To Father and Mother

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My wife for patiently waiting a long time in silence, while I was working here.

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ABSTRACT

Very little work has been done in the past on the hydrogenation of methyl acetylene using catalysts other than nickel, palladium and platinum metals. The kinetics of the hydrogenation of methyl acetylene have been investigated in a constant volume static system on supported iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum catalysts and unsupported nickel, in order to confirm and extend the previous work and to reconcile the apparent difference in behaviour between the catalyst preparations.

On the basis of the effect of the initial pressures of reactants on the initial rates, the order of reaction with respect to the reactants' initial pressures, the overall rate equations, the dependence of the rate constants upon temperature and the activation energies for various catalysts have been determined. The activation energies for pumice supported iron, cobalt, nickel, rhodium, palladium, iridium and platinum are 14.00, 13.30, 16.75, 8.60, 10.30, 9.15 and 12.85 k cal per mole respectively. The activation energy for nickel kieselguhr catalyst is 13.95 k cal per mole and for unsupported nickel, it varies from 17.16 to 19.99 k cal per mole.

The catalytic activities of the pumice supported metals are:

$$Pt > Pd > Ni > Ir > Rh > Co > Fe > Ru > Os$$

Correlations have been made between the catalytic activity and geometric and electronic structure of metals and also between the Arrhenius parameters.

An extensive study of the product analysis has been made over a nickel-pumice catalyst. The effects of various variables, such as initial pressure of reactants and reaction temperature, have been discussed. A possible mechanism has been proposed.

II INTRODUCTION

Catalysis is now the keystone of the structure of several major chemical industries. These industries at some stage use catalysts for increasing the yield, or getting the desired by-product. As a result of this, heterogeneous catalysis which was designated as an art in the past, has aroused considerable scientific interest in the last 50 years.

The catalytic hydrogenation of unsaturated hydrocarbons is of great theoretical and industrial importance. In the past, the hydrogenation of olefins over group VIII metal catalysts, has been studied by several authors. Though a considerable amount of work has been done on acetylene hydrogenation, the hydrogenation of methyl acetylene, the second one in the acetylene-series, has been much neglected in the past.

The catalytic hydrogenation of methyl acetylene was studied in a static constant volume system, over all the trancition metals of group VIII supported on pumice and also over a number of nickel catalysts, for a wide range of temperatures and reactant ratios.

The object of the detailed study of the catalytic hydrogenation of methyl acetylene was:

(1) to extend previous work on pumice supported nickel, palladium and platinum catalysts with a view to reconciling the apparent differences in behaviour among various catalysts,

(2) to study the behaviour shown by all the metals of the series and to determine their relative activities,

(3) to find if the electronic structure of the metals is related in any way to the catalytic activity, and finally

(4) to find a possible mechanism by studying the detailed product analysis over a pumice-supported nickel catalyst.

III LITERATURE SURVEY

Hydrogenation of unsaturated hydrocarbons is a subject of almost recent study. Three types of hydrogenation reactions - double bond, triple bond and aromatic rings - have been studied. Hydrogenation of double bond is easiest, triple bond is still more difficult and aromatic ring, by far, the most difficult. For hydrogenation of double bond unsaturated hydrocarbons, voluminous work has been reported in literature; more for ethylene and less for propylene. The hydrogenation of acetylenic bonds has been greatly neglected in comparison with the very large volume of work concerning the problems of olefin hydrogenation (1). Reasons for this neglect are not, however, far to seek. The reactions are more complicated, and it is frequently found that acetylenes act as catalyst poision (2). However, a number of papers dealing with the hydrogenation of acetylene have appeared recently. This reaction is very similar to the hydrogenation of methyl acetylene. For this reason, and because of the literature related to the hydrogenation of methyl acetylene being suprisingly very scarce; the literature pertaining to the hydrogenation of acetylene is reviewed first, followed by a review for methyl acetylene.

I. Literature Related to Acetylene

The industrialist's interest in the catalytic hydrogenation of acetylene reviewed here is of quite long standing. Considerable

effort has been devoted to the problems of obtaining high yields of ethylene from acetylene by hydrogenation. Ethylene so obtained is more costly than that produced from the cracking of natural gas. So the method of obtaining ethylene by hydrogenation of acetylene (3) is mostly of theoretical interest, and is only utilized when other sources of ethylene are not available.

Nickel as Catalyst

Sabatier and Senderens (4) observed considerable formation of higher hydrocarbons over reduced nickel powder, at room temperature, in addition to ethylene and ethane. Later investigators (5, 6, 7, 8, 9, 10, 11, 12) reported widely varying yields of these products. Most of them studied the products, without paying much attention to the kinetics of reaction. The differences among the results of these investigators were due to differences in the reaction conditions and difficulties encountered in controlling the variables in a flow system.

For accurate studies and greater control, Sheridan (13) employed a static system. The overall initial rate equation at 79° C over a nickel-pumice catalyst was

$$r_o = k\,(P_{H_2})^1\,(P_{C_2H_2})^0 \qquad (1)$$

where r_o = initial rate, mm. Hg., per minute

k = overall rate constant, per minute

P_{H_2} = initial pressure of hydrogen, mm. Hg.

and $P_{C_2H_2}$ = initial pressure of acetylene, mm. Hg.

He also found that for equimolar mixtures of reactants, the ratio of ethylene to ethane in the product was about six. Using hydrogen in excess, dePauw and Jungers (14) found the kinetics of the form

$$r_o = k (P_{H_2})^1 (P_{C_2H_2})^{-0.5} \qquad (2)$$

While Bond (15) reported a "two rate expression" over a nickel-pumice catalyst, Bond and Mann (16) confirmed the earlier findings of Bond (15) over various nickel catalysts and nickel powders.

Palladium as Catalyst

Palladium-Silica catalyst was employed in Germany during World War II for the production of ethylene from acetylene (3). Sheridan (17) found an activation energy, E, of about 12 kcal. per mole over palladium-pumice catalyst. Tamaru (18) reported the hydrogenation of acetylene over palladium-catalyst, taking place in two distinct steps. Bond, Dowden and Mackenzie (19) studied the hydrogenation of acetylene over a palladium-alumina catalyst, and found that the selectivity of the reaction (ratio of ethylene to ethylene plus ethane formed in the product)

could be increased to more than 96% by using greater than two fold excess of hydrogen over acetylene.

Platinum as Catalyst

Over platinum-pumice catalyst at 73°C, Sheridan (20) reported the kinetics of reaction as

$$r_o = k\,(P_{H_2})^{1.2}\,(P_{C_2H_2})^{-0.7} \qquad (3)$$

Over platinum-alumina catalyst, the selectivity was 0.86 (19).

Cobalt as Catalyst

Sabatier and Senderens (21) found that cobalt was active above 180°C and the main product was ethane. Sheridan (17) reported that the reaction orders were similar to nickel. Rapid deactivation of the catalyst prevented systematic study. Bond and Mann (22) investigated the kinetics of reaction over cobalt-pumice and cobalt-powder. In each case, they obtained the rate expression:

$$r_o = k\,(P_{H_2})^{1}\,(P_{C_2H_2})^{0} \qquad (4)$$

Rhodium as Catalyst

Sheridan and Reid (23) studied the reaction at 50° - 100°C over rhodium-pumice catalyst. The reaction orders were similar to those for nickel-pumice catalyst. The selectivity was 1.0 (19).

Iridium as Catalyst

Sheridan and Reid (23) found that the iridium-pumice catalyst had a smaller but distinct activity at about 175° C. The orders of reaction were similar to those over rhodium. Iridium catalyst became deactivated fast. The high yield of ethane, over partially deactivated catalyst, indicated a poor selectivity.

Iron as Catalyst

Using iron-pumice catalyst, Sheridan (17) investigated the reaction orders, which were similar to those over nickel. Reaction orders, determined by Bond and Mann (22), were in agreement with Sheridan's results.

Ruthenium as Catalyst

Sheridan and Reid (23) investigated the reaction over a ruthenium-pumice catalyst. They found that the reaction was very slow, even at 288° C. According to them the extremely small catalytic activity was due to its being poisoned rapidly.

Osmium as Catalyst

The behaviour of osmium-pumice catalyst was similar to the ruthenium-pumice catalyst, except that the former was slightly more active (23).

II. Literature Related to Methyl acetylene

Although catalytic hydrogenation of acetylene on group VIII metals has been studied by several investigators during last fifty years, there appears to be only one published report on methyl acetylene hydrogenation (24) over pumice supported nickel, palladium and platinum catalysts. The orders of reaction were first and zero with respect to hydrogen and methyl acetylene. The overall apparent activation energies were 14.2, 16.5 and 17.3 k cal. per mole respectively. A careful search of the literature revealed no further information. In view of lack of data reported on the kinetics of methyl acetylene hydrogenation, a detailed investigation, over all the metals of group VIII supported on pumice and a number of nickel catalysts, was undertaken.

IV EXPERIMENTAL

I. Apparatus

Experiments were carried out in a static system at constant volume, in a cylindrical Pyrex vessel, connected to a standard high vacuum system.

The apparatus consisted of four main sections: (i) a section for the purification, storage and exhaust of hydrogen, (ii) a section for the purification, storage and exhaust of methyl acetylene, (iii) a section for the study of the kinetics of hydrogenation reaction and (iv) a section for the analysis of the reaction products. A view of the apparatus is shown in Figure 1. Figure 2 is the schematic drawing of the apparatus.

(1) Hydrogen Section:

The hydrogen section consisted of a hydrogen cylinder connected to a 145 mm. long, 25 mm. O.D. glass thimble. It contained 20 gms of palladium-asbestos (5% palladium) catalyst, supplied by the Fisher Scientific Co., Ltd. The tube containing the catalyst was surrounded by an electric furnace whose temperature could be controlled to $\pm$ 1° C. The hydrogen then passed through a trap kept at liquid nitrogen temperature before being collected in a conventional 5 litre reservoir.

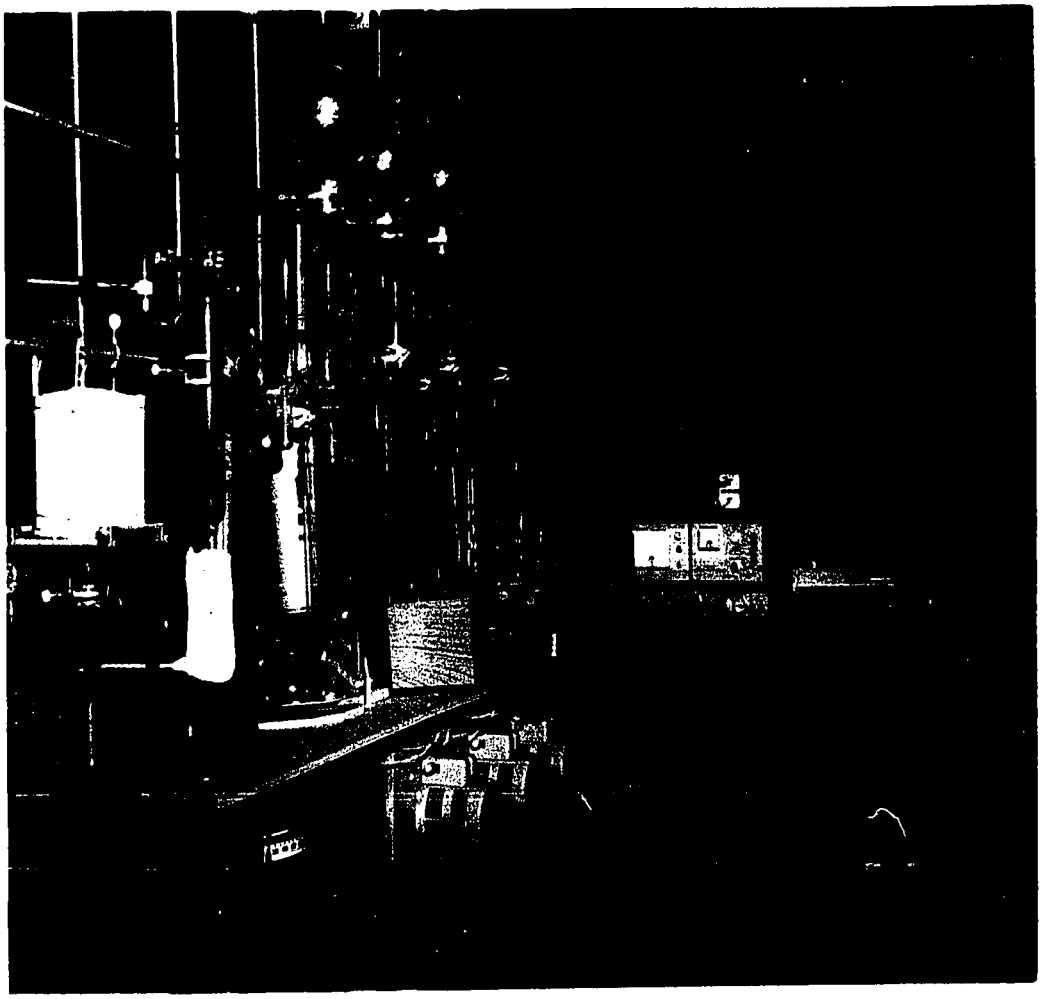


Fig. 1 View of the experimental apparatus

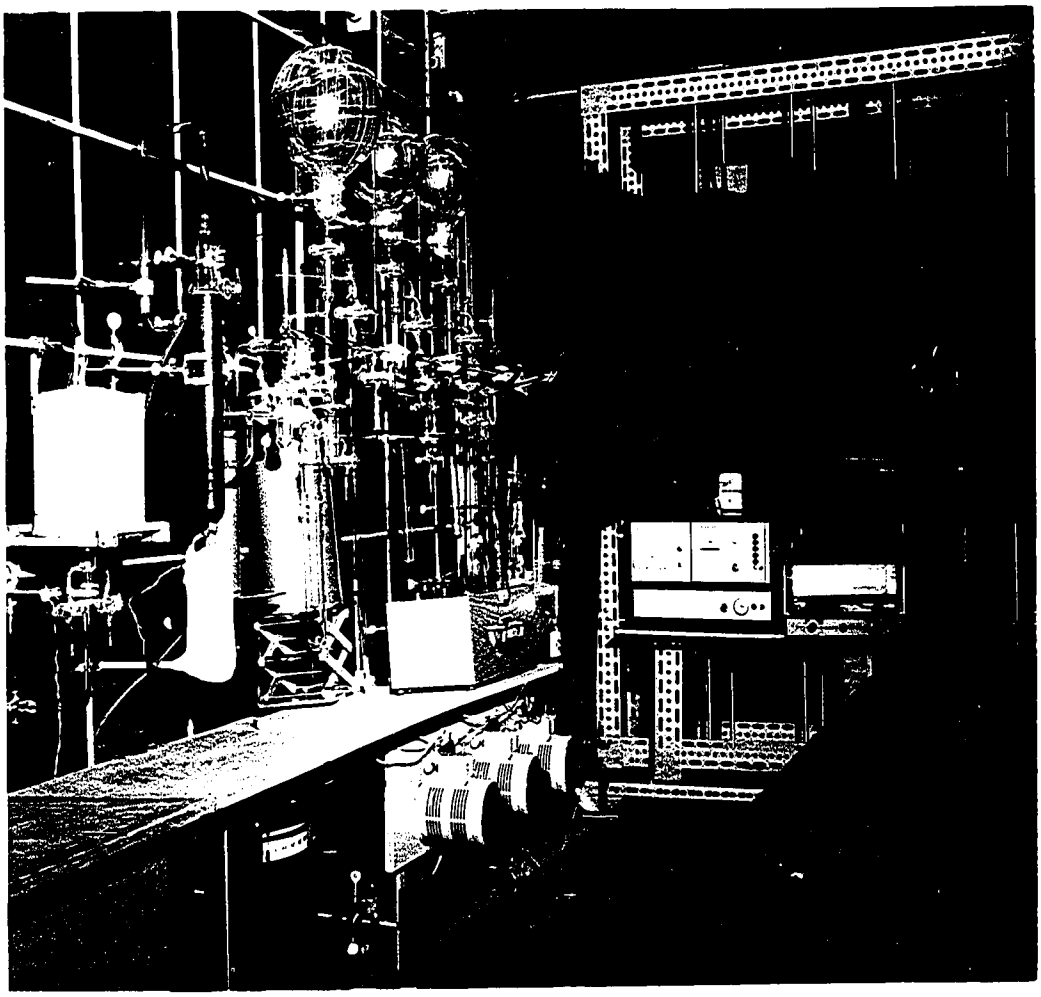


Fig. 1 View of the experimental apparatus

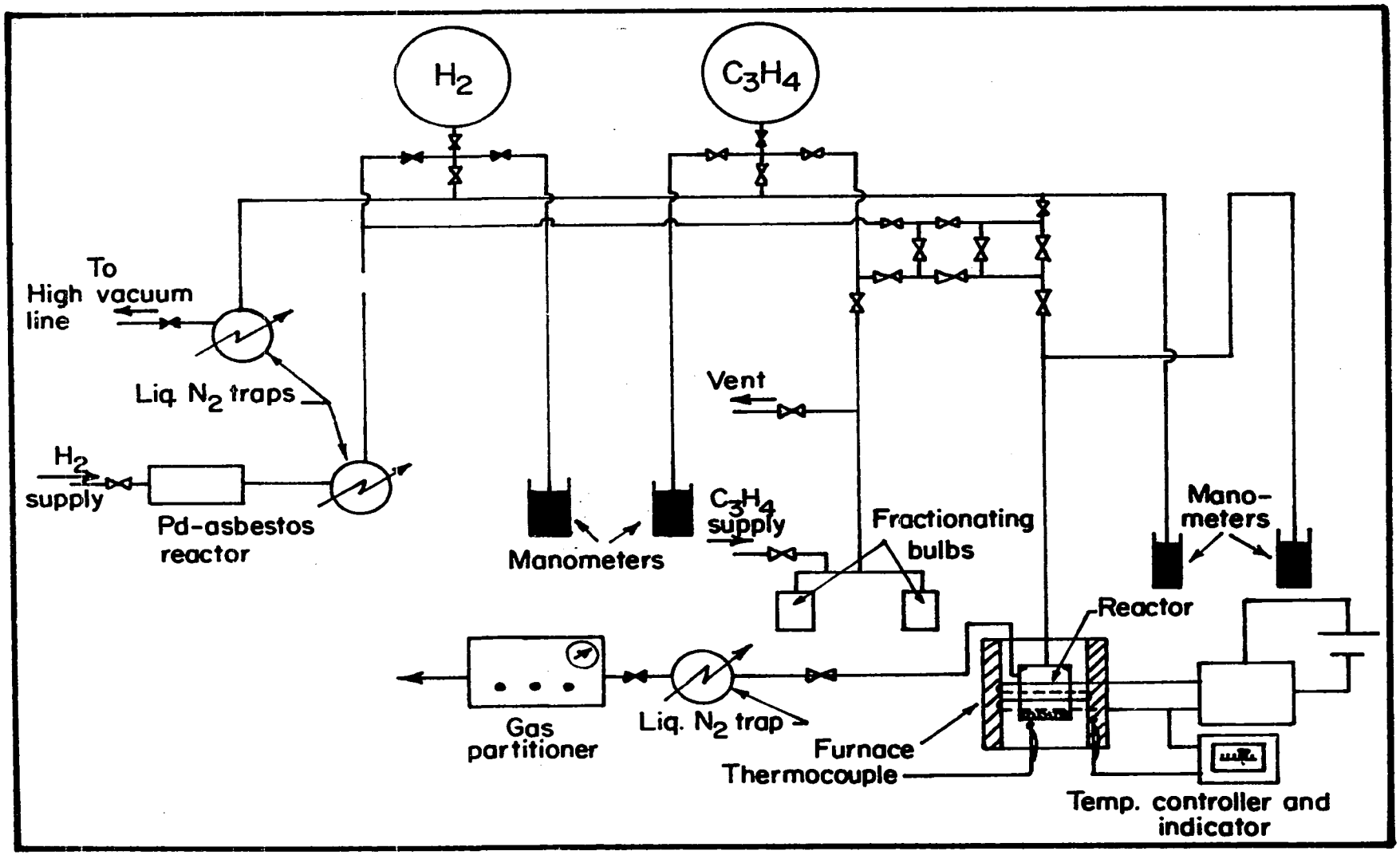


Fig. 2 Flow diagram of the experimental apparatus

(2) Methyl acetylene Section:

The methyl acetylene section consisted of a cylinder of methyl acetylene connected to a tube containing anhydrous silica gel and then to a system of two small traps. Methyl acetylene was purified by fractional distillation and stored in a 3 litre spherical reservoir.

(3) Reactor Section:

The reactor section was connected to hydrogen and methyl acetylene sections through 2 mm. Pyrex capillary tubes and stop cocks, wherever necessary. The cylindrical Pyrex reaction vessel was so designed as to keep the dead space to a minimum. It had a capacity of 86 ml. and was attached to a mercury manometer which measured the decrease in pressure as a function of time. A high temperature tubular furnace surrounded the reactor. The furnace was heated by nichrome wires, wrapped on the outside lower section of a ceramic tube. The reactor temperature was controlled by a Honeywell Pyr-O-Vane temperature indicator and controller, coupled with a variac, and actuated by an iron-constantan thermocouple located inside the furnace, next to the wall of the reactor. The temperature of the catalyst lying at the bottom of the reaction vessel was measured by placing the iron-constantan thermocouple, at the bottom of the reactor.

The main vacuum system, capable of an ultimate vacuum of 5×10^{-6} mm. Hg., consisted of a mercury diffusion pump and a Duo Seal Vacuum pump in series.

(4) Product Analysis Section:

The analysis section consisted of a Model 25 Gas Partitioner and a one millivolt Recorder, both supplied by the Fisher Scientific Co., Ltd. The reaction products from the reactor were transferred to a liquid nitrogen trap, evacuated previously. Later the products were removed and injected into the Gas Partitioner, by means of a gas sampling valve. The pressure of each gas in the product stream was recorded by the Recorder.

II Purification of Reactants

(1) Hydrogen:

The minimum hydrogen content of Linde hydrogen gas cylinder used was 99.8%. It contained less than 10 ppm of water and less than 10 ppm of oxygen. The rest of the impurities were nitrogen and argon and had no effect over the reaction. The water and oxygen contents of the hydrogen gas were removed by passing it at a very slow rate (10 ml. per minute) over palladium-asbestos catalyst at 200° C. The oxygen in the hydrogen was thus converted to water. The purified dry hydrogen was stored in a five-litre reservoir. The hydrogen was kept in the reservoir for not more than 15 days, when it was pumped

out and a new batch purified and collected in the reservoir.

(2) Methyl acetylene:

Research grade methyl acetylene supplied by the Matheson of Canada Ltd. was purified by passing through a glass tube containing anhydrous silica gel, at a rate of 10 ml. per minute. It was then condensed in one of the two traps by means of liquid nitrogen. The gas was released on gentle warming. The head and tail fractions were rejected and the middle fraction condensed in the second trap by dry ice. In doing so, the undesirable impurities like water and acetylene were removed. The second trap was warmed and the middle fraction containing pure dry methyl acetylene was collected and stored in the 3 litre reservoir. Methyl acetylene, like hydrogen, was kept in the reservoir for not more than 15 days.

III Preparation of Catalysts

The kinetics of the catalytic hydrogenation of methyl acetylene were investigated over transition metals of group VIII, supported on pumice and a number of supported and unsupported nickel catalysts.

(1) Supported Catalysts

As the catalytic components were very active, "a low-area carrier", i.e., pumice was selected. It was necessary to obtain kinetic data under such conditions that the effectiveness factor of catalytic

particles, E_A, (25) would approach unity. This was accomplished by decreasing the particle size and using catalyst with large and well-connected pores. The use of pumice, an inert porous support of 20-40 mesh size and low surface area (26, 27) ruled out the possibility of diffusion in the pores controlling the reaction rate.

All the pumice supported catalysts were prepared in a similar fashion by a slightly modified Ciapetta and Plank technique (28).

Two to five mm. diameter pumice granules, supplied by the Fisher Scientific Co., Ltd., were crushed and 20 - 40 mesh sizes selected for catalysts' support. The pumice granules were next boiled for 30 minutes in concentrated hydrochloric acid to expel the trapped air and to clean the surface. They were washed with warm distilled water several times till silver nitrate solution gave no precipitate, indicating that chloride ions were completely removed. The pumice stones were dried, thereafter. They had no effect on reactants at 350° C.

All the pumice supported catalysts contained 10% of metal by weight. They were prepared by impregnating and evaporating solutions containing the calculated weight of analar grade chemicals, in the presence of pumice. While iron, cobalt and nickel catalysts were prepared from their nitrates, ruthenium, rhodium, palladium and platinum catalysts were prepared from their chlorides. These

chemicals were obtained from the Fisher Scientific Co., Ltd. Iridium catalyst was prepared from iridic ammonium chloride, supplied by K and K Laboratories, Inc. Osmium catalyst was prepared from acid osmic, supplied by Fisher Scientific Co., Ltd.

The impregnated material was dried at 105° C for 15 hours and then calcined at 600° C in a muffle furnace for 6 hours.

Nickel kieselguhr catalyst was supplied by Chemetron, Louisville and contained 50% nickel by weight.

A known amount of supported catalyst was always placed inside the reactor. The catalyst was activated by reducing it in a 20 ml. per minute stream of hydrogen for 24 hours, at 400° C.

(2) Metallic powder Catalysts

(i) Nickel powder (I) - This was prepared by heating a known amount of nickel-oxalate, supplied by K and K Laboratories, Inc., at 400° C in reaction vessel in situ for 2 hours followed by reduction in a stream of purified hydrogen for 24 hours.

(ii) Nickel powder (II) - This was prepared from Analar grade nickel-nitrate, supplied by Fisher Scientific Co., Ltd. A known amount of nitrate was heated at 400° C in reaction vessel in situ for 2 hours, followed by reduction in a stream of purified hydrogen for 24 hours.

(iii) Nickel powder (III) - Basic nickel carbonate was coprecipitated from a solution containing known amount of nickel nitrate, in presence of ammonium hydrogen carbonate. The resulting precipitate was dried at 105°C for 15 hours and calcined at 600°C for 6 hours. A known amount of it was reduced in the reaction vessel at 400°C for 24 hours, in a 20 ml. per minute stream of purified hydrogen.

IV General Reaction Procedure

The reactor containing the reduced catalyst was heated at the required temperature and evacuated, till a hard vacuum was obtained. After hydrogen was admitted into the reactor, the connecting lines between the reaction vessel and storage vessels were evacuated by pumping for 3 minutes. The second reactant, methyl acetylene, was then admitted. Soon after the admission of the second reactant, the rate of reaction was followed by measuring the change in pressure, as indicated by a mercury manometer with time. After completion of each run, the reaction vessel was evacuated for 10 minutes. At the end of a series of runs, the catalyst was left over usually in 100 mm. of hydrogen, until the next series of runs were performed.

The initial hydrogen pressure, P_{H_2}, was varied in the range of 15 - 180 mm. and the initial pressure of methyl acetylene, $P_{C_3H_4}$, was maintained at 30 mm. Generally the time was noted

until the pressure change in the manometer, -dP, was equivalent to the initial pressure of methyl acetylene. The runs were made at random in order to nullify any effects due to changes in the catalyst activity. The change of temperature during the reactions was within $\pm$ 0.1°C. All the runs at a particular temperature were completed on the same day. The catalyst was found to be initially very active and reached a constant value after 3 - 4 runs.

Runs were taken at 5 different temperatures, generally, in 5 successive days. This series allowed a determination of hydrogen pressure dependency. A similar series of runs were made to determine methyl acetylene pressure dependency, where initial methyl acetylene pressure, $P_{C_3H_4}$, was varied, keeping initial hydrogen pressure, P_{H_2}, generally constant at 60 mm.

V. Analysis of Products

A series of reactions were carried out on a nickel-pumice catalyst and the products were analyzed by means of a Model 25 Fisher Gas Partitioner.

The Gas Partitioner was set on top of a Model 27 Fisher Thermal Stabilizer which regulated the temperature within the Partitioner sufficiently well to eliminate fluctuations due to changes in ambient temperature. The temperature of the Thermal Stabilizer was maintained at 50°C. The Gas Partitioner employed two columns, connected

in series. Column 1 was 12' long and was packed with 30% hexamethyl phosphoramide (HMPA) on 60 - 80 mesh Fisher Columpak. Column 2 was 13' long and was packed with activated 13X Molecular Sieve. Push-button controls of the Partitioner enabled the change in the sensitivity of the instrument at will. The Partitioner was used in conjunction with a one millivolt Fisher Laboratory Recorder. By adjusting the chart speed, sharp and narrow peaks for all the gases were obtained. The compositions of various gases, with an accuracy of $\pm$ 0.2%, were determined by measuring the peak heights.

The selection of a carrier gas, for the analysis of gaseous mixtures of propane, propylene, methyl acetylene and hydrogen, proved a very arduous and complicated task. Although argon and nitrogen gave high sensitivity for hydrogen, their sensitivity with propane and methyl acetylene were low and non linear as the thermal conductivities of argon and nitrogen were very near to those of the two hydrocarbons. Although the thermal conductivity of helium was much different from all the hydrocarbons, yet the analysis of hydrogen presented a very complicated problem.

At higher concentrations of hydrogen, Madison (29) obtained a negative and sometime a double peak. Pietsch (30) and Schmauch and Dinerstein (31) found that such a problem could be solved by adjusting the size of the sample loop and flow rate of helium and thereby keeping

the concentrations of hydrogen very low in comparison to helium.

With a volume of the sample loop as 5 ml. and a flow rate of helium as 83 ml. per minute, a positive linear peak was obtained for hydrogen.

Calibration curves for propane, propylene and methyl acetylene are given in Figure 3. Figure 4 gives the calibration curve for hydrogen. A typical analysis of products (Run Number 458) is given in Figure 5.

V RESULTS OF KINETIC STUDIES

The experimental data, obtained for the catalytic hydrogenation of methyl acetylene over various catalysts, are given in appendix B. The pressures were measured with the manometer with an accuracy of $\pm$ 0.5 mm. Hg.

Kinetic studies of the hydrogenation reaction over each catalyst involved three distinct steps:

I. Shape of pressure-time curves

Over a nickel-pumice, for acetylene hydrogenation, Bond (15) found that the kinetic form of pressure-time curves depended on

(i) the initial hydrogen: acetylene ratios,

(ii) the order of admission of reactants, if added separately, and (iii) the pretreatment of the catalyst, if the reactants were added together.

He classified the observed types of pressure-time curves as follows:

Type I: zero-order reaction, the rate being constant up to a pressure fall about equal to the initial acetylene pressure. Such curves were observed when acetylene was admitted first, provided that the initial hydrogen: acetylene ratios were greater than about two.

Type IIA: a broken curve, consisting of two linear portions of different rates. The inflexion occurred after a pressure fall equal to about one-half of the initial acetylene pressure. The initial hydrogen: acetylene ratios were always greater than about two and type IIA curves were obtained, only when a premixture was used and if there had been a hydrogen pretreatment before the first run, or if excess of hydrogen had remained from the previous experiment.

