KINETICS OF THE CATALYTIC HYDROGENATION OF ETHYLENE

by

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PREFACE

Many mechanisms have been postulated in the past for the ethylene hydrogenation reaction catalyzed by metal films. Two principal mechanisms, the Langmuir-Hinshelwood and the Rideal, have stood out from the other mechanisms as being the most probable. However the problem of deciding between these two mechanisms is much more difficult than the singling out of the two from the mass of other mechanisms.

Professor Laidler, partly on the basis of absolute rate calculations, has proposed that the investigation of the dependence of the hydrogenation reaction on the pressures of the reactants, ethylene and hydrogen, holds the answer to the problem of deciding between the two mechanisms. This approach to the problem allowed Laidler and Weber to favour the Langmuir-Hinshelwood mechanism for the ammonia-deuterium exchange catalyzed by iron.

The same approach has been used in the research described in this thesis on the ethylene hydrogenation reaction.

The hydrogenation reaction catalyzed by nickel films has been studied to only a limited extent in the past because heterogeneous reactions are very difficult and time consuming to study. For this thesis the reaction on nickel films has been studied extensively over wide pressure ranges, and by activation energy determinations and time course plots. The reaction on iron films has also been extensively

studied in this work because only qualitative results were obtained in the past.

As a result of these extensive studies, it has been concluded that depending upon the reaction conditions both the Rideal mechanism and the Langmuir-Hinshelwood mechanism may be the dominant one.

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ABSTRACT

The dependence of the kinetics of the ethylene hydrogenation reaction catalyzed by a nickel film on the pressures of ethylene and hydrogen has been studied over the pressure range of 1 to 30 cm.Hg of each reactant. The reaction, with simultaneous introduction of hydrogen and ethylene to the film, was first order in hydrogen, falling to 0.7 order at high pressure, and was -0.6 order in ethylene at 32.3°C. The activation energy was 7.8 kcal per mole over the temperature range 32.3°C to 80°C for equal initial pressures of 5 cm.Hg for each reactant. When ethylene was added to the nickel film prior to the hydrogen, the reaction was 0.7 order in hydrogen and -0.4 order in ethylene at 32.3°C, and 0.8 order in hydrogen and -0.2 order in ethylene at 80°C. The activation energy was 10 kcal. per mole.

When ethylene was introduced to an iron film prior to the hydrogen, the reaction was 0.9 order in hydrogen and -0.6 order in ethylene at 32.3°C, but 0.9 order in hydrogen and -0.2 order in ethylene at 80°C. The activation energy was 7.3 kcal. per mole.

Several time-course plots were made for the reaction on both nickel and iron films.

The ethylene hydrogenation reaction catalyzed by either nickel or iron was concluded to follow the Rideal mechanism if hydrogen was introduced to the film prior to the ethylene or if hydrogen was in large excess. The Langmuir-Hinshelwood mechanism is considered to hold for all other conditions.

CHAPTER I

INTRODUCTION

Investigations of the catalytic hydrogenation of ethylene have been fairly numerous in the past; however the results which have been published as a result of these experiments are neither complete nor extensive. Several theoretical mechanisms have been developed in some detail, but the experimental data to date have been insufficient or of such a doubtful nature that no one mechanism is firmly established.

The research described in this thesis was carried out in order to extend the pressure dependency studies. In particular the dependence of the rate of hydrogenation of ethylene on the pressure of ethylene was studied because the ethylene pressure dependency is a very important factor for deciding which mechanism gives the best correlation between theory and experiment.

LANGMUIR-HINSHELWOOD MECHANISM

The two principal mechanisms were both proposed for heterogeneous catalytic reactions by Langmuir in 1921 (1). One of these mechanisms was later applied by Hinshelwood (2) to numerous heterogeneous reactions with some measure of success and is thus now referred to as the Langmuir-Hinshelwood mechanism. In the Langmuir-Hinshelwood mechanism the reactants are considered to be in adsorptive equilibrium with the surface, and reaction then involves these adsorbed molecules. This adsorption equilibrium is considered to be established rapidly in comparison to the actual surface reaction. For the general case of two reactants A and B, the rate of reaction is proportional to the probability that A and B molecules are adsorbed on neighbouring sites, which in turn is proportional to the product of the fractions of the surface covered by A and by B. These fractions are given by

$$\theta = \frac{Kp}{1 + Kp + K'p'} \qquad (1)$$

for A, and

$$\theta' = \frac{K'p'}{1 + Kp + K'p'} \qquad (2)$$

for B. The rate of reaction is then given by

$$v = k_2\theta\ \theta' \qquad (3)$$

$$= \frac{k_2\ KK'\ pp'}{(1 + Kp + K'p')^2} \qquad (4)$$

This equation can be simplified for the special case of the hydrogenation of ethylene. It has been found that ethylene is much more strongly adsorbed than hydrogen on many metallic surfaces. Therefore if A represents hydrogen the term Kp in the denominator of equation (3) may be neglected in comparison with 1 + K'p', and the rate equation becomes

$$v = \frac{k_2 KK' pp'}{(1 + K' p')^2} \qquad (5)$$

The rate is now proportional to the pressure of hydrogen but as the pressure of ethylene is increased the rate passes through a maximum.

RIDEAL MECHANISM

The second principal mechanism proposed by Langmuir (1) involves the adsorption of one reacting substance which reacts with a gas molecule of the second reacting substance. The second reacting substance may or may not also be adsorbed but the reaction occurs between an adsorbed molecule and a gaseous molecule. Rideal (3,4) has proposed that this mechanism applies to certain reactions involving hydrogen; therefore this mechanism is usually referred to as the Rideal mechanism.

For the general case of two reactants A and B in which an adsorbed molecule of A reacts with a gaseous molecule of B, the rate of reaction is proportional to the fraction of surface covered by A and the pressure p' of B.

$$v = k_2 p' \theta \qquad (6)$$

$$= \frac{k_2 K pp'}{1 + Kp + K' p'} \qquad (7)$$

The term $K' p'$ corresponds to the adsorption of B. For this type of mechanism, if the pressure p of A is steadily increased, the rate at first increases and then levels off at a limiting rate. This pressure dependency of A is the feature which allows the Langmuir-Hinshelwood mechanism to be distinguished from the Rideal mechanism.

When this mechanism was first applied to the catalytic ethylene hydrogenation by Rideal, he assumed that adsorbed ethylene reacted with gaseous hydrogen. Thus since hydrogen is weakly adsorbed $K'p'$ can be neglected in comparison to $1 + Kp$, and therefore

$$v = \frac{k_2 Kpp'}{1 + Kp} \qquad (8)$$

Rideal (5) has more recently revised his application of the Rideal mechanism to the ethylene hydrogenation reaction. Rideal proposes now that adsorbed hydrogen reacts with gaseous ethylene. This revision does not change the general form of equation (7) which should now be written as

$$v = \frac{k_2 K' pp'}{1 + Kp} \qquad (9)$$

EXPERIMENTAL INVESTIGATIONS

The earliest investigation of the ethylene hydrogenation reaction was carried out by Grassi (6) in 1916 on copper. Grassi's data fitted a rate law which was first order in both ethylene and hydrogen.

A fairly extensive study of the hydrogenation of ethylene on copper was made by Pease (7,8) in 1923. Pease used both pure copper and copper supported on brick and glass beads. At 20°C he found that the reaction was 0.8 order in hydrogen and -0.4 in ethylene; at 100°C the hydrogen dependence was first order and the ethylene dependence was zero order, but at 200°C the reaction was 0.8 order in hydrogen and 0.66 order in ethylene.

Farkas and Farkas (9, 10), using platinum wire over a limited pressure range (10 mm. to 100 mm. Hg), determined the hydrogen pressure dependency to be first order and the ethylene pressure dependency to be negative first order.

Rideal's initial investigation (4, 11) of the ethylene hydrogenation reaction was on nickel foil. Over the limited pressure range from 0.1 to 10 cm. Hg with hydrogen in excess the reaction was first order in ethylene and zero order in hydrogen. The converse was found when ethylene was in excess; that is, the reaction was first order in hydrogen and zero order in ethylene.

Zur Strassen (12), working at very low pressure in the 0.03 to 0.2 mm. Hg pressure range with a nickel wire catalyst, found the reaction to be first order in hydrogen and zero order in ethylene at low temperatures; at higher temperatures the ethylene dependence became first order.

In an investigation of ethylene hydrogenation on nickel wire, Farkas, Farkas and Rideal (10) found that the decrease of ethylene pressure was linear in the first 30 minutes of the hydrogenation reaction indicating a zero order reaction at 20°C. But at 60°C the reaction ceased to be zero order indicating that the adsorbed layer of ethylene was no longer saturated. It was also assumed by these workers that the exchange reaction and the addition reaction proceed independently of each other since they have different temperature coefficients.

A valuable piece of research in this field was carried out in Japan by Toyama (13) in 1937. Using nickel in a powdered form he found that at 0°C, and in the pressure range 10 cm.Hg to 40 cm. Hg, increasing the ethylene pressure retards the reaction to some extent. With respect to hydrogen the reaction was nearly zero order with hydrogen in excess, and tended to be of the first order in hydrogen when ethylene was in excess. Toyama also carried out some constant pressure experiments in which he found that at a constant hydrogen pressure the reaction was always slightly accelerated as it proceeded, while at constant ethylene pressure the rate was only reduced as the hydrogen was consumed. At higher temperatures, that is 165°C, the reaction was approximately first order while at lower temperatures the order of the reaction was apparently lower.

Twigg and Rideal (14, 15, 16, 17) carried out a series of experiments on nickel wire to study the exchange as well as the hydrogenation of ethylene. The rate of exchange was found to be independent of the ethylene pressure but directly proportional to the hydrogen pressure. The absence of chemisorbed hydrogen atoms, as indicated by the lack of equilibration by direct $H_2 + D_2 \rightleftharpoons 2HD$ exchange during the ethylene exchange and hydrogenation reactions, suggests the associative mechanism, according to which ethylene is adsorbed by opening of the double bond. The associative mechanism is also indicated because the ethylene deuterium exchange occurs at a lower temperature than ethane deuterium exchange. It is suggested that the hydrogen is held in the molecular state in the van der Waals layer above and between the chemisorbed molecules of ethylene. The slow step in the exchange reaction is assumed to be the addition of one hydrogen atom to the adsorbed ethylene molecule. Since the addition reaction had a lower activation energy, the hydrogen molecule is assumed to add directly across the double bond of ethylene.

Beeck (18, 19) in 1940 made a great contribution to catalytic studies by his development of evaporated metal films. Prior to this period the catalysts were wires, foils, or bulk powder which were usually oxidized and then reduced with hydrogen at 500°C. The activity of evaporated films is dependent on the film thickness, the pressure of inert gas during the evaporation process, and the temperature of the surface on to which the metal condenses. The presence of a small pressure of inert gas, for example 1 mm. Hg of nitrogen, causes the film to be strongly oriented and more active. Beeck's preliminary studies of the ethylene hydrogenation on nickel films revealed that the reaction was first order with respect to hydrogen pressure and independent of ethylene pressure. Beeck assumed that some ethylene was adsorbed associatively on that part of the surface not covered with dehydrogenated complexes but no direct experimental evidence was given to support this postulate.

Beeck (20, 21, 22, 23, 24, 25) found that the activation energies for oriented and unoriented films of nickel as well as for iron, platinum, palladium, and rhodium covering a thousand-fold range in rate constant all gave about the same value of 10.7 kcal. per mole for the temperature range - 80°C to 150°C.

On nickel films at 23°C about 5×10^{18} molecules of ethylene were adsorbed on 100 mg. nearly instantaneously and irreversibly. Addition of more ethylene resulted in the formation of ethane and when 12.5×10^{18} molecules of ethylene were added, an equal number of ethane molecules appeared in the gas phase leaving acetylenic residues on the surface.

If ethylene was preadsorbed on films of the metals, the rates of hydrogenation were reduced by the following factors: Ni = 0.6 , Ta = 10 , W = 5 and Pt = 0.9 . Beeck considered the rate of hydrogenation of ethylene to be determined by the fraction of surface not covered by acetylenic residues. Hydrogen chemisorbed on the remaining surface reacts with gaseous ethylene. He assumed that the rate of removal of the poisoning acetylenic complexes by surface hydrogenation must be the rate controlling process. In a later paper (26) Beeck modified the last statement by assuming that the rate-controlling step is the removal of chemisorbed ethylene by chemisorbed hydrogen. Some acetylenic complexes are formed but these are limited to areas where four adjacent sites are empty.

Jenkins and Rideal (5) made an extensive study of the chemisorption of ethylene on a nickel film. When increments of ethylene were admitted to a clean film at 20°C three distinct phases were observed. The first few increments were completely and rapidly chemisorbed. On further additions more gas was rapidly adsorbed but there was then a rise in the residual gas pressure due to the formation of ethane. In the third phase both ethylene and ethane were present in the residual gas. From studies of hydrogen adsorption on films saturated with ethylene, it was concluded that 83.4 % of the surface sites were occupied by acetylenic complexes, 8.3 % were occupied by hydrogen atom pairs, and 8.3 % were unoccupied. From these studies Rideal has concluded that no associative adsorption occurs. Ethylene on chemisorption is dissociated to an acetylenic complex and chemisorbed hydrogen and there is no reversible adsorption of ethylene. These acetylenic complexes were only very slowly removed by hydrogen to form ethane.

Jenkins and Rideal from their investigations of the ethylene hydrogenation reaction obtained a value of 165°C for the inversion temperature and 10.2 kcal. per mole for the activation energy. The rate of the reaction was independent of the ethylene pressure over the pressure range from 2.0 to 9.6 cm. Hg but was directly proportional to the hydrogen pressure over the pressure range from 2.0 to 10 cm. Hg. If the reaction occurs between chemisorbed hydrogen and gaseous ethylene, the rate of chemisorption of hydrogen is given by $k_1 P_{H_2} (1 - \theta)$ where θ is the fraction of the surface covered by hydrogen, the rate of evaporation of hydrogen is $k_2 \theta$, and the rate of reaction with gaseous ethylene is $k_3 P_{C_2H_4} \theta$; then

$$k_1 P_{H_2} (1 - \theta) = k_2 \theta + k_3 P_{C_2H_4} \theta \qquad (10)$$

Hence the rate of hydrogenation is given by:

$$k_3 P_{C_2H_4} \theta = \frac{k_1 k_3 P_{H_2} P_{C_2H_4}}{k_2 + k_3 P_{C_2H_4} + k_1 P_{H_2}} \qquad (11)$$

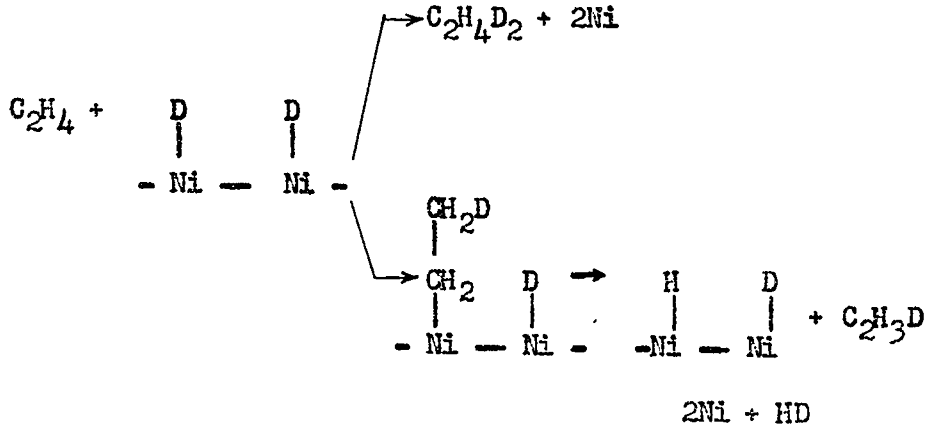
If $k_1 P_{H_2} << k_2 + k_3 P_{C_2H_4}$

$$\text{Rate} = \frac{k_1 k_3 P_{H_2} P_{C_2H_4}}{k_2 + k_3 P_{C_2H_4}} \qquad (12)$$

If further, at low temperature, $k_3 P_{C_2H_4} >> k_2$, then

$$\text{Rate} = k_1 P_{H_2} \tag{13}$$

On elevation of the temperature the rate of the evaporation of hydrogen $k_2 \theta$ increases more rapidly than the reaction rate with ethylene, of rate $k_3 P_{C_2H_4} \theta$, so that the inversion temperature is reached when $k_2 \approx k_3 P_{C_2H_4} \theta$. Above the inversion temperature the rate of hydrogenation becomes dependent on the ethylene pressure.



The relative rates of hydrogenation and exchange are given by $k_3 P_{C_2H_4}$ and k_2 respectively, k_2 being much smaller at low temperatures but of comparable magnitude at 165°C . In experimental agreement, the temperature coefficient of the exchange reaction is much greater than that of hydrogenation, both rates being comparable at 170°C .

