4.00	0.25	1.5	6.5	25.5	.475	8.75	19.02
50	0.0	0.5	0.0	13.2	23.5	.964	8.88	19.304
75	0.0	2.0	0.0	14.0	22.0	.935	8.00	17.39
100*	0.0	0.0	0.0	19.5	21.5	1.0	7.00	16.092
Co	0.75	2.0	.25	20.0	21.5	.87	1.50	3.26

* T = 185° C

APPENDIX C

Sample Calculation (For 80% Ni, 20% Cu alloy catalyst)

1) Equivalent weight of the metal

Weight of the catalyst taken = .0750 gm.

Weight of nickel oxide in the catalyst = $.075 \times \frac{80}{100}$

Weight of the copper oxide in the catalyst = $.075 \times \frac{20}{100}$

Equivalent weight of the metal

$$= .075 \times \frac{80}{100} \times \frac{58.71}{74.71} + \frac{0.75 \times 20}{100} \times \frac{63.55}{79.55} = 0.05914 \text{ gm}$$

2) Calculation of energy of activation (E)

Using equation 4 and figure 15 B

$$\text{Slope} = \frac{-E}{2.303 \times R} = \frac{-1.040 - (-1.712) \times 10^3}{2.7 - 3.1} = -1.68 \times 10^3$$

$$E = 1.68 \times 1.9872 \times 2.303 \times 10^3 \text{ cal/mol}$$

$$= 7.69 \text{ k cal/mol}$$

3) Calculation of overall rate constant $\bar{k}_{(60)}$ and the frequency factor

From figure 15B at 60° C ($\frac{1}{T} \times 10^3 = 3.0 \text{ K}^{-1}$)

The value of $\log_{10} \bar{k} = -1.553$

Rate constant $\bar{k}$ = 0.028 per min

$$= \frac{0.028}{.05914} = .4743 \text{ per min/gm.}$$

$$= \frac{.4743}{2.29} = .2071 \text{ per min per sq. meter.}$$

$\log_{10}$ = T .67605 = -.32395

$$\log_{10} = \log_{10} A - \frac{E}{2.303\,RT}$$

$$\log_{10} A = -.32395 + \frac{7.69 \times 10^3}{2.303 \times 1.9872 \times 333} = 4.6897$$

$A = 4.863\ \text{min}^{-1}/\text{gm}.$

4) Calculation of selectivity for Run Number 211

Initial hydrogen pressure = 50 mm

Initial 2-butyne pressure = 50 mm

Pressure of the product stream (mm Hg)

C_4H_{10}	1-C_4H_8	t-C_4H_8	C-C_4H_8	C_4H_6
0.5	1.0	0.0	15.0	26.5

$$S = \frac{15.0}{15.0 + 1.0 + 0.5} = \frac{15.0}{16.5} = .909$$

51 mm of C_4H_6 (in the reactor) at 80° C = 47.0 mm at room temperature (24° C).

butyne lost = 47.0 - (26.5 + 1.0 + 0.5 + 15.0)

= 47.0 - 43.0 = 4.0

$$\text{Percent polymerized} = \frac{4.0}{47.0} \times 100 = 8.51.$$