Type IIB: a broken curve, consisting of a curved portion (order greater than zero) followed by a linear (zero order) portion. Such curves were obtained when the initial hydrogen: acetylene ratios were greater than two and hydrogen was admitted first into the reaction vessel. The break occurred after a pressure fall equal to about one-half of the initial acetylene pressure.

Type IIC: as type IIA, but with the inflexion occurring after a greater percentage reaction. The inflexion occurred after a pressure fall equal to about five-sixths of the initial acetylene pressure. Type IIC curves were obtained with the premixture following acetylene treatment for 10 minutes. However, the initial hydrogen: acetylene ratios were greater than two.

Type III: first-order reaction in hydrogen. Such curves were obtained with initial hydrogen: acetylene ratios less than about two. Acetylene was admitted first into the reaction vessel.

Examples of various pressure-time curves are shown in Figure 6.

For methyl acetylene hydrogenation, the pretreatment of each catalyst remained the same and the reactants were added separately. The pressure-time curves for different initial hydrogen: methyl acetylene ratios were studied for each catalyst.

II. Overall rate equations

A surface reaction between two substances involves, interaction between two adsorbed molecules, the adsorption occurring on neighbouring surface sites (32). For reaction occurring between reactants A and B, whose initial pressures are P_A and P_B respectively, the overall initial rate equations could be written as

$$r_o = k (P_A)^x (P_B)^y \qquad (5)$$

where x and y are order of reaction with respect to A and B respectively. For hydrogenation of methyl acetylene, equation 5 could be written as

$$r_o = k (P_{H_2})^x (P_{C_3H_4})^y \qquad (6)$$

In this work, the overall initial rate equations of the form of equation 6 were found out for each catalyst.

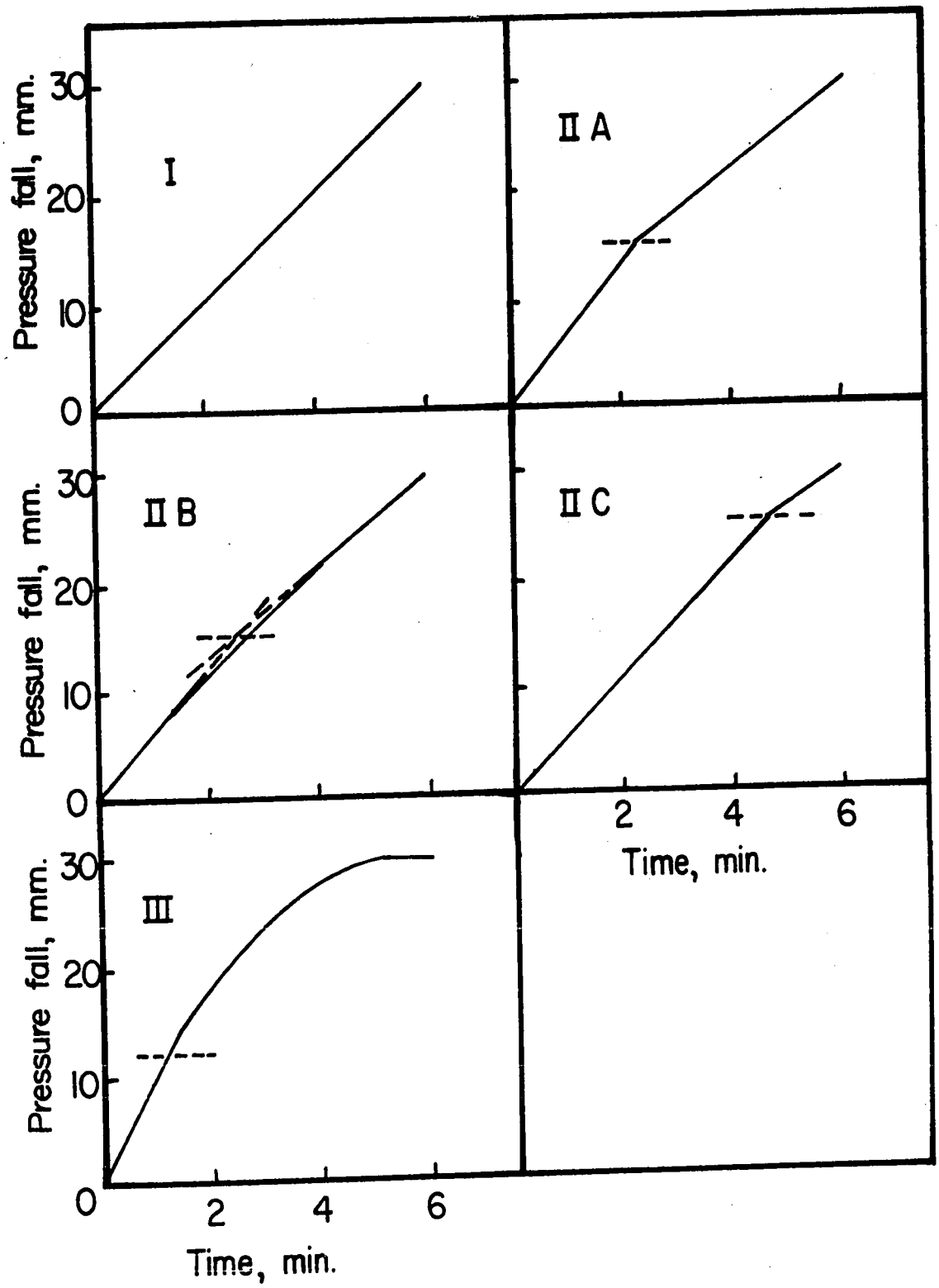


Fig. 6 Examples of various pressure-time curves

III. Activation Energies

The temperature variation of the rate constant is related to the activation energy by the Arrhenius equation (33)

$$k = A \exp. (-E/RT) \qquad (7)$$

where k is the rate constant at T °K,
A and E are parameters, which are assumed to be constants for a given reaction. Arrhenius considered that the activation energy, E, represented the energy difference between the reactants and an activated species, presumably a tautomer, which has a structure intermediate between those of the reactants and products, but has a weakness in a particular vibration leading to its decomposition (34), although in many ways it is a normal molecule. Activation energy is the minimum energy difference between the reactants and the transition state and is generally called as the height of the energy barrier opposing the reaction. System whose energy is greater than the activation energy can surmount the barrier.

Application of the above concept for a Boltzmann distribution of energies leads to the exponential form in which E occurs in the Arrhenius equation. The pre-exponential factor A is a constant of integration in the differential form of the Arrhenius equation:

$$d (\log_e k)/dT = E/RT^2 \qquad (8)$$

A is often divided into a true collision number Z multiplied by a probability factor P. Equation 7 involves the assumption that the activation energy does not vary with temperature. The activation energy is a thermodynamic quantity which should vary with temperature just as the heat of reaction does (35) and so equation 7 is at best but a good approximation. Deviations are quite small for gas phase reactions (36); only in a few instances they are readily detectable and hence the use of equation 7 is justified.

In methyl acetylene hydrogenation, using equation 7, when $\log_{10} k$ was plotted against 1/T, invariably a straight line of gradient $-E/2.303R$ was obtained for each catalyst. Within the particular range of temperature employed, no detectable deviation was observed. Activation energy, E, was calculated from the slopes of the plots of $\log_{10} k$ against 1/T. The kinetic behaviour of each catalyst is described below, in detail for nickel pumice, and briefly for others.

1) Nickel-pumice catalyst

Experimental data obtained for the hydrogenation of methyl acetylene over pumice supported nickel catalysts are given in Table 1.

The reaction had a measurable rate at 50° C. When the catalyst attained a constant activity, the series of runs were taken.

The shape of pressure-time curves observed at 88° C, for initial hydrogen: methyl acetylene ratios, $\overline{R}$, of 1, 2 and 3 are shown in Figure 7. They resembled type IIA curves obtained by Bond (15) for acetylene hydrogenation. The slope of the first linear curve gave initial rate, r_o.

The reaction order with respect to hydrogen was obtained by using a constant initial methyl acetylene pressure and varying the hydrogen pressures, to give hydrogen: methyl acetylene ratios between 1 and 6, at 5 different temperatures between 50° and 88° C. The reaction order with respect to methyl acetylene was similarly obtained by using a constant initial hydrogen pressure and varying methyl acetylene pressures. Rewriting equation 6,

$$r_o = k (P_{H_2})^x (P_{C_3H_4})^y$$

as

$$\log_{10} r_o = \log_{10} k + x \log_{10} P_{H_2} + y \log_{10} P_{C_3H_4} \qquad (9)$$

it would be seen that the orders of reaction, x and y, could be obtained by keeping the initial pressure of one reactant constant and varying the other. The logarithmics of the reaction rate constants were then calculated at different temperatures.

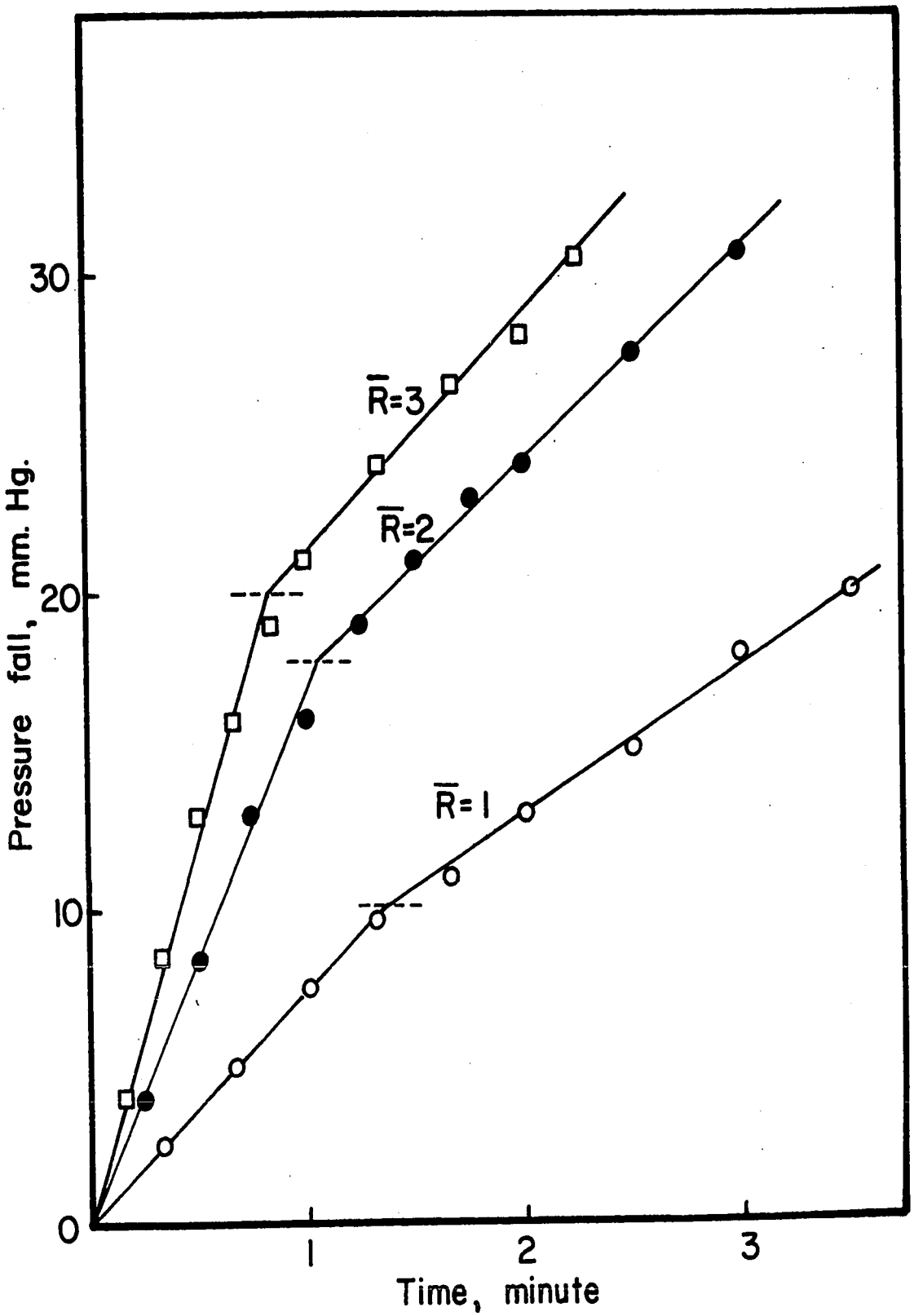


Fig. 7 Pressure-time curves over nickel-pumice at 85° C

The initial rate dependence on the initial hydrogen pressure and methyl acetylene pressure at 80°C is shown in Figure 8. For nickel pumice catalyst, the order of reaction with respect to hydrogen was 1.14 ± 0.02 and with respect to methyl acetylene zero. The overall initial rate was represented by the equation

$$r_o = k (P_{H_2})^{1.14 \pm 0.02} (P_{C_3H_4})^0 \qquad (10)$$

Methyl acetylene was more strongly adsorbed than hydrogen.

The Arrhenius plot of $\log_{10} k$ against $1/T$ for the reaction between the temperature range of 50° - 88°C is given in Figure 9. An activation energy of 16.75 k cal. per mole was obtained from the slope of the line. A sample calculation is given in appendix D.

2) Nickel kieselguhr catalyst

This catalyst was much more active than nickel-pumice, due to large difference in crystalline size (16). The reaction appeared fast even at room temperature.

The kinetics were studied from 5° to 48°C. The experimental data obtained are given in Table 2. The pressure-time curves were similar to those obtained for nickel-pumice. The orders of reaction with respect to both the reactants were determined from the influence of initial pressures on initial rates. Figure 10 shows the effect

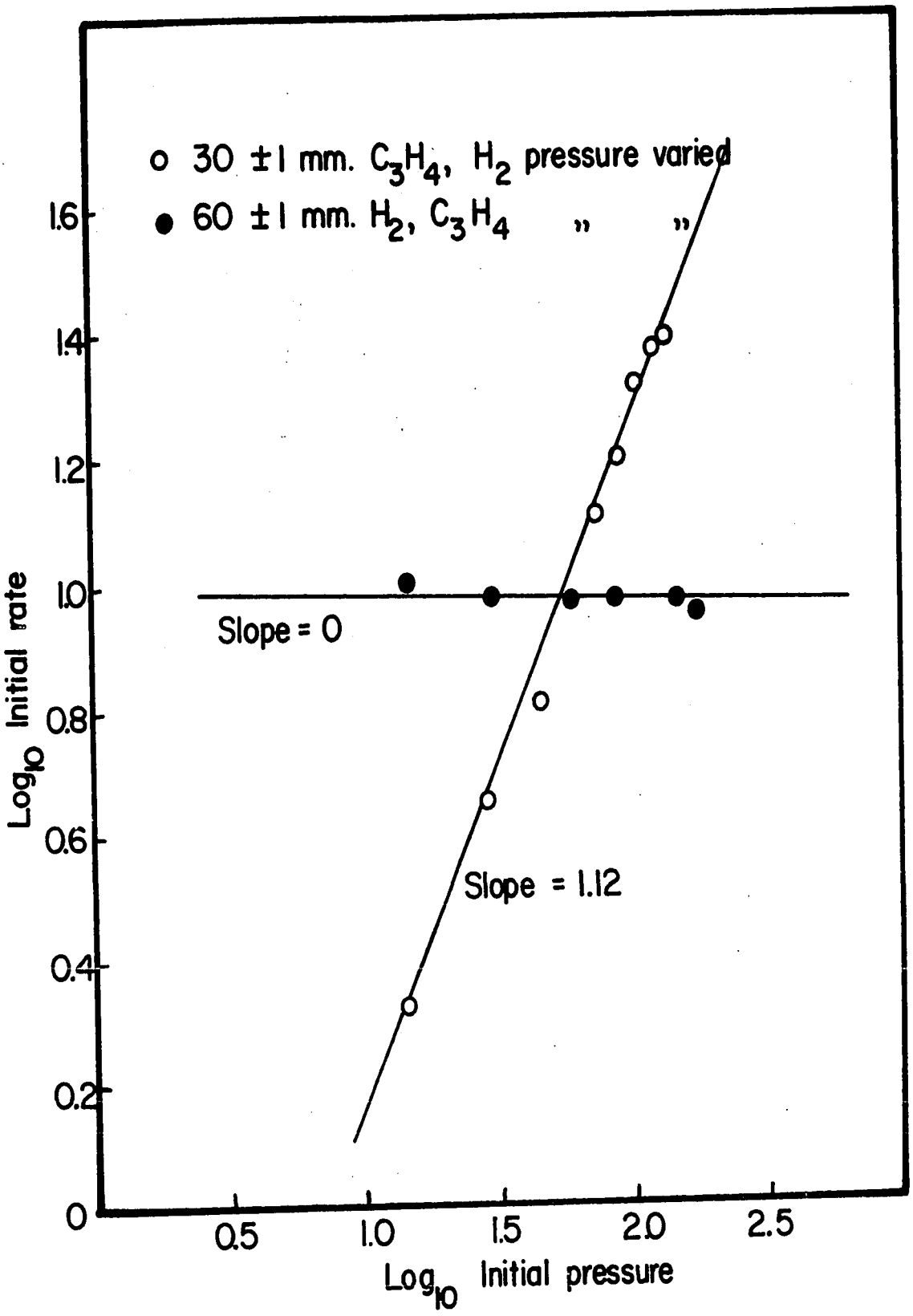


Fig. 8 The dependence of initial rates upon initial pressures, nickel-pumice at 88°C

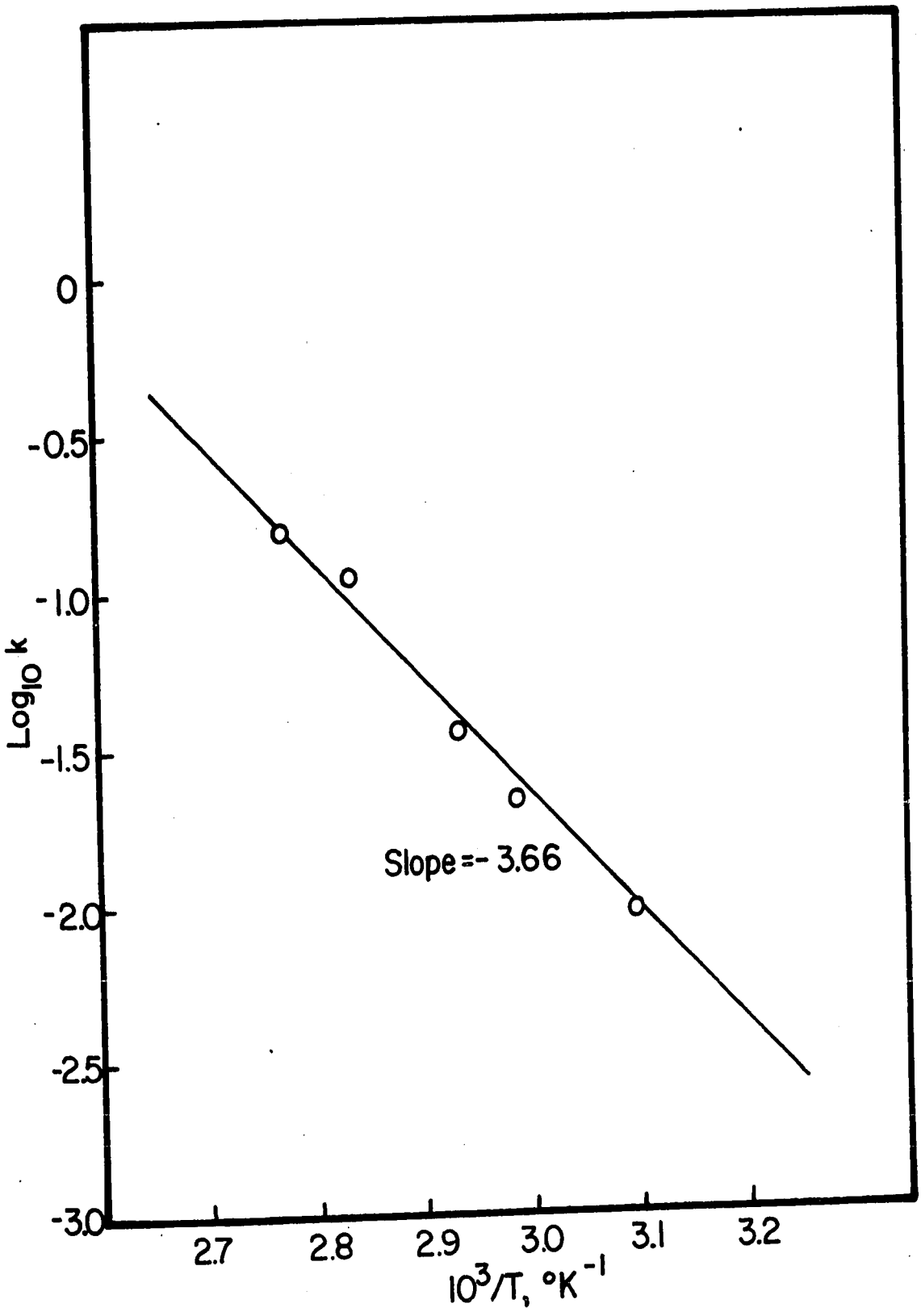


Fig. 9 The dependence of rate constants upon temperature, nickel-pumice

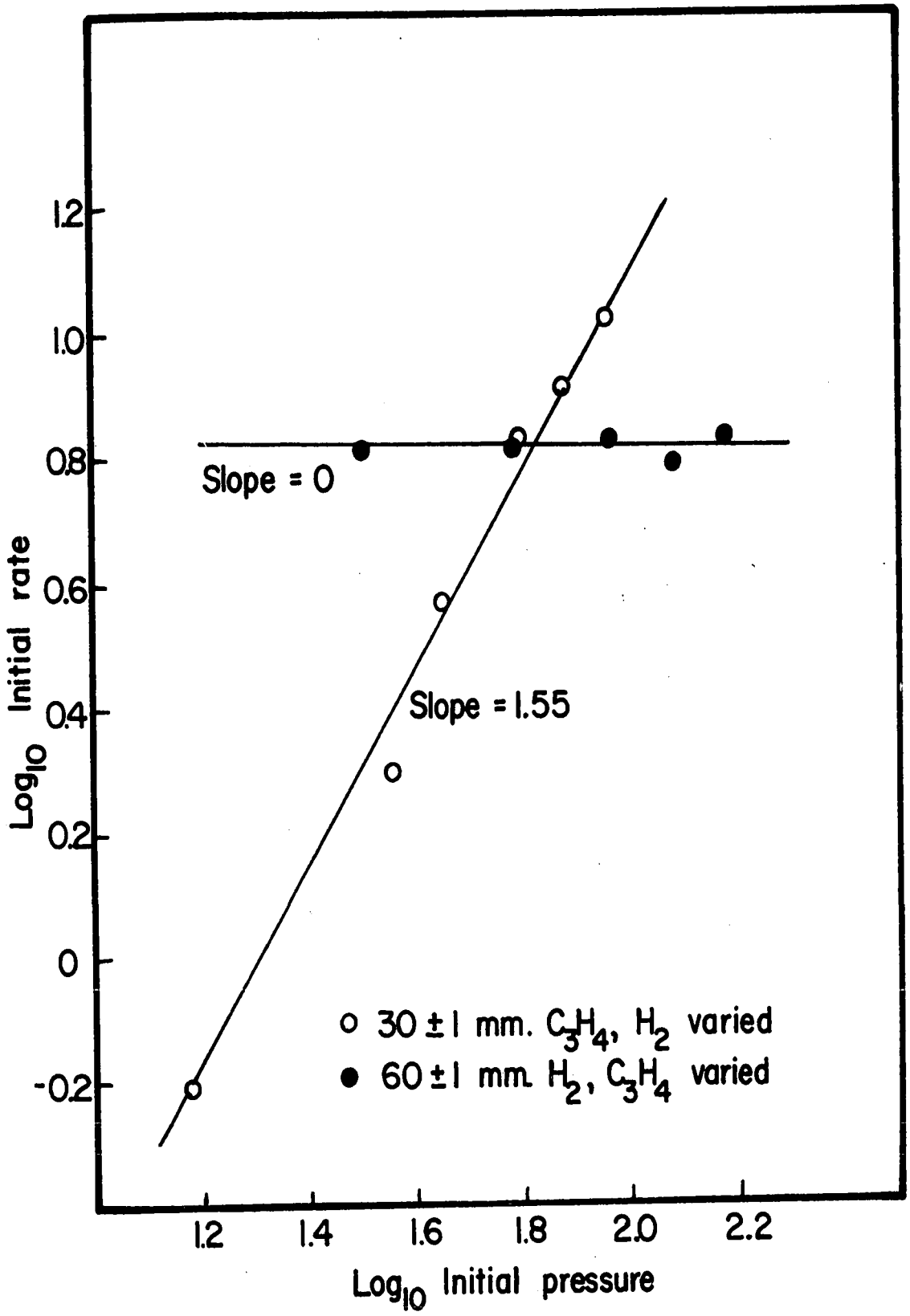


Fig. 10 The dependence of initial rates upon initial pressures, nickel-bicoeigubr at 39° C

of initial pressures on initial rates. The order was zero with respect to methyl acetylene. The order varied from 1.98 to 1.55 with respect to hydrogen, presumably due to high sensitivity of the catalyst. The initial rate equation was

$$r_o = k\,(P_{H_2})^{1.765 \pm 0.215}\,(P_{C_3H_4})^{0} \qquad (11)$$

The Arrhenius plot for determination of activation energy is shown in Figure 11. An activation energy of 13.95 kcal. per mole was obtained.

3) Nickel-powder (I) catalyst

The results for this catalyst are listed in Table 3.

Measurable rates were observed at 72° C. A series of runs were taken in a temperature range from 72° to 108° C, after the catalyst had attained a constant activity. The pressure-time curves were similar to those obtained for supported nickel catalysts.

The orders of reaction with respect to hydrogen and methyl acetylene were determined from the influence of varying the initial pressure of one while keeping the other constant, on the initial rates. Figure 12 shows the results of such variations at 90° C. The orders with respect to hydrogen varied between 1.29 and 1.15. The orders were zero with respect to methyl acetylene. However, the orders with respect to methyl acetylene were slightly negative for higher pressures.

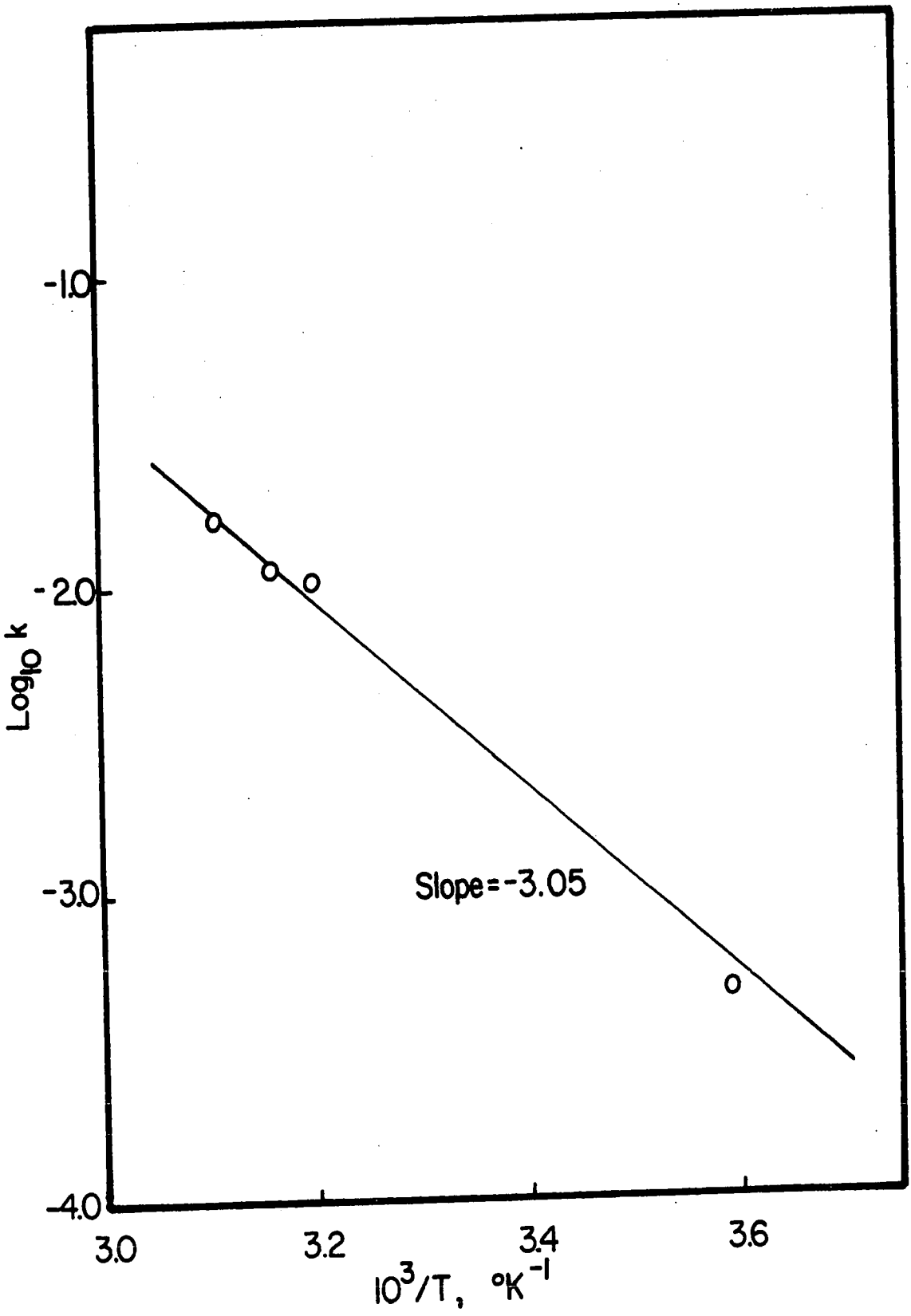


Fig. 11 The dependence of rate constants upon temperature, nickel-bissalicylal

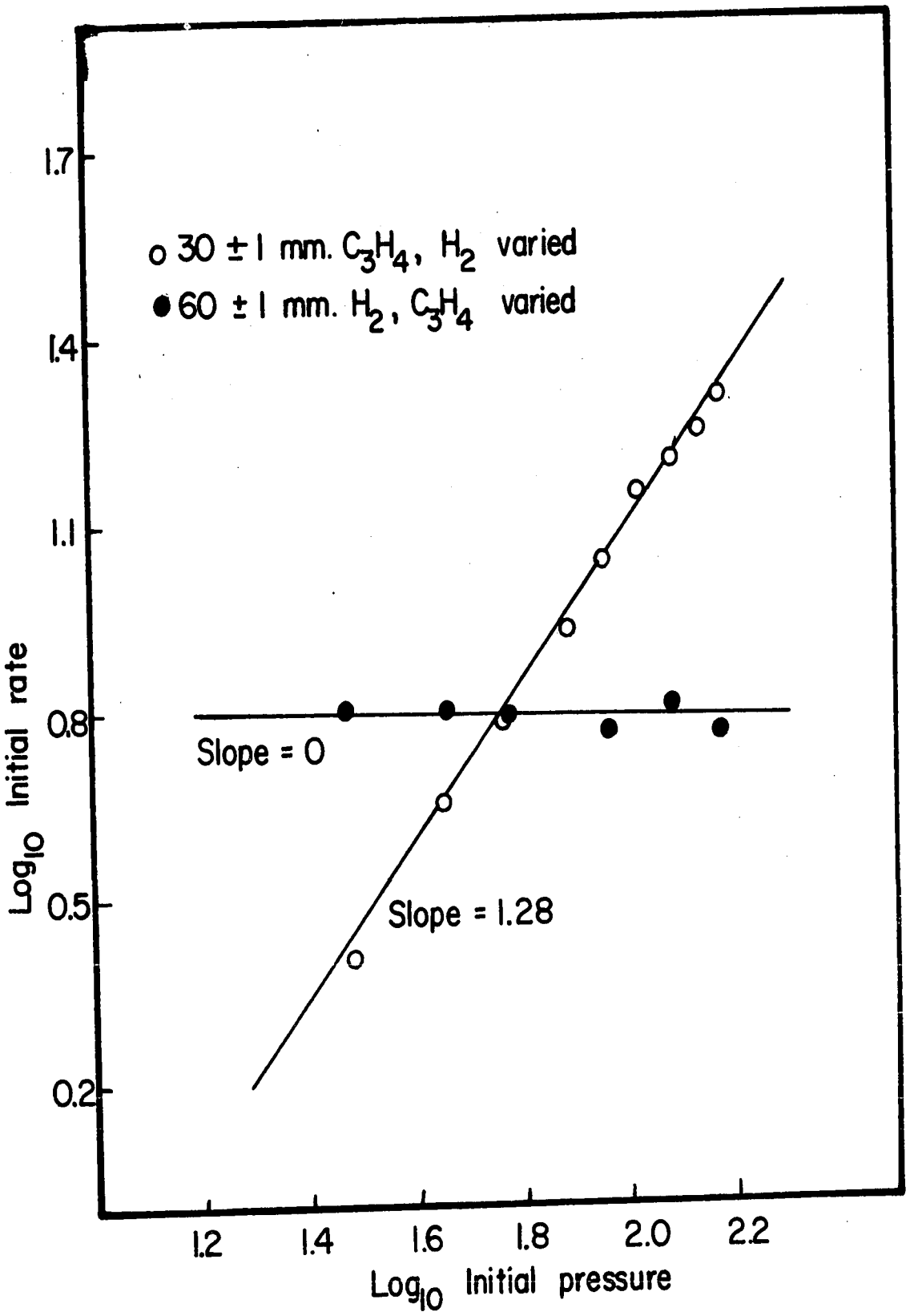


Fig. 12 The dependence of initial rates upon initial pressures, nickel-powder (I) at 90° C

The rate equation was

$$r_o = k (P_{H_2})^{1.22 \pm 0.07} (P_{C_3H_4})^{0} \qquad (12)$$

The activation energy, E, was determined from the Arrhenius plot shown in Figure 13. An activation energy of 18.58 kcal. per mole was found over nickel powder (I) catalyst.