Kemball (27, 28) has made a recent study of the deuteration and exchange of ethylene on evaporated metal catalysts at low temperatures. At temperatures between - 120°C and - 100°C both deuteration and exchange rates were independent of ethylene pressure and were proportional to the square root of the deuterium pressure. Kemball put forward a general theory not based on any particular mechanism which would explain the distribution of deuterated ethylenes and ethanes. The theory is based on the probabilities of the various changes which the adsorbed entities may undergo on the surface. These entities are adsorbed ethylene and adsorbed ethyl radicals. The assumptions of the theory are: (a) Every adsorbed ethylene molecule must either become an adsorbed ethyl radical or leave the surface. The chances of these two events are independent of isotopic content and are given by $P/(1 + P)$ and $1/(1 + P)$ respectively, P being the ratio of the chances. (b) When an ethylene molecule becomes an ethyl radical there is an equal chance of the new hydrogen atom adding to either end of the ethylene molecule. The chances of obtaining a deuterium or hydrogen atom in this process are $q/(1 + q)$ or $1/(1 + q)$, respectively. (c) Every adsorbed ethyl radical must either revert to an adsorbed ethylene molecule or leave the surface as an ethane molecule. The chances of these two events are independent of isotopic content and are given by $r/(1 + r)$ and $1/(1 + r)$, respectively. (d) When an ethyl radical reverts to an adsorbed ethylene molecule, it has an equal chance of losing any of the three "hydrogen" atoms in the methyl group. (e) When an ethyl radical takes up a "hydrogen" atom to become a gaseous ethane molecule, the chances of obtaining a deuterium or hydrogen atom are $s/(1 + s)$ and $1/(1 + s)$ respectively. By using one fundamental generating equation, one can write down eighteen simultaneous equations which upon solution give the fraction of each of the possible eighteen deuterated compounds. The Jenkins and Rideal mechanism alone is not sufficient to account for the initial production of tri and tetra deutero-ethylenes observed by Kemball. It is probable that the presence of added hydrogen would favour the existence of the more highly hydrogenated entities such as ethylene molecules and ethyl radicals and thus reduce the number of acetylenic complexes. It is Kemball's opinion that perhaps several of the different mechanisms suggested in the past all play a part in the hydrogenation and exchange reactions.

Foss and Eyring (29) carried out an investigation of the catalytic hydrogenation of ethylene over evaporated nickel films in order to see if earlier work done on wire and powdered nickel could be reproduced on nickel films. They also attempted to develop a technique for obtaining very reproducible results on reproducible nickel films. Over the pressure range from 0.03 to 300 mm. Hg, the hydrogenation reaction was found to be first order in hydrogen pressure and zero order in ethylene pressure. However, in order to increase the life time of the films, most of the work was done in the 15 to 100 μ pressure range. Potassium-sodium eutectic mixture bubblers were used to purify the reactants. With these improvements a film's activity was found to have decreased only sixfold after thirty-one runs over a period of six days. On the addition to the routine of a baking period at 300°C with 5 cm. Hg of hydrogen between runs, very good reproducibility was obtained. For example for one series of five runs the initial first order rate constants were found to vary by less than 1 %. The activation energy determined by Foss and Eyring was 8 kcal. per mole. Other groups (5, 18) have obtained 10 kcal. per mole for the activation energy and Foss and Eyring concluded that their lower value must be due to the presence of some unknown contaminant, probably oxygen. However the possibility of oxygen as a contaminant seems unlikely since Foss and Eyring used more rigorous methods of purification than former authors.

ABSOLUTE RATE TREATMENT

The rate expressions formulated by Langmuir in the early developement of catalytic research have, in more recent times, been confirmed by an analysis of the problem using absolute rate theory (30, 31, 32). However absolute rate theory shows that a study of the magnitudes of the various rate constants will not allow one to decide between these mechanisms. Absolute rate theory calculations have shown that the rate constants are of the same magnitude regardless of which mechanism is assumed. It is however instructive to follow through the absolute rate calculations to confirm the expressions developed by Langmuir and thus to show the importance of pressure dependency studies in a decision of the type of mechanism.

A brief outline will now be given of the application of the theory of absolute reaction rates to the ethylene hydrogenation reaction first formulated by Laidler, Glasstone, and Eyring (31, 32, 33, 34, 35, 36, 37). The simple process of adsorption in which the activated complex is localized will be given. Let N_s, N_g, and $N_\ddagger$ be the numbers of sites, gas molecules, and activated complexes, respectively, and let the corresponding concentrations be c_s (= N_s/S), c_g (= N_g/V), and $c_\ddagger$ (= $N_\ddagger/S$). The assumption of equilibrium between the activated complexes and the reactants then gives rise to the equation:

$$\frac{c_\ddagger}{c_g\ c_s} = \frac{f^\ddagger}{F_g\ f_s}\ e^{-\epsilon_1/kT} \qquad (14)$$

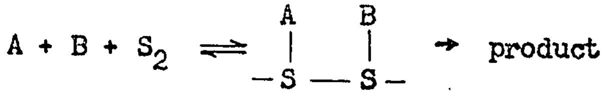
is the energy of the complexes with reference to the reactants at the absolute zero, and is therefore the activation energy at that temperature. f is the complete partition function and F is the partition function per unit volume. One of the vibrational factors in the partition function of the complex is a very loose vibration which allows the complex to dissociate into the products of the reaction. By taking the expression for this vibration out of $f^{\ddagger}$, this expression results:

$$\frac{c^{\ddagger}}{c_g\, c_s} = f^{\ddagger} \frac{(kT/h\nu)}{F_g\, f_s}\, e^{-\epsilon_1/kT} \qquad (15)$$

Thus, the rate is given by:

$$v = c^{\ddagger}\nu = c_g\, c_s \frac{kT}{h} \frac{f^{\ddagger}}{F_g\, f_s}\, e^{-\epsilon_1/kT} \qquad (16)$$

An extension of this to a Langmuir-Hinshelwood bimolecular reaction, formulated as:



$$A + B + S_2 \rightleftharpoons \overset{A}{\underset{-S}{|}} \!\!-\!\! \overset{B}{\underset{S-}{|}} \rightarrow \text{product}$$

where A and B are the reacting molecules and S_2 is a dual site, gives the rate as:

$$v = c_g\, c'_g\, c_{s_2} \frac{kT}{h} \frac{f^{\ddagger}}{F_g\, F'_g\, f_{s_2}}\, e^{-\epsilon_0/kT} \qquad (17)$$

where c_g and c'_g are the gas-phase concentrations of A and B , and

F_g and F'_g are the corresponding partition functions per unit volume. The concentration of bare dual sites is related to the concentration of bare single sites by

$$c_{s_2} = \frac{1}{2} s c_s^2 / L \tag{18}$$

where L is the total number of sites.

$$v = \frac{1}{2} s \frac{c_g \, c'_g \, c_s^2}{L} \frac{kT}{h} \frac{f_{\ddagger}}{F_g \, F'_g \, f_{s_2}} e^{-\epsilon_o/kT} \tag{19}$$

By the use of isotherms

$$\frac{c_a}{c_g \, c_s} = K \tag{20}$$

$$\frac{c'_a}{c'_g \, c_s} = K' \tag{21}$$

where c_a and c'_a are the concentrations of adsorbed A and adsorbed B , equation (19) can be put into a more general form. Also

$$c_a + c'_a + c_s = L \tag{22}$$

and therefore

$$c_s = \frac{L}{1 + k \, c_g + k' \, c'_g} \tag{23}$$

Equation (19) can now be expressed as:

$$v = \frac{\frac{1}{2}\, s c_g c'_g\, L}{(1 + Kc_g + K'c'_g)^2}\ \frac{kT}{h}\ \frac{f_{\ddagger}}{F_g\, F'_g\, f_{s_2}}\ e^{-\epsilon_0/kT} \qquad (24)$$

If B is only weakly adsorbed $K'c'_g$ may be neglected and the equation becomes:

$$v = \frac{1}{2}\, s\ \frac{L\, c_g\, c'_g}{(1 + K\, c_g)^2}\ \frac{kT}{h}\ \frac{f_{\ddagger}}{F_g\, F'_g\ f_{s_2}}\ e^{-\epsilon_0/kT} \qquad (25)$$

which passes through a maximum as c_g is increased.

If A is strongly adsorbed also, Kc_g is large compared with unity and equation (25) can be expressed as

$$v = \frac{1}{2}\, s\, \frac{L}{K^2}\ \frac{c'_g}{c_g}\ \frac{kT}{h}\ \frac{f_{\ddagger}}{F_g\, F'_g\ f_{s_2}}\ e^{-\epsilon_0/kT} \qquad (26)$$

The application of the absolute rate theory to the Rideal mechanism gives a slightly different equation. For the reaction between an adsorbed molecule A, of concentration c_g in the gas phase, and a gaseous molecule B, of concentration c'_g, the concentration of adsorbed A is expressed as:

$$c_a = \frac{L\, K\, c_g}{1 + K\, c_g + K'\, c'_g} \qquad (27)$$

The rate of the reaction is:

$$v = c'_g \, c_a \, \frac{kT}{h} \, \frac{f_{\ddagger}}{F'_g \, f_a} \, e^{-\epsilon'_0/kT} \qquad (28)$$

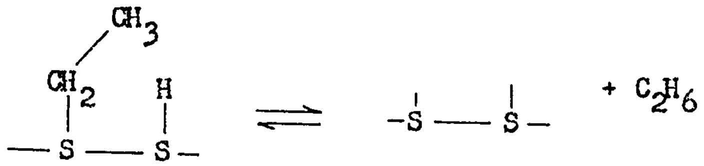
where ϵ'_0 is the activation energy for the reaction at the absolute zero. Substitution of (27) in equation (28) gives

$$v = \frac{L \, c_g \, c'_g \, K}{1 + K \, c_g + K' \, c'_g} \; \frac{kT}{h} \; \frac{f_{\ddagger}}{F'_g \, f_a} \; e^{-\epsilon'_0/kT} \qquad (29)$$

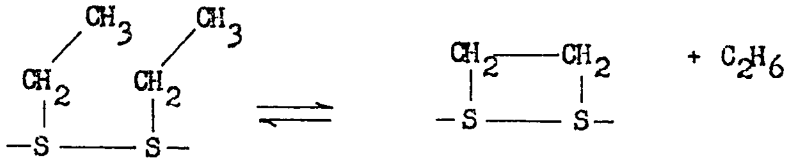
In order to apply the Langmuir-Hinshelwood treatment to the hydrogenation of ethylene the following reactions must be considered.

(1)

(2)



(3)



The isotherm for ethylene adsorption is

$$\frac{c_a}{c_{s_2}} = K\,c_g \tag{30}$$

where c_{s_2} is the concentration of dual sites, equal to $sc_g^2/2L$. Since the surface is only very sparsely covered by hydrogen,

$$L = 2c_a + c_s \tag{31}$$

Thus

$$2sKc_g\,c_a^{\,2} - L(1 + 2sKc_g)c_a + \frac{1}{2}\,sKL^2\,c_g = 0 \tag{32}$$

The solution of this is

$$c_a = L\,\frac{1 + x - (1 + 2x)^{1/2}}{2x} \equiv L\,A \tag{33}$$

where $x = 2sKc_g$. Also

$$c_s = L\,\frac{(1 + 2x)^{1/2} - 1}{x} \equiv L\,B \tag{34}$$

The isotherm for hydrogen adsorption is

$$\frac{c_a'}{c_s} = (K'c_g')^{1/2} \tag{35}$$

so that

$$\theta' = \frac{c'_a}{L} = B\,K'^{1/2}\,c'^{1/2}_g \qquad (36)$$

The concentration of adsorbed ethylene molecules which have a neighbouring hydrogen atom is given by $c_{aa'} = sc_a\,\theta'$. Therefore the concentration of adsorbed ethyl radicals, $c_{a''}$, is given by

$$\frac{c_{a''}}{c_{aa'}} = \frac{c_{a''}}{sc_a\theta'} = \frac{f_{a''}}{f_{aa'}}\,e^{\epsilon''/kT} \qquad (37)$$

The fraction of the surface covered by ethyl radicals is

$$\theta'' = \frac{c_{a''}}{L} = \frac{sc_a\theta'}{L}\,\frac{f_{a''}}{f_{aa'}}\,e^{\epsilon''/kT} \qquad (38)$$

The concentration of ethyl radicals which have a neighbouring hydrogen atom is

$$c_{a'a''} = sc_{a''}\,\theta' = s^2c_a\,\theta'^2\,\frac{f_{a''}}{f_{a'}}\,e^{\epsilon''/kT} \qquad (39)$$

The rate of reaction is

$$v = s^2LAB^2c'_g\,\frac{kT}{h}\,\frac{1}{F_g'}\,e^{-(\epsilon_o - \epsilon'' - 2\epsilon)/kT} \qquad (40)$$

where ϵ is the energy of adsorption per atom of hydrogen. The rate varies directly with the hydrogen pressure c_g' but goes through a complex maximum on variation of the ethylene pressure.

If the reaction proceeds by mechanism (3), that is, the interaction between two ethyl radicals adsorbed on neighbouring sites, the rate of reaction is given by

$$v = c_{a''a''} \frac{kT}{h} \frac{f_{\ddagger}}{f_{a''a''}} e^{-\epsilon_o/kT} \tag{41}$$

The concentration of ethyl radicals adsorbed on neighbouring sites is

$$c_{a''a''} = \frac{1}{2} s c_{a''} \theta''$$

$$= \frac{1}{2} s^3 \frac{c_a{}^2 \theta'^2}{L} \frac{f^2_{a''}}{f^2_{aa'}} e^{2\epsilon''/kT} \tag{42}$$

Therefore the rate can be expressed as

$$v = \frac{1}{2} s^3 LA^2B^2c_g' \frac{kT}{h} \frac{1}{F_g'} e^{-(\epsilon_o - 2\epsilon' - 2\epsilon)/kT} \tag{43}$$

The rate is again proportional to c_g' but goes through a very flat maximum as the ethylene pressure is increased.

Twigg's mechanism which involves the interaction between adsorbed ethylene and gaseous hydrogen gives the following rate equation.

$$v = LA\, c'_g \frac{kT}{h} \frac{1}{F'_g} e^{-\epsilon_0/kT} \qquad (44)$$

At high values of c_g the rate reaches a limiting value of

$$v_{max} = (1/2)\, Lc'_g \frac{kT}{h} \frac{1}{F'_g} e^{-\epsilon_0/kT} \qquad (45)$$

The foregoing mechanisms cannot be distinguished quantitatively because all the expressions give rate values of similar magnitude.

The absolute rate treatment of the ethylene deuterium exchange has been developed for the Langmuir-Hinshelwood mechanism. It is assumed that there is at least one bare site adjacent to an ethyl radical, so that the exchange rate is controlled by the unimolecular breakdown of adsorbed ethyl radicals. The rate expression is:

$$v = sLABc'_g{}^{1/2} \frac{kT}{h} \frac{f_{a'}\, f_{\ddagger}}{f_{aa'}\, f_s\, F'_g} e^{-(\epsilon_0 - \epsilon'' - \epsilon)/kT} \qquad (46)$$

If this expression is compared with that for hydrogenation, it is evident that the activation energy for exchange should be greater than for hydrogenation by the heat of adsorption per atom of hydrogen. The agreement with experimental activation energy differences is quite good.

SUMMARY OF THE DISCUSSIONS FOR ASSOCIATIVE AND DISSOCIATIVE ADSORPTION

It is now generally accepted that saturated hydrocarbons are chemisorbed on metals by the dissociation of one or two hydrogen atoms (38, 39, 40, 41). The principal piece of research was carried out by Kemball (42, 43, 44, 45). Kemball has done extensive studies on the exchange of deuterium with saturated hydrocarbons using the mass spectrometer for the analysis of the products during the course of the reaction. Kemball has shown that some hydrocarbons on certain metals (e.g. rhodium) are adsorbed by two point contact with the loss of two hydrogen atoms.

This knowledge of saturated hydrocarbon chemisorption has been used as evidence in support of dissociative adsorption of unsaturated hydrocarbons. However Wagner (46) and Taylor (47, 48) have shown that ethylene exchanged with deuterium at -80°C while ethane did not exchange until temperatures of the order of 100°C were reached, so that different mechanisms must be involved for saturated and unsaturated hydrocarbon exchange reactions.

Farkas and Farkas (10) have supported the dissociative mechanism and experiments along the following general lines have been studied to confirm the dissociative mechanism. (1) Rates of addition of hydrogen to the double bond were determined. (2) The rate of ethylene-deuterium exchange was determined from the increase in hydrogen content of the deuterium as measured by microthermal conductivity. (3) The rates of conversion of para to ortho hydrogen in the presence of ethylene and also the rates of equilibration of mixtures of hydrogen and deuterium in the presence of ethylene were measured. They obtained an activation energy of 10 kcal. per mole for ethylene hydrogenation and 22 kcal. per mole for the exchange reaction on platinum. However no inversion temperature was observed for the exchange reaction as was found for the hydrogenation reaction.

During the reactions of para-hydrogen and ortho-deuterium with ethylene, the rates of the addition reactions were of the same magnitude as the rates of the conversions. This indicated to them that the rate controlling step in the addition reaction was the dissociation of hydrogen. The differences in the activation energies of the exchange and addition reactions led them to postulate that the two reactions proceeded by entirely different mechanisms. For the exchange reaction, the dissociation of the adsorbed ethylene was assumed to be rate controlling. They also suggested that for hydrogenation two hydrogen atoms added simultaneously. However more recent infra-red studies (16, 17) have shown this postulate to be incorrect. The difference in activation energies of the exchange and hydrogenation reactions has, however, been explained using absolute rate calculations as seen previously.

Cis addition of deuterium to a double bond (49, 50, 51) was thought to be further support of the simultaneous addition of two hydrogen atoms, but Polanyi (52, 53) has been able to explain cis addition using the associative mechanism.

Pliskin and Eischens' infra-red studies (54, 55) of olefin adsorption on metallic films would seem to support associative adsorption. They found a CH_2 deformation band but no $C-H$ stretching band when ethylene and propylene were adsorbed on nickel. There was also no evidence for a $C = C$ stretching band. The $C-H$ stretching band for a hydrogen attached to a doubly bonded carbon appears in the region above 3030 cm^{-1}.

Studies of double bond migration (53, 56, 57) lend support to the dissociative mechanism since the associative mechanism does not predict the correct ratios of products.

Twigg and Rideal (14) found that hydrogen and deuterium were not equilibrated during the exchange between deuterium and ethylene and they concluded that the concentration of chemisorbed hydrogen atoms must be very small. Also the hydrogen coming from the catalyst surface initially was low in deuterium. They supported the associative chemisorption of ethylene but assumed that chemisorbed ethylene reacts with deuterium molecules held in a van der Waals layer.

Twigg and Conn (16) using infra-red analysis found no exchange between ethylene and tetra-deutero-ethylene on nickel between 76°C and 360°C, and this tends to support the associative mechanism. However Wright and Taylor (58) and Rabinovitch (59), using mass spectrometric and infra-red analyses, did find exchanged products. Sheridan (60, 61) found that acetylene and di-deutero acetylene were equilibrated in two hours at 119°C on nickel.

Jenkins and Rideal (5) have found that when ethylene was adsorbed on a nickel film a self-hydrogenation took place to form ethane. The dissociative mechanism is required to explain self-hydrogenation. The ethylene on adsorption is thought to dissociate into two hydrogen atoms and an acetylenic complex which is held to the surface by four-point bonding.

THEORY OF METALS

The metal film plays such an important role in heterogeneous catalysis that it is necessary to obtain all possible information about the structure of metals. Whenever a gas comes in contact with a metal, it is important to know how the gas is physically adsorbed or chemisorbed. This requires a complete knowledge of the energy levels of the electrons in the metal and in the gas molecule to determine whether an electron transfer or sharing takes place. Theories of metals which have been developed to the present time are capable of giving qualitative or semi-quantitative results only.

QUANTUM MECHANICAL THEORIES

Metals have been treated theoretically from a quantum-mechanical point of view (62) and from a resonant bond point of view (63). In the quantum-mechanical treatment the possible energy levels available to the electrons are calculated from a knowledge of the potential fields set up by the nuclei of the metal atoms. The resonant bond treatment, due mainly to Pauling, regards the atoms in the metal as held together by ordinary localized bonds, and considers the possible resonance states existing between them.

SOMMERFELD THEORY. Sommerfeld (64) developed the simplest quantum-mechanical treatment by regarding the potential field of the nuclei as uniform throughout the metal. The electrons therefore can move freely through the metal, as an electron gas. The Schroedinger equation for the case of zero potential is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 mE}{h^2} \psi = 0 \qquad (47)$$

and its solution is

$$\psi = e^{ikx} \tag{48}$$

where

$$k^2 = \frac{8\pi^2 mE}{h^2} \tag{49}$$

The energy E is equal to $1/2\ mv^2$ and h/mv is equal to λ, the de Broglie wave length so that

$$k = \frac{2\pi}{\lambda} \tag{50}$$

The electrons are confined in a metal of length L and in order for to satisfy this boundary condition, L must be equal to $n\lambda/2$ where n is an integer. Thus

$$k = \frac{\pi n}{L} \tag{51}$$

and the allowed energy levels are given by

$$E = \frac{k^2h^2}{8\pi^2 m} = \frac{n^2h^2}{2mL^2} \tag{52}$$

This corresponds to a series of very closely spaced levels. Since the Sommerfeld theory does not properly account for the specific heats of metals, a more elaborate theory was necessary.

BLOCH, KROENIG, AND PENNEY THEORY. A more satisfactory theory was developed by Bloch, Kroenig, and Penney (65). They used a periodic square-wave potential field. The potential V consists of rectangular barriers of height V_o and width "b" separated by intervals of length "a" as seen in Figure 1 (a). The Schroedinger equation takes the following forms:

From x = 0 to x = a

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} \Psi E = 0 \qquad (53)$$

and from x = 0 to x = -b

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - V_o) \Psi = 0 \qquad (54)$$

The general solution of these equations is of the form

$$\Psi = Ue^{ikx} \qquad (55)$$

where U is a periodic function having the same periodicity as V .

The actual solutions must satisfy four boundary conditions. (1) The values of U satisfying equations (53) and (54) must be identical at the point x = 0 . (2) Also du/dx must be identical for both solutions at x = 0 . (3) The value of U at -b must be equal to the value of U at "a" . (4) The value of du/dx at -b and "a" must be identical. These boundary conditions result in four simultaneous equations, which on elimination of the four constants lead to

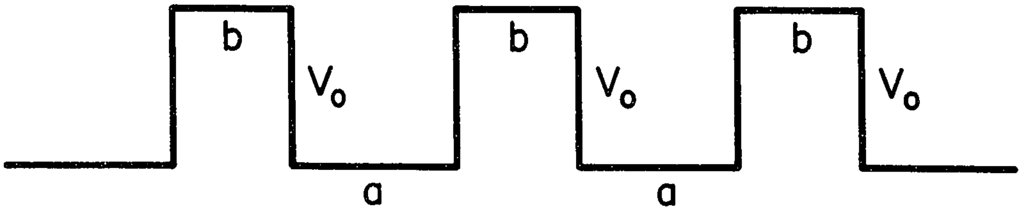


Figure 1a Rectangular potential-energy barrier.

$$\frac{\gamma^2 - \beta^2}{2\beta} \sinh \gamma b \sin \beta a + \cosh \gamma b \cos \beta a = \cos k(a + b) \tag{56}$$

where

$$\beta = \left(\frac{8\pi^2 m E}{h^2}\right)^{1/2} \tag{57}$$

and

$$\gamma = \frac{8\pi^2 m(V_0 - E)^{1/2}}{h^2} \tag{58}$$

Certain values of E do not satisfy this equation; therefore there are certain forbidden regions of energy which occur periodically and are separated by regions crowded with permitted energy states. When these zones of permitted and impossible levels are marked out in terms of momentum coordinates the permitted regions are referred to as Brillouin zones.

If the potential barriers are very high, the only solution of equation (56) is

$$\sin \beta a = 0 \tag{59}$$

and

$$E = \frac{n^2 h^2}{8ma^2} \tag{60}$$

The energy levels are discrete, the electrons being confined to individual potential wells. This is the situation for the innershell electrons.

The number of possible states in each Brillouin zone is limited. An electron in a completely filled zone cannot participate in conduction phenomena unless it acquires enough energy to pass across the forbidden zone into a higher zone. If this energy is great, the probability of such a passage is small, and the solid is an insulator. If the barrier is small, the solid is a semi-conductor. Only solids with incompletely filled zones are conductors.

As seen in Figure 1(b) certain electrons are localized in the potential wells at each nucleus and are unable to pass from one nucleus to another. There are also groups of energy levels corresponding to values higher than the maxima that overlap all the nuclei, and these groups are referred to as bands. If these bands are incompletely filled, conduction can take place upon application of an electric field. If the band is filled conduction can arise only if the field is sufficiently strong to excite electrons into an upper band. The number of energy levels in any band is equal to the total number of atoms present in the crystal. In general the bands formed from s states show a greater energy spread than those formed from p states, while the d bands are narrower still.

THE RESONATING BOND THEORY OF METALS.

The theory of metals developed by Pauling (66, 67, 68) regards the metallic bond as involving resonance between covalent and ionic bonds formed between the individual atoms. The resonance forms

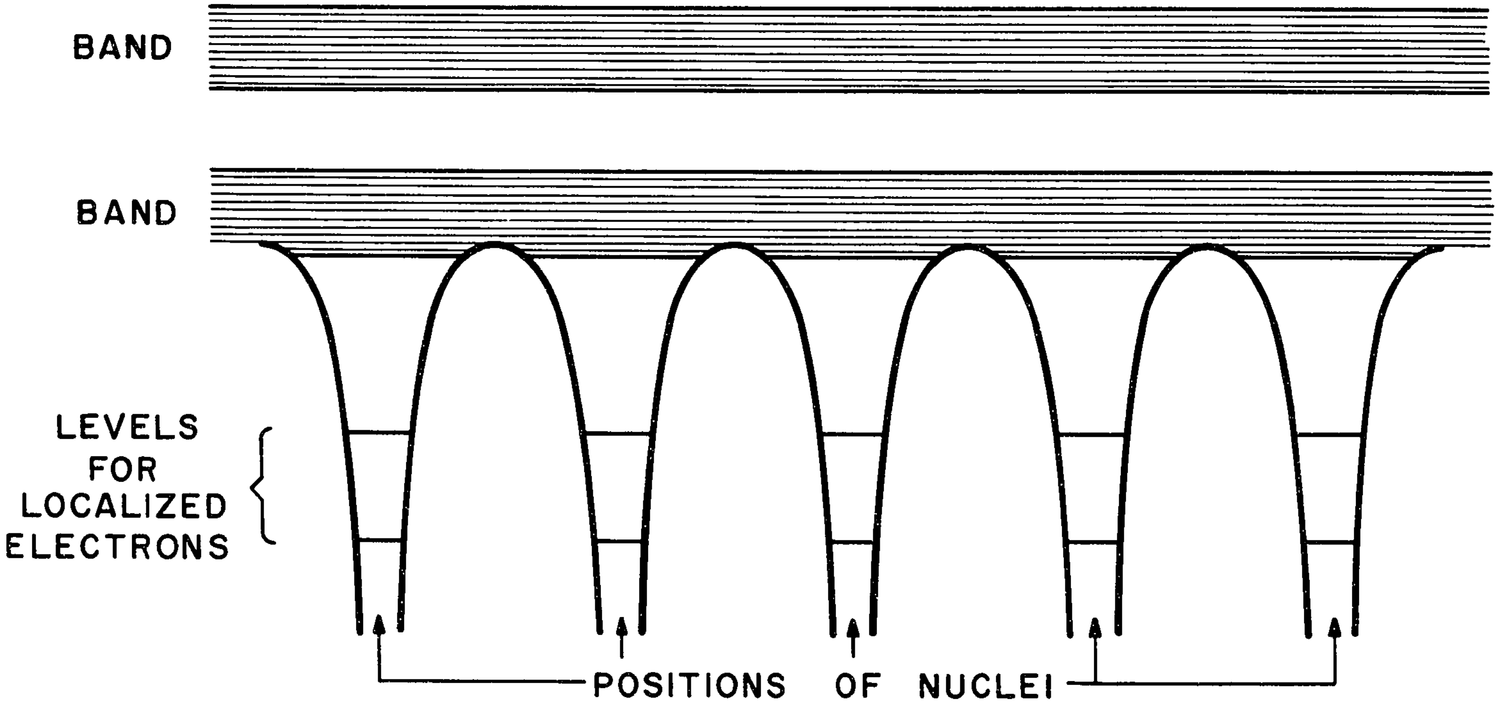
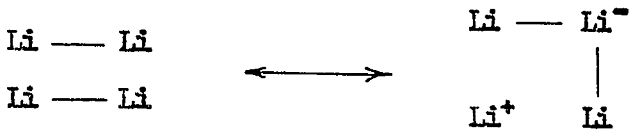


Figure 1b Potential-energy barriers for electrons in a metal, showing the positions of bands.

in lithium, for example, are given as:



In order for this resonance to be possible the atom must be capable of forming a structure of the type $-\mathrm{Li}^{-}-$ and this 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. The metallic orbital in lithium is a p orbital, but in transition metals it is frequently a d orbital.

The scheme in Table I represents the situation with iron, cobalt, nickel, and copper. This table indicates the relative percentages of the forms that are believed to exist in the metal, the average valency of the bonds in the metals, and the percentage d character (69, 70).

Iron will be used as an example to show how the percentage d character is determined. In the first iron structure there are two unpaired d electrons, whereas in the second there are three . According to the theory of paramagnetism each unpaired d electron contributes a value of one Bohr magneton to the magnetic dipole moment. Experimentally the magnetic moment of iron is 2.22 magnetons; thus iron must consist of 22 % of the B form and 78 % of the A form in order to explain this magnetic moment. In structure A there are three d electrons, and altogether seven orbitals are involved in the bonding; in structure B there are two d electrons

Table I

Electronic Configuration of Forms of Iron, Cobalt, Nickel and Copper

Metal	Number of Outer Electrons			Resonance Ratio	Valency		Percentage d Character
	3d	4s	4p				
Fe A	↑ ↑ ● ● ●	●	● ● ○	78	6	5.78	39.7
Fe B	↑ ↑ ↑ ● ●	●	● ● ○	22	5		
Co A	↑ ↑ ↑ ● ●	●	● ● ●	35	6	6	39.5
Co B	↑↓ ↑ ● ● ●	●	● ● ○	65	6		
Ni A	↑↓ ↑ ↑ ● ●	●	● ● ●	30	6	6	40.0
Ni B	↑↓ ↑↓ ● ● ●	●	● ● ○	70	6		
Cu A	↑↓ ↑↓ ● ● ●	●	● ● ●	25	7	5.5	35.7
Cu B	↑↓ ↑↓ ↑↓ ● ●	●	● ● ○	75	5		

↑ Electron

● Electron involved in bonding

○ Empty orbital

and six orbitals involved in bonding. Therefore the percentage d character is given by:

$$78 \times \frac{3}{7} \times 22 \times \frac{2}{6} = 39.7$$

In the band treatment described by Mott and Jones (62) only the outer s electrons are considered to be involved in bond formation. But in Pauling's theory all the outer electrons are involved in bond formation. Since in the band theory there is frequent overlapping of bands with no clear distinction as to type of orbital, Pauling's percentage d character concept has no counterpart in band theory.

THE d-BAND IN METALS.

In copper the d band is completely filled and copper has no paramagnetism. For nickel the saturation magnetic dipole moment is 0.6 and this indicates that there are on the average 9.4 electrons per atom in the d band, and 0.6 in the s band. From the standpoint of chemisorption the d band holes seem to be a more significant factor than the percentage d-character.

The initial heats of chemisorption of hydrogen are given in Table II along with other properties of the metals, including the valency, the percentage d-character, the magnetic moment, and the product of the valency and the percentage d-character. Beeck (26) has suggested that there is a correlation between the initial heat of chemisorption and the percentage d-character. However apart from tungsten and copper this order is the inverse of that for the initial heats of chemisorption. Trapnell (71) considers that the bond

Table II

Heats of Chemisorption of Hydrogen

	Ta	W	Cr	Fe	Ni	Pt	Rh	Cu
Observed heat	45	45	45	32	31	30	28	9
Valency	5	6	6.3	5.8	6	6	6	5.5
% d-character	39	43	39	39.7	40	44	50	36
Vxd	195	258	246	230	240	264	300	198
Magnetic moment	-	-	-	2.22	0.6	0.6	0.55	0
Calculated heat (Eley)	32	44	15.7	17	17	-	23	13.6
Calculated heat (Trapnell)	47	50	31.5	18	18	37	23	-

Heats of Chemisorption in kcal. per mole.
Magnetic momemt in Bohr magnetons.

between the metal and the adsorbed species involves an electron in the adsorbed species and an electron in the d-band. Thus the greater the percentage d-character of the bond in the metal the fewer electrons are available for such bonding, and the lower will be the heat of adsorption. Since the correlation is poor other more important factors must be involved. In actual fact a correlation with the magnetic moment of the metal, which is a measure of the number of holes in the d-band, is more satisfactory.

Eley (72), using an equation due to Pauling, equates the energy of a surface-hydrogen bond to the arithmetic mean of the energies of the surface-surface and hydrogen-hydrogen bonds, corrected by a term which involves the square of the differences between the electronegativities. Eley's treatment gives a slightly improved correlation but does not take into consideration the details of what occurs at the surface when adsorption takes place, nor the possibility that some type of surface bond has to be broken.

The band theory as yet is only capable of giving qualitative results. The band theory does give a more concrete picture than some of the former theories. It is expected that the band energies will increase as the surface of the metal is approached. As a molecule approaches the surface the energy levels in the metal will become more horizontal, and there will be a movement of electrons either to or from the metal in order for equilibrium to be established. The direction and extent of this movement depends upon the work function of the metal, ϕ , and the ionization potential, I, of the adsorbed molecule. If the ionization potential of the approaching molecule is very low there will be a tendency for electrons to move from the adsorbed molecule to the surface and conversely.