4) Nickel-powder (II) catalyst

In order to find if the kinetics and activation energies would vary considerably for the same metal catalyst prepared from different compounds, the kinetics of the reaction were investigated for the nickel powder prepared from nickel nitrate.

Measurable reaction was observed at 46° C. After the catalyst attained constant activity, the series of runs were taken. The results are given in Table 4.

The pressure-time curve consisted of two linear portions of different rates and resembled that obtained for nickel-pumice catalyst. The orders of reaction with respect to both the reactants were determined from the influence of initial pressures on the initial rates. Figure 14 shows the results for nickel catalyst at 60° C. The orders with respect to hydrogen varied from 1.2 to 1.0, decreasing with decrease of temperature. But the orders with respect to methyl acety-

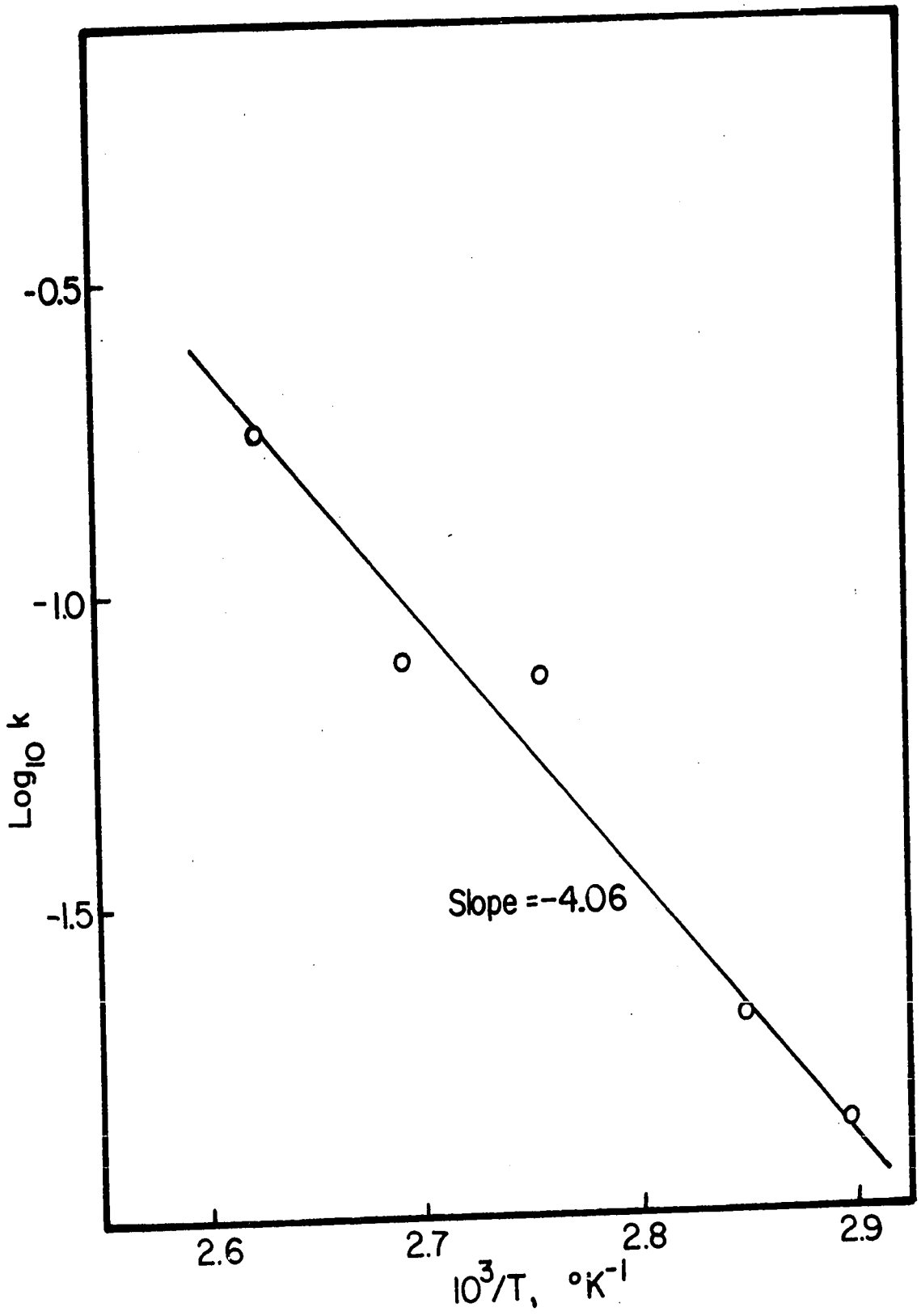


Fig. 13 The dependence of rate constants upon temperature, nickel-powder (I)

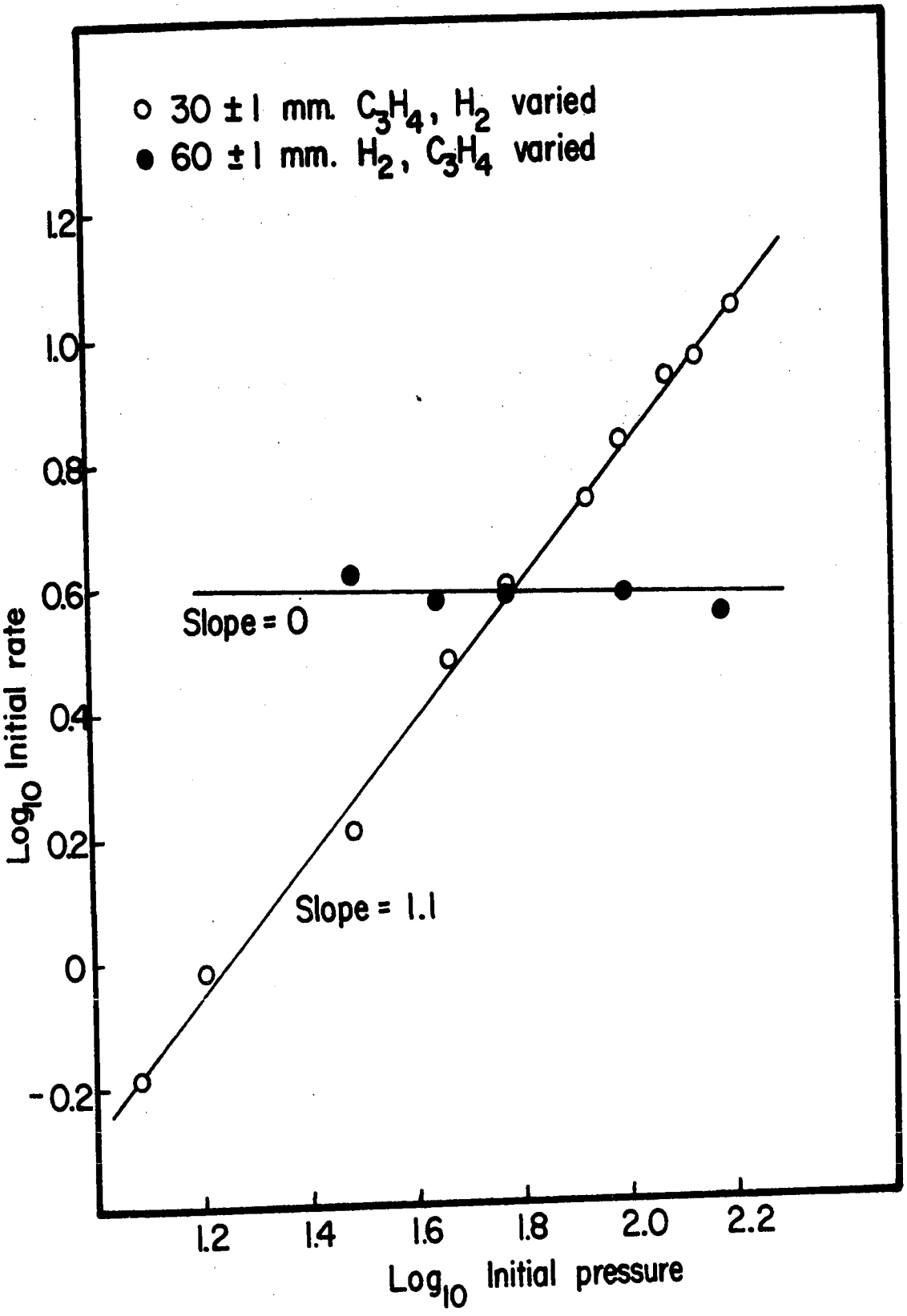


Fig. 14 The dependence of initial rates upon initial pressures, nickel-powder (II) at 60° C

lene always remained zero. The rate equation for the reaction was

$$r_o = k (P_{H_2})^{1.1 \pm 0.1} (P_{C_3H_4})^{0} \qquad (13)$$

From the Arrhenius plot of $\log_{10} k$ against $1/T \times 10^3$, as shown in Figure 15, an activation energy of 17.16 kcal. per mole was obtained.

Both the nickel-powder catalysts behaved in a similar fashion. The activity, the orders of reaction with respect to hydrogen and the activation energy were little higher for the nickel-powder (I) catalyst, prepared from nickel oxalate, as compared to other catalysts.

5) Nickel-powder (III) catalyst

In the hydrogenation of acetylene over nickel powder, the catalyst was poisoned when acetylene was admitted first (16). In order to verify if the findings of the acetylene hydrogenation on nickel powder would be true for methyl acetylene hydrogenation as well, kinetics were investigated over nickel powder obtained from basic nickel carbonate, coprecipitated from a solution of nickel nitrate in presence of ammonium hydrogen carbonate.

Measurable reaction rates were observed at 60° C. Runs were taken when constant activity was attained by the catalyst. The results are given in Table 5. Linear pressure time curves, similar

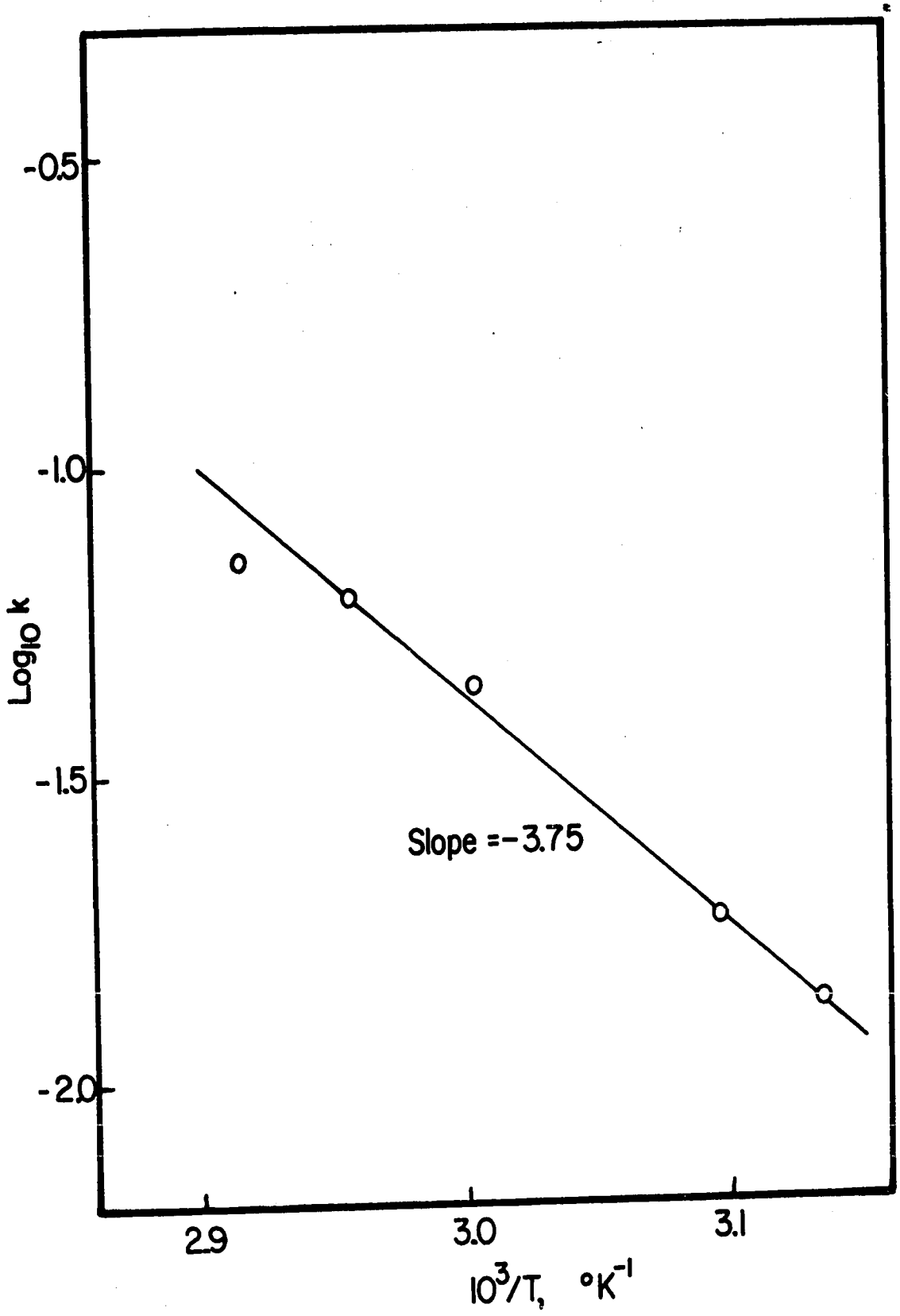


Fig. 15 The dependence of rate constants upon temperature, nickel-powder (II)

to other nickel catalysts, were obtained. The order with respect to hydrogen was between 1.34 and 1.16 and decreased with decreased temperatures. The order with respect to methyl acetylene was always zero. The overall rate equation was

$$r_o = k (P_{H_2})^{1.25 \pm 0.09} (P_{C_3H_4})^0 \qquad (14)$$

From the Arrhenius plot of $\log_{10} k$ against $1/T$, an activation energy of 19.99 kcal. per mole was evaluated. Figure 16 shows the effect of initial pressures of hydrogen and methyl acetylene on initial rates at 66° C. The Arrhenius plot is shown in Figure 17.

Unlike the findings of Bond and Mann (16) on the catalytic hydrogenation of acetylene over unsupported nickel, when methyl acetylene was admitted first into the reaction vessel, the catalyst did not lose activity fast. However, the comparable activity of the catalyst was higher when hydrogen was admitted first.

6) Palladium-pumice catalyst

The kinetics of the methyl acetylene hydrogenation over a pumice supported palladium catalyst was studied between 80° and 116° C. Below 80° C, the reaction was slow and it was difficult to measure the rates accurately. Table 6 gives the results obtained for palladium-pumice catalyst.

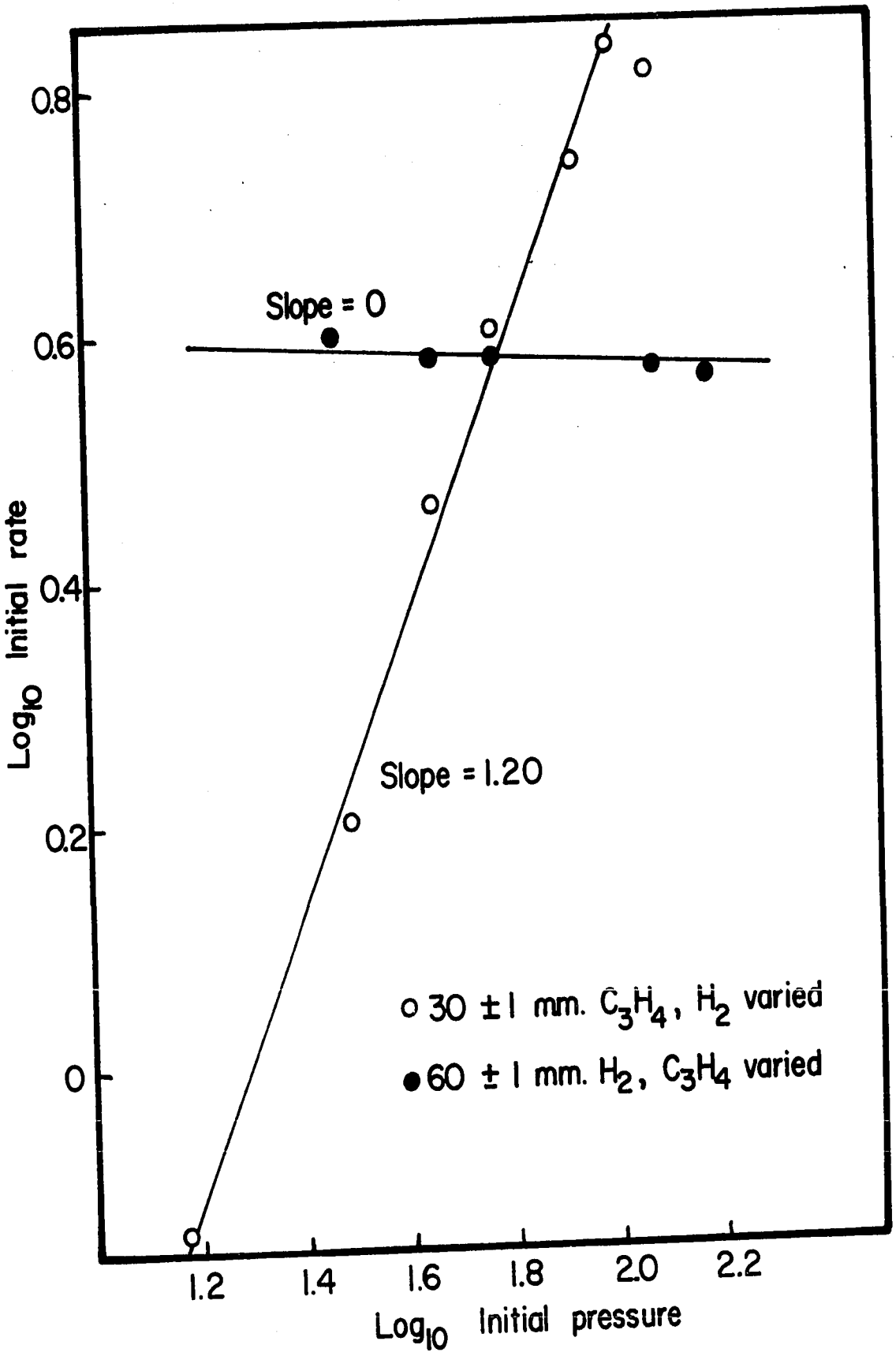


Fig. 16 The dependence of initial rates upon initial pressures, ~~nickel powder (wet)~~ at 66°C. methyl acetylene added first

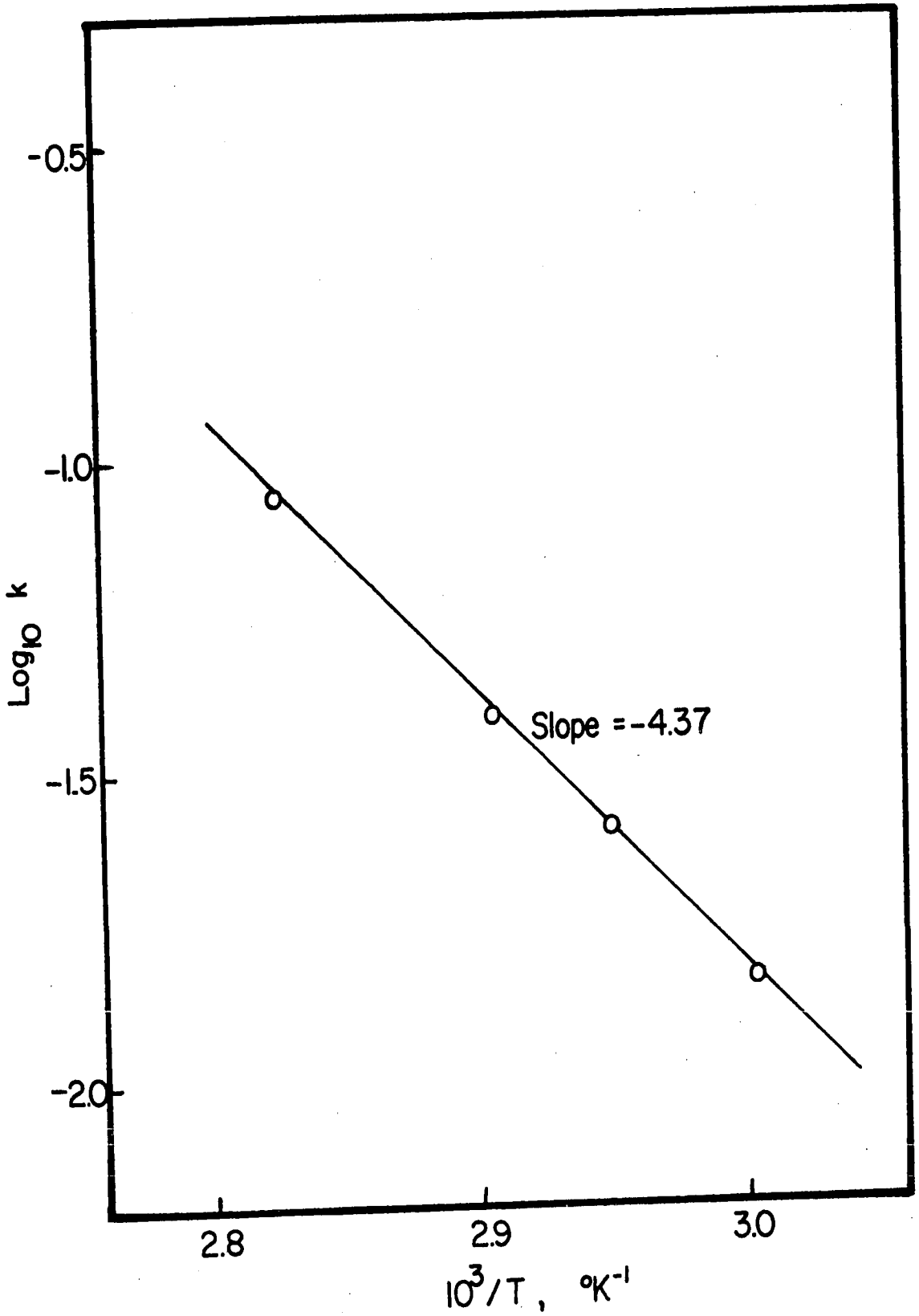


Fig. 17 The dependence of rate constants upon temperature, nickel-powder (III), methyl acetylene added first

Pressure-time curves having two linear portions, with different slopes, were obtained and resembled those obtained for nickel-pumice catalyst. The orders of reaction were 0.94 ± 0.03 and zero with respect to hydrogen and methyl acetylene respectively. The overall reaction rate was expressed by the equation

$$r_o = k (P_{H_2})^{0.94 \pm 0.03} (P_{C_3H_4})^0 \qquad (15)$$

The Arrhenius plot of $\log_{10} k$ against $1/T$ gave a straight line from whose slope an activation energy of 10.3 kcal. per mole was evaluated.

Figure 18 shows the effect of initial pressures of reactants on initial rates at 94° C. The Arrhenius plot is shown in Figure 19.

7) Platinum-pumice catalyst

Over platinum-pumice catalyst, measurable rates were observed at 61° C. A series of runs were taken in a range of 61° to 133.5° C, after the catalyst had attained the constant activity. All the results are given in Table 7.

The forms of pressure-time curves were similar to those obtained for nickel-pumice catalyst. The orders of reaction were determined from the initial rate data. The orders were 1.87 ± 0.02 with respect to hydrogen, and -0.50 with respect to methyl acetylene.

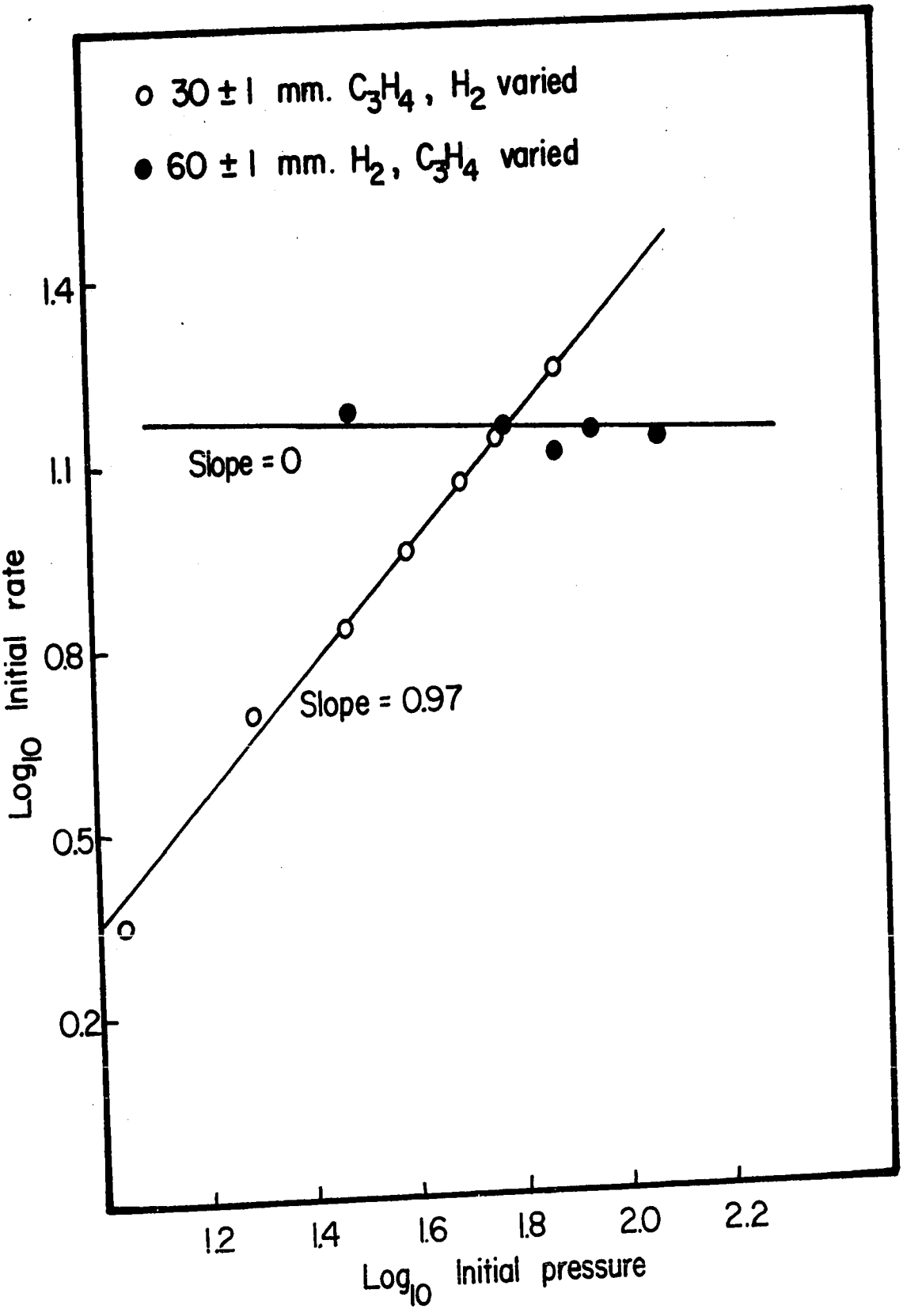


Fig. 18 The dependence of initial rates upon initial pressures, palladium-quartz at 64° C

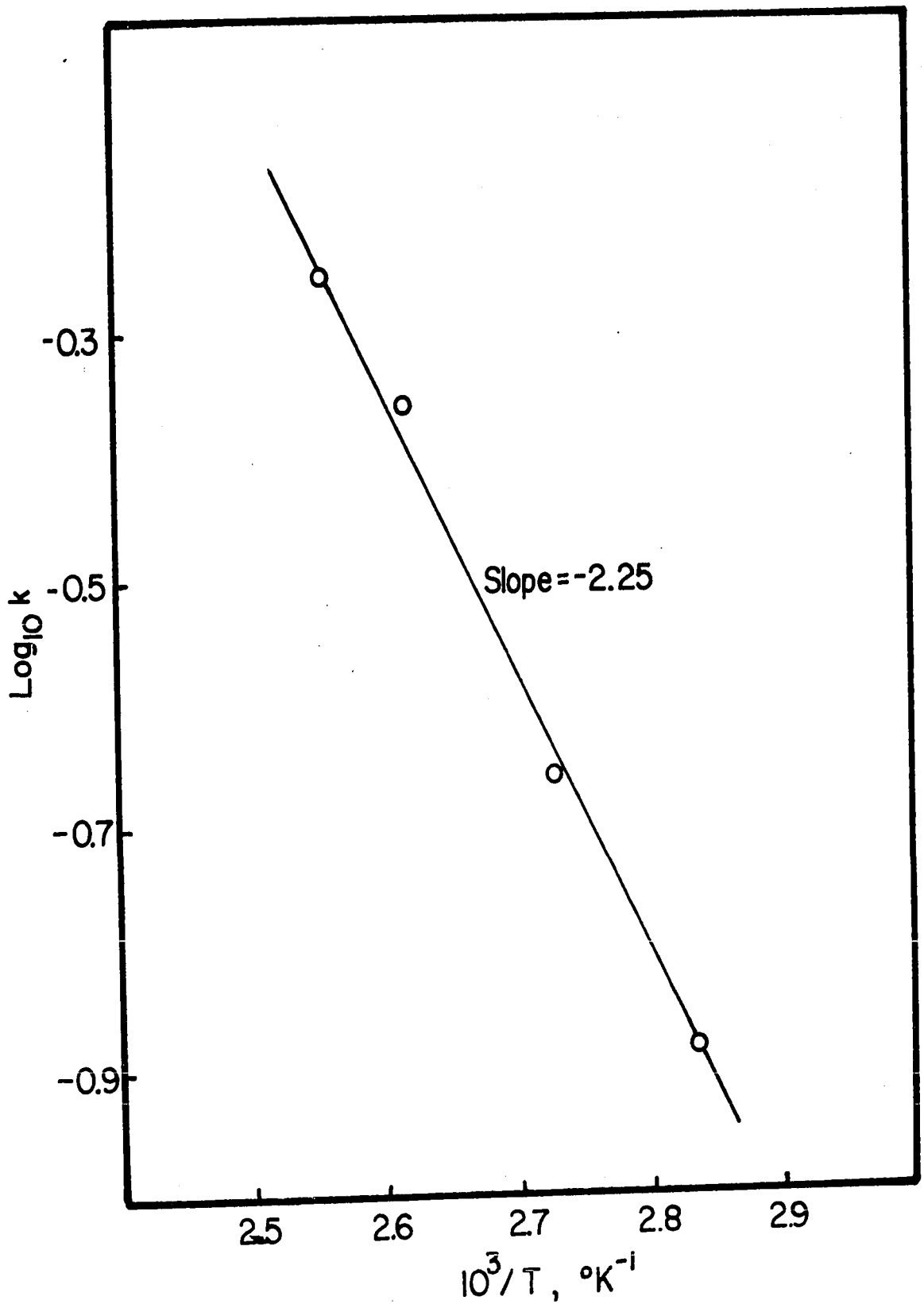


Fig. 19 The dependence of rate constants upon temperature, palladium-pumice

Figure 20 shows the effect of reactants' pressures on initial rates at 133.5° C. The overall rate equation was

$$r_o = k (P_{H_2})^{1.87 \pm 0.02} (P_{C_3H_4})^{-0.5} \qquad (16)$$

It seems likely that the reactions occurred through the interaction of adjacently adsorbed methyl acetylene and hydrogen. Methyl acetylene was not as strongly adsorbed on platinum as on other catalysts. It appears that hydrogen was able to displace methyl acetylene from the surface when the former was present in sufficient excess. This was in agreement with observations of Sheridan (20) for the hydrogenation of acetylene over platinum-pumice catalyst.