Schwab and his co-workers (73, 74, 75) studied the zero-order decomposition of formic acid over catalysts consisting of various metals dissolved in silver. In all cases the addition of the solute metal caused an increase in the activation energy; with antimony, lead, and bismuth the activation energy was increased by 15 to 20 kcal. per mole over the value of 17.6 kcal. per mole for pure silver. The addition of a solute metal increases the electron concentration and the reaction is therefore favoured by empty levels in the conduction band, so that the rate determining step is probably the addition of electrons from a chemisorbed formic acid molecule to the conduction band of the metal.

Couper and Eley (76) carried out a series of experiments on the para-hydrogen conversion on palladium-gold alloy wires. The activation energy was found to increase abruptly as soon as the proportion of gold reached approximately 60 atomic percent. Since pure palladium has 0.55 holes in its d-band, the reaction must be favoured by holes in the d-band because at 60 atomic percent gold all the d-band holes are filled.

Similar results were obtained by Dowden and Reynolds (77) using copper-nickel alloys. The rate of decomposition of methanol into carbon monoxide and water decreased as the proportion of copper was increased but the rate of decomposition of hydrogen peroxide was favoured by the addition of copper. Thus the rate determining step for hydrogen peroxide decomposition involves the transfer of electrons from the surface to the adsorbed species.

It is hoped that in the future more quantitative results will be obtained from these theories when a greater knowledge of metals is obtained experimentally. The further development of these theories is hindered by a lack of accurate knowledge of the properties of metals.

This introduction has been restricted to only the pertinent facts and experimental results which pertain directly to the research described in this thesis. A more general picture of heterogeneous catalysis and chemisorption can be obtained from the many excellent reviews and books written by Laidler (32), Trapnell (71), Eley (78), Anderson (38), Boudart (79), Burwell (80), Rabinovitch (81), Taylor (82), and Stone (84).

CHAPTER II

EXPERIMENTAL

APPARATUS

The apparatus consisted of three main components: (1) a section for the purification, storage, and dispensing of hydrogen; (2) a similar section for ethylene; and (3) a reaction section. A schematic diagram is given in Figure 2.

The hydrogen treatment component consisted of a cylinder of hydrogen connected to a palladium thimble. The palladium thimble was a Johnson Matthey ZX001 palladium thimble consisting of a palladium tube 4 mm. O.D. by 0.2 mm. wall and length 50 mm. attached to a platinum tube 4 mm. O.D. by 0.2 mm. wall and 25 mm. long. The thimble was continuously maintained at a temperature of 400°C. It was found that, if the temperature of the palladium thimble was lowered to room temperature and then again raised to 400°C, the thimble would become misshapen and develop leaks. (Palladium undergoes a phase transition at 310°C). A liquid air trap was put between the palladium thimble and the rest of the system to prevent the entrance of any mercury vapour to the graded seal on the palladium thimble which contained gold. A two-litre reservoir with a manometer attached was used to store the hydrogen. The dispensing system consisted of a small bulb of one litre and a

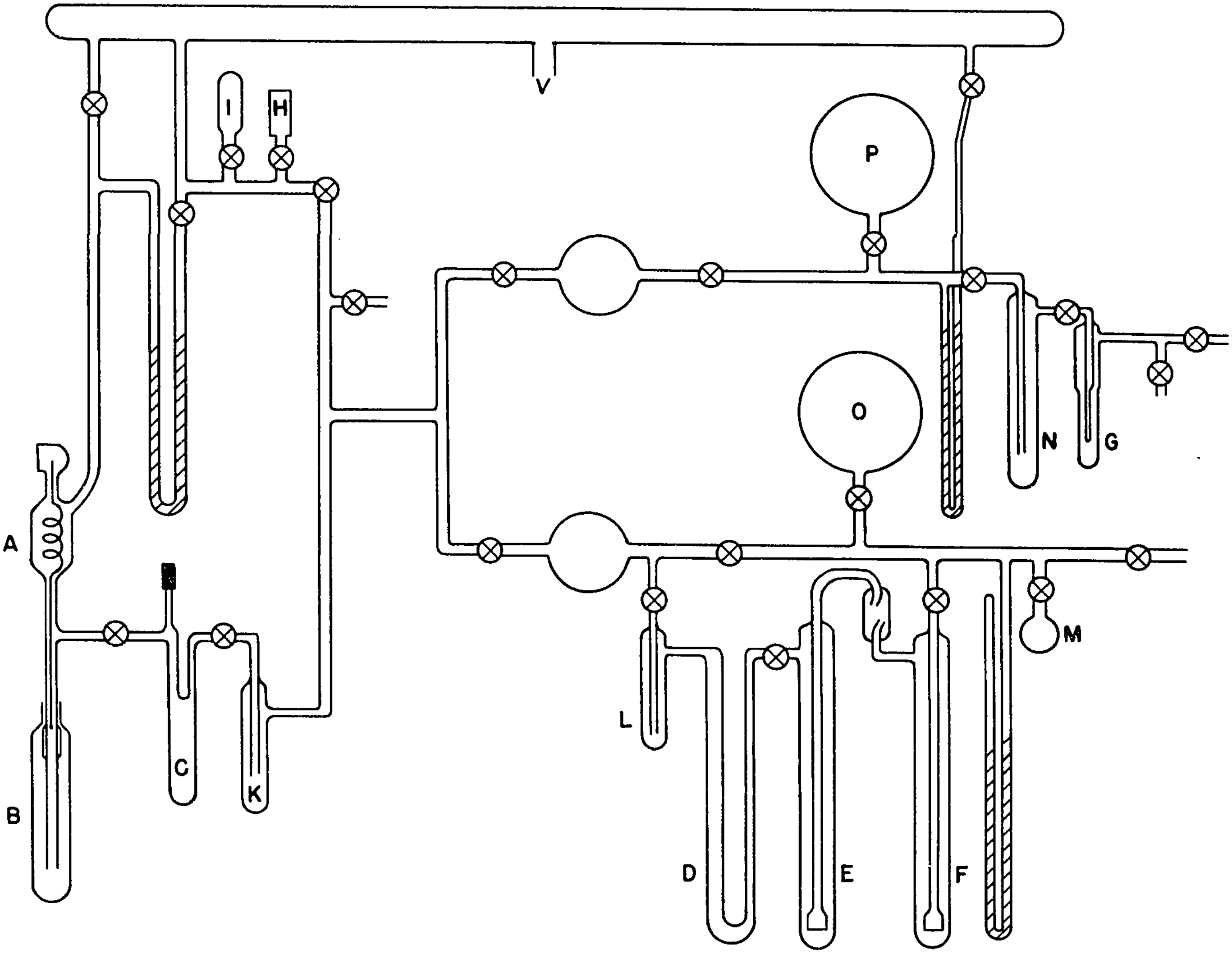


Figure 2 Schematic diagram of the apparatus.

A.	Quartz spiral gauge.	I.	Ionization gauge.
B.	Reaction vessel.	K.	Trap.
C.	Premix chamber.	L.	Trap.
D.	Drying column.	M.	Liquid ethylene reservoir.
E.	Lead acetate bubbler.	N.	Trap.
F.	Fieser's solution bubbler.	O.	Ethylene storage reservoir.
G.	Palladium thimble.	P.	Hydrogen storage vessel.
H.	Pirani gauge.	V.	Lead to oil diffusion pump.

couple of 5 cc. and 7 cc. sections which allowed small quantities of hydrogen to be introduced into the reaction system.

The ethylene dispensing system consists of a cylinder of ethylene connected to a small bulb with an attached manometer into which the ethylene could be condensed with liquid air. The small bulb was connected to a two-litre storage bulb which in turn was connected to a series of bubblers and driers. The first bubbler contained Fieser's solution, and the second contained a saturated solution of lead acetate. The bubblers were fourteen inches long and contained a coarse sintered glass tube. The drying column contained Linde molecular sieve number 5A and was three feet long. The drier was followed by a trap which was kept in a Dewar of cyclohexene at its melting point. The purification train led into a dispensing system consisting of a one-litre bulb and a 7 cc section closed off by stopcocks.

The reaction system was connected to the rest of the system through a trap. The trap led into a premix chamber of 140 cc. volume which had an attached Pirani head. The Pirani was manufactured by Consolidated Electrodynamics Corp. and the head was of small volume; the filament operated at 170°C. The premix chamber was connected to the actual reaction vessel by three millimeter capillary and a high vacuum stainless steel Hoke valve.

The reaction vessel was designed to keep dead-space to a minimum. The reaction vessel as seen in Figure 3 consisted of a 35 mm. tube 20 cm. long containing a thermocouple well. The 24/40 ground glass joint at the mouth of the reaction vessel was actually 6 cm. from the actual reaction chamber. This was made possible by using a through

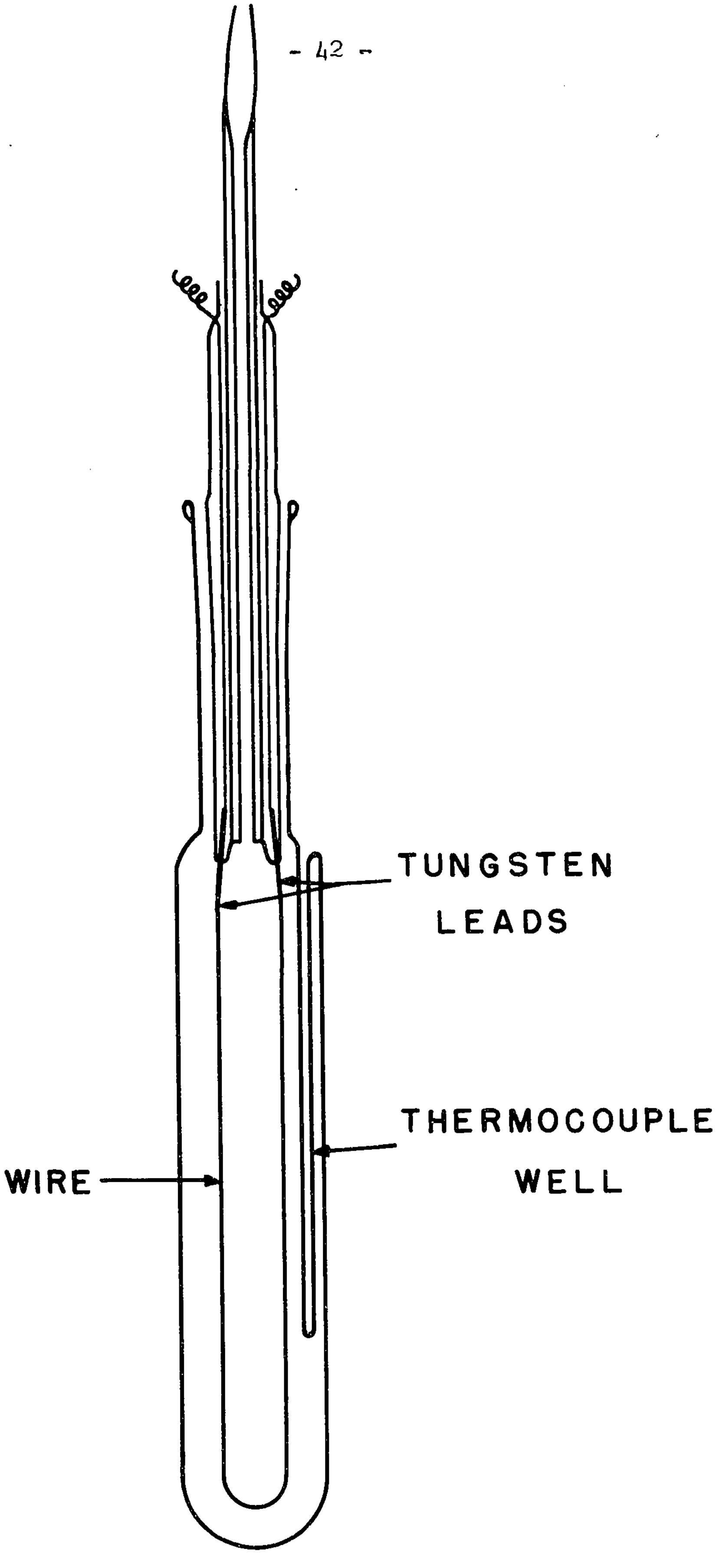


Figure 3 Reaction vessel.

male 24/40 joint with a 6 cm. nose which closely fitted inside the neck of the reaction vessel. A two millimeter capillary tube ran from the end of the nose up through the male joint and terminated in a male 10/30 joint. Two copper leads passed through the male 24/40 joint and terminated in the nose at two one millimeter diameter tungsten wires sealed into the glass and protruding 15 millimeters into the interior of the reaction chamber.

Above the reaction vessel a quartz spiral gauge for measuring the pressure decrease during reaction was located. The quartz spiral consisted of four loops of 4 cm. diameter which were immersed in silicon oil to minimize small vibrations. The outer section of the spiral gauge was connected to the main vacuum manifold. A 5 cm. pointer was connected to the spiral. At the upper end of the pointer was attached a small galvanometer mirror. The long pointer was necessary to keep the oil from spraying the mirror.

The optical system consisted of a 500 watt projection bulb which was focused on the spiral mirror by one lens. The image fell on the phototubes of a Beckman Photopen recorder placed four feet from the mirror. The complete optical system was enclosed in a black box to prevent the intervention of stray light. With this system a change of 2.8 cm. Hg pressure within the quartz spiral resulted in a deflection of one inch by the photopen in the recorder. The spiral gauge was strong enough to withstand a pressure difference of one atmosphere between the interior of the spiral and the surrounding enclosure.

Below the reaction vessel there was a high temperature furnace mounted on two scissor jacks. The use of two jacks allowed the furnace a travel of 18 inches up the frame which surrounded the reaction vessel. Thereby the furnace could be raised so that it completely surrounded the reaction vessel, but when the furnace was lowered to its limit it allowed a small 5 × 5 inch water bath to be placed around the reaction vessel. The temperature of the water bath was controlled by a Thermistemp Temperature Controller built by the Yellow Springs Instrument Co. The Thermistemp Controller uses a thermister as the sensing element. The bath was rapidly stirred and the temperature maintained to within one tenth of a degree.

The temperature inside the reaction vessel was measured by means of a chromel-alumel thermocouple one end of which was placed inside the reaction vessel thermocouple well and the other end was placed in a $0^{\circ}C$ ice bath. The potential of the thermocouple was measured on a Tinsley portable potentiometer.

The main vacuum system consisted of an Edwards Speedivac oil diffusion pump, type 203, backed by a Welch rotary pump. There were liquid air traps before the mechanical pump and the diffusion pump. The diffusion pump had a pumping speed of 50 to 55 litres per second and was capable of an ultimate vacuum of 5×10^{-6} mm. Hg. The vacuum was measured by an Edwards Pirani gauge and an ionization gauge made by Consolidated Vacuum Corporation.

PROCEDURE

PURIFICATION OF CHEMICALS.

Hydrogen - Dominion Gas cylinder hydrogen was passed through a palladium thimble heated to $400^{\circ}C$. The hydrogen was stored in a two-litre bulb after passing through a liquid air trap. A hydrogen pressure of 5 p.s.i. was applied to the one side of the palladium thimble. The hydrogen diffused through the palladium thimble at such a rate that the pressure in the storage reservoir increased at a rate of 0.2 cm. Hg per minute. The hydrogen was kept in the storage reservoir for not more than 24 hours after which time the old hydrogen was pumped out and a new batch of hydrogen was purified by diffusion.

Ethylene. - Matheson's C.P. grade ethylene was condensed into a small bulb with liquid air. This ethylene was then purified by the freeze-thaw method; that is, the ethylene was frozen by liquid air and pumped out under high vacuum. After closing off the vacuum the ethylene was warmed until it was completely liquified, then frozen and pumped out once more. This procedure was repeated three times, after which the ethylene was passed through the bubbler train.

The first bubbler contained Fieser's solution prepared by mixing 26.7 grams of sodium hydroxide, 8 grams of anthraquinone-β-sulphonate, and 32 grams of sodium hydrosulphite in 200 cc. of water under an atmosphere of nitrogen. The second bubbler contained a saturated solution of lead acetate to remove any hydrogen sulphide formed by the reaction of oxygen and Fieser's solution. The lead acetate solution was followed by a four foot drying column of number 5A molecular sieve. The last component of the purification train was a trap kept in a freezing mixture of cyclohexene. Cyclohexene has a melting point of -103.7°C, at which temperature the vapour pressure of ethylene is 76 cm. Hg. Thus the coldest trap temperature was attained while allowing an atmosphere of ethylene to pass. The freezing mixture of cyclohexene was prepared by mixing liquid air with cyclohexene until half the cyclohexene was frozen. The ethylene was passed through this purification train at least three times before being stored. At the beginning of each day of reactions, the stored ethylene was passed through the purification train once again.