The Arrhenius plot of $\log_{10} k$ against $1/T$ is shown in Figure 21. From the slope of this plot, an activation energy of 12.85 kcal. per mole was evaluated.

8) Cobalt-pumice catalyst

Measurable rates were observed only above 87° C. When the catalyst attained a constant activity, a series of runs were taken. The results are given in Table 8.

After the runs were taken at three different temperatures, the catalyst lost its activity. Any further increase in temperature did not increase the initial rates. The decomposition started at 190° C.

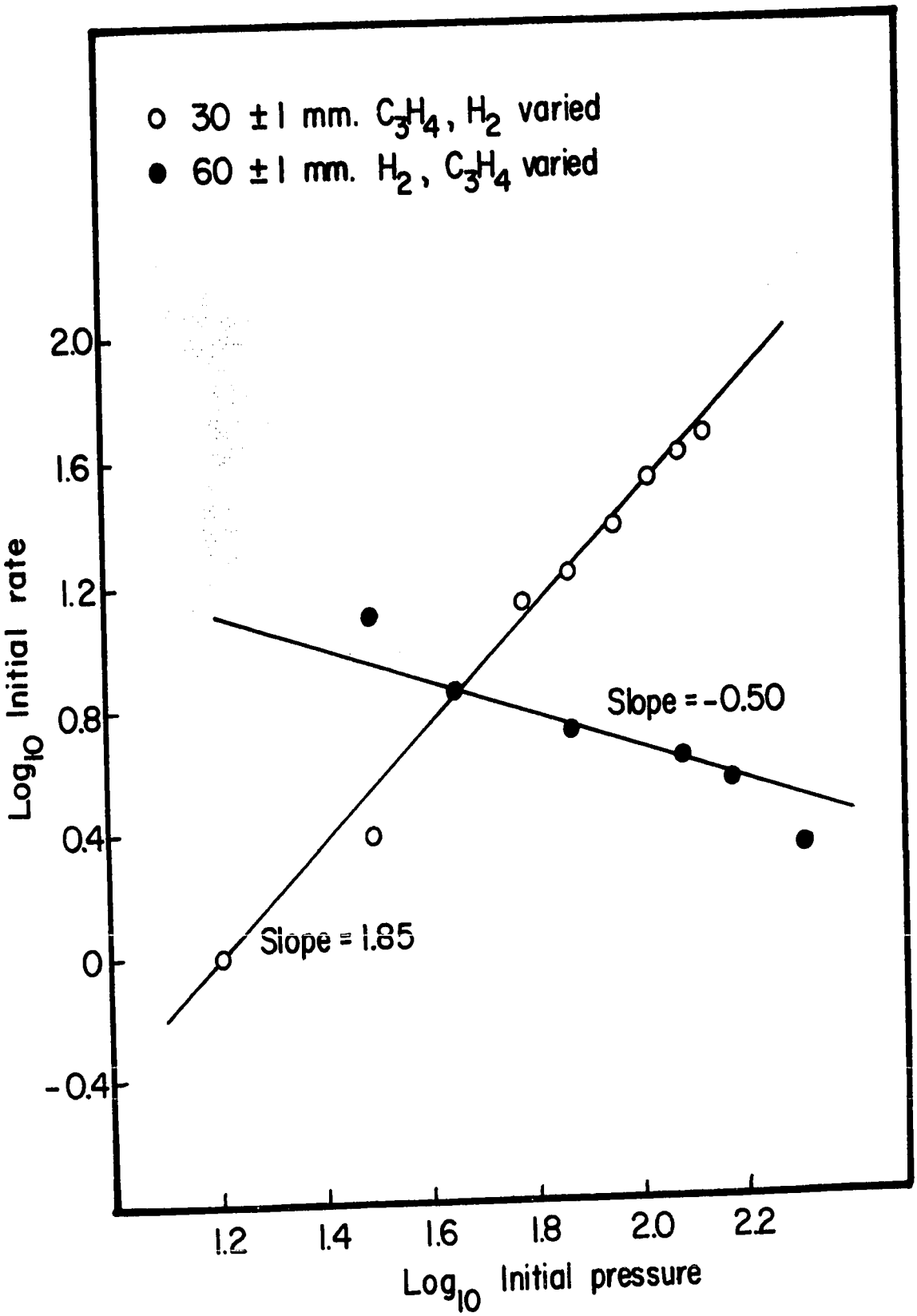


Fig. 20 The dependence of initial rates upon initial pressures, [illegible] at 133.5°C

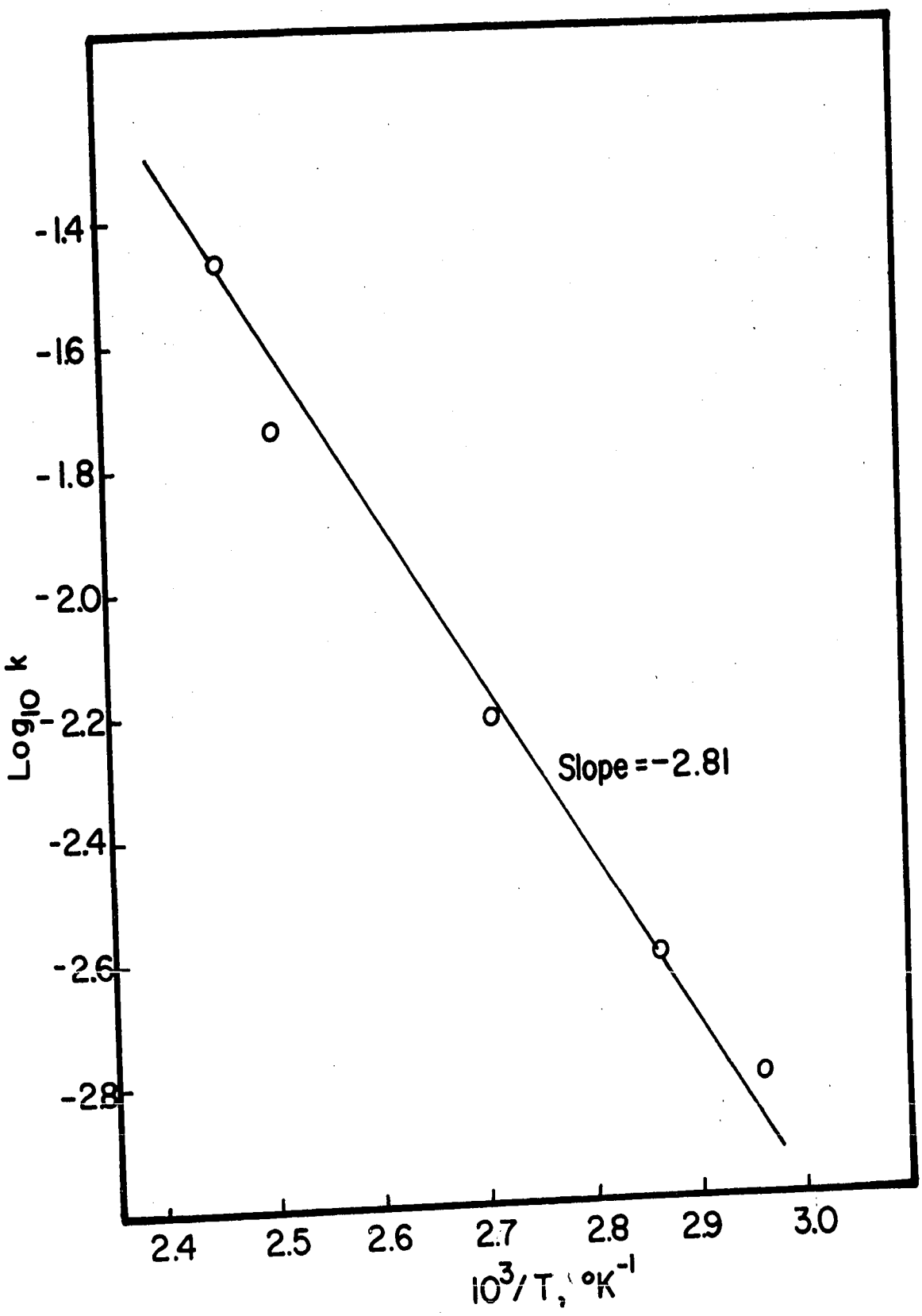


Fig. 21 The dependence of rate constants upon temperature, platinum-pumice

However, the kinetic analysis was based on runs taken at three different temperatures. Pressure-time curves similar to nickel-pumice catalyst were obtained. The orders were always 2.6 with respect to hydrogen and zero with respect to methyl acetylene. Figure 22 shows the effect of initial pressures of reactants on initial rates at 105° C. The overall initial rate equation was of the form

$$r_o = k\,(P_{H_2})^{2.6}\,(P_{C_3H_4})^{0} \qquad (17)$$

implying a remarkably high adsorption of hydrogen.

Figure 23 shows the Arrhenius plot of $\log_{10} k$ against 1/T. From the slope of this plot, an activation energy of 13.30 k cal. per mole was evaluated.

9) Rhodium-pumice catalyst

Measurable rates were observed at 60° C. Runs were taken at four different temperatures, in a range of 60° to 104° C. The results are given in Table 9.

The forms of pressure-time curves were similar to those obtained for nickel-pumice catalyst. The orders of reaction with respect to hydrogen and methyl acetylene were 1.5 and zero respectively. There was no temperature dependence of the orders of reaction. Figure 24 shows the effect of initial pressures of reactants on initial rates at 90° C. The overall initial rate equation was

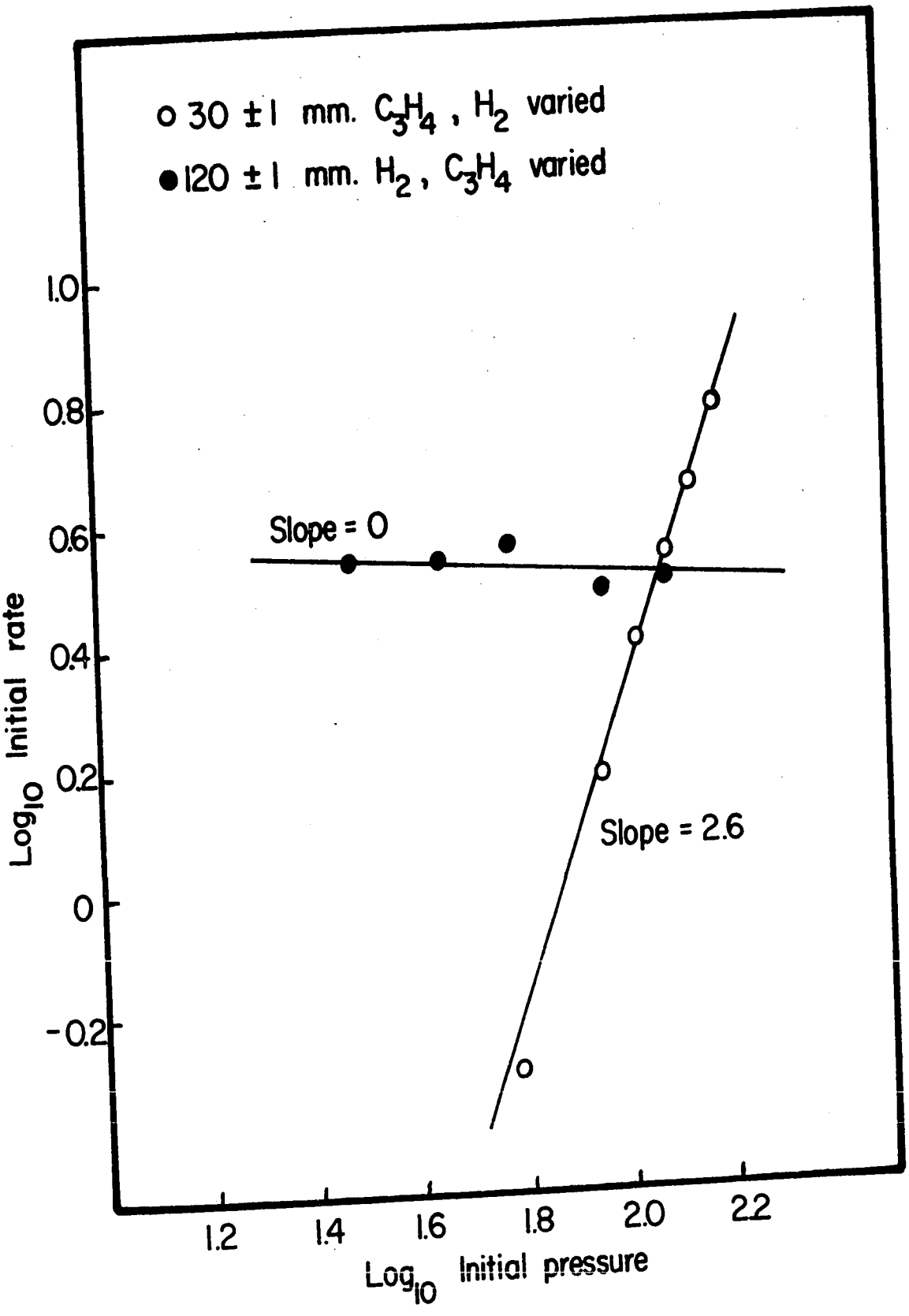


Fig. 22 The dependence of initial rates upon initial pressures, ethyl-pumice at 185° C

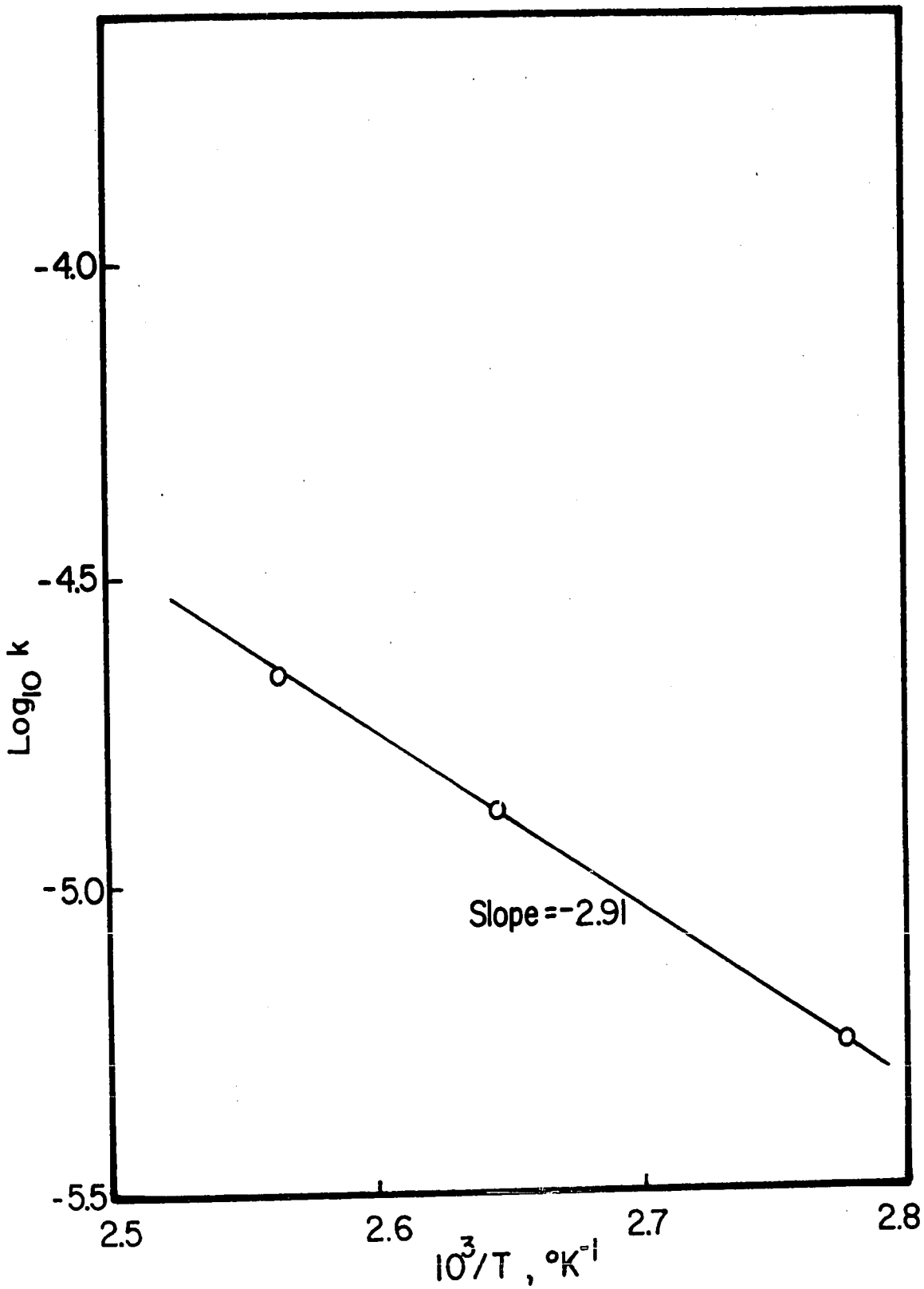


Fig. 23 The dependence of rate constants upon temperature, cobalt-pumice

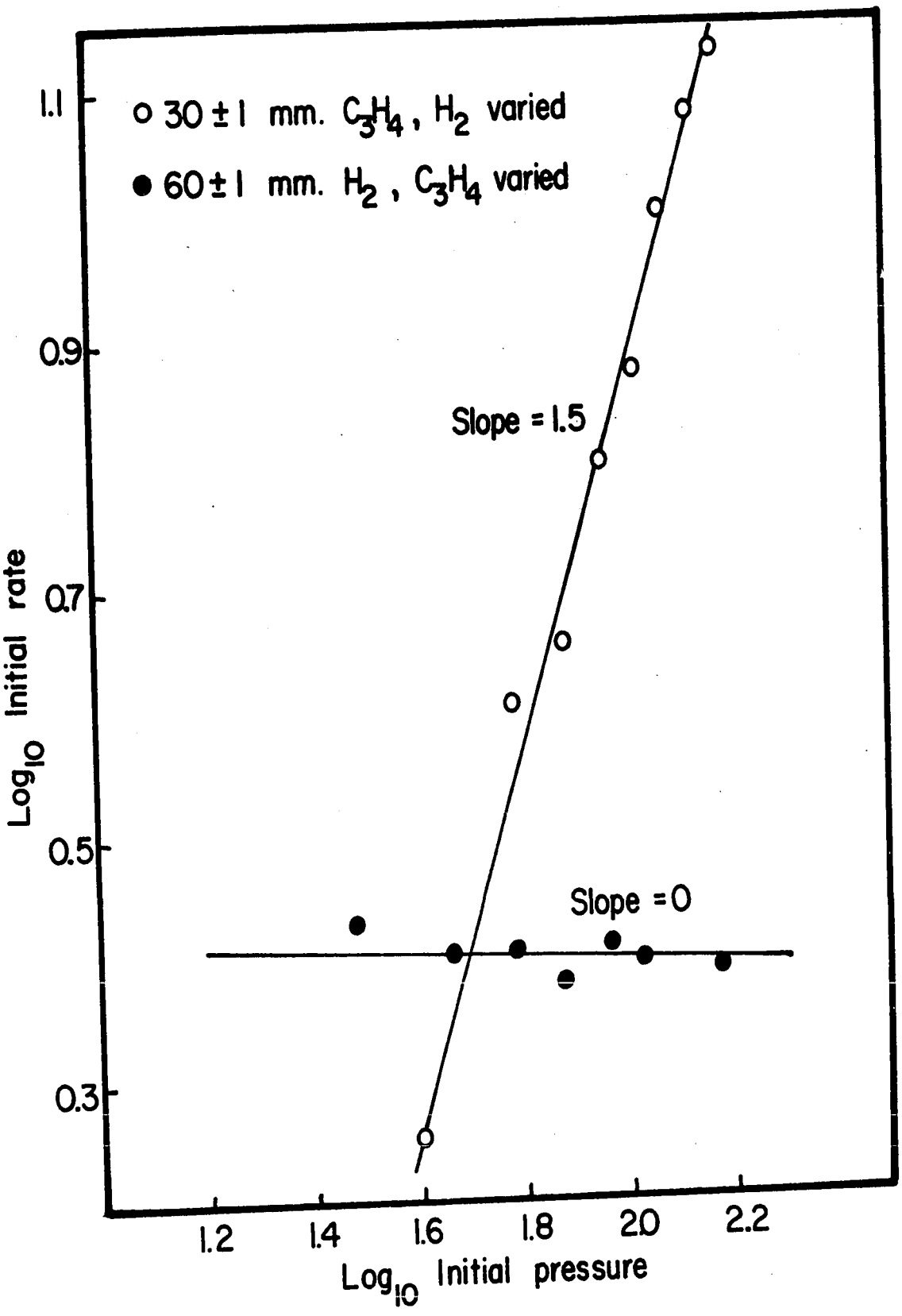


Fig. 24 The dependence of initial rates upon initial pressures, rhodium-pumice at 90° C

$$r_o = k (P_{H_2})^{1.5} (P_{C_3H_4})^0 \qquad (18)$$

The Arrhenius plot of $\log_{10} k$ against $1/T$ is shown in Figure 25. An activation energy of 8.60 k cal. per mole was obtained from the slope of the line.

10) Iridium-pumice catalyst

With iridium-pumice catalyst, measurable rates were observed at 56.5° C. When the catalytic activity became constant, the series of runs were taken. The experimental results are given in Table 10. The runs were taken at four different temperatures.

The pressure-time curves obtained with iridium-pumice catalyst, were similar to those with nickel-pumice catalyst. The orders with respect to hydrogen and methyl acetylene were 1.24 and zero respectively. Figure 26 shows the effect of initial pressures of reactants on initial rates at 100.8° C. The overall rate expression could be expressed as

$$r_o = k (P_{H_2})^{1.24} (P_{C_3H_4})^0 \qquad (19)$$

The Arrhenius plot of $\log_{10} k$ against $1/T$ is shown in Figure 27. For the temperature range of 56.5° to 116.2° C, it was a straight line. The slope of thie line gave an activation energy of 9.15 k cal. per mole.

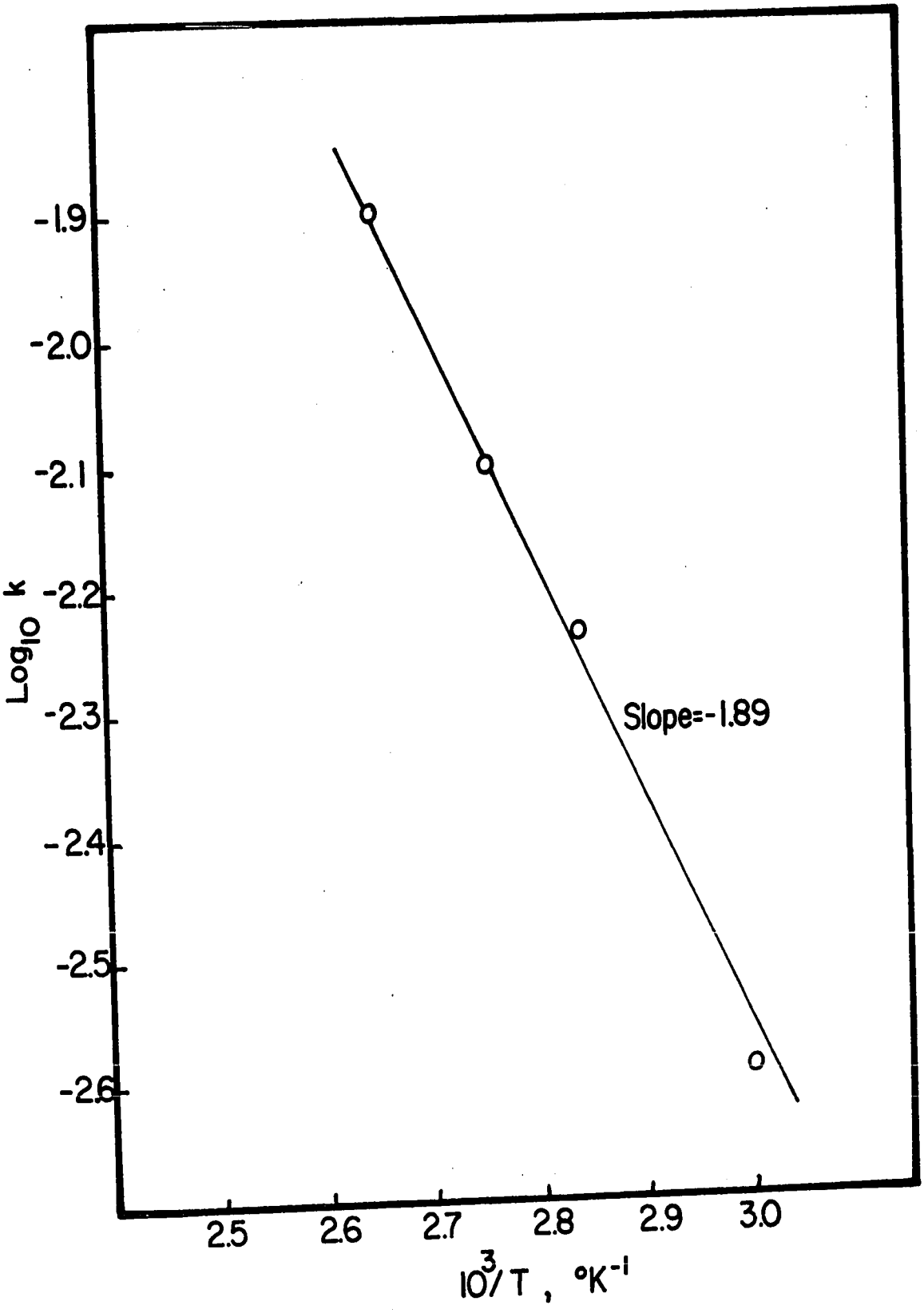


Fig. 25 The dependence of rate constants upon temperature, ~~medium-pumice~~

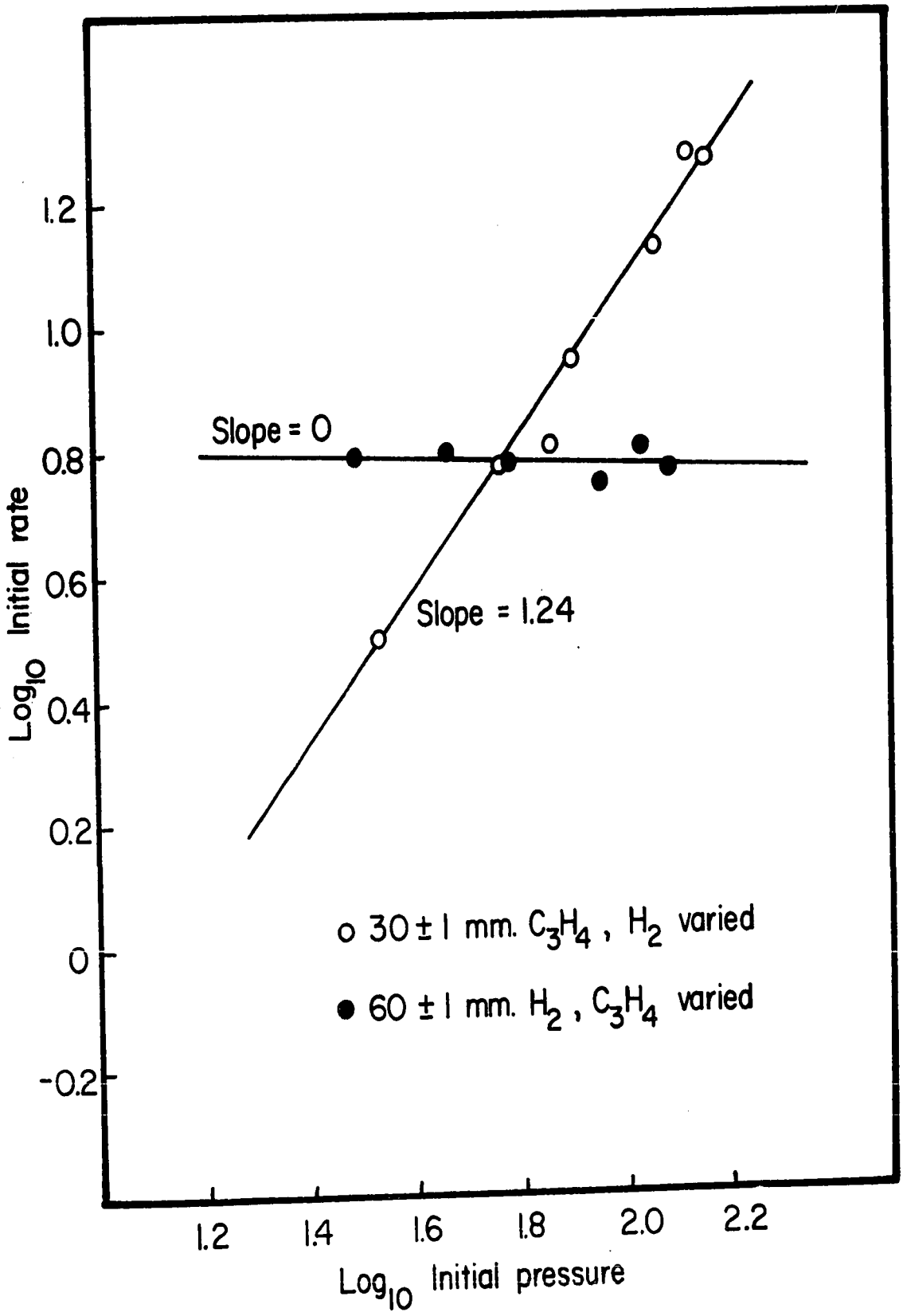


Fig. 26 The dependence of initial rates upon initial pressures, iridium-pumice at 100.8° C