PREPARATION OF METAL FILMS

The reaction vessel was cleaned with hot chromic acid cleaning solution and then washed for 15 minutes in a continuous stream of water. The vessel was thoroughly dried in an oven. A 35 cm. length of the metal wire to be evaporated was then spot-welded to the two tungsten leads. The 24/40 ground glass joint was greased with Dow Corning Silicon high vacuum grease and the reaction vessel put together so that the metal filament did not touch the walls of the vessel. The reaction vessel was placed on the main apparatus and the high temperature furnace was then moved up around the reaction vessel by means of two scissor jacks. The top of the furnace was 6 cm. below the ground glass joint and well insulated to prevent the greased joint from becoming too hot. The vessel was heated to 500°C and pumped out under high vacuum for at least four hours but usually overnight. A vacuum of 10^{-5} mm. Hg was attained. A current of 4 amps. was passed through the metal filament for 15 minutes to thoroughly degas the metal wire. The furnace was then lowered and the reaction vessel allowed to cool to room temperature. An ice water bath in a large dewar was placed around the reaction vessel. A current sufficient to cause the metal to evaporate at the rate of one milligram per minute was then passed through the filament for approximately twenty minutes. The metal film formed was then ready for reactions. This method of evaporating films is due mainly to Beeck and Kemball.

Nickel - Johnson Matthey spectroscopically pure nickel wire of 0.5 mm. diameter was used as the filament for the preparation of nickel films. To prepare a typical nickel film a voltage of 7.8 volts was applied to the filament to pass a current of 6 amperes for 15 minutes. The resulting nickel film weighed 22 milligrams. The weight of a nickel film was determined, after a series of reactions was completed, by dissolving it in nitric acid and precipitating the nickel as nickel glyoxime. The nickel nitrate was diluted with water to a concentration of 50 milligrams of nickel per 200 cc. of water. This solution was heated to boiling and then treated with a slight excess of a 1 percent solution of dimethyl glyoxime in ethanol. After neutralization with ammonia the solution was allowed to stand for one hour and then filtered and washed with hot water. The precipitate collected in a sintered glass filter was dried at 100°C for one hour.

Palladium - Johnson Matthey pure palladium wire of 0.5 mm. diameter was used as the filament for the preparation of the palladium films. A typical palladium film was prepared by applying 7.2 volts to the filament resulting in a current of 7.0 amperes for 9 minutes. The film so prepared weighed 85 milligrams. The palladium films were also precipitated by dimethyl glyoxime to determine their weight. Aqua regia was used to dissolve the palladium film off the reaction vessel. After dilution with water the procedure was the same as that used for nickel.

Iron - Johnson Matthey spectroscopically pure iron wire of diameter 0.5 mm. was used as the filament in the preparation of iron films. For the preparation of a typical iron film a current of 4.8 amperes requiring a voltage of over 10 volts was passed for 15 minutes.

The film thus prepared weighed 27 milligrams. The iron was determined as the ferric oxide. Concentrated hydrochloric acid was used to dissolve the iron film off the reaction vessel. After dilution to 200 cc. with water and the addition of 1 cc. of concentrated nitric acid, the solution was heated to boiling and neutralized with 1 : 1 ammonia solution. After being boiled for one minute the precipitate was allowed to settle. Then 100 cc. of boiling one percent ammonium nitrate solution was added and the precipitate filtered with a 41 H filter paper. The precipitate was heated at 1000°C to constant weight.

GENERAL REACTION PROCEDURE

In all former investigations of ethylene hydrogenation on metallic films, except for the work done by Kemball, Jenkins and Rideal, and Foss and Eyring, each metallic film was used only once. It was thought that a great saving in time could be effected by using a film more than once. However, in order to use films several times the gases must be of very high purity, and must especially be oxygen-free. Also, to make for greater facility in operation a reaction vessel similar to Kemball's was used which included a ground glass joint. However, the Kemball model has been modified in this work to reduce dead-space to a minimum as described in the apparatus section. Former investigators used all-glass systems with no joints or stopcocks. Mercury cut-offs and cold traps were used instead of stopcocks but the amount of dead-space was great. For each new film it was necessary to cut open the reaction vessel, and after cleaning to reseal the vessel.

However in order to use a metallic film more than once some technique must be developed to determine the activity of the film between individual runs. Since Jenkins and Rideal had found some correlation between the quantity of hydrogen chemisorbed and the film activity, chemisorption of hydrogen was investigated. However no correlation was found in this research so that a standard hydrogenation, using 5 cm. Hg of ethylene and 5 cm. Hg of hydrogen introduced into the reaction vessel simultaneously at 32.3°C, was used as a measure of the film's activity.

As in the work done by Jenkins and Rideal, the film was found to be initially very active but decreased rapidly in activity reaching a constant value after three or four runs. The initial great activity was eliminated by treating each new film with 10 cm. Hg of ethylene for 30 minutes. After this treatment the film activity decreased slowly. In order to reduce this rate of decrease in film activity even further, Foss and Eyring worked at very low pressures, between 15 to 100 microns. However in the present research it was found that, by treating the film between reactions with 10 cm. Hg of hydrogen for 15 minutes at 32.3°C, the activity of the film now decreased quite slowly. This technique allowed as many as thirty runs to be done on one film.

The procedure for the standard hydrogenation was as follows. The premix vessel was filled with 10 cm. Hg of ethylene which had passed through a trap cooled in a freezing mixture of cyclohexene. The ethylene was then condensed in the bottom of the premix vessel with liquid air. The trap, after being warmed up and pumped out, was cooled with liquid air. A hydrogen pressure of 10 cm. Hg was then introduced into the premix chamber. The stopcock between the trap and the premix chamber was closed and the premix chamber allowed to come to room temperature. By rapidly opening and closing the stainless steel stopcock between the reaction vessel and the premix chamber the gas mixture was introduced into the reaction vessel. The reaction vessel was maintained at 32.3°C by a water bath controlled by a thermistor regulator. The decrease in pressure due to the hydrogenation reaction was automatically recorded on chart paper by the photopen recorder via the quartz spiral gauge.

Nickel Reactions - The preceding procedure was used for all the hydrogenation reactions on nickel in which the ethylene and hydrogen were introduced to the nickel film at the same time. Between each reaction the reaction vessel and the premix chamber were evacuated under high vacuum for three-quarters of an hour. The film was then treated with 10 cm. Hg of hydrogen for fifteen minutes after which time the reaction vessel was again rigorously evacuated for one hour.

An activation energy was determined for the temperature range from 32.3°C to 80°C . In this case it was necessary to average the rates of the standard hydrogenations at 32.3°C , which were carried out before and after the reaction done at the elevated temperature, in order to get a true indication of the activity change since the film's activity decreases with increasing temperature.

A series of reactions was carried out on nickel in which the initial ethylene pressure was maintained at 5 cm. Hg and the initial hydrogen pressure was varied from 1 cm. Hg to 55 cm. Hg. This series allowed a determination of the hydrogen pressure dependence of the hydrogenation reaction to be made. A similar series was done to determine the ethylene pressure dependency. In this series the initial hydrogen pressure was maintained at 5 cm. Hg for each run and the initial ethylene pressure was varied from 1 cm. Hg to 20 cm. Hg .

In order to investigate whether the initial rate of the hydrogenation reaction depends upon which reactant gas is introduced first, several runs were carried out introducing hydrogen first and a series of runs was completed introducing ethylene first.

The following procedure was used to introduce the hydrogen first. The premix chamber was filled with 25 cm. Hg of ethylene which had passed through a cyclohexene freezing mixture cold trap. The ethylene was condensed into the bottom of the premix chamber. The stopcock between the premix chamber and the reaction vessel was opened and 7 cm. Hg of hydrogeh which had passed through a liquid air cold trap was introduced into both the reaction vessel and the premix vessel. Then the stopcock to the reaction vessel was closed and the premix chamber was warmed to room temperature. The recorder was started and the stopcock to the reaction vessel was rapidly opened and closed to introduce the ethylene and hydrogen mixture.

To introduce ethylene to the reaction vessel first, 8 cm. Hg of ethylene was introduced through a melting cyclohexene cold trap into both the reaction vessel and the premix chamber. The stopcock to the reaction vessel was then closed and the ethylene in the premix chamber was condensed in the bottom of the vessel with liquid air. Next, 23 cm. Hg of hydrogen was introduced through a liquid air cold trap into the premix chamber and then the premix chamber was allowed to warm up to room temperature. By rapidly opening and closing the reaction vessel stopcock the ethylene and hydrogen mixture was introduced into the reaction vessel.

An activation energy over the temperature range from 32.3°C to 80°C was determined using this latter procedure which introduces the ethylene to the reaction vessel prior to the hydrogen. Using a similar procedure an ethylene pressure dependence was determined at both 32.3°C and 80°C over an ethylene pressure range from 2 cm. Hg to 50 cm. Hg while the initial hydrogen pressure was kept constant at 5.5 cm. Hg for each run. To determine how the reaction rate depends upon the hydrogen pressure at 32.3°C when ethylene was introduced first, a series of runs was carried out using the above procedure with the initial ethylene pressure maintained at 6 cm. Hg and the initial hydrogen pressure varied from 1.5 cm. Hg to 26 cm. Hg.

Several runs were carried out using initial pressures of 10 cm. Hg of ethylene and 10 cm. Hg of hydrogen and all three methods of introducing the reactants. The rates throughout the course of these reactions were measured and a time course plot was made for each run.

Reactions on Palladium Films - Several exploratory reactions were carried out on palladium films. A few of the standard hydrogenations were attempted along with some reactions with very high initial hydrogen pressures. A number of runs were carried out with the introduction of ethylene first at both high and low initial hydrogen pressures. A couple of runs were attempted introducing hydrogen first. The results of these runs were so unpromising that only two palladium films were made.

Reactions on Iron Films - An activation energy for the ethylene hydrogenation reaction catalyzed by iron films was determined for the temperature range from 32.3°C to 80°C. For this activation energy determination, the runs were carried out by introducing the ethylene to the reaction vessel first using the same technique as that used for the nickel films. The initial pressures in the reaction vessel were

5 cm. Hg of hydrogen and 5 cm. Hg of ethylene. Standard hydrogenations were carried out at 32.3°C between each run carried out at an elevated temperature. As a measure of the iron film's activity for each of these runs at higher temperatures, an average of the initial rates for the standard hydrogenations, carried out before and after the run in question, was used.

The dependence of the initial reaction rate on the initial ethylene pressure was determined at 32.3°C. The ethylene was introduced to the reaction vessel first for each of these runs. While the initial hydrogen pressure was kept constant at 5 cm. Hg, the initial ethylene pressure was varied from 2.5 cm. Hg to 50 cm. Hg. A similar pressure range was used to determine the ethylene pressure dependence at 80°C. The ethylene was again introduced into the reaction vessel first for this series at 80°C.

In order to determine how the initial reaction rate depends on the initial hydrogen pressure a series of runs was carried out at 32.3°C. In this series the ethylene was introduced to the reaction vessel first and its initial pressure was maintained at 5 cm. Hg for the series. The initial hydrogen pressure was varied from 1 cm. Hg to 20 cm. Hg. For the hydrogen pressure dependence at 80°C a similar pressure range was studied, the initial ethylene pressure still being kept constant at 5 cm. Hg.

For all the runs used to determine pressure dependencies at 32.3°C, a measure of the film's activity for a particular run was given by the standard hydrogenation at 32.3°C carried out just before the run in question. In the case of the reactions carried out at 80°C for pressure dependency determinations, standard hydrogenations at 80°C were carried out before each dependency run and used as a measure of the film's activity for the run which followed the standard hydrogenation.

A number of runs was carried out at 32.3°C and analyzed throughout their complete course to determine a time course order for the hydrogenation reaction. Most of these runs were carried out introducing the ethylene to the reaction vessel first but one reaction was analyzed throughout its course with the hydrogen introduced to the reaction vessel first. In the series for which the ethylene was introduced first, some reactions were carried out with almost equal pressures of hydrogen and ethylene, some reactions had ethylene in large excess, and still others had hydrogen in excess over ethylene.

CHROMATOGRAPHIC ANALYSIS

A series of reactions was carried out on an iron film and the products were analyzed on a Perkin Elmer Vapour Fractometer. The products of a reaction were transferred to a sample bulb by means of a Toepler pump. The products were fed from the bulb into the chromatograph by a gas sampling valve. Helium was used as a carrier gas at a flow rate of 8 cc. per minute. The temperature of the column and detector was 30°C . The column consisted of silica gel and brought about a complete separation of ethylene and ethane. Two reactions were carried out on an iron film introducing both ethylene and hydrogen to the reaction vessel, simultaneously. One reaction had hydrogen in excess and the other reaction had ethylene in excess. The second set of two reactions on the iron film was carried out introducing ethylene to the reaction vessel first, but as in the other set, one reaction had excess hydrogen, and the other excess ethylene.

A similar series of four runs was carried out on a nickel film and the products were analyzed by the chromatograph.

CHAPTER III

RESULTS

ACCURACY

The accuracy of the measurements quoted in the following results is much greater than the reproducibility of reaction rates. All the pressures measured with a manometer and cathetometer are good to ± 0.01 cm. Hg and pressures measured with the spiral gauge have an error of ± 0.06 cm. Hg. However in heterogeneous catalysis the film is very sensitive to impurities and thus it is very difficult to reproduce a reaction rate. The use of a standard run between each experimental run gives a measure of activity but it cannot give an exact measure since any impurity introduced after the standard run will reduce the activity of the film.

This sensitivity of the film has resulted in a scatter in the results, as can be seen in many of the graphs; the pressure dependency orders cannot, therefore, be expected to be better than ± 0.05 and the activation energies will have a probable error of approximately ± 0.5 kcal. per mole.

All the pertinent runs in this research have been listed in Tables III to XVIII. The initial hydrogen and ethylene pressures, the method of reactant introduction, temperature, and initial rate have

TABLE III

RESULTS FOR METALLIC FILM 26 NICKEL

All pressures given in cm.Hg.
14.9 mg.
Temperature 32.3°C

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Initial rate cm.Hg/min.	Remarks
1	5.75	4.71	A	1.90	Std.
2	5.53	9.27	A	2.25	C_2H_4 dependence
3	5.58	12.67	A	1.12	C_2H_4 dependence
4	5.47	4.82	A	0.970	Std.
5	5.22	19.19	A	0.986	C_2H_4 dependence
6	6.26	25.68	A	0.626	
7	5.44	4.62	A	0.499	Std.
8	5.59	10.54	A	0.648	C_2H_4 dependence
9	5.87	12.70	A	0.490	C_2H_4 dependence
10	5.33	4.85	A	0.392	Std.
11	5.39	4.67	A	0.516	Std.

Method of Reactant Introduction

A	Ethylene and hydrogen were introduced to the film simultaneously.
B	Ethylene was introduced to the film prior to the hydrogen.
C	Hydrogen was introduced to the film prior to the ethylene.

Table IV

RESULTS FOR METALLIC FILM 27 NICKEL

31.9 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min.	Remarks
1	5.64	4.65	A	32.3	5.56	Std.
2	5.58	15.25	A	32.3	8.24	C_2H_4 dependence
3	5.53	4.82	A	32.3	4.43	Std.
4	5.86	26.83	A	32.3	4.78	C_2H_4 dependence
5	5.56	4.79	A	32.3	3.07	Std.
6	8.70	50.85	A	32.3	1.91	
7	5.53	5.04	A	32.3	1.14	Std.
8	23.50	4.34	A	32.3	5.84	H_2 dependence
9	5.95	4.76	A	32.3	3.53	Std.
10	6.12	14.03	A	32.3	2.38	C_2H_4 dependence
11	6.32	4.76	A	32.3	1.33	Std.
12	5.53	4.73	A	32.3	2.96	Std. Film treated with H_2 prior to this run.
13	5.39	10.60	A	32.3	2.03	C_2H_4 dependence
14	5.64	4.65	A	32.3	1.00	Std.

Table V

RESULTS FOR METALLIC FILM 28 NICKEL

22.3 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min.	Remarks
1	5.84	5.10	A	32.3	3.78	Std.
2	14.97	11.87	A	32.3	9.18	Time course plot
3	5.84	4.68	A	32.3	5.74	Std.
4	15.45	8.67	A	32.3	1.37	
5	5.73	4.36	A	32.3	5.47	Std.
6	14.60	6.12	A	32.3	8.41	H_2 dependence
7	5.84	4.90	A	32.3	4.71	Std.
8	15.02	8.22	A	32.3	6.96	
9	5.95	4.88	A	32.3	3.58	Std.
10	14.85	6.15	A	32.3	5.76	H_2 dependence
11	5.73	4.87	A	32.3	2.82	Std.
12	18.48	3.09	A	32.3	5.32	
13	5.95	4.79	A	32.3	2.07	Std.
14	14.80	7.00	A	32.3	2.60	H_2 dependence
15	6.04	4.93	A	32.3	1.28	Std.
16	13.52	14.80	A	32.3	1.36	Time course plot
17	5.50	4.93	A	32.3	0.772	Std.