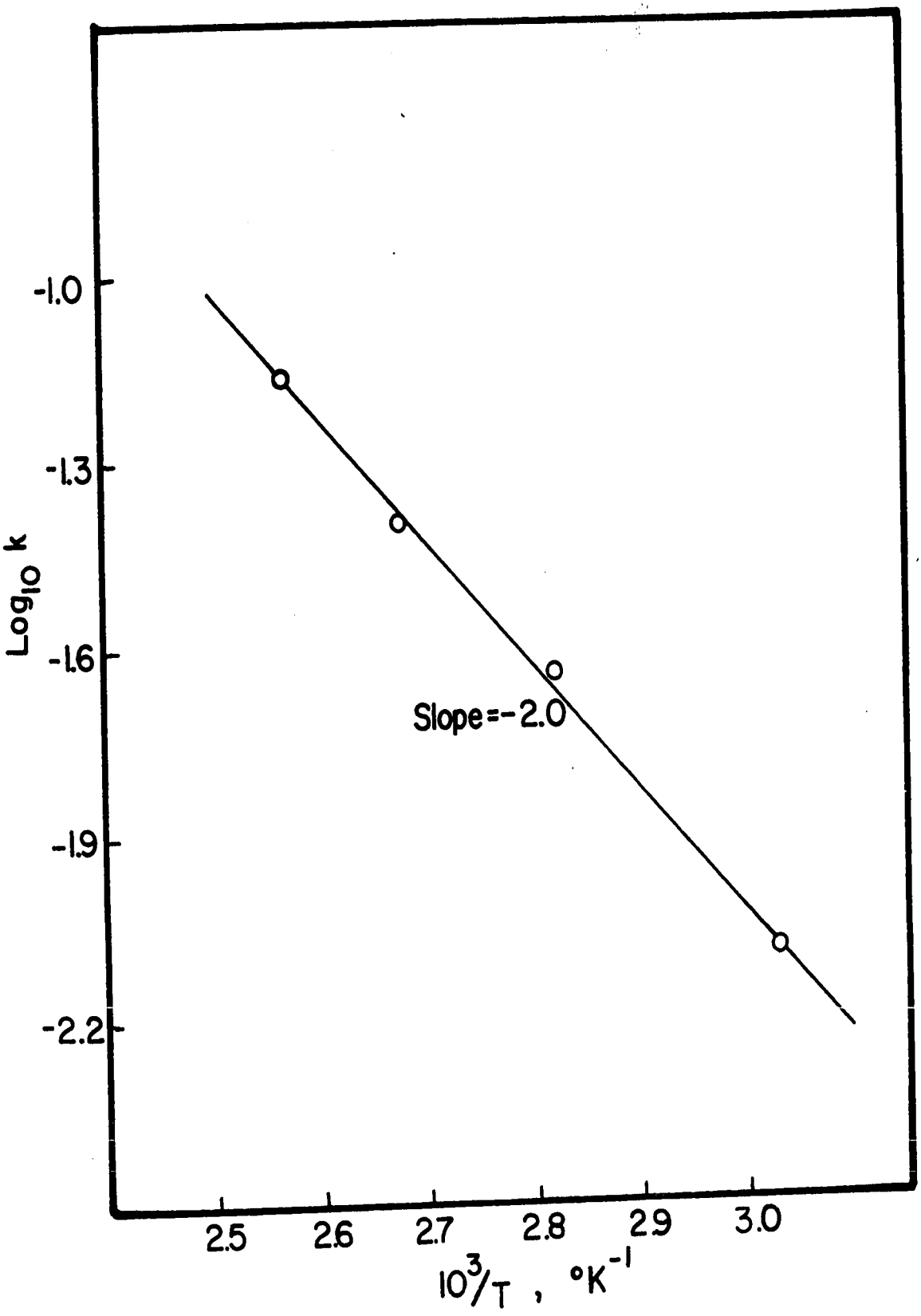


Fig. 27 The dependence of rate constants upon temperature, iridium-pumice

Sheridan (23) observed that the iridium-pumice catalysts were readily deactivated in the acetylene hydrogenation and that the rhodium-pumice catalysts were more active than the iridium-pumice catalysts. In case of methyl acetylene hydrogenation, it was found that the iridium was more active than rhodium and the catalytic activity for both remained constant for sufficient period.

11) Iron-pumice catalyst

Over iron-pumice catalyst, measurable reaction did not occur below 185°C. When the catalytic activity became constant, the series of runs were taken. The results are given in Table 11.

Iron behaved very similar to nickel catalysts, in agreement with the observations of Sheridan (17) for acetylene hydrogenation.

The orders of reaction with respect to hydrogen and methyl acetylene were 1.28 and zero respectively. Figure 28 shows the effect of initial pressures of reactants on initial rates at 185°C. The overall rate equation was

$$r_o = k\,(P_{H_2})^{1.28}\,(P_{C_3H_4})^{0} \qquad (20)$$

Figure 29 shows the Arrhenius plot of $\log_{10} k$ against $1/T$. From the slope of the line, an activation energy of 14.0 kcal. per mole was evaluated.

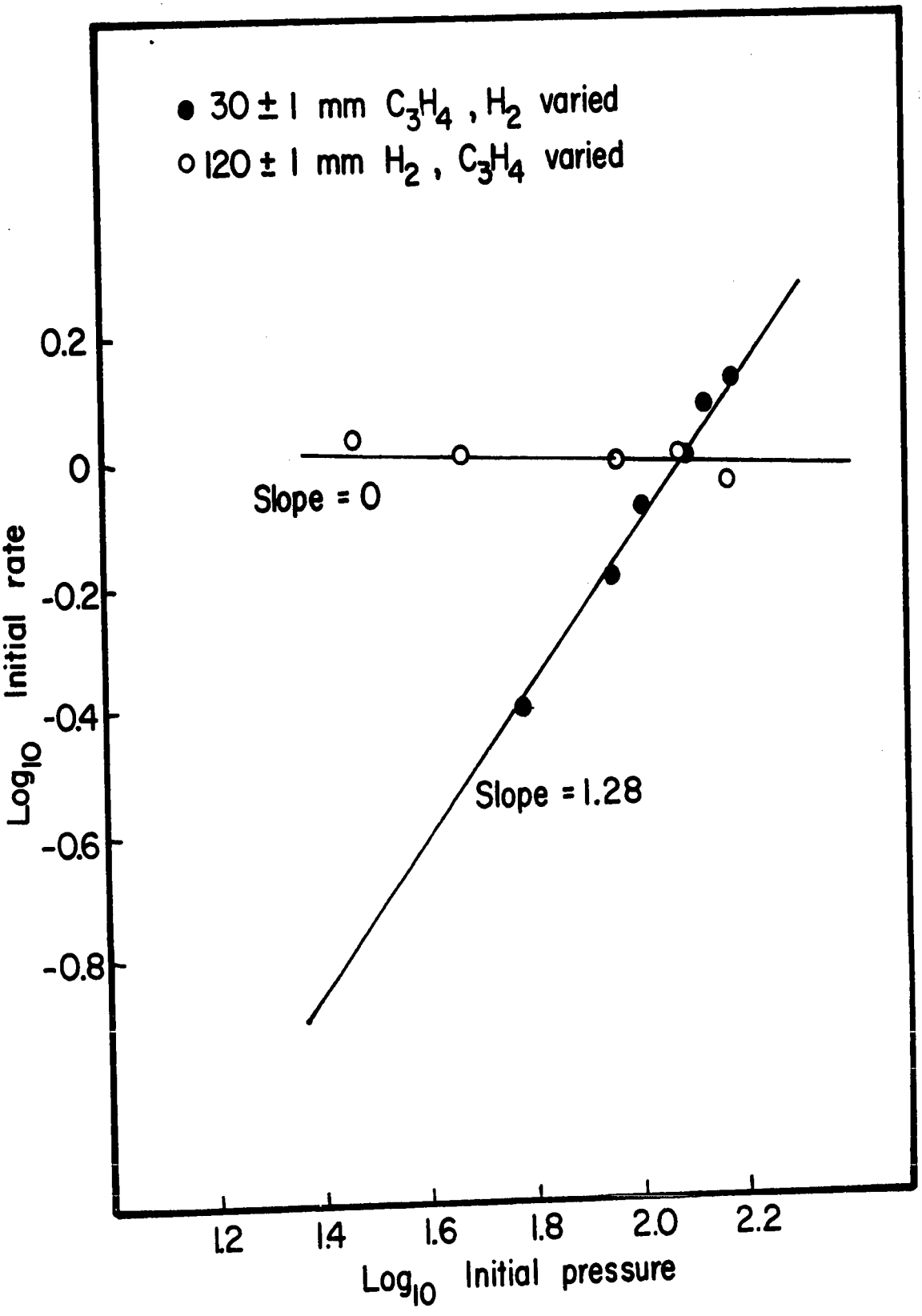


Fig. 28 The dependence of initial rates upon initial pressures, iron-pumice at 185° C

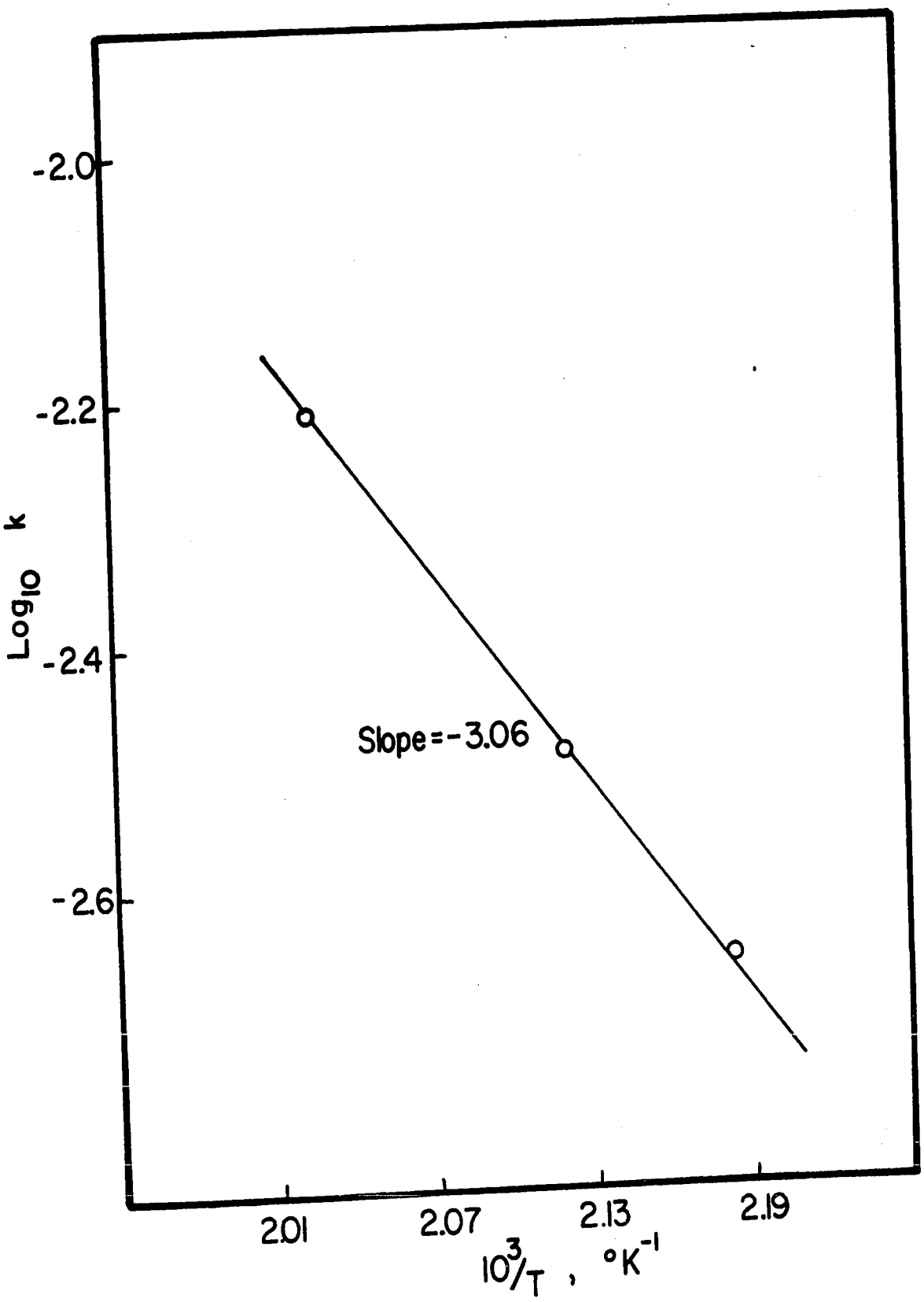


Fig. 29 The dependence of rate constants upon temperature, iron-pumice

Like cobalt-pumice catalyst, the iron-pumice catalyst lost its catalytic activity after the runs were taken at three different temperatures. Any further increase of temperature above 226°C, did not increase the initial rates. The decomposition started at 370°C. The catalytic activity of iron-pumice was less than that of cobalt-pumice.

12 and 13) Ruthenium-pumice and Osmium-pumice catalysts

Sheridan (23) observed that ruthenium and osmium were very less active even at 288° and 210°C respectively for acetylene hydrogenation. The catalytic activity of osmium was slightly higher than that of ruthenium. However, Sheridan (23) could not make any systematic studies on these two catalysts for acetylene hydrogenation.

For methyl acetylene hydrogenation, pumice supported ruthenium and osmium catalysts were slightly active at temperatures higher than 270°C. Further, the activity of these catalysts decreased rapidly and they got deactivated within 24 hours or so. Since these catalysts lost their catalytic activity very rapidly, a systematic study could not be undertaken.

However, with an initial hydrogen: methyl acetylene ratios of five, the fall of activity (initial rates) against time was noted ; until the catalyst became completely inactive. The shape of the pressure-

time curves were different from those obtained for nickel-pumice catalyst. They were linear for the first stages of reaction. Towards the end of the reaction, the fall in pressure gradually became slower. At a late stage, the rate did not increase. Farkas and Farkas (37) had obtained such pressure-time curves for hydrogen-acetylene mixtures over platinum. Also Cremer, Knorr and Plieninger (38) obtained such curves for hydrogen-acetylene mixtures over palladium. These curves were identical with type III curves obtained by Bond (15) for acetylene hydrogenation over nickel-pumice catalyst.

The slopes of first linear portions of the pressure-time curves, gave initial rates.

2 gm. of ruthenium-pumice (0.1778 gm. of ruthenium) catalyst gave an initial rate of 7 mm. Hg. per minute, when the temperature was 280° C. The initial rates decreased rapidly and the catalyst became inactive after 23 hours. The results are given in Table 12. Figure 30 shows the time dependence of the initial rates.

With 2 gm. of osmium-pumice (0.1802 gm. of osmium) catalyst, runs were taken at 296° C. The initial rate was 6 mm. Hg. per minute in the beginning and decreased very rapidly. The catalyst became completely deactivated after 24 hours. Results of time dependence on initial rates are given in Table 13. Figure 31 shows the effect of time on initial rates.

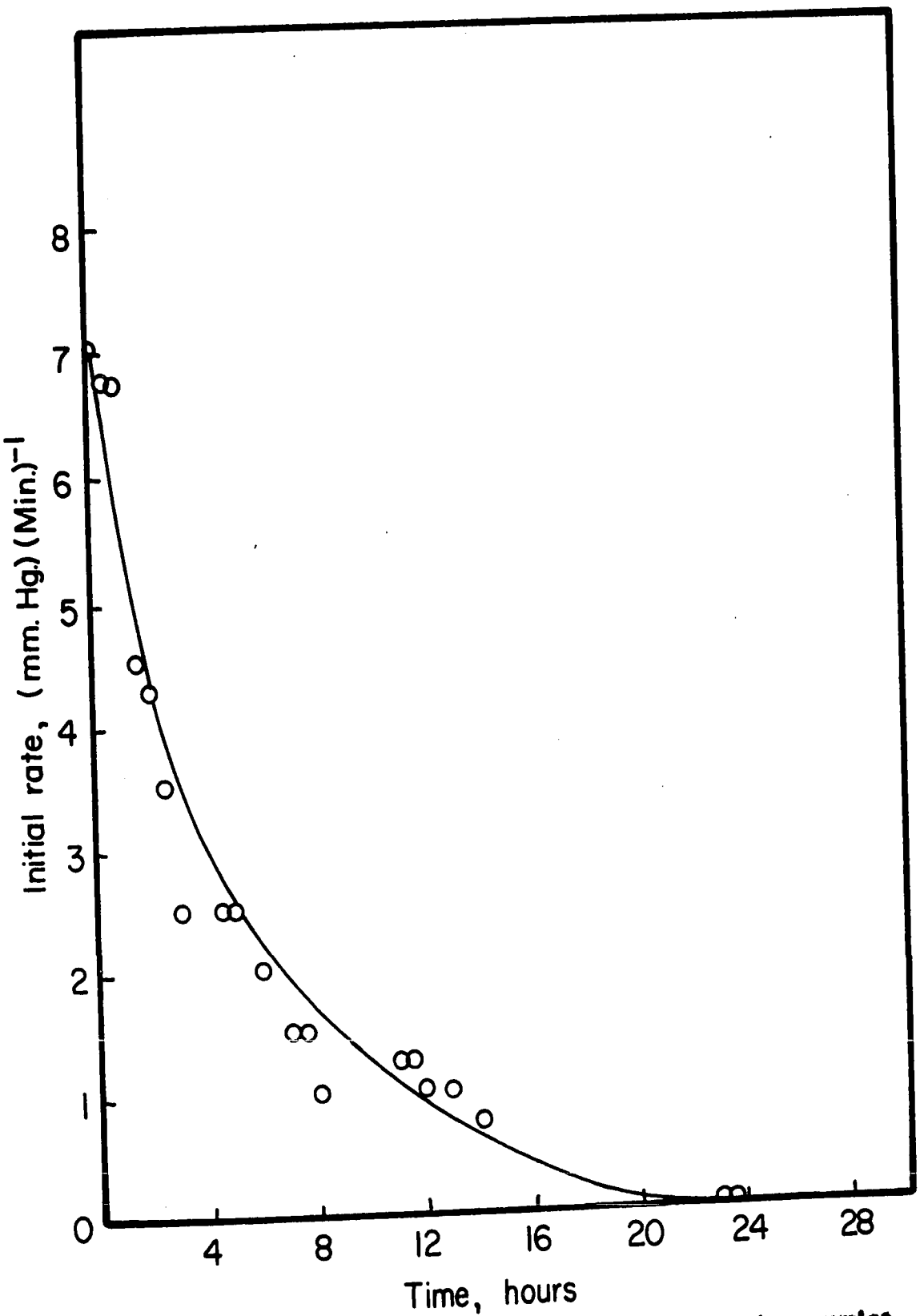


Fig. 20 The dependence of initial rates upon time, ruthenium-pumice

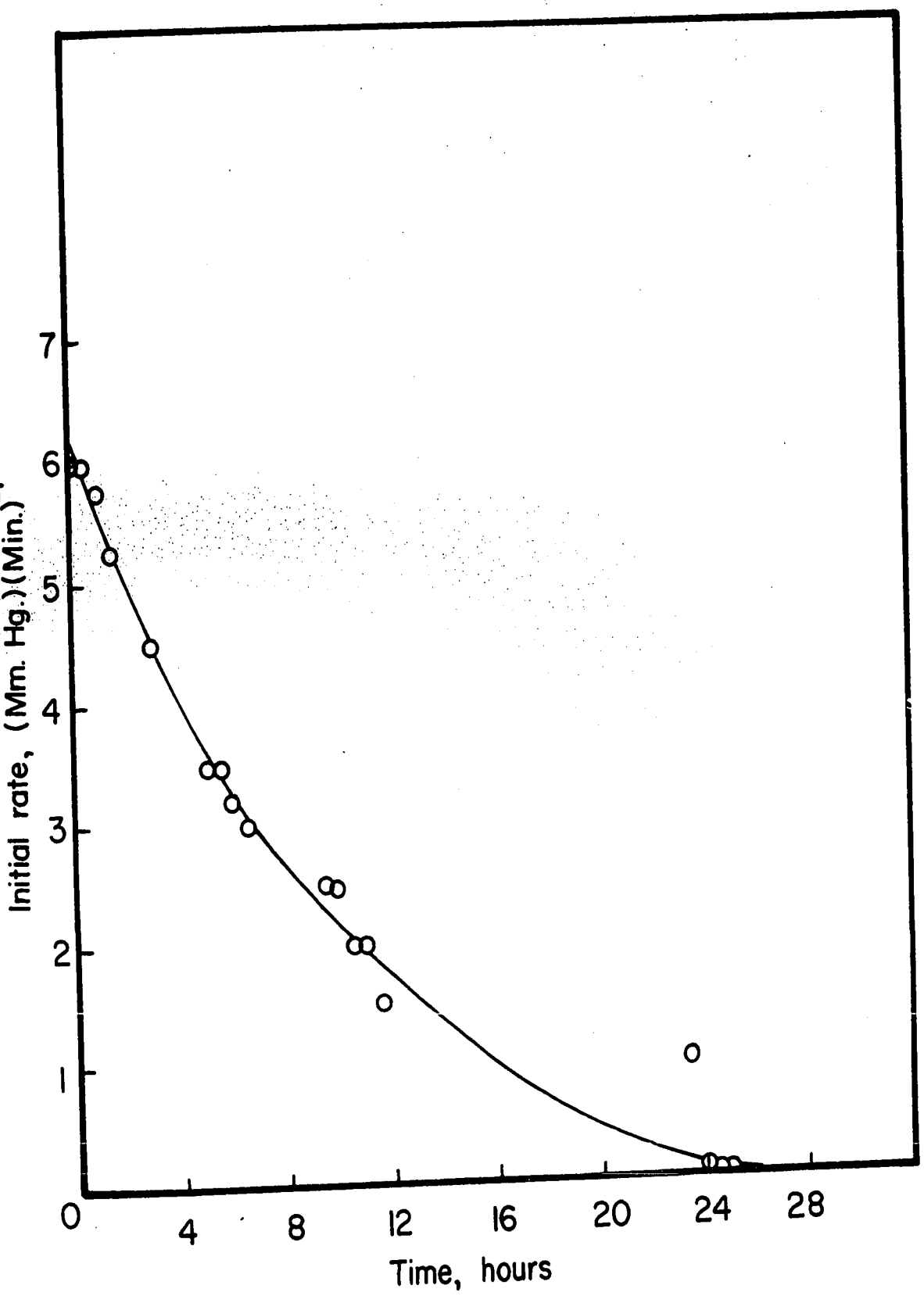


Fig. 31 The dependence of initial rates upon time, osmium-pumice

The initial ratios of reactants were five for both the catalysts. Hence the temperature employed and the initial rates, weight for weight, obtained enabled to conclude that ruthenium was slightly more active than osmium. However, both were unsuitable for detailed kinetic studies.

VI RESULTS OF PRODUCT ANALYSES

The overall rate equations were found to be solely dependent on the initial pressures of reactants for all the catalysts. Except platinum-pumice catalyst, the initial rates for all other catalysts were independent of methyl acetylene pressure and decreased slightly with increase of methyl acetylene pressure. The initial rate equation suggested that methyl acetylene was strongly chemisorbed on the surface of the catalyst.

Although the rate equations for all but platinum catalyst were identical, the activation energies were different. Therefore the rate controlling steps could not be the same, though the same mechanism might be operating.

While hydrogenating acetylene over nickel powder, Sabatier and Senderens (4) recorded formation of ethylene, ethane and higher hydrocarbons. Bond and Sheridan (24) hydrogenated methyl acetylene over pumice supported nickel and platinum catalysts. They found propylene, propane and polymers as products. They could not detect propane over palladium-pumice catalyst. They did not investigate the kinetics of the reaction systematically and did not study some of the variables, like the effect of temperature on products.

In the present work, a very systematic product analysis was made over a nickel-pumice catalyst.

I. The course of reaction

The course of reaction was investigated, using the same amount of nickel-pumice catalyst as was used for kinetic studies. The temperature employed was 97° C. An equimolar mixture of reactants (90 mm. of each) was always used. The course of reaction was followed by means of analysis after various falls in pressures, after the catalyst had attained a constant activity. The results are given in Table 14 and the sample calculations are given in appendix D.

Figures 32 and 33 show the course of reaction. The formation of propylene was 3-4 times that of propane at all stages. The selectivity varied from 0.75 to 0.80. Loss of methyl acetylene was always slightly higher than that of hydrogen. Recoveries of hydrogen and methyl acetylene were above 84% and 76% respectively.

II. Effect of initial pressure of hydrogen on the yields

The dependence of yields on the initial pressure of hydrogen was studied at 97° C. While the initial methyl acetylene pressure was kept constant at 30 mm., the initial hydrogen pressure was always varied. Products were analysed, when the total pressure fall was equal to the initial methyl acetylene pressure. The results are given in Table 15.

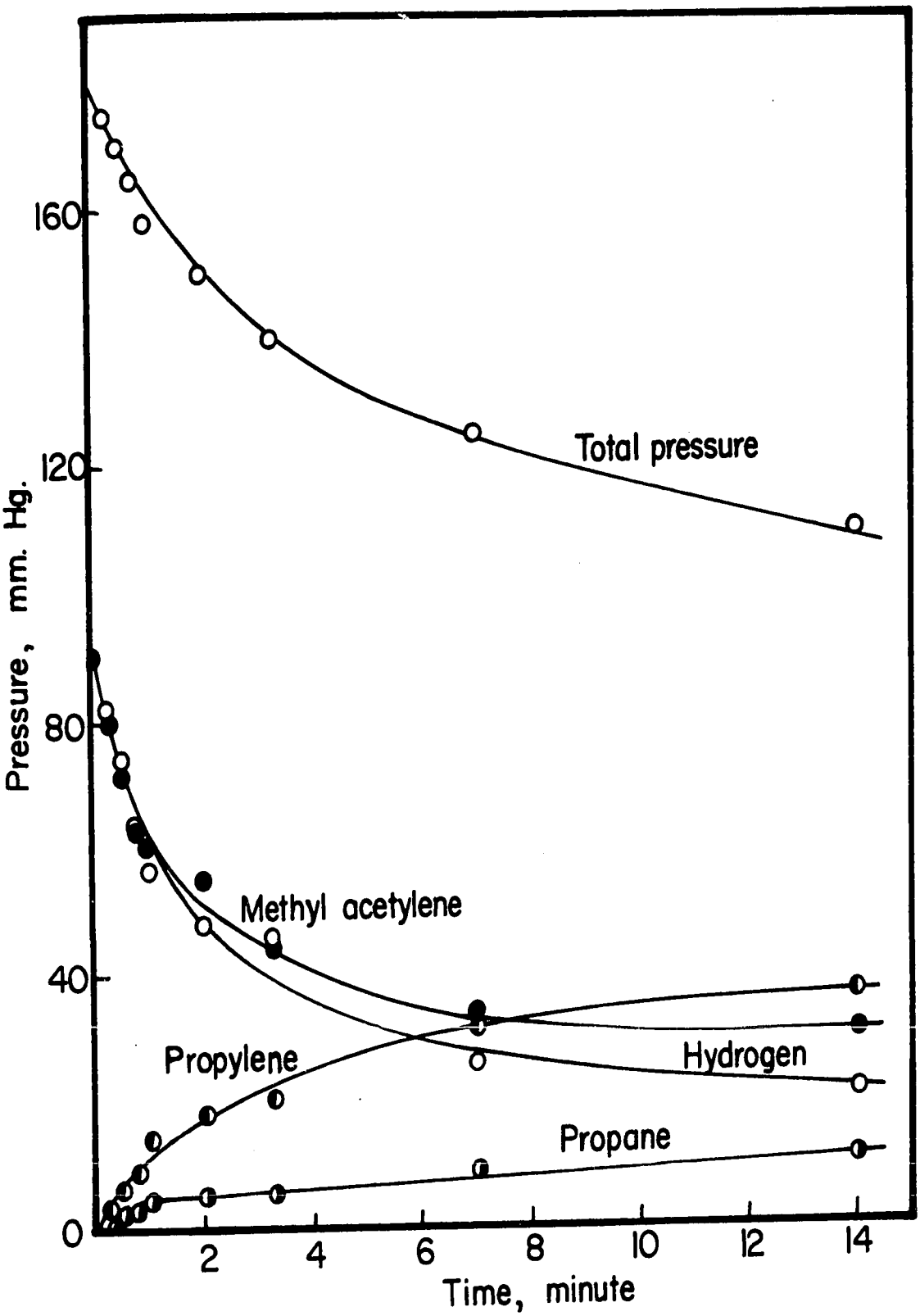


Fig. 12 Course of reaction over nickel-pumice at 97° C

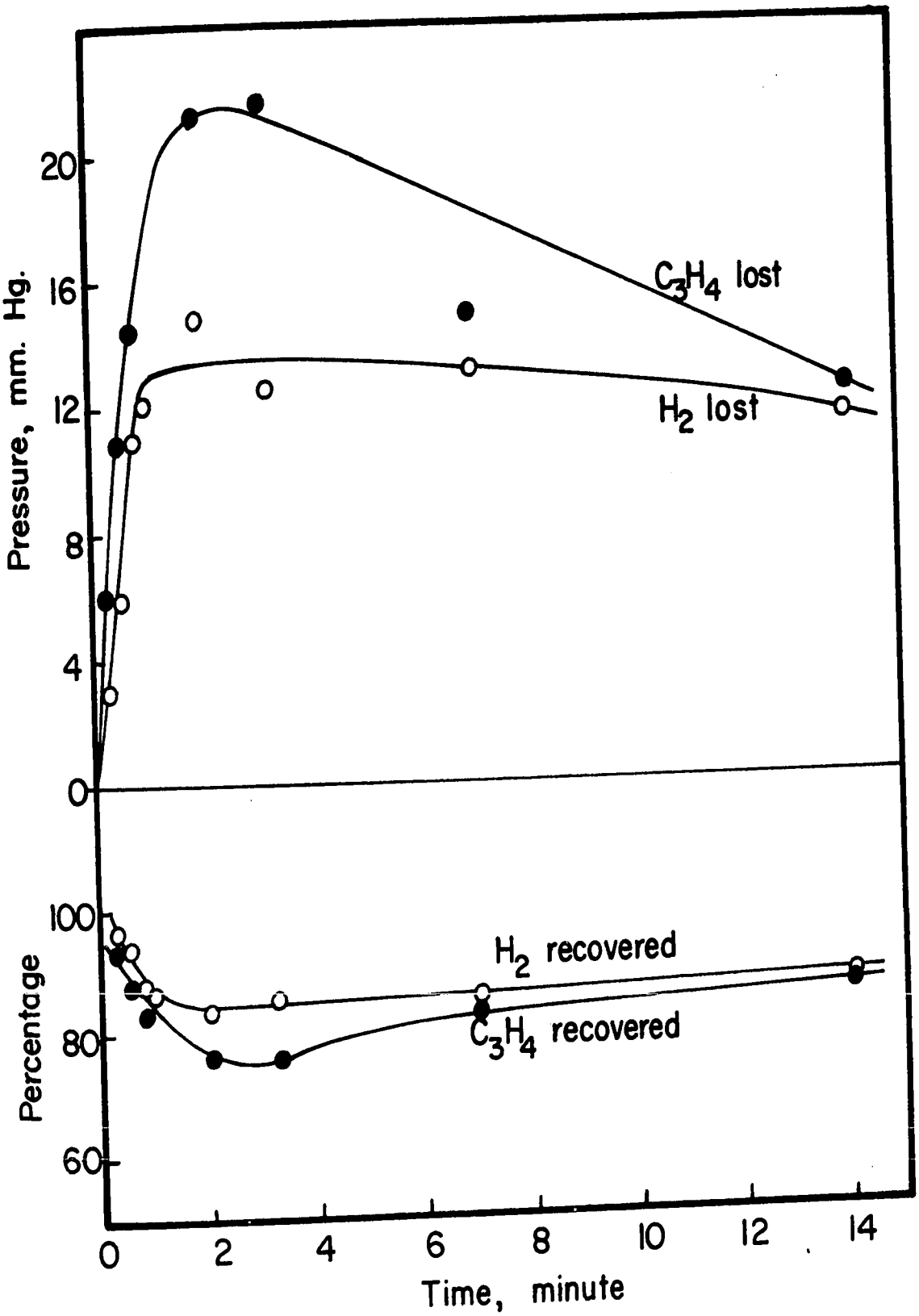


Fig. 33 Course of reaction over nickel-pumice at 97° C

The overall rate equation 10 suggested that the rate would increase with increase of initial hydrogen pressure. So a study of the effect of initial hydrogen pressures on products was desired to correlate the products and the selectivity with the initial ratios of reactants.

Higher ratios of reactants lowered the propylene: propane ratios in the product. Figure 34 shows a plot of propylene and propane yields (as percentage of methyl acetylene not recovered) against initial ratios of reactants. With the increase of initial ratios of reactants, yield of propane increased and that of propylene decreased. When the initial ratio of reactants was 4.25, yields of propylene and propane were equal and each was 33.5%.

An identical behaviour was observed when acetylene was hydrogenated over rhodium-pumice catalyst (23). However, when acetylene was hydrogenated over nickel-pumice catalyst (13), yields of ethylene and ethane increased in a parallel manner.

Figure 35 shows the effect of initial ratios of reactants on partial pressures of propylene and propane in the product stream. Figures 36a and 36b show the effect of initial ratios of reactants on propylene: propane ratios and on selectivity respectively. The selectivity S decreased with the increased initial ratios of hydrogen: methyl acetylene $\overline{R}$. The results were fed into the computer and the equation

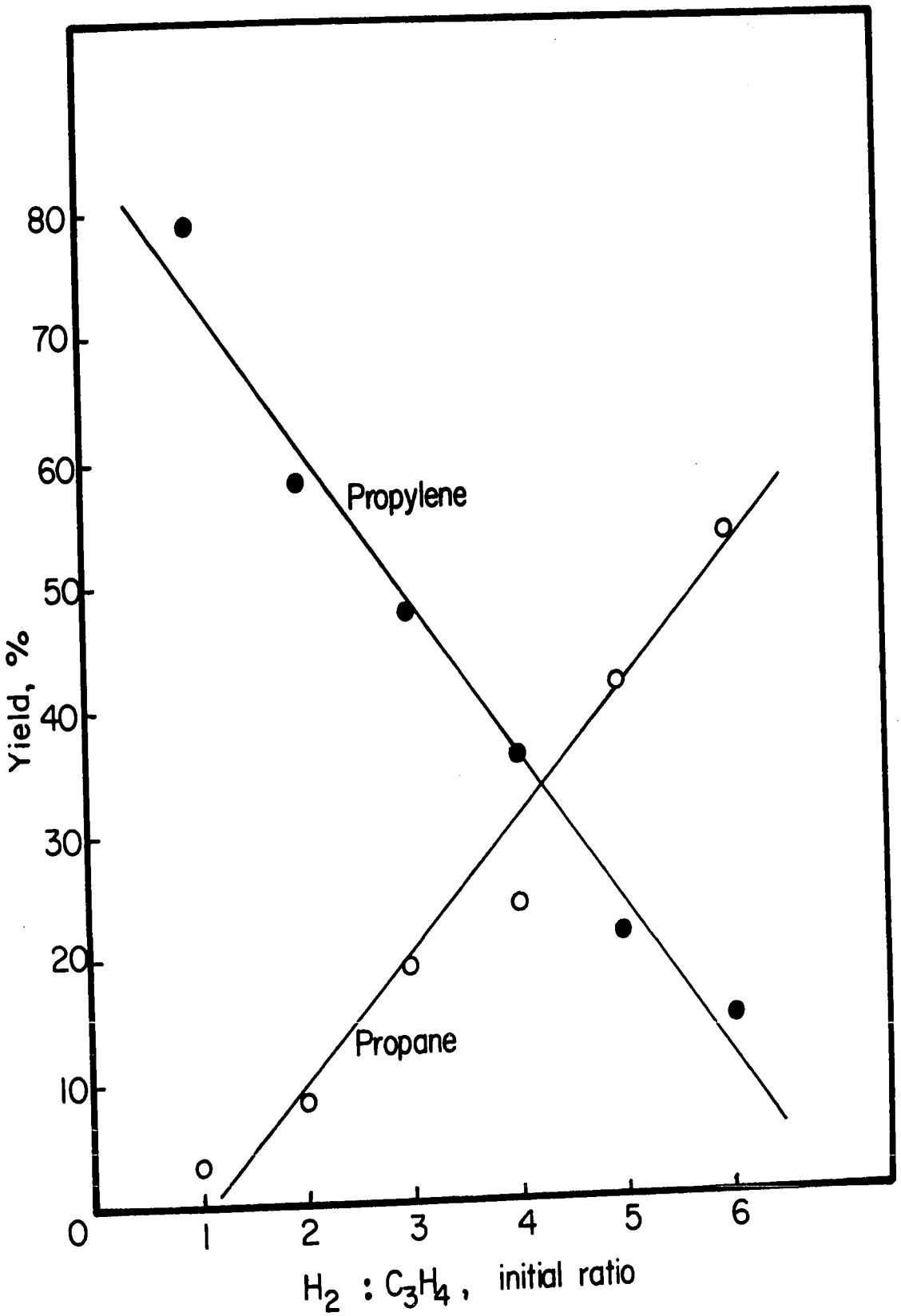


Fig. 34 The dependence of yields upon initial $H_2:C_3H_4$ ratios

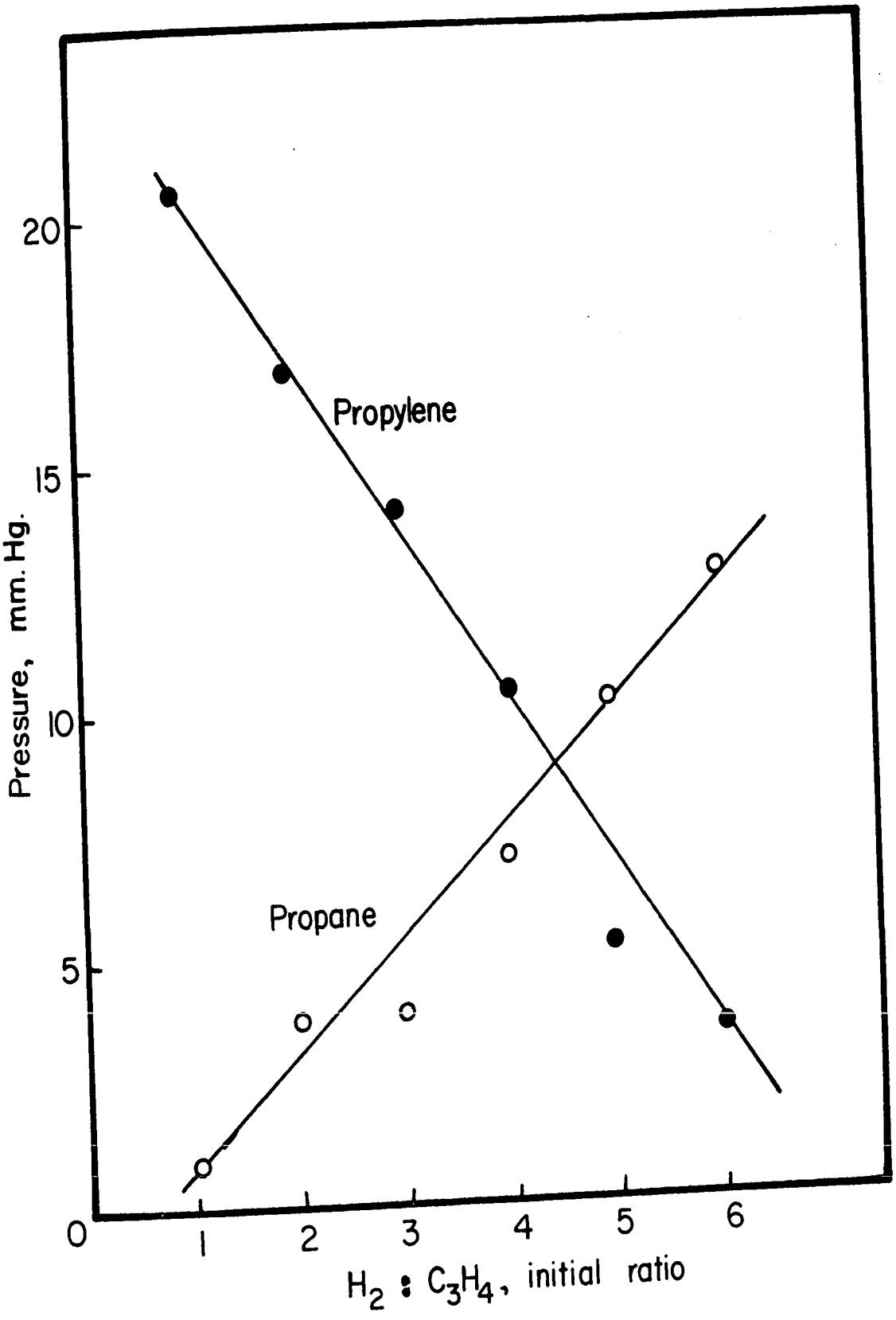


Fig. 35 The dependence of products' pressure upon initial H_2:C_3H_4 ratios

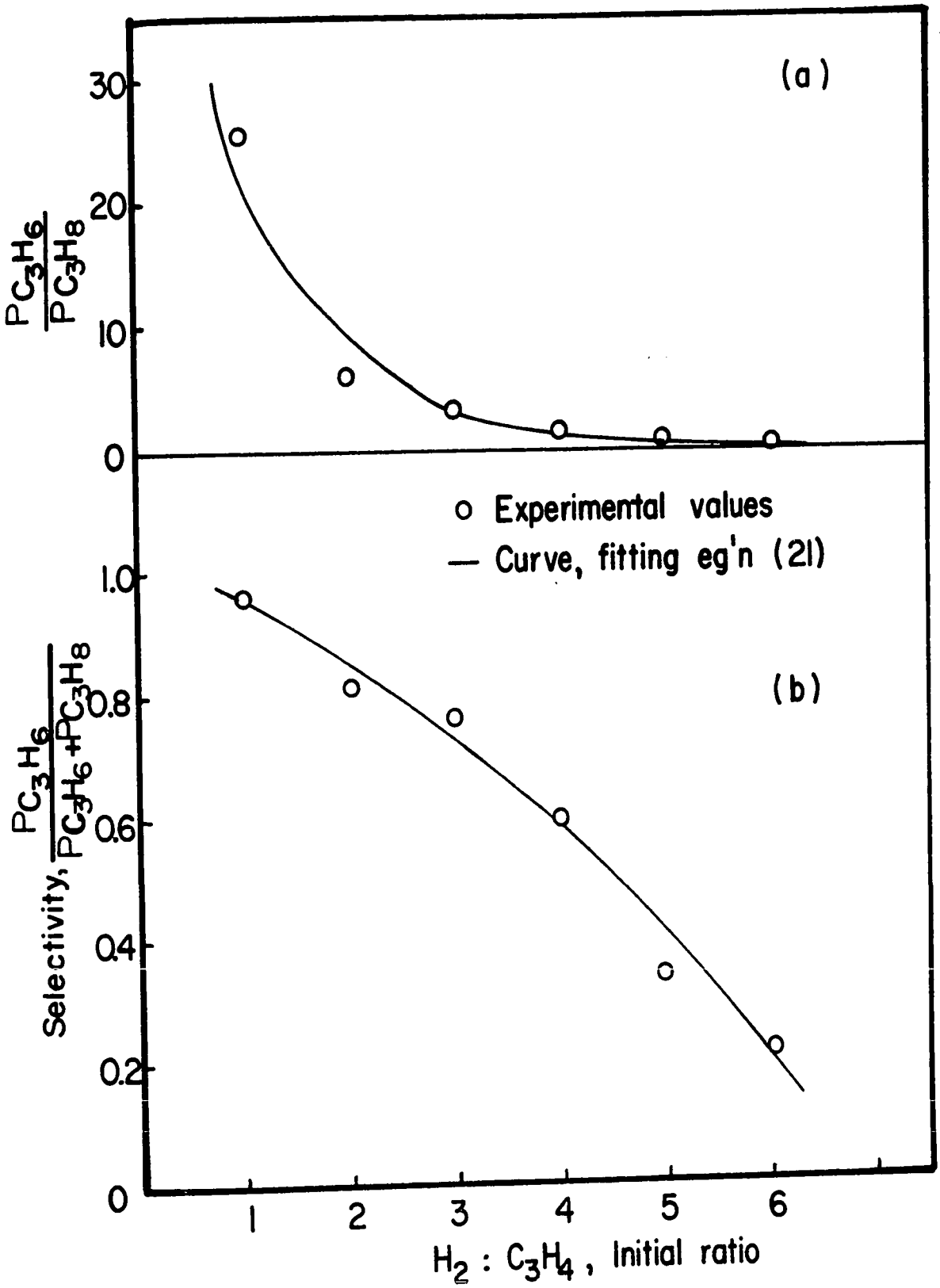


Fig. 36 The dependence of propylene:propane ratios and selectivity upon initial H_2:C_3H_4 ratios

$$S = 1.028 - 0.060\,\overline{R} - 0.013\,\overline{R}^{2} \qquad (21)$$

was obtained to give the best fit of the data. In Figure 36b, while the experimental points are indicated by the open circles, the solid curve represents the one obtained from equation 21.

III. Effect of initial methyl acetylene pressure on the yields

The initial methyl acetylene pressure dependence of yield was studied at 97° C by maintaining a constant initial hydrogen pressure of 90 mm. and varying the initial methyl acetylene pressure. The products were analysed after reaction took place for one minute, for each run. Results of analysis are given in Table 16.

Propylene: propane ratios in the products varied from 2.70 to 3.09. The selectivity ranged between 0.73 and 0.75. Increase of initial methyl acetylene pressure increased the loss of methyl acetylene and decreased the loss of hydrogen.

Figure 37 shows the effect of initial methyl acetylene pressures on polymer formation. The amount of polymers increased with methyl acetylene pressure, giving a nonlinear relationship. The polymers thus formed poisoned the catalyst, decreasing the initial rate at the same temperature. In agreement with the kinetic studies, it was now confirmed that for higher initial methyl acetylene pressure, the initial rate would decrease.

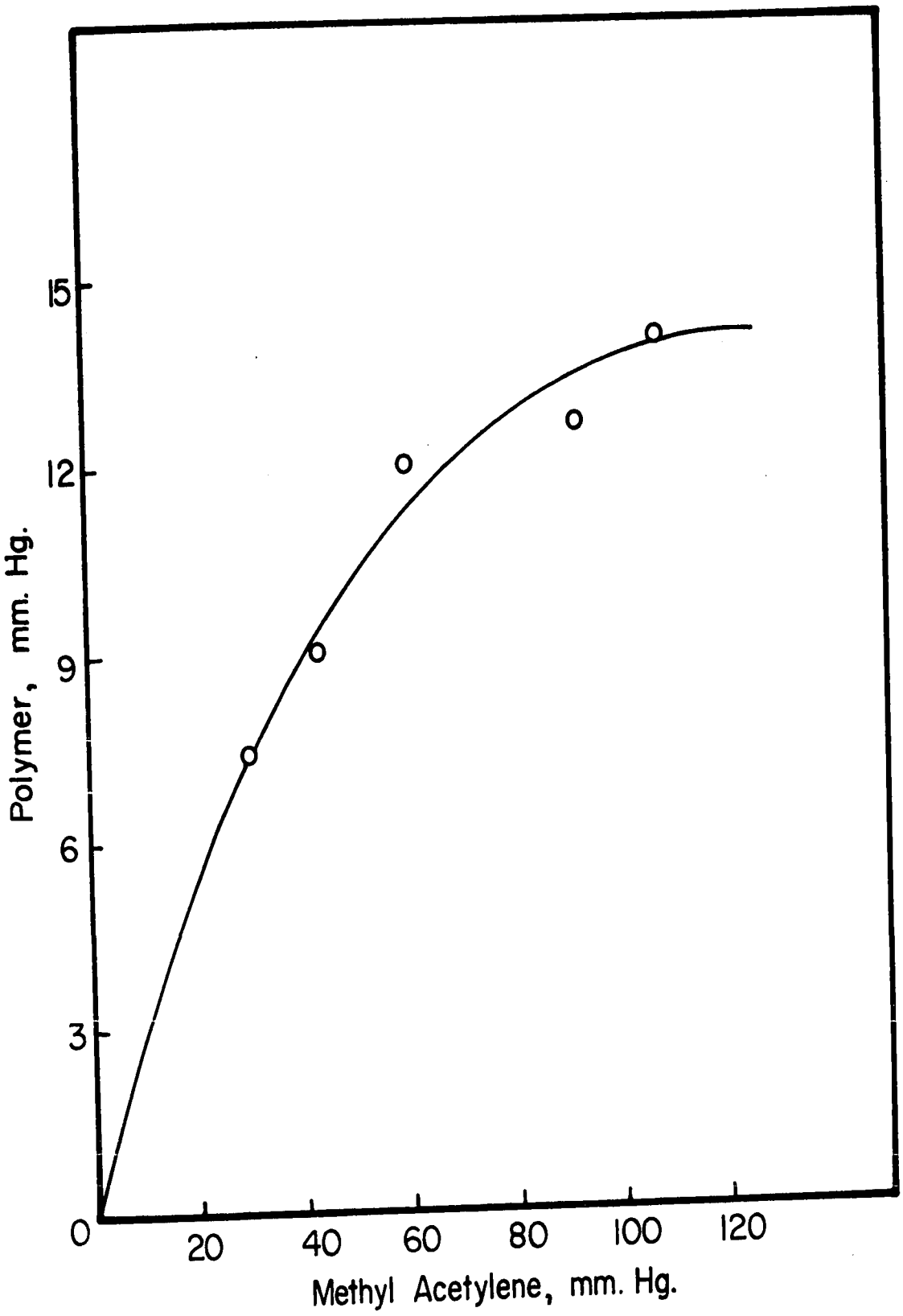


Fig. 37 The dependence of polymers upon initial methyl acetylene pressure

IV. Effect of temperature on yields

The temperature dependence of the yields was studied with an equimolar mixture of reactants (90 mm. of each). The products were analyzed at several temperatures, for a total pressure fall of 45 mm. The results are given in Table 17.

With increased temperatures, the amount of propylene and propane in the product stream decreased rapidly. But the propylene: propane ratios and the selectivity increased. Figure 38 shows the affect of temperatures on partial pressures of propylene and propane in the product-stream.

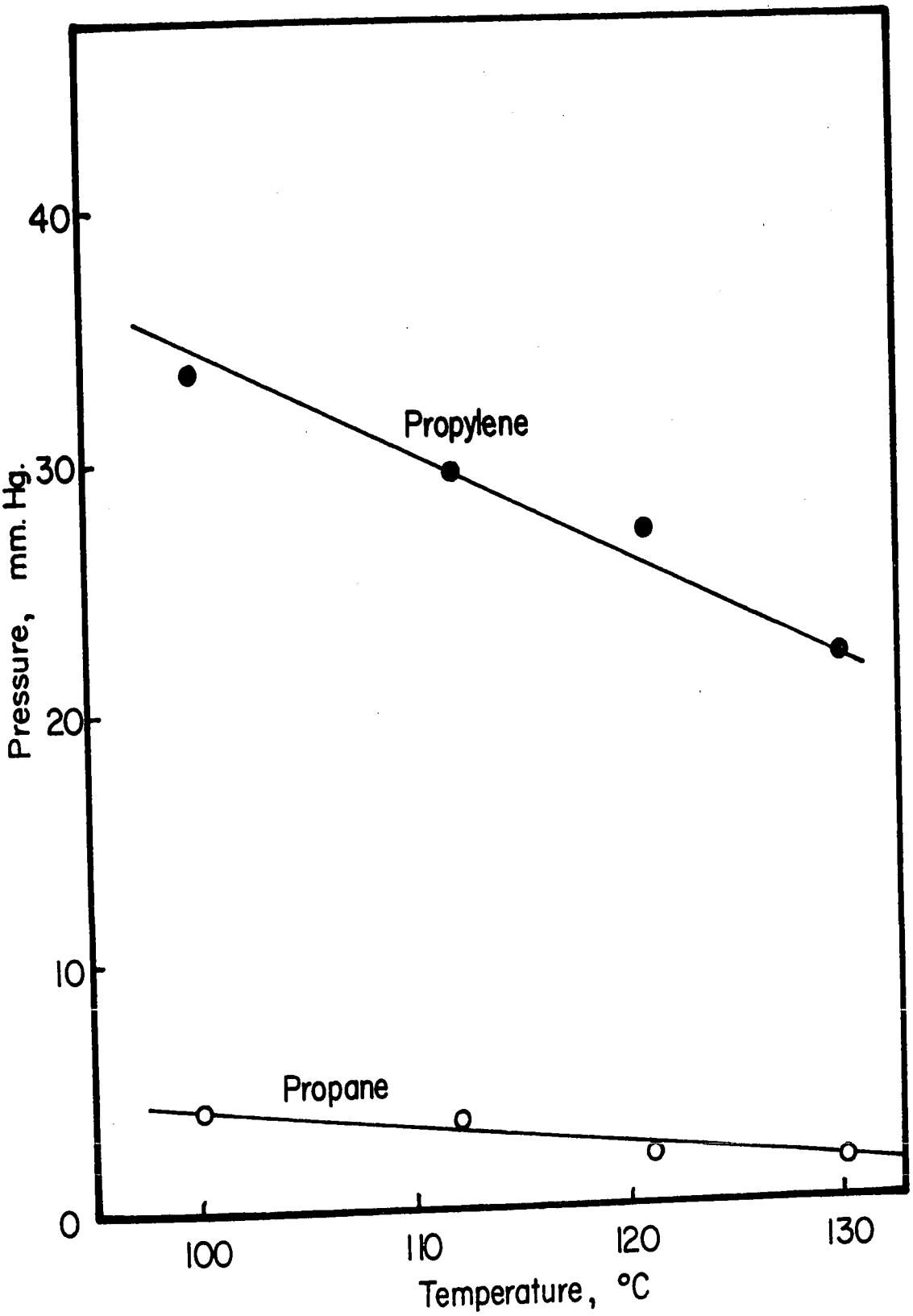


Fig. 38 The dependence of products upon temperature

VII DISCUSSIONS AND CORRELATIONS

I Activity of Catalysts

The rate of reaction expressed in millimeters of mercury per unit time per unit weight of metal can be considered as one of the best methods available for comparing the catalytic activity of the catalysts, provided all the catalysts are prepared in the same manner on the same support. However, the rate of reaction thus expressed is not suitable for being used as a parameter for correlations, since the reaction rate is a function of temperature, pressure and composition. It is possible to calculate the overall rate constant $\bar{k}$ (per minute per gram). The parameter $\bar{k}$ depends on temperature and not on pressure (except perhaps at a very high pressure) or composition.

Since the overall rate constant $\bar{k}$ depends on temperature, it is necessary to use a reference temperature T_r for all the catalysts.

Selecting the reference temperature as 80° C, rate constants ks were either intrapolated or extrapolated from the Arrhenius plot. The rate constants were experimentally found to increase proportionally with the amount of metal present in the catalysts. Knowing the proportionality factor, the overall rate constants $\overline{ks}$ per minute per gram weight of metal for various metals were calculated. Such values are given in Table 18 and the sample calculations are given in appendix D.

Considering the overall rate constant $\bar{k}$ as a measure of the catalytic activity, it would appear that the order of catalytic activity for pumice supported catalysts is:

$$Pt > Pd > Ni > Ir > Rh > Co > Fe > Ru > Os$$

Ruthenium and osmium were compared on the basis of their initial rates, as systematic investigation for these two metals could not be made due to their rapid deactivation. According to Sheridan (23), the order of activity, for acetylene hydrogenation over pumice supported catalysts, was:

$$Pd > Pt > Ni,\ Rh > Co > Fe > Ir > Ru,\ Os$$

Platinum, palladium, nickel, iridium and rhodium were found to be most active catalysts for hydrogenating methyl acetylene. All these metals have face-centred cubic structure. Ruthenium and osmium were least active. Both have close-packed hexagonal structure. Cobalt might contain crystals of both these structures (39) and its activity was presumably due to the cubic form. Iron is the only metal having a body-centred cubic structure. It had thus a smaller activity than face-centred cubic metals and cobalt. Maximum activity in each horizontal row of group VIII metals, occurred in the column of nickel, palladium and platinum. This was in agreement with the observations of Sheridan and Reid (23) for acetylene hydrogenation.

II Geometric Factor

Differences in the catalytic activities can be explained in terms of geometric factor. In 1929, Balandin (40) proposed that a group of properly spaced atoms only on a certain plane of the metal might be responsible for the catalytic activity. Herington (41) and Sheridan (42) considered the geometry of the associatively adsorbed state of acetylene and shed further light on such spatial considerations. Bond lengths for acetylene and methyl acetylene are same. Hence, an analogous discussion can be made for methyl acetylene hydrogenation.

From the knowledge of carbon-metal distances and carbon-carbon distance, optimum metal-metal distances can be calculated. The optimum metal-metal distances for nickel, palladium and platinum are 3.33, 3.43 and 3.43 Å respectively. Planes having metal-metal distances very near to these values are suitable for adsorption of methyl acetylene. Available metal-metal distances for these metals in (110) plane are 3.50, 3.91 and 3.88 Å respectively. Available metal-metal distances in other planes are much different. Therefore, (110) planes of face-centred cubic metals are favourable for adsorption of methyl acetylene. The catalytic activities of platinum, palladium, nickel, iridium and rhodium are attributed to these metals' favourable metal-metal distances in (110) planes.

$(10\bar{1}0)$ planes of cobalt, ruthenium and osmium resemble the (110) planes of face-centred cubic metals. But the metal-metal

distances in $(10\bar{1}0)$ planes for cobalt, ruthenium and osmium are 4.11, 4.27 and 4.31 Å respectively. These distances are much longer than the optimum metal-metal distances are are probably too long to be spanned by adsorbed methyl acetylene without considerable strain.

III Electronic Factor

Further attempts in elucidating the phenomenon of heterogeneous catalysis usually involve the correlation of the strength of surface bonds with the nature of the chemical bonds in metals, in the light of the theory of metals. The theory of metals, developed by Pauling (43, 44, 45), regards the metallic bond as involving a resonance between covalent and ionic bonds formed between the individual atoms. The resonance forms in lithium, for example, are given as:

$$\begin{matrix} Li - Li \\ \\ Li - Li \end{matrix} \longleftrightarrow \begin{matrix} Li - \bar{Li} \\ + \\ Li \quad Li \end{matrix}$$

In order for this resonance to be possible, the atom must be capable of forming a structure of the type - $\bar{Li}$ - which in turn requires the atom to have an available orbital, known as the metallic orbital. The metallic orbital consists of a vacancy which can receive an electron and then share it with a neighbouring atom.

As an example, the scheme in Table 19 represents the electronic configuration of nickel. In nickel A structure, there are two unpaired d electrons, whereas in nickel B, there are no unpaired electrons. From the experimental values of the magnetic moment, nickel consists of 30% of A form and 70% of B form. In nickel A, there are two d electrons and altogether six orbitals are involved in bonding. In nickel B, there are three d electrons and seven orbitals (empty p orbital is the metallic orbital) are involved in bonding. Therefore, the percentage d-character in nickel is given by:

$$30 \times \frac{2}{6} + 70 \times \frac{3}{7} = 40\%$$

Similarly, percentage d-character for group VIII metals have been calculated. Table 20 shows the percentage d-character of these metals.