TABLE VI

RESULTS FOR METALLIC FILM 29 NICKEL

26.3 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min.	Remarks
1	6.09	4.26	A	32.3	19.97	Std.
2	10.46	3.91	A	32.3	28.02	
3	6.01	4.73	A	32.3	15.70	Std.
4	17.01	3.40	A	32.3	32.00	
5	6.21	4.42	A	32.3	13.91	Std.
6	7.74	4.56	A	32.3	14.61	H_2 dependence
7	5.90	4.13	A	32.3	7.66	Std.
8	5.87	4.65	A	32.3	8.97	Std.
9	7.06	4.68	A	32.3	11.19	H_2 dependence
10	5.58	4.65	A	32.3	7.92	Std.
11	12.25	4.13	A	32.3	11.81	H_2 dependence
12	5.78	4.88	A	32.3	7.86	Std.
13	14.54	4.28	A	32.3	13.81	H_2 dependence
14	5.61	4.65	A	32.3	8.09	Std.
15	16.70	3.96	A	32.3	13.42	
16	5.75	4.65	A	32.3	7.66	Std.
17	5.87	4.31	A	32.3	9.30	Std.
18	16.89	4.11	A	32.3	21.13	H_2 dependence
19	5.84	4.79	A	32.3	8.78	Std.
20	18.17	4.19	A	32.3	15.58	H_2 dependence
21	5.90	4.98	A	32.3	8.72	Std.

TABLE VI - (Cont'd)

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
22	21.37	3.86	A	32.3	13.12	
23	5.87	4.82	A	32.3	6.59	Std.
24	21.40	3.71	A	32.3	12.08	
25	5.90	4.73	A	32.3	6.18	Std.
26	1.98	4.88	A	32.3	2.78	H_2 dependence
27	5.36	5.04	A	32.3	2.36	Std.
28	21.32	4.42	A	32.3	5.08	Time course plot
29	5.78	4.74	A	32.3	3.11	Std.
30	5.84	4.73	A	32.3	3.75	Std.
31	25.92	4.31	A	32.3	1.06	H_2 was impure
32	5.92	4.91	A	32.3	2.21	Std.
33	31.35	4.62	A	32.3	1.19	H_2 was impure
34	5.95	4.88	A	32.3	1.97	Std.
35	15.73	4.68	A	32.3	1.83	H_2 was impure
36	5.92	4.79	A	32.3	1.74	Std.

TABLE VII

RESULTS FOR METALLIC FILM 30 NICKEL

7.33 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min.	Remarks
1	5.81	4.73	A	32.3	14.07	Std.
2	8.25	4.28	A	32.3	15.86	H_2 dependence
3	5.92	4.71	A	32.3	12.30	Std.
4	5.73	4.64	A	32.3	13.60	Std.
5	12.47	3.89	A	32.3	19.70	H_2 dependence
6	5.75	4.37	A	32.3	11.59	Std.
7	17.29	3.52	A	32.3	26.12	H_2 dependence
8	5.87	4.45	A	32.3	9.71	Std.
9	2.66	5.36	A	32.3	5.25	H_2 dependence
10	5.70	4.70	A	32.3	7.62	Std.
11	16.16	3.60	A	32.3	17.71	H_2 dependence
12	5.90	4.50	A	32.3	7.56	Std.
13	9.92	3.94	A	32.3	10.77	H_2 dependence
14	5.44	4.85	A	32.3	6.73	Std.
15	17.43	4.40	A	32.3	15.01	H_2 dependence
16	5.84	4.51	A	32.3	6.42	Std.
17	25.11	3.60	A	32.3	19.76	H_2 dependence
18	5.75	4.54	A	32.3	5.68	Std.
19	2.18	4.88	A	32.3	2.59	H_2 dependence
20	5.47	4.62	A	32.3	3.65	Std.
21	31.70	3.43	A	32.3	17.63	H_2 dependence

TABLE VII - (Cont'd)

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min.	Remarks
22	5.39	4.48	A	32.3	3.97	Std.
23	13.55	4.45	A	32.3	7.21	H_2 dependence
24	5.78	4.42	A	32.3	3.63	Std.
25	8.56	4.42	A	32.3	4.48	H_2 dependence
26	5.53	4.76	A	32.3	3.66	Std.
27	5.50	4.53	A	32.3	3.48	Std.
28	5.78	4.82	A	32.3	2.96	Std.
29	9.78	4.80	A	32.3	3.97	H_2 dependence
30	15.87	4.45	A	32.3	5.59	H_2 dependence
31	5.64	4.51	A	32.3	3.04	Std.
32	24.51	4.14	A	32.3	7.75	H_2 dependence
33	5.56	4.47	A	32.3	2.55	Std.
34	26.50	4.25	A	32.3	7.10	H_2 dependence
35	5.53	4.56	A	32.3	2.13	Std.
36	53.68	3.74	A	32.3	10.25	H_2 dependence
37	5.47	4.65	A	32.3	2.13	Std.
38	51.09	3.77	A	32.3	8.19	H_2 dependence
39	5.30	4.59	A	32.3	1.67	Std.
40	46.69	3.97	A	32.3	6.12	H_2 dependence
41	5.53	4.42	A	32.3	1.57	Std.
42	54.71	3.94	A	32.3	6.39	H_2 dependence
43	5.67	4.73	A	32.3	0.988	Std.

TABLE VIII

RESULTS FOR METALLIC FILM 31 NICKEL

26.7 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
1	5.84	4.39	A	32.3	23.23	Std.
2	5.84	4.53	A	32.3	26.12	Std.
3	0.71	4.51	A	32.3	2.97	H_2 dependence
4	5.75	4.17	A	32.3	17.67	Std.
5	0.82	4.68	A	32.3	2.97	H_2 dependence
6	5.92	4.09	A	32.3	15.82	Std.
7	1.48	4.76	A	32.3	4.23	H_2 dependence
8	5.58	4.54	A	32.3	14.57	Std.
9	5.71	6.77	A	32.3	12.48	C_2H_4 dependence
10	5.75	4.31	A	32.3	13.06	Std.
11	2.81	4.79	A	32.3	7.08	H_2 dependence
12	5.84	4.34	A	32.3	10.67	Std.
13	5.78	6.52	A	32.3	9.73	C_2H_4 dependence
14	5.81	4.59	A	32.3	10.53	Std.
15	5.78	11.57	A	32.3	7.16	C_2H_4 dependence
16	5.87	4.39	A	32.3	8.26	Std.
17	5.87	4.50	A	32.3	7.73	Std.
18	5.72	12.70	A	32.3	4.40	C_2H_4 dependence
19	5.61	4.45	A	32.3	4.44	Std.
20	14.85	4.06	A	32.3	9.33	H_2 dependence
21	5.78	4.54	A	32.3	5.87	Std.

TABLE VIII - (Cont'd)

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
22	5.93	17.43	A	32.3	4.41	C_2H_4 dependence
23	5.73	4.59	A	32.3	4.27	Std.
24	6.10	12.47	A	32.3	3.84	C_2H_4 dependence
25	5.75	4.43	A	32.3	3.65	Std.
26	5.62	2.43	A	32.3	3.55	C_2H_4 dependence
27	5.44	4.59	A	32.3	3.29	Std.
28	5.58	4.60	A	32.3	4.70	Std.
29	19.47	4.14	A	32.3	11.83	H_2 dependence
30	5.70	4.67	A	32.3	4.25	Std.
31	7.03	19.81	A	32.3	4.06	Time course plot
32	5.75	4.77	A	32.3	3.42	Time course plot
33	5.44	0.77	A	32.3	2.69	C_2H_4 dependence
34	5.78	4.76	A	32.3	3.07	Std.
35	5.61	2.30	A	32.3	2.85	C_2H_4 dependence
36	6.18	4.56	A	32.3	2.92	Std.
37	44.45	4.36	A	32.3	10.26	Time course plot
38	5.56	4.70	A	32.3	2.75	Std.
39	2.75	19.36	B	32.3	0.73	
40	5.47	4.71	A	32.3	2.10	Std.
41	8.59	14.46	C	32.3	3.09	Time course plot
42	5.70	4.53	A	32.3	2.08	Std.
43	22.39	1.68	C	32.3	4.23	
44	5.44	4.59	A	32.3	2.01	Std.

TABLE VIII - (Cont'd)

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
45	2.38	16.02	A	32.3	1.09	
46	5.33	4.65	A	32.3	1.83	Std.

TABLE IX

RESULTS FOR METALLIC FILM 32 NICKEL

29.2 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
1	5.62	4.28	A	32.3	28.10	Std.
2	5.30	16.27	B	32.3	6.30	C_2H_4 dependence
3	5.90	4.62	A	32.3	25.48	Std.
4	4.08	15.59	C	32.3	12.52	
5	5.98	4.28	A	32.3	18.96	Std.
6	4.26	14.60	C	32.3	17.37	
7	5.70	4.42	A	32.3	15.42	Std.
8	9.41	10.77	B	32.3	7.84	Time course plot
9	5.64	4.25	A	32.3	11.98	Std.
10	10.37	8.48	C	32.3	21.94	Time course plot
11	5.64	4.45	A	32.3	12.20	Std.
12	8.59	10.32	A	32.3	16.72	
13	5.61	4.45	A	32.3	11.37	Std.
14	5.84	4.42	A	40.0	14.53	Activation Energy
15	5.41	4.45	A	32.3	11.77	Std.
16	5.70	4.73	A	50.0	19.76	Activation Energy
17	6.09	4.40	A	32.3	10.09	Std.
18	6.38	4.62	A	60.0	29.71	Activation Energy
19	5.53	4.42	A	32.3	8.40	Std.
20	5.90	4.62	A	70.0	24.76	Activation Energy
21	5.73	4.39	A	32.3	7.32	Std.
22	5.44	4.76	A	32.3	6.58	Std.

TABLE IX - (Cont'd)

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
23	5.98	4.96	A	80.0	37.76	Activation Energy
24	5.58	4.57	A	32.3	6.85	Std.
25	5.36	20.38	B	32.3	2.18	C_2H_4 dependence
26	5.27	4.68	A	32.3	4.79	Std.
27	4.65	6.01	B	32.3	2.37	C_2H_4 dependence
28	5.73	4.47	A	32.3	4.29	Std.
29	5.70	42.59	B	32.3	1.33	C_2H_4 dependence
30	5.78	4.72	A	32.3	3.60	Std.
31	3.91	2.61	B	32.3	1.68	
32	6.07	4.50	A	32.3	3.46	Std.
33	14.29	6.32	B	32.3	4.05	H_2 dependence
34	5.56	4.62	A	32.3	2.96	Std.
35	25.80	6.09	B	32.3	5.17	H_2 dependence
36	5.50	4.65	A	32.3	2.46	Std.
37	4.71	30.53	B	32.3	0.604	C_2H_4 dependence
38	5.58	4.85	A	32.3	1.15	Std.
39	2.16	5.61	B	32.3	0.496	H_2 dependence
40	5.70	4.53	A	32.3	1.08	Std.
41	2.13	5.75	B	32.3	0.434	H_2 dependence
42	5.50	4.82	A	32.3	0.971	Std.

TABLE X

RESULTS FOR METALLIC FILM 33 NICKEL

25.7 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
1	5.56	4.13	A	32.3	23.02	Std.
2	3.91	4.85	A	32.3	18.52	
3	1.88	6.60	B	32.3	2.57	H_2 dependence
4	6.01	4.31	A	32.3	17.17	Std.
5	12.56	6.23	B	32.3	13.38	H_2 dependence
6	5.75	4.37	A	32.3	12.02	Std.
7	9.72	6.47	B	32.3	7.84	H_2 dependence
8	5.56	4.28	A	32.3	10.33	Std.
9	26.44	6.94	B	32.3	14.13	H_2 dependence
10	5.73	4.42	A	32.3	7.96	Std.
11	1.42	5.92	B	32.3	1.19	H_2 dependence
12	5.84	4.36	A	32.3	6.55	Std.
13	1.87	6.24	B	32.3	1.23	H_2 dependence
14	5.75	4.51	A	32.3	5.00	Std.
15	5.50	20.32	B	32.3	1.86	C_2H_4 dependence
16	5.61	4.51	A	32.3	3.64	Std.
17	5.67	4.62	A	32.3	4.12	Std.
18	5.81	10.49	B	32.3	1.96	C_2H_4 dependence
19	5.70	4.62	A	32.3	3.09	Std.
20	4.73	2.87	B	32.3	1.69	C_2H_4 dependence
21	5.67	4.45	A	32.3	3.06	Std.

TABLE X - (Cont'd)

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
22	5.59	27.32	B	32.3	0.984	C_2H_4 dependence
23	5.41	4.65	A	32.3	1.85	Std.
24	5.56	7.31	B	32.3	1.10	C_2H_4 dependence
25	5.64	4.56	A	32.3	1.39	Std.
26	6.26	4.88	A	80.0	9.69	Std.
27	6.77	43.53	B	80.0	4.19	C_2H_4 dependence
28	6.26	4.82	A	80.0	7.00	Std.
29	5.41	1.99	B	80.0	5.13	C_2H_4 dependence
30	6.01	4.87	A	80.0	7.52	Std.
31	4.37	10.20	B	80.0	4.09	C_2H_4 dependence
32	6.18	4.68	A	80.0	6.57	Std.

TABLE XI

RESULTS FOR METALLIC FILM 34 NICKEL

2.60 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
1	5.58	4.60	A	32.3	2.21	Std.

RESULTS FOR METALLIC FILM 35 NICKEL

9.43 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
1	5.56	4.45	A	32.3	2.52	Std.
2	4.96	41.82	B	32.3	0.259	C_2H_4 dependence
3	5.39	4.90	A	32.3	0.501	Std.
4	5.44	1.39	B	32.3	0.259	C_2H_4 dependence
5	5.66	4.77	A	32.3	0.259	Std.
6	6.07	4.84	A	80.0	1.786	Std.
7	3.19	44.11	B	80.0	0.255	
8	5.80	5.17	A	80.0	0.640	Std.

TABLE XII

RESULTS FOR METALLIC FILM 36 NICKEL

15.2 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
1	5.67	4.25	A	32.3	5.70	Std.
2	7.54	48.89	B	32.3	1.14	C_2H_4 dependence
3	5.50	4.70	A	32.3	2.43	Std.
4	4.99	2.55	B	32.3	1.04	C_2H_4 dependence
5	5.67	4.73	A	32.3	1.45	Std.
6	5.36	10.94	B	32.3	0.577	C_2H_4 dependence
7	5.61	4.65	A	32.3	0.877	Std.
8	5.19	5.44	B	32.3	0.474	C_2H_4 dependence Activation Energy
9	5.47	4.76	A	32.3	0.671	Std.
10	4.99	5.78	B	40.0	0.599	Activation Energy
11	5.17	4.89	A	32.3	0.411	Std.
12	5.70	4.79	B	50.0	0.720	Activation Energy
13	5.45	4.81	A	32.3	0.385	Std.
14	5.64	5.22	B	60.0	0.877	Activation Energy
15	5.54	4.83	A	32.3	0.318	Std.
16	6.04	5.07	B	70.0	1.02	Activation Energy
17	5.45	4.84	A	32.3	0.250	Std.
18	5.30	5.47	B	80.0	1.22	Activation Energy
19	5.02	4.76	A	32.3	0.174	Std.
20	6.26	4.88	A	80.0	1.49	Std.
21	6.18	5.02	A	80.0	1.42	Std.

TABLE XII - (Cont'd)

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. ºC	Initial Rate cm.Hg/min	Remarks
22	5.81	42.61	B	80.0	0.550	C_2H_4 dependence
23	5.39	4.96	A	80.0	1.16	Std.
24	5.56	2.29	B	80.0	1.06	C_2H_4 dependence
25	6.04	4.93	A	80.0	0.930	Std.
26	5.08	11.42	B	80.0	0.550	C_2H_4 dependence
27	6.01	5.07	A	80.0	0.586	Std.
28	5.53	1.56	B	80.0	0.456	C_2H_4 dependence
29	5.69	5.17	A	80.0	0.532	Std.
30	6.80	31.55	B	80.0	0.331	C_2H_4 dependence
31	5.90	5.21	A	80.0	0.300	Std.
32	5.24	2.67	B	80.0	0.277	C_2H_4 dependence

TABLE XIII

RESULTS FOR METALLIC FILM 37 PALLADIUM

85.0 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
1	4.50	4.54	A	32.3		Extensive H_2 Solution
2	7.16	4.89	A	32.3	very slow	
3	2.61	5.78	B	32.3		
4	12.3	5.4	C	32.3		

METALLIC FILM 38 PALLADIUM

139.7 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
1	8.2	4.72	A	32.3		Extensive H_2 Solution
2	5.2	14.1	B	32.3		
3	24.4	5.7	C	32.3		

TABLE XIV

RESULTS FOR METALLIC FILM 39 IRON

14.5 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
1	6.26	3.94	A	32.3	20.69	Std.
2	5.75	4.37	A	32.3	13.73	Std.
3	7.48	10.66	A	32.3	16.46	Time course plot
4	8.82	10.37	B	32.3	3.49	Time course plot
5	10.71	8.62	C	32.3	10.56	Time course plot
6	5.81	4.39	A	32.3	8.27	Std.
7	3.26	36.14	B	32.3	0.877	C_2H_4 dependence
8	5.70	4.45	A	32.3	3.41	Std.
9	5.56	4.39	A	32.3	4.85	Std.
10	4.43	9.86	B	32.3	1.06	C_2H_4 dependence
11	5.78	4.62	A	32.3	1.56	Std.
12	5.13	2.52	B	32.3	0.832	C_2H_4 dependence
13	5.84	4.56	A	32.3	1.05	Std.
14	5.22	4.73	B	32.3	0.599	C_2H_4 dependence
15	5.41	4.68	A	32.3	0.635	Std.
16	14.34	5.25	B	32.3	0.886	H_2 dependence
17	5.50	4.65	A	32.3	0.519	Std.
18	18.23	5.92	B	32.3	0.908	Time course plot
19	5.23	4.78	A	32.3	0.452	Std.
20	5.95	4.85	A	80.0	4.67	Std.
21	5.24	16.36	B	80.0	2.57	C_2H_4 dependence

TABLE XIV - (Cont'd)

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
22	6.04	4.70	A	80.0	4.19	Std.
23	8.24	47.22	B	80.0	2.29	C_2H_4 dependence
24	6.04	4.70	A	80.0	2.55	Std.
25	5.27	2.27	B	80.0	1.66	C_2H_4 dependence
26	5.61	4.93	A	80.0	3.43	Std.
27	15.76	5.64	B	80.0	3.29	H_2 dependence
28	6.15	4.79	A	80.0	2.40	Std.
29	5.81	4.93	A	80.0	1.53	Std.
30	1.76	5.61	B	80.0	0.510	H_2 dependence
31	5.95	4.91	A	80.0	1.52	Std.