According to Pauling (45), the number of empty atomic orbitals decreases as the d-band is filled. Assuming that the surface states are related to the electronic configuration of the bulk of the metals, metals with high percentage d-characters will have less orbitals available for bonding with the adsorbate and will have high activity.

Attempt to find a correlation between the catalytic activity of metals and their percentage d-characters was made as early as 1950 by Beeck (46). Using the results obtained for ethylene hydrogenation on metal films at 0°C, he plotted logarithm of activity against per-

A smooth nonlinear curve was obtained and metals with higher percentage d-character were more active. Schuit's modification (47) of plotting logarithm of activity against percentage d-character x metallic valency improved the situation and a linear plot was obtained, again activity increasing with the increased percentage d-character x metallic valency.

However, Beeck's correlation appeared to be poor when Kemball's (48) results for ethylene hydrogenation over metal films at -100° C and results of Schuit and van Reijen (49) for ethylene hydrogenation over silica supported metals at 0° C were used. Also, Beeck's correlation of activity order did not follow the percentage d-character for propane deuteration. Further, Beeck's correlation suffered a serious set back when Sheridan and Reid (23) considered acetylene hydrogenation over various pumice supported metal catalysts. They plotted logarithm of activity against percentage d-character. A maxima was reached for palladium. Unlike the findings of Beeck for ethylene hydrogenation, rhodium with highest percentage d-character was found not to have the highest activity. It was less active than palladium, platinum and nickel which lesser percentage d-character. Further, ruthenium, osmium and iridium with higher percentage d-character than nickel, palladium, platinum, cobalt and iron were lower in activity. Since Beeck's (46) correlation did not include ruthenium, osmium, cobalt

and iridium; there does not appear to be enough reasons for accepting his postulation that catalytic activity is directly dependent on percentage d-character. The same reasonings are applicable to Schuit's (47) modification. Their correlation is limited to their own work on ethylene hydrogenation over a limited number of group VIII metal films.

It appears that Beeck's correlation is of not much significance for methyl acetylene hydrogenation over pumice supported catalysts, since nickel, palladium and platinum with lesser percentage d-character than ruthenium, osmium, rhodium and iridium were much more active. Iron and cobalt with percentage d-characters close to nickel were less active than nickel.

Emmett (50) correlated Kemball's (51) results of activation energy against percentage d-character, for ammonia deuteration over metal films. A linear plot was obtained, the activation energy decreased with increased percentage d-character. However, Kemball's (51) work did not include cobalt, iridium, ruthenium and osmium. Also iron, nickel and platinum were far away from the sequence.

For methyl acetylene hydrogenation over supported metal catalysts, activation energy was plotted against percentage d-character. A nonlinear plot, shown in Figure 39, was obtained. The activation energy decreased with increased percentage d-character. However, cobalt and

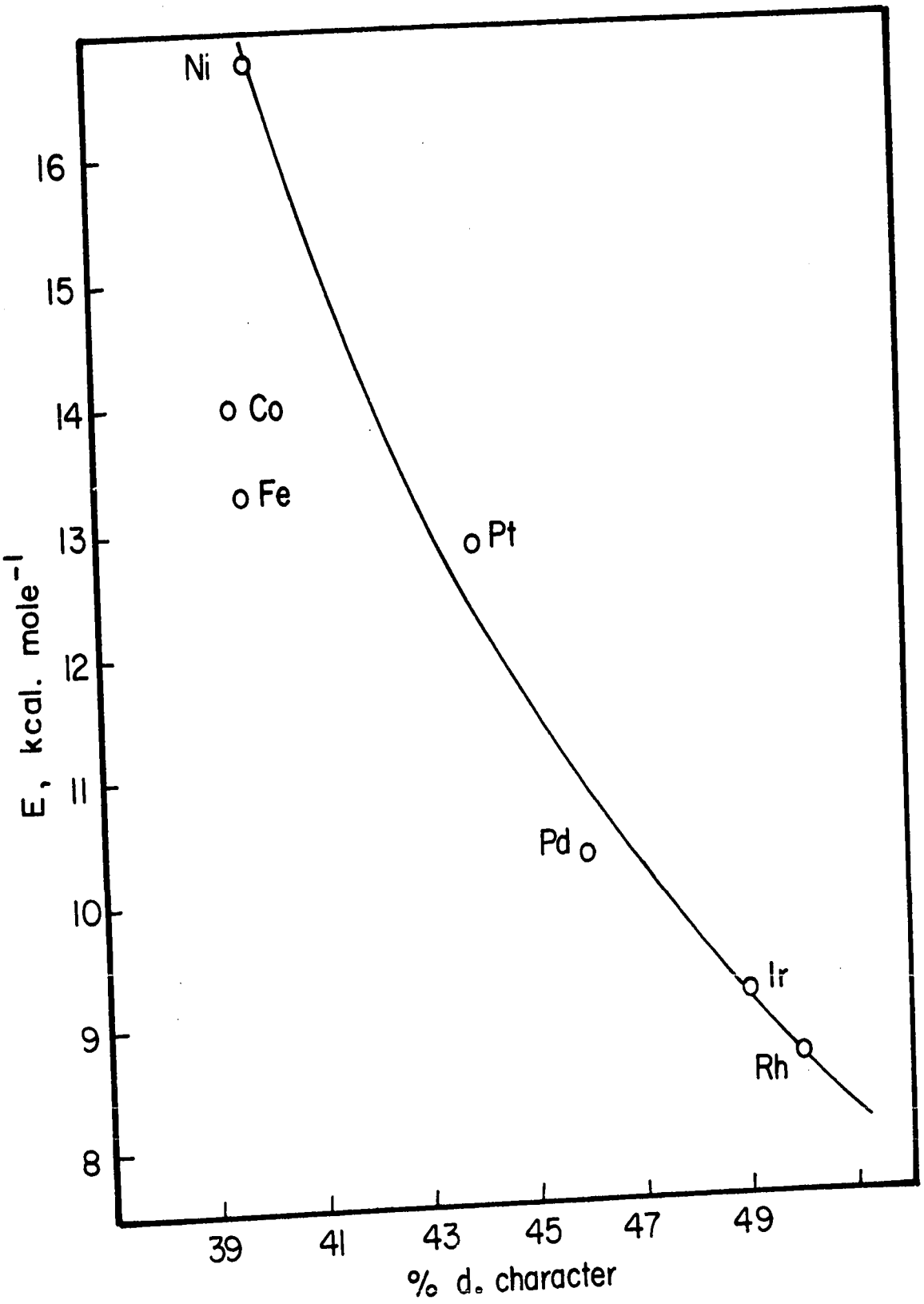


Fig. 39 Effect of percentage d-characters on activation energies

iron fall out of smooth sequence. The possible explanations are: (1) cobalt and iron do not have face-centred cubic structures like other metals and (2) activation energies for cobalt and iron were determined in a much higher temperature range.

However, no suitable theory has been established as yet to explain the dependence of catalytic activity on geometric and electronic factor (52, 53).

IV Compensation Effect

Variations of activity defined by the overall reaction rate constant $\bar{k}$ shown by a series of related catalysts, such as a series of different metals or a given metal treated in a variety of ways, may be due to the variations in activation energy E or in the pre-exponential factor A or in both simultaneously. The frequently observed relationship between activation energy E and the pre-exponential factor A is of the form

$$\log_{10} A_i = m E_i + c \qquad (22)$$

and is referred to as a "compensation effect". When $\log_{10} A_i$ is plotted against E_i, m and c are slope and intercept respectively.

(1) An increase in $\log_{10} A$ at constant activation energy E implies a higher rate, (2) an increase in activation energy E at constant $\log_{10} A$ implies a lower rate and (3) simultaneous increase or

decrease in both tend to compensate from the stand point of the rate. (1) and (2) are "no compensation effects". (3) has a "compensation effect". For methyl acetylene hydrogenation, both activation energy and the pre-exponential factor were variable. "Compensation effect" is, therefore, anticipated.

Since variations in the catalytic activity is best studied at a reference temperature (54), $\log_{10} A$ values were obtained at 80° C. These values have been tabulated in Table 18. Plots of $\log_{10} A_i$ against activation energies are shown separately for nickel catalysts in Figure 40 a and for pumice supported catalysts in Figure 40 b. Linear plots were obtained for both cases. The slope and intercept for Figure 40 a were 0.50 and 1.80 respectively. The Arrhenius parameters for nickel catalysts can be correlated by the following equation:

$$\log_{10} A_i = 0.50\, E_i + 1.80 \qquad (23)$$

The slope and intercept for Figure 40 b were 0.75 and -2.50 respectively. The Arrhenius parameters for pumice supported catalysts can be correlated by the equation

$$\log_{10} A_i = 0.75\, E_i - 2.50 \qquad (24)$$

Bond and Mann (22) have found the following corresponding equations for acetylene hydrogenation:

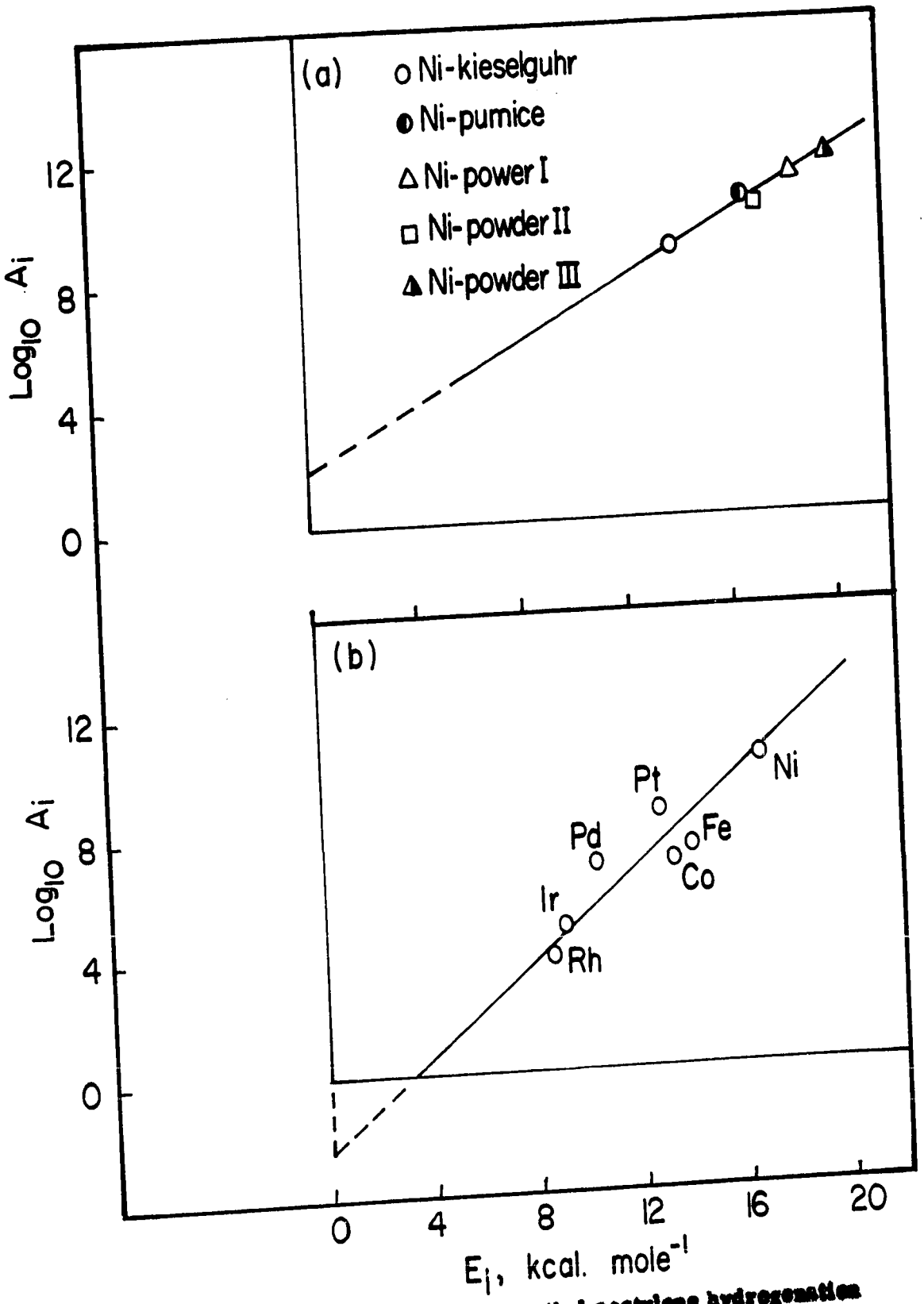


Fig. 40 Compensation effects for methyl acetylene hydrogenation

$$\log_{10} A_i = 0.48\ E_i + 0.40 \quad (25)$$

$$\log_{10} A_i = 0.55\ E_i - 1.50 \quad (26)$$

V Reaction Mechanism

The establishment of a mechanism for a heterogeneous catalytic reaction is more difficult and of greater complexity than a homogeneous reaction. The main reason for this is that in case of a heterogeneous reaction, the surface is an active participant and has to be considered as a reactant. The concentration of the active surface in the steady state is not directly accessible. Further, the normal state of the free surface may be disturbed when adsorption occurs on it. The transition state of a heterogeneous reaction is more difficult to define both in geometric and energetic terms, than that of a homogeneous reaction. Therefore, the reaction mechanism of a heterogeneous reaction is usually explained by the results over simplified models.

Although the hydrogenation of olefins results in saturated products containing the same number of carbon atoms, hydrogenation of acetylenes is accompanied by the formation of polymers with the unsaturated and saturated products. Hence, the reaction mechanism for acetylenes' hydrogenation becomes still more complicated. For acetylene hydrogenation, Bond and Wells (55) suggested three types of

mechanisms. Their discussions are based on the experimental observations and deductions obtained for acetylene deuteration.

There appears to be no published data on methyl acetylene deuteration. Therefore, in this work, an attempt has been made to suggest a mechanism based on product analyses over nickel-pumice catalyst and by analogy with those postulated by Sheridan (42) for acetylene hydrogenation.

The results of the kinetic investigations show that strongly adsorbed methyl acetylene and weakly adsorbed hydrogen are involved in the steps, determining formation of propylene, propane and higher hydrocarbons (polymers). Adsorption of methyl acetylene follows an "associative mechanism", analogous to adsorption of acetylene. Gaseous methyl acetylene and hydrogen are adsorbed at the catalyst surface. The reactions may be represented as:

$$H_3C - C \equiv CH + 2* = H_3C - \underset{*}{C} = \underset{*}{CH} \qquad (I)$$

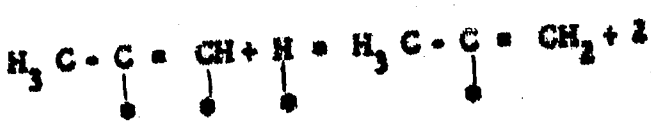
(adsorbed methyl acetylene)

$$H - H + 2* = \underset{*}{2H} \qquad (II)$$

(adsorbed hydrogen atom)

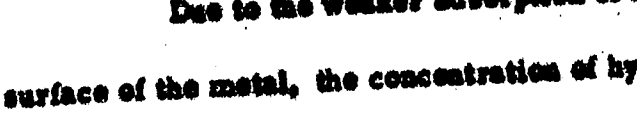
where * represents a catalyst atom.

Reaction between adsorbed methyl acetylene and hydrogen may occur as follows:



(III)

Due to the weaker adsorption of hydrogen on the surface of the metal, the concentration of hydrogen atoms on the surface would be low. The initial reaction (III) may therefore be represented by the equation

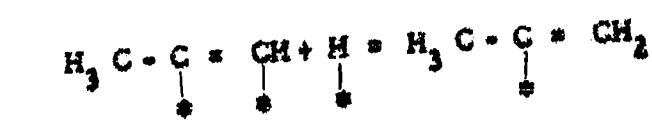


(IV)

(half-hydrogenated state)

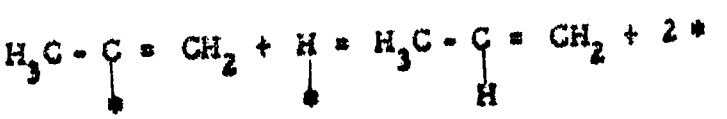
implying that the adsorbed hydrogen atom reacted immediately with an adsorbed methyl acetylene molecule to form a half-hydrogenated state

The activation energy for methyl acetylene hydrogenation on nickel-pumice catalyst was constant in the temperature range of 50° - 88°C. Products were analyzed at 97° C at which temperature the activation energy may be assumed to be the same. Constancy of the activation energy and absence of hydrogen exchange reactions (24, 37) reduced the possibility for the reversibility of reaction (IV). Therefore, the reaction may be represented as



(V)

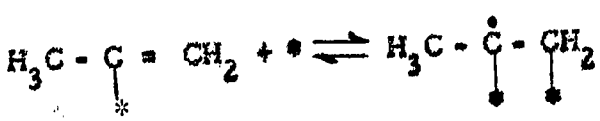
The half-hydrogenated state, an adsorbed radical, would react with an adsorbed hydrogen atom to form gaseous propylene:



(VI)

(Propylene)

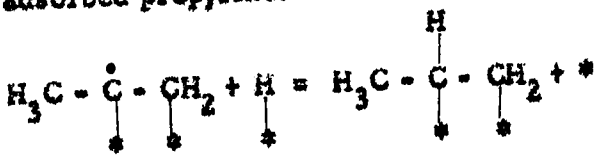
The adsorbed radical would further isomerize into a free radical:



(VII)

(free radical)

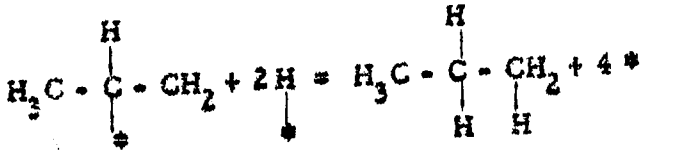
The free radical would react with an adsorbed hydrogen atom to give adsorbed propylene:



(VIII)

(adsorbed propylene)

Propane was formed in the early stages of methyl acetylene hydrogenation. This would have come from the further hydrogenation of adsorbed propylene in (VIII).

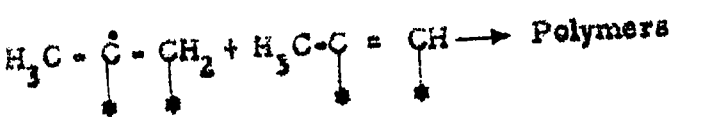


(IX)

(Propane)

Propane can not be formed from re-adsorption of gaseous propylene on planes because methyl acetylene is more strongly adsorbed. Nor can it be formed from re-adsorption of propylene on planes which can not adsorb methyl acetylene, otherwise no selectivity would be observed where the rate of propylene hydrogenation is faster than the rate of methyl acetylene hydrogenation. Propane is eventually formed by the hydrogenation of adsorbed propylene as represented in (IX). The selectivity is controlled by the reaction (VII) and by the rate of evaporation of propylene from the surface.

When methyl acetylene was hydrogenated, polymers were formed. The free radical formed in (VII), initiated the polymerization with adsorbed methyl acetylene molecules.



(X)

Methyl acetylene hydrogenation produced less polymers than acetylene hydrogenation. Bond and Sheridan (24) estimated steric effects of the methyl group in adsorbed methyl acetylene. They believed that the steric effects might prevent extensive polymerization in the chemisorbed layer. Also physically adsorbed methyl acetylene might cause polymerization.

This work agrees with the observations of Bond and Sheridan (24) as it explains the reasons for the increase of the polymers with increased initial methyl acetylene pressure. It appears that the concentration of the physically-adsorbed methyl acetylene was not affected by the temperature. Hence the yield of polymer was found to be almost independent of temperature.

Polymerisation is probably initiated by the free radicals in the chemisorbed layer and then proceeds through methyl acetylene adsorbed in the van der Waal's layer.

VIII CONCLUSIONS

The kinetics of methyl acetylene hydrogenation over the transition metal catalysts of group VIII, supported on pumice and several other supported and unsupported nickel catalysts, have been investigated in a static system over a wide range of temperature and reactant ratios.

The initial rate equation depended on the initial hydrogen pressures for all the catalysts except platinum, in which case it depended on the initial pressures of methyl acetylene as well.

The catalytic activities of the pumice supported catalysts for methyl acetylene hydrogenation were in the sequence:

$$Pt > Pd > Ni > Ir > Rh > Co > Fe > Ru > Os$$

The face-centred cubic metals appeared to be most active. Such high activity has been explained in terms of metal-metal distances.

Like acetylene hydrogenation and propane deuteration, the order of catalytic activities did not follow the percentage d-character for methyl acetylene hydrogenation.

The Arrhenius parameters, activation energy E and the pre-exponential factor A were variable in this work. Therefore, "compensation effects" were expected and equations relating the pre-exponential factors and the activation energies have been evaluated.

The initial rate equations suggested that the reaction took place due to "adjacent adsorption" of both the reactants, methyl acetylene being more strongly adsorbed than hydrogen.

A possible reaction mechanism has been postulated based on the product analyses over a nickel-pumice catalyst.

It has been proposed that the adsorbed methyl acetylene molecule and the adsorbed hydrogen atom react and form a half-hydrogenated state, which further hydrogenates to form gaseous propylene. The adsorbed half hydrogenated species could also exist in free radical forms which further hydrogenate to gaseous propane and also initiate polymerization.

IX RECOMMENDATIONS

The systematic study of methyl acetylene hydrogenation marks a mile stone in the history of catalysis, for it fills a gaping need in the field of catalytic hydrogenation of unsaturated hydrocarbons. However, certain informations are still needed to explain the mechanism more formly.

(i) The study of selectivity is very important from the industrialist's point of view, besides academic interest. Selectivity is a function of the nature and state of the catalyst, the temperature and the initial pressures of the reactants. Hence, a thorough study over all the catalysts should be made to find the highest selective catalyst.

(ii) The deuteration of methyl acetylene over all the catalysts should be investigated to obtain informations on the reversibility of adsorption of the reactants.

(iii) Nature of adsorbed methyl acetylene species should be determined by infrared spectroscopy. Also nature of polymers should be determined.

(iv) To obtain a better unified knowledge, the work should be extended to more metals, supported and unsupported, particularly on noble metals.

X NOMENCLATURE

A	reactant A
A	pre-exponential factor in Arrhenius equation
B	reactant B
c	intercept in the plot of compensation effects
dP	pressure fall, mm. Hg.
E	activation energy, k cal per mole
E_A	effectiveness factor of catalyst particles
k	overall reaction rate constant, min^{-1}
$\bar{k}$	overall reaction rate constant, $min^{-1} g^{-1}$
m	slope in the plot of compensation effect
P	probability factor in Arrhenius equation
P	pressure of reactants
$P_{C_2H_2}$	initial acetylene pressure, mm. Hg.
$P_{C_3H_4}$	initial methyl acetylene pressure, mm. Hg.
$P_{C_3H_6}$	pressure of propylene, mm. Hg.
$P_{C_3H_8}$	pressure of propane, mm. Hg.
P_{H_2}	initial hydrogen pressure, mm. Hg.
R	gas constant, cal. per mole per degree Kelvin
$\bar{R}$	initial hydrogen: methyl acetylene ratio
r_o	initial reaction rate, mm. Hg. per minute

S	selectivity, propylene: propylene + propane
T	temperature, °K
x	order of reaction with respect to hydrogen
y	order of reaction with respect to hydrocarbon
Z	collision number in Arrhenius equation

Subscripts

A	reactant A
B	reactant B
i	catalyst i
o	initial
r	reference

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XII APPENDICES

Appendix A

Calibration and typical analysis curves

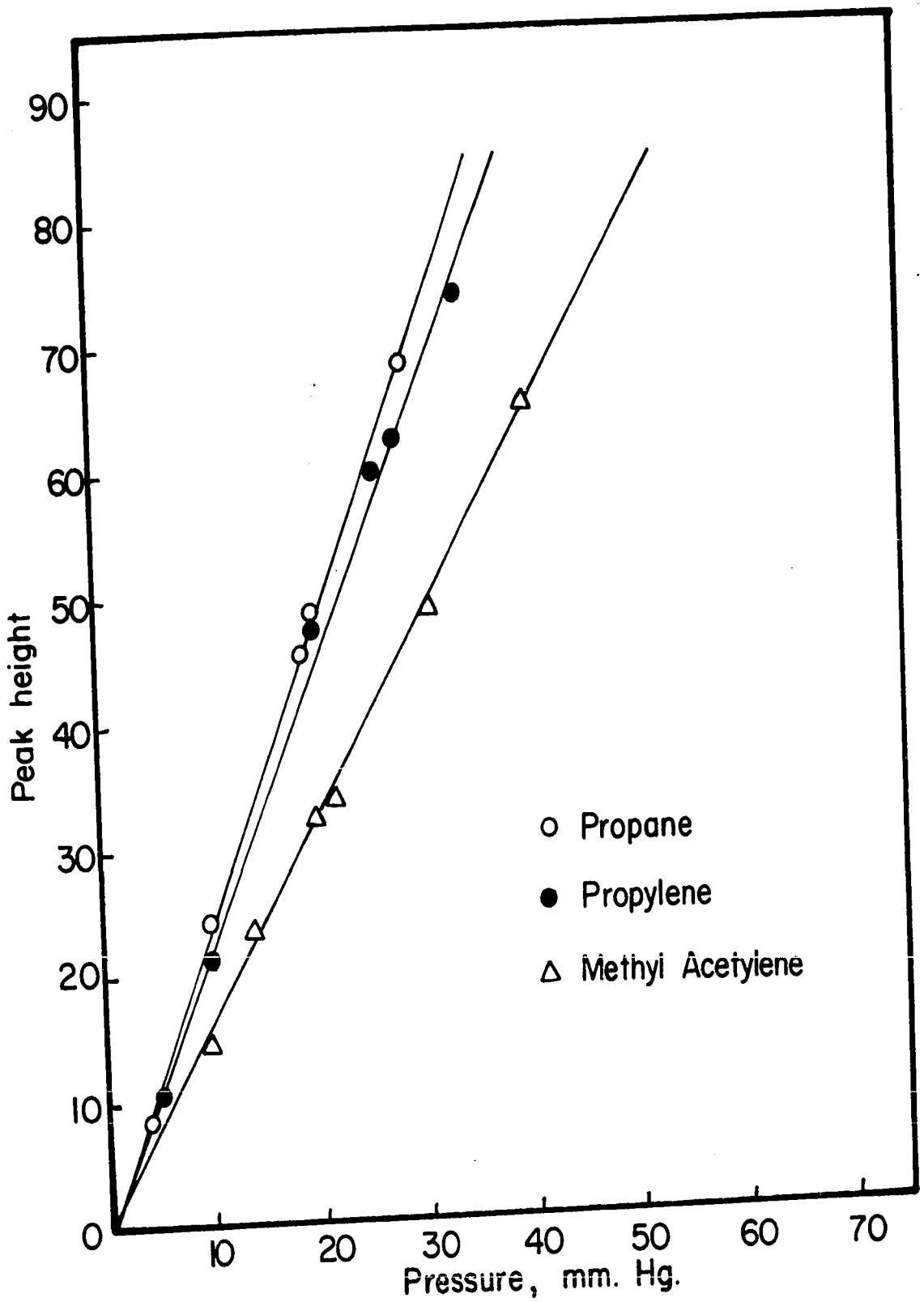

Fig. 3 Calibration of hydrocarbons at 50°C

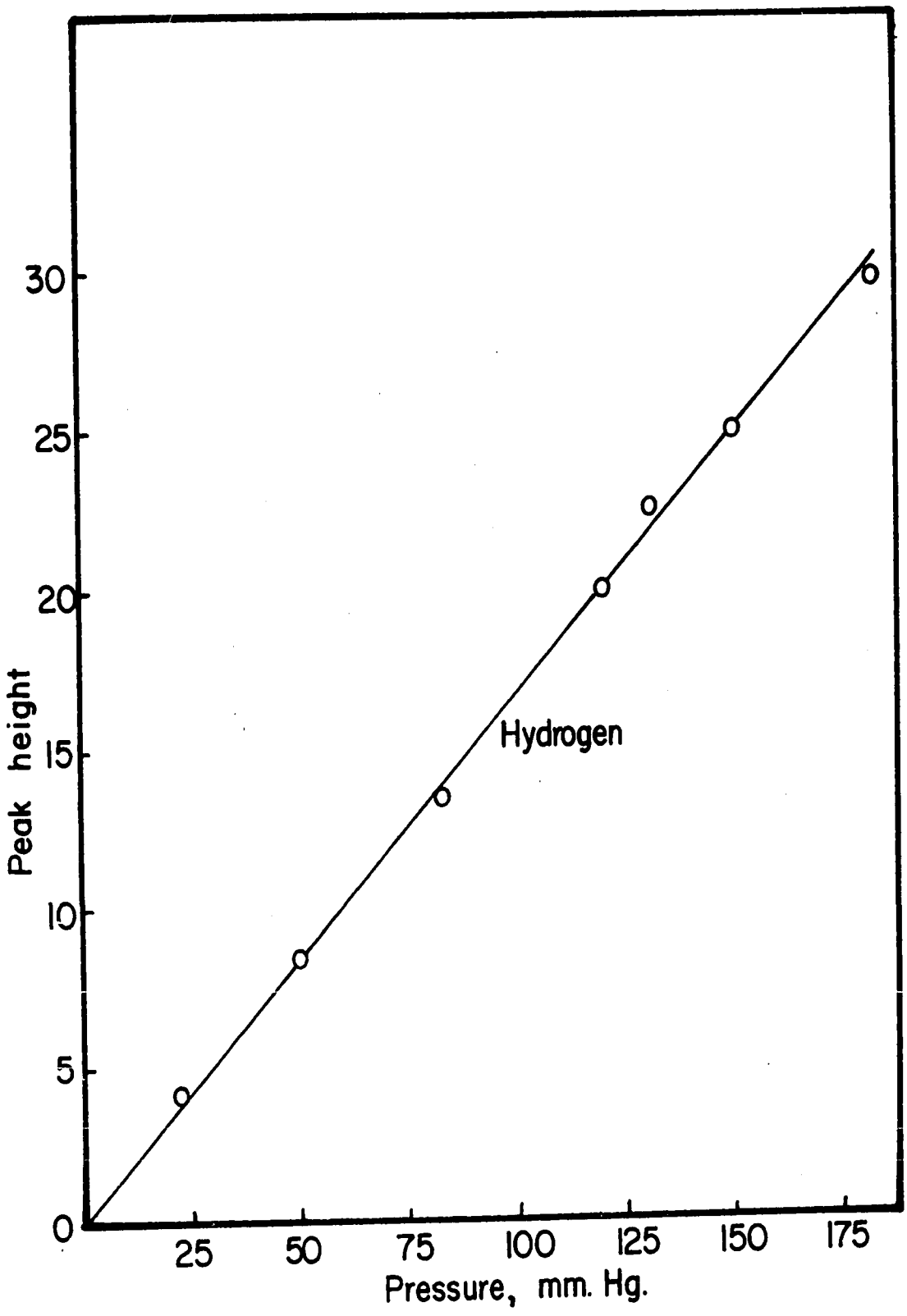

Fig. 4 Calibration of hydrogen at 50°C

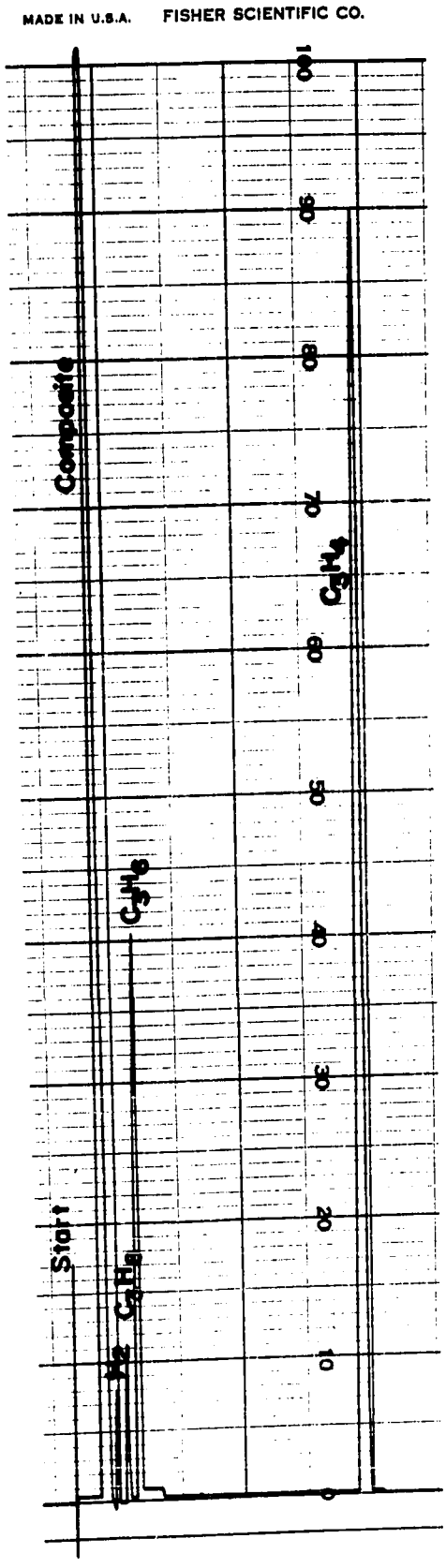

Fig. 5 Typical analysis of gases

Appendix B

Experimental data and kinetic results

Table 1 Results for nickel-pumice catalyst

Weight of catalyst = 2 gms

Equivalent amount of nickel = 0.1777 gm

(i) Initial methyl acetylene pressure = 30 ± 1 mm. Hg.