TABLE XV

RESULTS FOR METALLIC FILM 40 IRON

7.46 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
1	5.47	4.42	A	32.3	6.99	Std.
2	5.64	48.63	B	32.3	0.604	C_2H_4 dependence
3	5.53	4.45	A	32.3	0.742	Std.
4	13.58	5.16	B	32.3	0.537	H_2 dependence
5	5.35	4.77	A	32.3	0.268	Std.
6	5.95	4.57	B	32.3	0.966	C_2H_4 dependence
7	5.32	4.77	A	32.3	0.224	Std.
8	6.29	4.65	A	80.0	1.81	Std.
9	6.77	5.73	B	80.0	0.890	C_2H_4 dependence
10	6.01	4.87	A	80.0	0.890	Std.
11	21.17	6.38	B	80.0	1.81	H_2 dependence
12	5.87	5.21	A	80.0	0.756	Std.

TABLE XVI

RESULTS FOR METALLIC FILM 41 IRON

27.3 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
1	5.64	4.45	A	32.3	22.50	Std.
2	5.89	39.39	B	32.3	2.29	Time course plot
3	5.78	4.40	A	32.3	9.94	Std.
4	9.21	6.13	B	32.3	3.42	H_2 dependence
5	5.75	4.34	A	32.3	5.93	Std.
6	11.68	12.39	B	32.3	3.16	Time course plot
7	5.58	4.57	A	32.3	3.65	Std.
8	17.53	10.95	B	32.3	2.69	Time course plot
9	5.75	4.88	A	32.3	2.10	Std.
10	5.22	4.87	B	40.0	1.48	Activation Energy
11	5.24	4.51	A	32.3	1.62	Std.
12	5.16	5.78	B	50.0	1.72	Activation Energy
13	5.53	4.50	A	32.3	1.06	Std.
14	5.30	5.47	B	60.0	2.58	Activation Energy
15	5.53	4.67	A	32.3	1.50	Std.
16	5.08	5.75	B	70.0	3.19	Activation Energy
17	5.78	4.65	A	32.3	0.890	Std.
18	5.13	5.36	B	80.0	3.51	Activation Energy
19	5.50	4.68	A	32.3	1.06	Std.
20	5.64	4.71	A	32.3	1.62	Std.
21	1.11	5.41	B	32.3	0.250	H_2 dependence

TABLE XVI - (Cont'd)

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Remarks
22	5.47	4.45	A	32.3	0.702	Std.
23	4.79	5.50	B	32.3	0.470	C_2H_4 dependence
24	5.58	4.65	A	32.3	0.461	Std.
25	6.52	4.82	A	80.0	3.28	

TABLE XVII

RESULTS FOR METALLIC FILM 42 IRON

49.6 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Introduction of Reactants	Temp. °C	Initial Rate cm.Hg/min	Ratio C_2H_4 / Ethane	Remarks
1	11.96	6.10	A	32.3	31.32	0.026	Products
2	7.26	9.78	A	32.3	24.03	0.026	analyzed
3	10.83	13.63	B	32.3	7.05	0.158	by
4	13.41	9.83	B	32.3	7.45	0.013	chromatograph

TABLE XVIII

RESULTS FOR METALLIC FILM 43 NICKEL

16.6 mg.

Run Number	Initial H_2 Pressure	Initial C_2H_4 Pressure	Method of Reactant Introduction	Temp. °C	Initial Rate cm.Hg/min	Ratio C_2H_4 Ethane	Remarks
1	12.47	7.46	A	32.3	14.27	0.019	Products
2	8.00	10.03	A	32.3	8.11	0.117	analyzed
3	9.72	6.78	B	32.3	3.05	0.010	by
4	6.54	12.59	B	32.3	1.76	0.073	chromatograph

been given for each run. All pressures given in cm.Hg.

FILM ACTIVITY

Beeck found a good correlation between the film weight and the film activity. However, in the present work the nickel films seemed to divide into two groups as seen in Figure 4. One group of low activity films, numbers 25 to 28, 35 and 36, gave very good correlation between the initial reaction rate of the first run carried out on the film and the film weight. The second group contained very active films, numbers 29 to 34, which gave only fair correlation between the initial reaction rate and the film weight . The low activity films had not more than 17 runs carried out on them; whereas on the high activity films the numbers of runs varied from a minimum of 31 to a maximum of 43 runs.

Only four iron films were used in this research and the correlation between film weight and initial reaction rate of the first run carried out on the film was not better than 20% .

On a per mole basis, the active nickel films had the same activity as the iron films at 32.3°C. However the active nickel films were five times more active than the group of low activity nickel films.

HYDROGEN CHEMISORPTION

The attempt to correlate the quantity of hydrogen chemisorbed with the film activity proved to be unsatisfactory. The Autovac Pirani gauge head attached to the premix vessel was used to

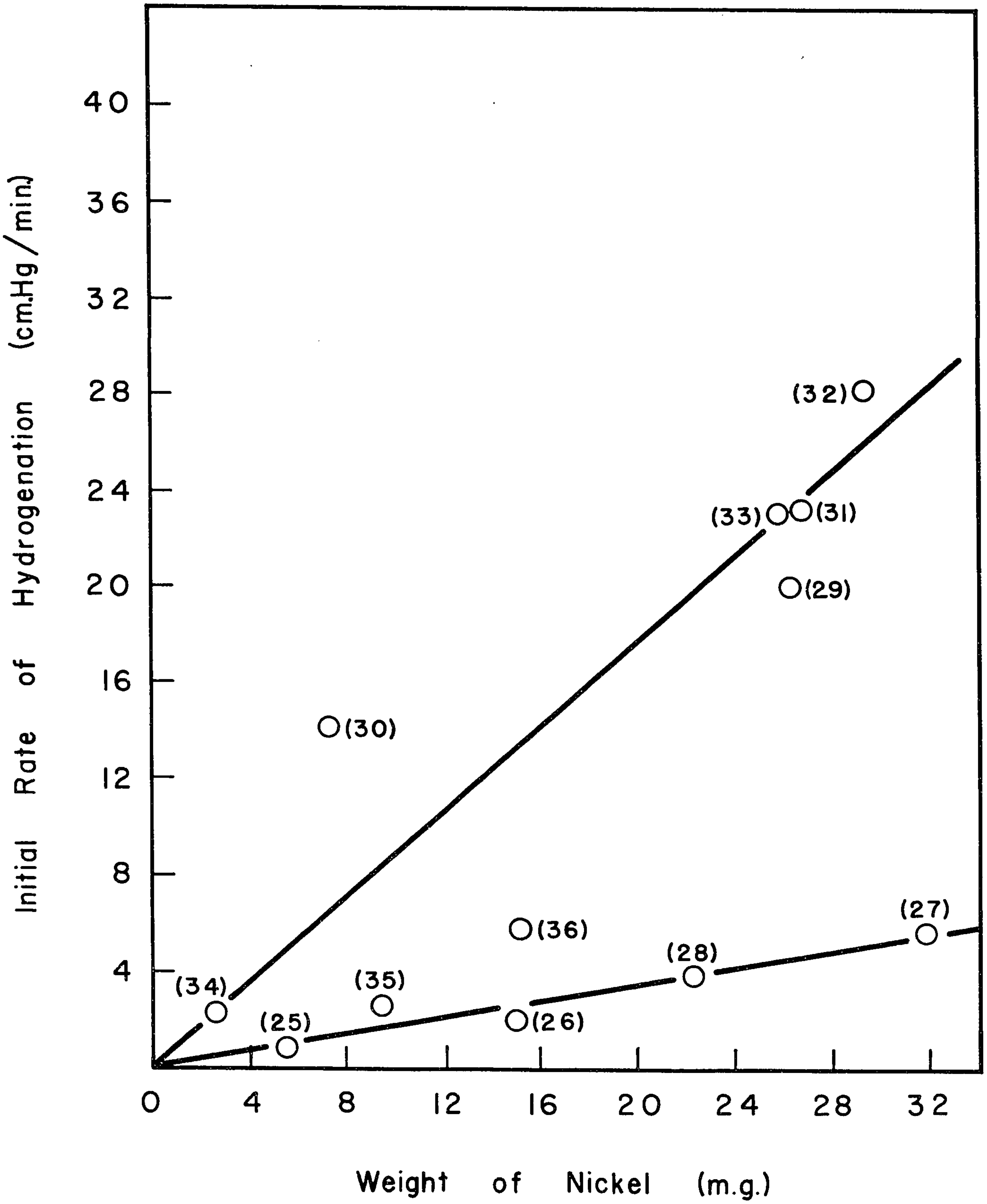


Figure 4. Plot of the initial rate of a standard hydrogenation against the weight of the nickel film.

measure the decrease in the hydrogen pressure in the reaction vessel and the premix chamber. The measurements were made with an initial hydrogen pressure of 1 mm.Hg. There proved to be a rough one to one correlation between the quantity of hydrogen chemisorbed at 0°C and the initial rate of reaction of the standard type hydrogenation. However at low reaction rates (below 4 cm.Hg. per minute) there was no agreement between the reaction rate and the quantity of hydrogen chemisorbed. Thus because there was no correlation with hydrogen chemisorption at low reaction rates and very rough correlation at high reaction rates, the measurement of the quantity of hydrogen chemisorbed as an indication of the film activity was discarded in favour of the use of a standard hydrogenation reaction even though the latter involved a greater expenditure of time.

By taking great care in the purification of the hydrogen and the ethylene and by rigorous evacuation of the reaction vessel and premix chamber, the film activity could be maintained at a reasonable level over numerous runs if the film was treated between the runs with hydrogen for fifteen minutes. Figure 5 gives the initial rate of the standard-hydrogenation reaction against the number of the standard done on only one nickel film, number 30. After fourteen runs the activity of the nickel film was reduced to one half of the initial value. The activity of the film was reduced to a tenth of the initial activity after 41 runs. All the intervening runs were carried out at total initial pressures of ethylene and hydrogen from 6 cm. Hg. to 45 cm. Hg.

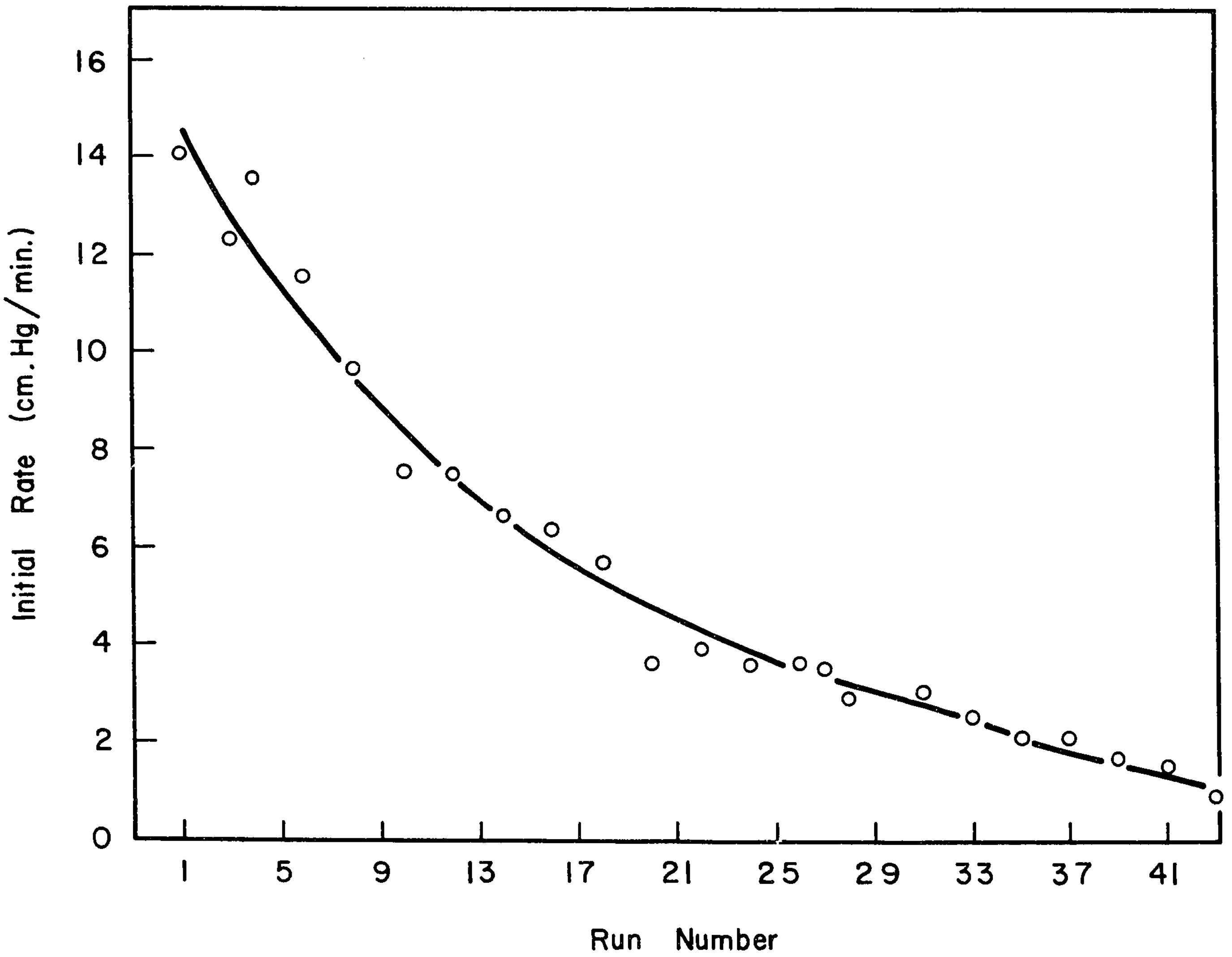


Figure 5 Plot of the initial rate in cm. Hg per min. against the number of the standard run carried out on nickel film number 30.

NICKEL FILM REACTIONS

ACTIVATION ENERGY

The results for the activation energy determination for the temperature range from 32.3°C to 80°C are given in Figure 6. For this activation energy determination the hydrogen and ethylene were introduced into the reaction vessel together from the premix vessel. The average initial ethylene pressure was 4.8 cm.Hg and for hydrogen the average was 5.8 cm.Hg. The slope of the graph is 1.70×10^3 which gives an activation energy of 7.8 kcal. per mole.

A second activation energy was determined in the temperature range from 32.3°C to 80°C but in this case the ethylene was introduced into the reaction vessel first. The average initial hydrogen pressure was 5.5 cm.Hg and for ethylene the initial pressure was 5.3 cm.Hg. These results are given in Figure 7 and the slope of the line is 2.176×10^3 which corresponds to an activation energy of 9.96 kcal. per mole.