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
50	1	30	0.33
	2	45	0.80
	3	105	2.00
	4	75	1.33
	5	135	2.66
	6	90	1.50
	7	120	2.10
62	8	45	1.36
	9	61	1.90
	10	106	5.00
	11	76	3.00
	12	90	3.75
	13	120	6.00
	14	150	7.50
	15	135	7.00
68	16	15	0.80
	17	30	1.80
	18	60	4.50
	19	45	3.00
	20	75	5.60

Table 1 (Continued)

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
	21	91	7.70
	22	120	10.50
	23	135	11.50
	24	105	8.70
80	25	134	24.00
	26	104	21.00
	27	121	23.00
	28	74	13.00
	29	91	16.00
	30	45	6.50
	31	59	9.50
	32	15	2.10
	33	29	4.50
88	34	90	24.70
	35	15	2.70
	36	47	15.00
	37	30	7.25
	38	76	24.00
	39	60	17.00

Table 1 (Continued)

(ii) Initial hydrogen pressure = 60 ± 1 mm. Hg.

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
50	40	31	1.10
	41	59	1.00
	42	90	1.00
	43	151	0.90
	44	75	1.00
	45	120	0.95
80	46	45	9.60
	47	60	9.50
	48	91	9.50
	49	150	9.30
	50	180	8.90
	51	30	10.00

(iii) Summary of Results

Temperature °C	x	y	$\log_{10} k$	$\frac{1}{T} \times 10^3$ ($°K^{-1}$)	Activation energy k cal/mole
50	1.15	0	-2.03	3.094	16.75
62	1.14		-1.67	2.985	
68	1.15		-1.45	2.934	
80	1.12	0	-0.95	2.835	
88	1.16		-0.80	2.770	

Table 2 Results for nickel-kieselguhr catalyst

Weight of catalyst = 0.2 gm

Equivalent amount of nickel = 0.088 gm

(i) Initial methyl acetylene pressure = 30 ± 1 mm. Hg.

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
5	52	150	9.00
	53	121	7.00
	54	135	8.00
	55	104	4.92
	56	90	3.66
	57	60	1.50
	58	74	2.62
	59	45	0.93
39	60	30	2.00
	61	62	6.87
	62	75	8.25
	63	45	3.75
	64	15	0.63
	65	90	10.50
43	66	70	14.80
	67	45	9.25
	68	60	13.00
	69	15	1.33
	70	31	5.00

Table 2 (Continued)

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
48	71	75	15.00
	72	62	13.00
	73	34	7.00
	74	44	9.50
	75	25	3.37
	76	14	1.35

(iii) Initial hydrogen pressure = 60 ± 1 mm. Hg.

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
39	77	32	6.4
	78	91	6.6
	79	60	6.4
	80	120	6.2
	81	151	6.6
64	82	42	17.30
	83	60	17.10
	84	25	17.30
	85	30	17.35
	86	15	17.35
	87	73	17.00

Table 2 (Continued)

(iii) Summary of results

Temperature °C	x	y	$\log_{10} k$	$\frac{1}{T} \times 10^3$ ($°K^{-1}$)	Activation energy kcal/mole
5	1.98		-3.32	3.597	13.98
39	1.55	0	-1.99	3.205	
43	1.76		-1.94	3.164	
48	1.68		-1.78	3.115	
64		0			

Table 3 Results for nickel-powder (I)

Weight of catalyst = 6 gms

Equivalent amount of nickel = 0.1826 gm

(i) Initial methyl acetylene pressure = 30 ± 1 mm. Hg.

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
72	88	30	0.65
	89	45	1.25
	90	151	4.50
	91	105	3.00
	92	125	3.90
	93	95	2.40
	94	75	2.16
	95	60	1.70
78	96	30	1.71
	97	45	2.86
	98	140	9.00
	99	120	8.00
	100	100	6.75
	101	60	3.80
	102	80	5.00

Table 3 (Continued)

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
90	103	150	20.00
	104	30	2.50
	105	45	4.50
	106	135	18.00
	107	120	16.00
	108	58	6.00
	109	76	8.50
	110	90	11.00
	111	105	14.00
99	112	91	25.5
	113	76	19.0
	114	45	10.0
	115	60	15.0
	116	30	5.0
108	117	76	25.5
	118	16	3.9
	119	30	9.0
	120	60	20.0
	121	44	17.0

Table 3 (Continued)

(ii) Initial hydrogen pressure = 60 ± 1 mm. Hg.

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
90	122	30	6.3
	123	60	6.1
	124	46	6.3
	125	92	5.7
	126	121	6.3
	127	150	5.7

(iii) Summary of Results

Temperature °C	x	y	$\log_{10} k$	$\frac{1}{T} \times 10^3$ ($°K^{-1}$)	Activation energy k cal/mole
72	1.15		-1.854	2.898	18.58
78	1.29		-1.682	2.849	
90	1.28	0	-1.138	2.755	
99	1.28		-1.110	2.688	
108	1.15		-0.743	2.625	

Table 4 Results for nickel-powder (II)

Weight of catalyst = 3 gms

Equivalent amount of nickel = 0.604 gm

(i) Initial methyl acetylene pressure = 30 ± 1 mm. Hg.

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
46	122	120	1.0
	123	50	0.45
	124	90	0.84
	125	30	0.32
	126	80	0.70
	127	15	0.16
	128	60	0.50
50	129	45	1.30
	130	57	1.80
	131	77	2.30
	132	170	5.50
	133	130	4.30
	134	104	3.30
	135	94	2.80
	136	30	0.70
	137	17	0.50
60	138	162	11.00
	139	137	9.25
	140	120	8.50
	141	12	0.65
	142	16	0.83
	143	31	1.60

Table 4 (Continued)

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
	144	47	3.00
	145	61	4.00
	146	85	5.40
	147	99	6.80
65	148	90	15.00
	149	15	1.60
	150	30	3.70
	151	40	4.75
	152	60	9.00
	153	80	14.50
	154	100	15.50
70	155	90	18.00
	156	80	16.50
	157	15	2.00
	158	31	5.20
	159	40	6.50
	160	60	13.00

(ii) Initial hydrogen pressure = 60 ± 1 mm. Hg.

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
60	161	60	3.9
	162	31	4.2
	163	152	3.5

Table 4 (Continued)

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
	164	100	3.8
	165	45	3.7
70	165	61	13.00
	166	45	13.50
	167	32	13.70
	168	150	12.80
	169	121	12.90
	170	90	13.00

(iii) Summary of Results

Temperature °C	x	y	$\log_{10} k$	$\frac{1}{T} \times 10^3$ ($°K^{-1}$)	Activation energy kcal/mole
46	1.0		-1.87	3.135	17.16
50	1.1		-1.74	3.096	
60	1.1	0	-1.35	3.003	
65	1.2		-1.21	2.956	
70	1.2	0	-1.15	2.915	

Table 5 Results for nickel-powder (III)

(Methyl acetylene admitted first)

Weight of nickelous nitrate = 3 gms

Equivalent amount of nickel = 0.604 gm

(i) Initial methyl acetylene pressure = 30 ± 1 mm. Hg.

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
60	171	45	1.20
	172	57	1.70
	173	77	2.00
	174	145	4.70
	175	126	3.75
	176	104	3.25
	177	94	2.60
66	178	15	0.73
	179	120	6.50
	180	31	1.60
	181	45	2.90
	182	60	4.00
	183	100	6.75
	184	85	5.50
71	185	149	20.00
	186	135	18.00
	187	120	16.50
	188	59	6.25
	189	74	8.50
	190	104	14.00

Table 5 (Continued)

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
81	191	31	2.20
	192	45	4.40
	193	90	11.00
	194	15	3.75
	195	73	27.75
	196	31	9.00
	197	44	14.50
	198	60	22.00

(ii) Initial hydrogen pressure = 60 ± 1 mm. Hg.

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
66	199	60	3.80
	200	45	3.80
	201	122	3.70
	202	151	3.65
	203	30	4.00
88	204	30	24.00
	205	150	23.00
	206	121	23.00
	207	61	23.50
	208	105	23.50
	209	46	23.70

Table 5 (Continued)

(iii) Summary of Results

Temperature °C	x	y	$\log_{10} k$	$\frac{1}{T} \times 10^3$ ($°K^{-1}$)	Activation energy kcal/mole
60	1.16		-1.835	3.003	19.99
66	1.20	0	-1.585	2.949	
71	1.25		-1.406	2.906	
81	1.34		-1.054	2.825	
80		0			

Table 6 Results for palladium-pumice catalyst

Weight of catalyst = 0.5 gm

Equivalent amount of palladium = 0.0448 gm

(i) Initial methyl acetylene pressure = 30 ± 1 mm. Hg.

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
80	210	90	7.50
	211	60	5.00
	212	30	2.75
	213	74	6.50
	214	44	4.00
	215	15	1.00
94	216	11	2.25
	217	20	5.00
	218	30	6.75
	219	41	9.00
	220	50	11.50
	221	59	13.50
	222	76	17.50
109	223	30	10.00
	224	46	15.00
	225	60	18.50
	226	17	5.00
	227	9	2.50

Table 6 (Continued)

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
118	228	19	9.50
	229	31	13.00
	230	12	5.00
	231	40	15.0
	232	60	23.5
	233	90	35.0

(ii) Initial hydrogen pressure = 60 ± 1 mm. Hg.

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
94	234	60	14.1
	235	31	15.1
	236	76	12.8
	237	90	13.8
	238	122	13.2
118	239	60	23.7
	240	46	24.0
	241	32	24.5
	242	90	23.7
	243	40	24.2
	244	105	23.0

Table 6 (Continued)

(iii) Summary of Results

Temperature °C	x	y	$\log_{10} k$	$\frac{1}{T} \times 10^3$ ($°K^{-1}$)	Activation energy kcal/mole
80	0.91		-0.885	2.833	10.30
94	0.97	0	-0.656	2.725	
109	0.92		-0.359	2.618	
118	0.92	0	-0.254	2.557	

Table 7 Results for platinum-pumice catalyst

Weight of catalyst = 0.01 gm

Equivalent amount of platinum = 0.000894 gm

(i) Initial methyl acetylene pressure = 30 ± 1 mm. Hg.

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
61	245	75	0.90
	246	59	0.50
	247	120	2.50
	248	90	1.37
	249	133	3.25
	250	105	1.66
76	251	50	0.80
	252	105	2.83
	253	120	3.90
	254	134	8.00
	255	75	1.80
	256	152	6.30
	257	58	1.00
	258	165	6.60
96	259	31	1.25
	260	75	3.17
	261	105	7.00
	262	150	12.60
	263	45	1.30
	264	74	3.17

Table 7 (Continued)

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
	265	120	9.10
	266	58	2.33
	267	90	5.00
124	268	119	27.50
	269	150	35.40
	270	74	10.00
	271	135	32.00
	272	90	14.10
	273	104	18.60
133.5	274	105	34.00
	275	75	17.00
	276	120	39.80
	277	135	45.70
	278	60	13.00
	279	31	2.50
	280	16	1.00

(ii) Initial hydrogen pressure = 60 ± 1 mm. Hg.

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
96	281	30	2.50
	282	46	2.60
	283	60	2.30

Table 7 (Continued)

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
	284	78	1.90
	285	93	1.60
	286	122	1.40
133.5	287	148	3.60
	288	31	12.50
	289	45	7.00
	290	75	5.20
	291	120	4.30
	292	201	2.10

(iii) Summary of Results

Temperature °C	x	y	$\frac{1}{T} \times 10^3$ ($°K^{-1}$)	$\log_{10} k$	Activation energy kcal/mole
61	1.86		3.003	-2.801	12.85
76	1.89		2.865	-2.600	
96	1.88	-0.50	2.710	-2.209	
124	1.87		2.512	-1.744	
133.5	1.85	-0.50	2.460	-1.477	

Table 8 Results for cobalt-pumice catalyst

Weight of catalyst = 0.00189 gm

Equivalent amount of cobalt = 0.000114 gm

(i) Initial methyl acetylene pressure = 30 ± 1 mm. Hg.

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
87	293	150	2.50
	294	134	2.00
	295	120	1.50
	296	104	1.00
	297	91	0.83
105	298	135	4.50
	299	150	6.00
	300	121	3.50
	301	105	2.50
	302	90	1.50
	303	61	0.80
117	304	119	5.50
	305	134	6.50
	306	150	10.00
	307	60	0.75
	308	90	2.20

Table 8 (Continued)

(ii) Initial hydrogen pressure = 120 ± 1 mm. Hg.

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
105	309	30	3.50
	310	61	3.60
	311	45	3.50
	312	92	3.00
	313	120	3.20

(iii) Summary of Results

Temperature °C	x	y	$\frac{1}{T} \times 10^3$ ($°K^{-1}$)	$\log_{10} k$	Activation energy kcal/mole
87	2.6		2.777	-5.260	13.30
105	2.6	0	2.645	-4.880	
117	2.6		2.564	-4.658	

Table 9 Results for rhodium-pumice catalyst

Weight of catalyst = 2 gm

Equivalent amount of rhodium = 0.1792 gm

(i) Initial methyl acetylene pressure = 30 ± 1 mm. Hg.

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
60	314	30	0.40
	315	45	0.90
	316	60	1.00
	317	76	1.70
	318	104	2.70
	319	121	3.30
	320	136	4.00
78.5	321	150	10.50
	322	90	5.00
	323	135	8.50
	324	76	3.33
	325	60	2.50
	326	118	7.50
	327	105	6.00
	328	46	1.66
90	329	148	13.50
	330	105	7.50
	331	61	4.00
	332	119	10.00
	333	90	6.30
	334	76	4.50
	335	134	12.00

Table 9 (Continued)

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
	336	46	2.50
	337	40	1.78
104	338	150	22.90
	339	105	12.00
	340	45	3.50
	341	135	19.90
	342	91	10.00
	343	75	8.00
	344	120	15.00
	345	60	5.75

(ii) Initial hydrogen pressure = 60 ± 1 mm. Hg.

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
90	346	31	2.70
	347	46	2.50
	348	75	2.30
	349	60	2.50
	350	91	2.60
	351	106	2.40
	352	150	2.40

Table 9 (Continued)

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
	336	46	2.50
	337	40	1.78
104	338	150	22.90
	339	105	12.00
	340	45	3.50
	341	135	19.90
	342	91	10.00
	343	75	8.00
	344	120	15.00
	345	60	5.75

(ii) Initial hydrogen pressure = 60 ± 1 mm. Hg.

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
90	346	31	2.70
	347	46	2.50
	348	75	2.30
	349	60	2.50
	350	91	2.60
	351	106	2.40
	352	150	2.40

Table 9 (Continued)

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
110	353	31	8.00
	354	60	7.50
	355	74	7.50
	356	121	7.20
	357	150	7.00
	358	92	7.50
	359	47	7.70

(iii) Summary of Results

Temperature °C	x	y	$\frac{1}{T} \times 10^3$ ($°K^{-1}$)	$\log_{10} k$	Activation energy k cal/mole
60	1.5		3.003	-2.598	8.60
78.5	1.5		2.844	-2.243	
90	1.5	0	2.755	-2.105	
104	1.5		2.652	-1.904	
110		0			

Table 10 Results for iridium-pumice catalyst

Weight of catalyst = 2 gms

Equivalent amount of iridium = 0.1804 gm

(i) Initial methyl acetylene pressure = 30 ± 1 mm. Hg.

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
56.5	360	152	5.00
	361	35	0.90
	362	118	2.60
	363	199	3.25
	364	125	2.90
	365	51	1.20
	366	90	1.90
81.8	367	162	33.50
	368	36	2.50
	369	148	32.00
	370	134	22.50
	371	106	14.50
	372	48	4.00
	373	79	4.25
100.8	374	116	13.50
	375	34	3.20
	376	73	6.50
	377	82	9.00
	378	131	19.00
	379	144	18.50
	380	57	6.00

Table 10 (Continued)

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg./min.
116.2	381	80	17.50
	382	36	6.50
	383	124	39.00
	384	39	6.00
	385	201	31.00

(ii) Initial hydrogen pressure = 60 ± 1 mm. Hg.

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
80	386	61	4.2
	387	32	4.5
	388	75	4.2
	389	91	4.0
	390	120	3.9
100.8	391	31	6.2
	392	60	6.0
	393	46	6.3
	394	91	5.6
	395	106	6.4
	396	122	5.9

Table 10 (Continued)

(iii) Summary of Results

Temperature °C	x	y	$\frac{1}{T} \times 10^3$ ($°K^{-1}$)	$\log_{10} k$	Activation energy kcal/mole
56.5	1.24		3.034	-2.097	9.15
80.0		0			
81.8	1.24		2.818	-1.638	
100.8	1.24	0	2.675	-1.398	
116.2	1.24		2.569	-1.155	

Table 11 Results for iron-pumice catalyst

Weight of catalyst = 0.016 gm

Equivalent amount of iron = 0.0014 gm

(i) Initial methyl acetylene pressure = 30 ± 1 mm. Hg.

Temperature °C	Run number	Initial hydrogen pressure mm. Hg.	Initial rate mm. Hg.
185	397	61	0.4
	398	150	1.33
	399	104	0.83
	400	136	1.20
	401	120	1.00
	402	90	0.64
198	403	150	5.00
	404	105	1.25
	405	75	0.80
	406	60	0.60
	407	46	0.50
226	408	150	3.00
	409	31	0.50
	410	136	2.00
	411	143	2.50

(ii) Initial hydrogen pressure = 120 ± 1 mm. Hg.

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
185	412	122	1.00
	413	90	1.10

Table 11 (Continued)

Temperature °C	Run number	Initial methyl acetylene pressure mm. Hg.	Initial rate mm. Hg./min.
	414	150	0.90
	415	91	1.00
	416	47	1.05

(iii) Summary of Results

Temperature °C	x	y	$\frac{1}{T} \times 10^3$ ($^\circ K^{-1}$)	$\log_{10} k$	Activation energy kcal/mole
185	1.28	0	2.183	-2.662	14.00
198	1.28		2.120	-2.490	
226	1.28		2.025	-2.211	

Table 12 Results for ruthenium-pumice catalyst

Weight of catalyst = 2 gms

Equivalent amount of ruthenium = 0.1778 gm

Temperature = 280°C

Initial hydrogen pressure = 150 ± 1 mm. Hg.

Initial methyl acetylene pressure = 30 ± 1 mm. Hg.

Run number	Time, Hours	Initial rate mm. Hg.
417	0	7.00
418	0.5	6.75
419	1.0	6.75
420	1.5	4.50
421	2.0	4.25
422	2.5	3.50
423	3.0	2.50
424	4.5	2.50
425	5.0	2.50
426	6.0	2.00
427	7.0	1.50
428	7.5	1.50
429	8.0	1.00
430	11.0	1.25
431	11.5	1.25
432	12.0	1.00
433	13.0	1.00
434	14.0	0.75
435	23.0	0
436	23.5	0

Table 13 Results for osmium-pumice catalyst

Weight of catalyst = 2 gms

Equivalent amount of osmium = 0.1802 gm

Temperature = 296°C

Initial hydrogen pressure = 150 ± 1 mm. Hg.

Initial methyl acetylene pressure = 30 ± 1 mm. Hg.

Run number	Time, Hours	Initial rate mm. Hg./min.
437	0	6.00
438	0.5	6.00
439	1.0	5.75
440	1.5	5.25
441	3.0	4.50
442	5.0	3.50
443	5.5	3.50
444	6.0	3.20
445	6.5	3.00
446	9.5	2.50
447	10.0	2.50
448	10.5	2.00
449	11.0	2.00
450	11.5	1.50
451	23.5	1.00
452	24.0	0
453	24.5	0

Appendix C

Experimental data and results for product analyses

Table 14 Product analysis for course of reaction at 97° C

Initial hydrogen pressure = 90 mm. Hg.

Initial methyl acetylene pressure = 90 mm. Hg.

Run number	Total pressure fall, mm. Hg.	Pressure in product stream, mm. Hg.				
		Hydrogen	Propane	Propylene	Methyl acetylene	Polymers (by difference)
454	5.0	82.0	1.0	3.0	80.0	9.0
455	10.0	74.1	2.0	6.0	71.1	16.8
456	15.0	64.0	3.0	9.0	63.5	25.5
457	22.0	56.5	3.9	13.6	60.5	23.5
458	30.0	48.0	4.6	18.0	56.0	23.4
459	40.0	46.0	5.6	20.2	42.5	25.7
460	55.0	26.0	9.6	31.6	34.0	23.8
461	70.0	21.0	10.6	36.2	30.8	11.4

Table 14 (Continued)

Run number	Reactants lost, mm. Hg.		Reactants recovered %		Propylene: Propane	Selectivity, S
	Hydrogen	Methyl acetylene	Hydrogen	Methyl acetylene		
454	3.0	6.0	96.7	93.3	3.00	0.75
455	5.9	10.9	93.4	87.9	3.00	0.75
456	11.0	14.5	87.8	83.9	3.00	0.75
457	12.1	12.0	86.6	86.7	3.49	0.78
458	14.8	21.4	83.6	76.2	3.91	0.80
459	12.6	21.7	86.0	75.9	3.61	0.78
460	13.2	14.8	85.3	83.6	3.30	0.76
461	11.6	12.4	87.1	86.2	3.41	0.77

Table 15 Effect of initial reactants' ratios, $\overline{R}$, on products at 97° C

Initial methyl acetylene pressure = 30 mm. Hg.

Total pressure fall = 30 mm. Hg.

Run number	Initial hydrogen: methyl acetylene ratios, $\overline{R}$	Pressure in products, mm. Hg.			
		Hydrogen	Propane	Propylene	Methyl acetylene
462	6.00	150.0	12.6	3.4	6.6
463	4.93	118.0	10.2	5.2	5.6
464	4.00	91.0	7.0	10.4	1.0
465	3.00	63.0	4.2	14.0	0.6
466	2.00	33.5	3.8	16.8	1.2
467	1.00	4.0	0.8	20.6	4.0

Table 15 (Continued)

Run number	Yield (%)		Propylene: Propane	Selectivity, S
	Propylene	Propane		
462	14.50	53.80	0.27	0.212
463	21.31	41.80	0.51	0.337
464	35.86	24.13	1.48	0.597
465	47.61	19.28	3.33	0.769
466	58.32	8.28	4.42	0.815
467	79.23	1.07	25.75	0.963

Table 16 Effect of initial methyl acetylene pressures on polymers at 97° C

Initial hydrogen pressure = 90 mm. Hg.

Duration of reaction = 1 minute

Run number	Initial methyl acetylene pressure, mm. Hg.	Total pressure fall, mm. Hg.	Pressure in products, mm. Hg.				
			Hydrogen	Propane	Propylene	Methyl acetylene	Polymers (by difference)
468	197	21	69.0	4.0	12.0	77.0	14.0
469	92	22	64.0	4.2	13.0	66.2	12.6
470	60	22	63.0	4.2	13.0	35.8	12.0
471	43	23	60.0	4.8	12.8	23.4	9.0
472	30	23	59.9	4.6	12.9	12.2	7.4

Table 17 Effect of temperature on products

Initial hydrogen pressure = 90 mm. Hg.
Initial methyl acetylene pressure = 90 mm. Hg.
Total pressure fall = 45 mm. Hg.

Run number	Temperature °C	Pressure in products, mm. Hg.				
		Hydrogen	Propane	Propylene	Methyl acetylene	Polymers (by difference)
473	100	28	4.0	33.6	28.0	41.4
474	112	34	3.6	29.4	33.0	35.0
475	121	33	2.0	27.2	26.5	46.3
476	130	40	1.6	22.0	32.0	39.4

Table II7 (Continued)

Run number	Reactants lost, mm. Hg.		Propylene: Propane	Selectivity, S
	Hydrogen	Methyl acetylene		
473	20.4	24.4	8.40	0.893
474	19.4	24.0	8.17	0.890
475	25.8	34.3	13.60	0.931
476	24.8	34.4	13.75	0.932

Appendix D

Sample Calculations

I. Calculation of activation energy E for nickel pumice catalyst:

Using equation 7 and Figure 9,

$$\text{Slope} = -\frac{E}{2.303\,R} = -3.66 \times 10^3$$

$$E = 3.66 \times 10^3 \times 2.303 \times 1.9872 \text{ cal per mole}$$

$$= 3.66 \times 2.303 \times 1.9872 \text{ k cal per mole}$$

$$= 16.75 \text{ k cal per mole}$$

II. Calculations of products for Run Number 454:

Initial hydrogen pressure = 90.0 mm

Initial methyl acetylene pressure = 90.0 mm

Total pressure of product stream = Total initial pressures of reactants - Total pressure fall = 180 - 5 = 175 mm

Gases recorded from the product stream:

Hydrogen	=	82.0 mm
Propane	=	1.0 mm
Propylene	=	3.0 mm
Methyl acetylene	=	80.0 mm
Total		166.0 mm

Polymers (by difference) = 175.0 - 166.0 = 9.0 mm

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II. Calculations of products for Run Number 454:

Initial hydrogen pressure = 90.0 mm

Initial methyl acetylene pressure = 90.0 mm

Total pressure of product stream = Total initial pressures of reactants - Total pressure fall = 180 - 5 = 175 mm

Gases recorded from the product stream:

Hydrogen	=	82.0 mm
Propane	=	1.0 mm
Propylene	=	3.0 mm
Methyl acetylene	=	80.0 mm
Total		166.0 mm

Polymers (by difference) = 175.0 - 166.0 = 9.0 mm

Hydrogen balance:

Unreacted hydrogen	=	82.0 mm
Hydrogen used to form propane = 1.0 x 2	=	2.0 mm
Hydrogen used to form propylene = 3.0 x 1	=	3.0 mm
Total		87.0 mm

Hydrogen lost = 90.0 - 87.0 = 3.0 mm

Hydrogen recovered = $\frac{87.0}{90.0}$ x 100 = 96.7%

Methyl acetylene balance:

Unreacted methyl acetylene	=	80.0 mm
Methyl acetylene used to form propane	=	1.0 mm
Methyl acetylene used to form propylene	=	3.0 mm
Total		84.0 mm

Methyl acetylene lost = 90.0 - 84.0 = 6.0 mm

Methyl acetylene recovered = $\frac{84.0}{90.0}$ x 100 = 93.3%

Propylene: Propane in product = $\frac{3.0}{1.0}$ = 3.0

Selectivity, S = $\frac{3.0}{3.0 + 1.0}$ = 0.75

III. Calculation of overall rate constant $\bar{k}$ and the logarithmic pre-exponential factor $\log_{10} A$ at 80° C, for nickel-pumice catalyst:

From Figure 9, at 80° C, the intrapolated value of $\log_{10}$ rate constant = -1.02

Rate constant $k = 0.09549$ per minute

Weight of nickel in the catalyst $= 0.1777$ gm

Overall rate constant $\bar{k} = \frac{0.09549}{0.1777} = 0.5395$ per minute per gram

$\log_{10} \bar{k} = -0.2680$

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

$E = 16.75 \times 10^3$ cal per mole

$\log_{10} A = -0.2680 + \frac{16.75 \times 10^3}{2.303 \times 1.9872 \times 353} = -0.2680 + 10.37$

$= 10.102$

Appendix E

The Arrhenius parameters, electronic configuration and percentage d-character

Table 18 The Arrhenius-Parameters for different catalysts

Catalysts	Activation energy E kcal/mole	Overall Rate constant $\bar{k}$ min.$^{-1}$ gm^{-1} (Tr = 80° C)	$\log_{10} \bar{k}$	$\log_{10} A$
Ni - pu	16.75	0.5395	-0.2680	10.102
Ni - k	13.95	1.3040	-0.1152	8.751
Ni - p (I)	18.58	0.3760	-0.4248	11.078
Ni - p (II)	17.16	0.2944	-0.5311	10.092
Ni - p (III)	19.99	0.1377	-0.8611	11.514
Pd - pu	10.30	2.9080	0.4636	6.840
Pt - pu	12.85	3.3000	0.5185	8.474
Co - pu	13.30	0.0330	-1.4810	6.753
Rh - pu	8.60	0.0334	-1.4755	3.849
Ir - pu	9.15	0.1106	-0.9564	4.708
Fe - pu	14.00	0.0320	-1.4950	7.173

pu = pumice support
k = kieselguhr support
p = metallic powder

Table 19 Electronic configuration of nickel

Forms	Number of outer electrons			Resonance ratio	Percentage d-character
	3d	4s	4p		
Ni A				30	40.0
Ni B				70	

. Electron involved in bonding

0 Empty orbital

Table 20 Percentage d-character of Group VIII metals

Iron (39.7)	Cobalt (39.5)	Nickel (40.0)
Ruthenium (50.0)	Rhodium (50.0)	Palladium (46.0)
Osmium (49.0)	Iridium (49.0)	Platinum (44.0)