HYDROGEN AND ETHYLENE PRESSURE DEPENDENCIES

For the ethylene hydrogenations on nickel films in which both the ethylene and hydrogen were introduced simultaneously to the film, the initial reaction rate dependence on hydrogen pressure at 32.3°C with a constant initial pressure of 4.7 cm.Hg of ethylene, is given in Figure 8. This is a double logarithmic plot and the slope at any point gives the order with respect to concentration of hydrogen. The hydrogen pressure range was 0.7 to 54.7 cm.Hg. At low pressures of hydrogen the

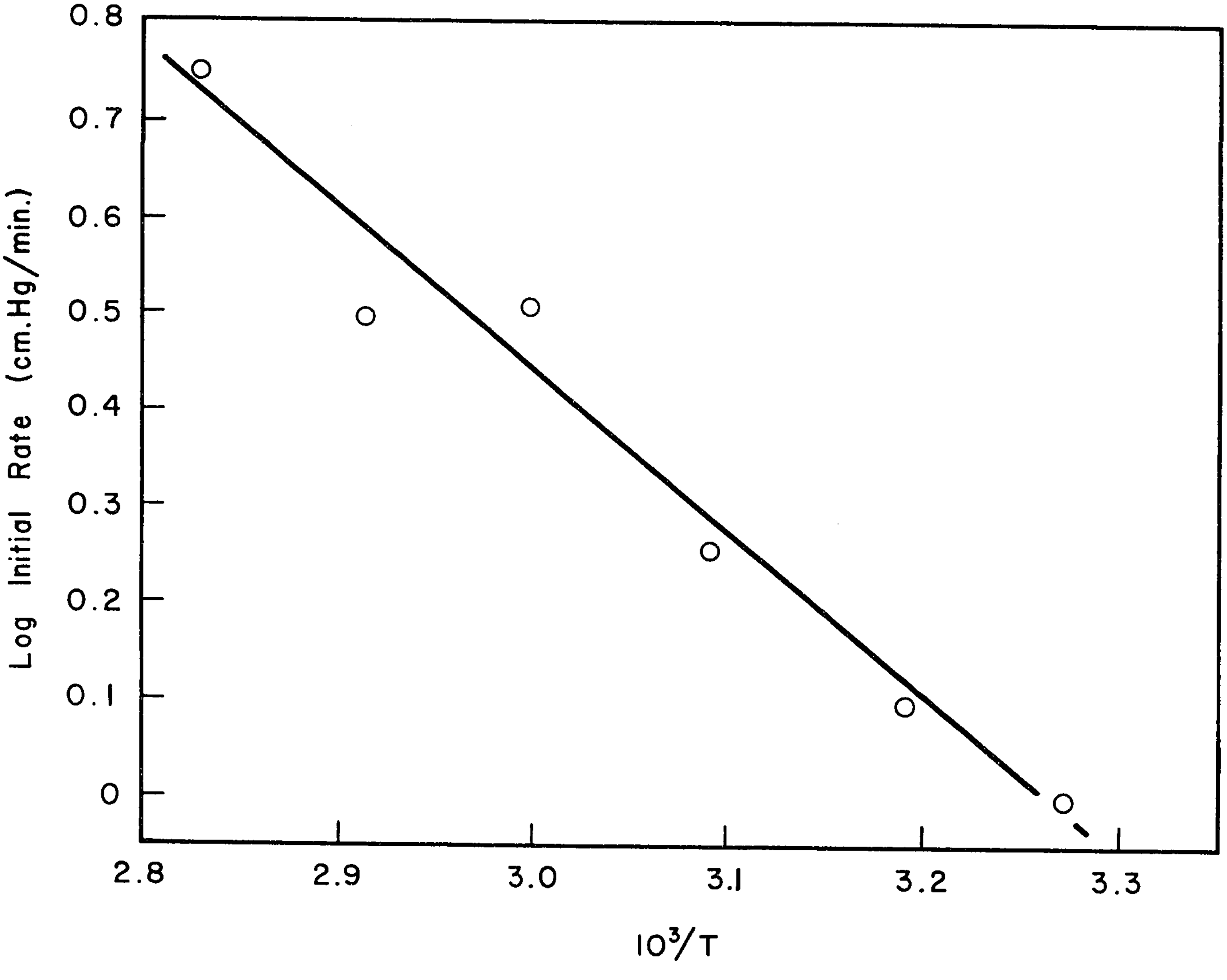


Figure 6 Plot of the logarithm of the initial rate on nickel film in cm. Hg per min. against 1/T. Hydrogen and ethylene introduced to the film simultaneously.

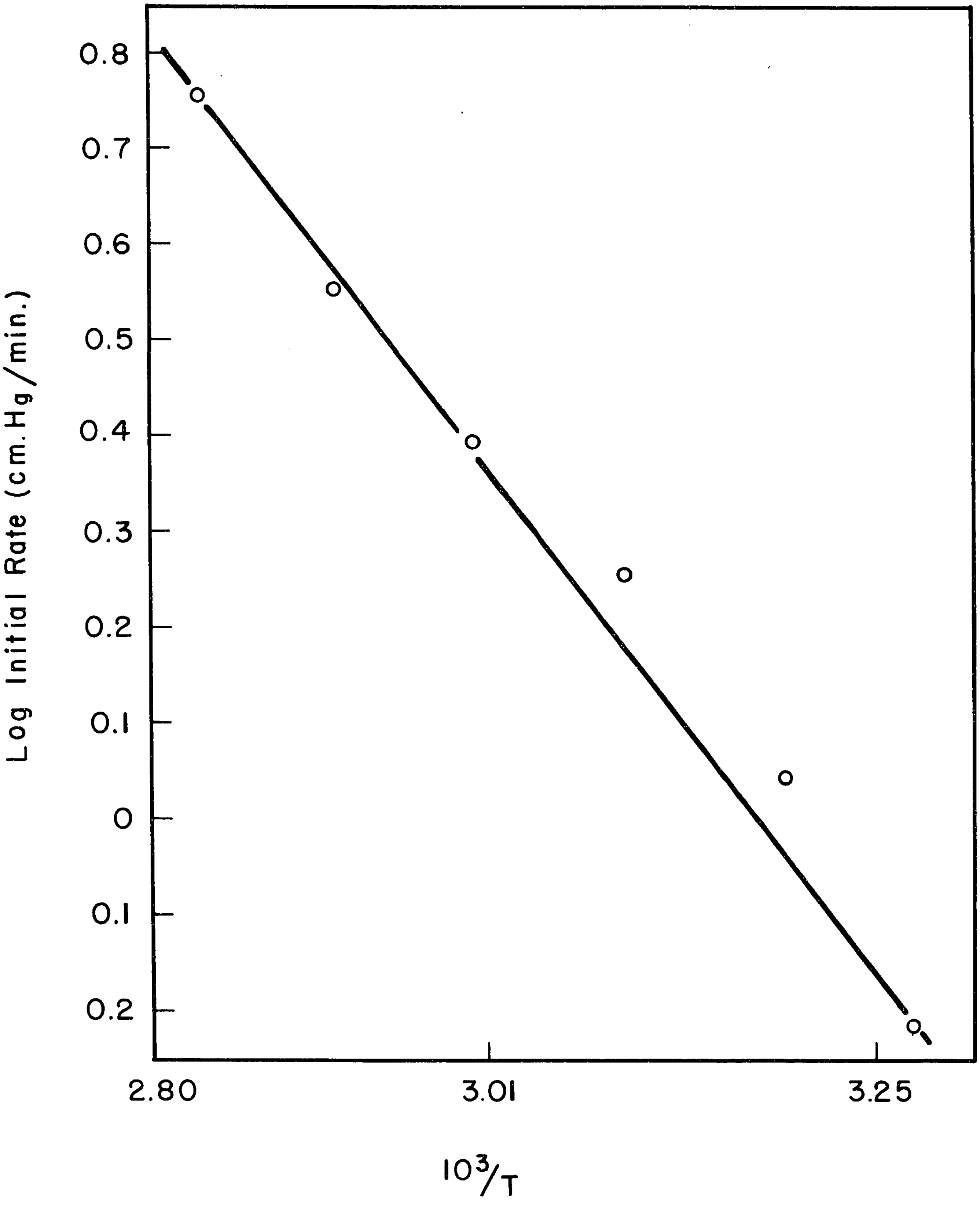


Figure 7 Plot of the logarithm of the initial rate on nickel film in cm. Hg per min. against 1/T. Ethylene introduced to the film prior to the hydrogen.

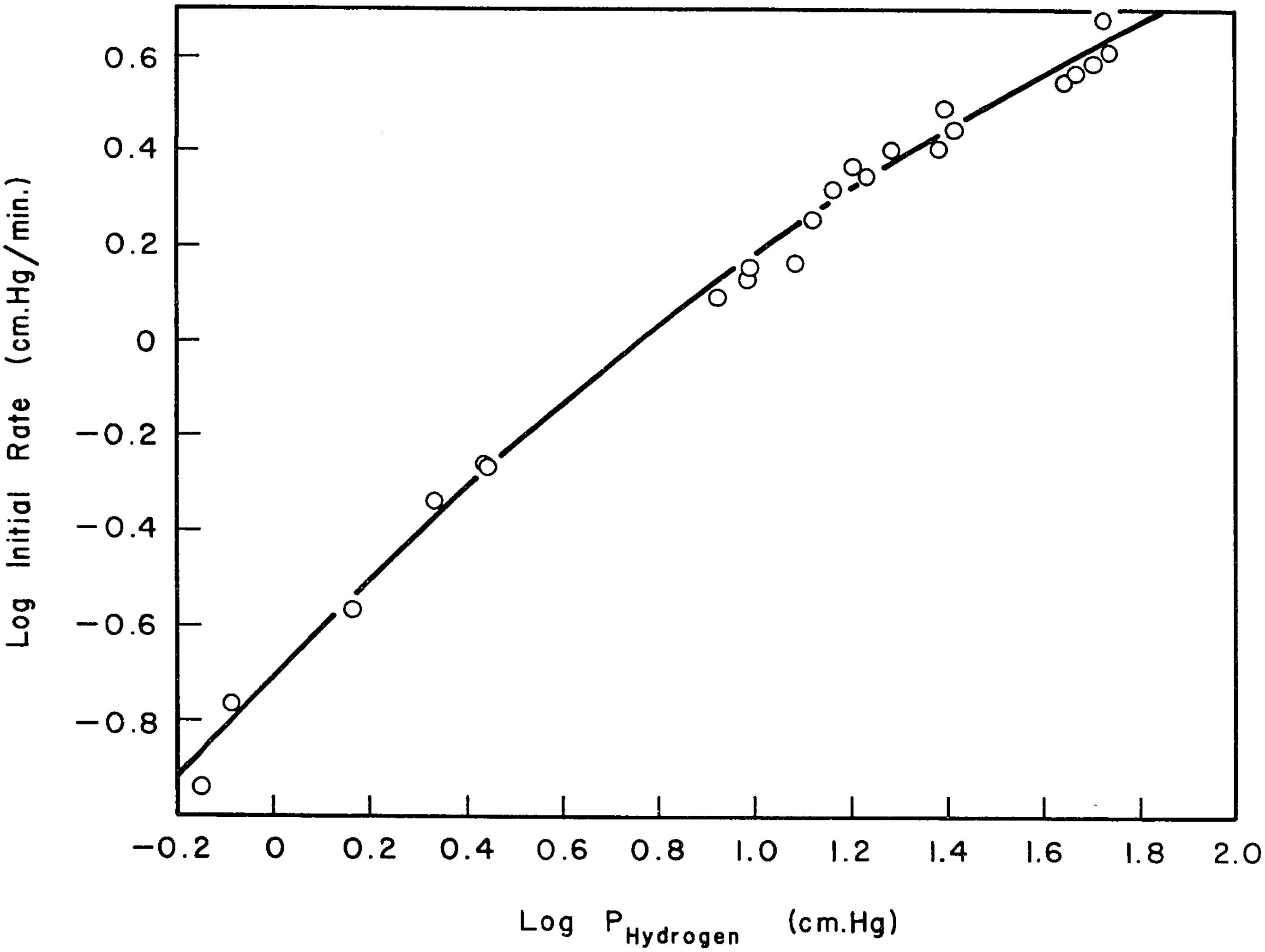


Figure 8 Plot of the logarithm of the initial rate at 32.3°C on nickel film in cm. Hg per min. against the logarithm of the initial hydrogen pressure. Ethylene and hydrogen introduced simultaneously to film. Average initial ethylene pressure 4.5 cm. Hg.

reaction rate was first order in hydrogen, but the order decreased to 0.85 at a hydrogen pressure of 6.3 cm.Hg. At the highest hydrogen pressure studied, 54.7 cm.Hg, the hydrogen order had fallen off to 0.67.

The dependence of the initial rate of ethylene hydrogenation on ethylene pressure is shown in Figure 9. This is for the case in which ethylene and hydrogen were introduced into the reaction vessel together. The ethylene pressure range was from 2.3 to 17.4 cm.Hg, while the initial hydrogen pressure was a constant 5.7 cm.Hg. The points scatter to some extent but at high pressures of ethylene the order with respect to ethylene pressure was -0.6 . At low ethylene pressures there would seem to be a slight trend to leveling off to zero order or at least a more positive order.

Figure 10 shows the course of three ethylene hydrogenations on a nickel film in which the method of introduction of ethylene and hydrogen was different for each run. In run number 32.12 the ethylene and hydrogen were introduced simultaneously to the reaction vessel; the initial hydrogen pressure was 10.3 cm.Hg and the initial ethylene pressure was 8.6 cm.Hg. The hydrogen was introduced to the reaction vessel first for run number 32.10, and the initial pressures of hydrogen and ethylene were 10.4 cm.Hg and 8.5 cm.Hg respectively. For run number 32.8, ethylene was introduced to the reaction vessel first with an initial pressure of 9.4 cm.Hg. The initial pressure of hydrogen was 10.8 cm.Hg. The initial rate for the most rapid reaction was 21.9 cm.Hg per minute, which was for run number 32.10 with hydrogen introduced to the film first. The next most rapid reaction was run number 32.12 with an initial rate of 16.7 cm.Hg per minute. The

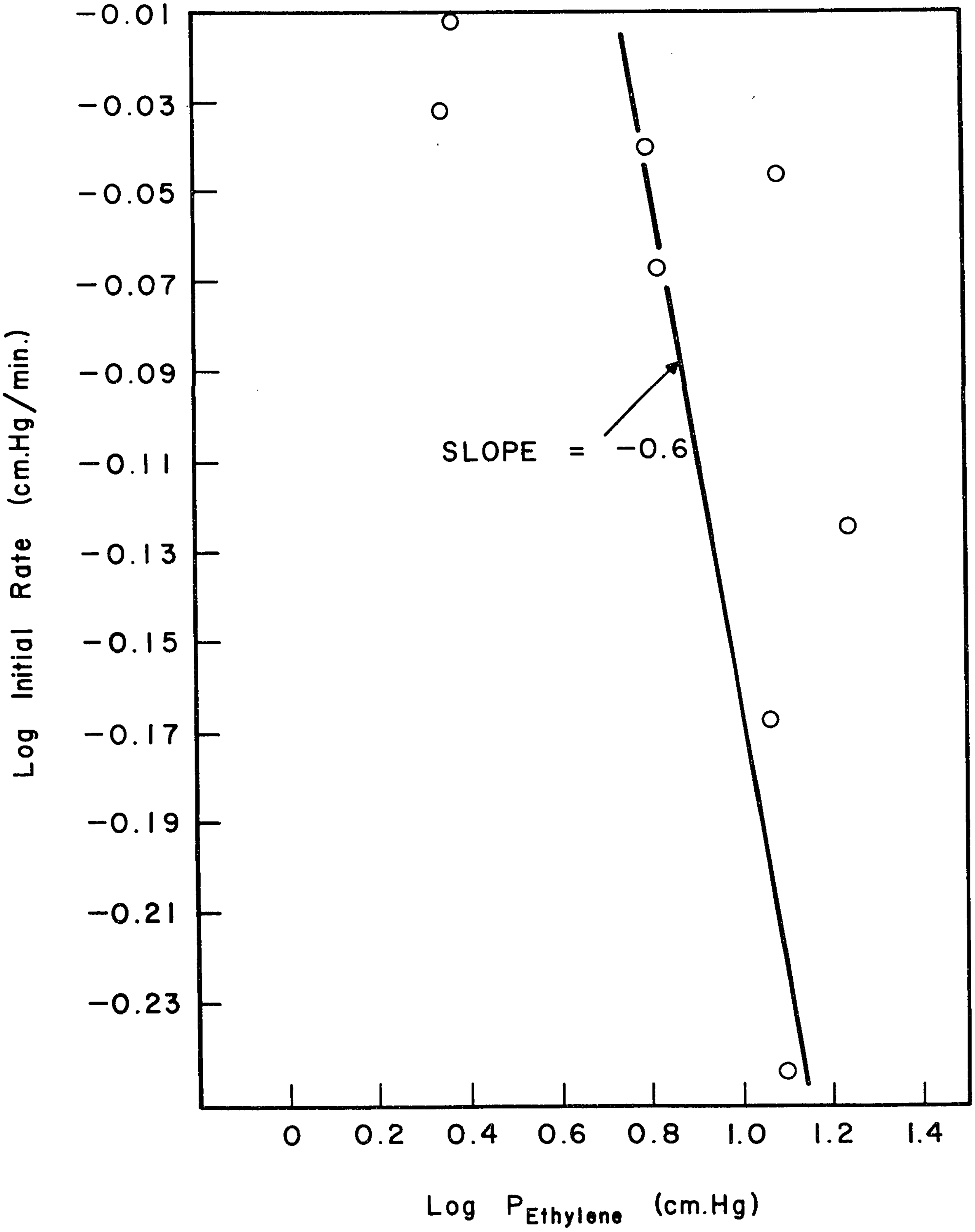


Figure 9 Plot of the logarithm of the initial rate at 32.3°C on nickel film in cm. Hg per min. against the logarithm of the initial ethylene pressure. Ethylene and hydrogen introduced to film simultaneously. Average initial hydrogen pressure 6.0 cm. Hg.

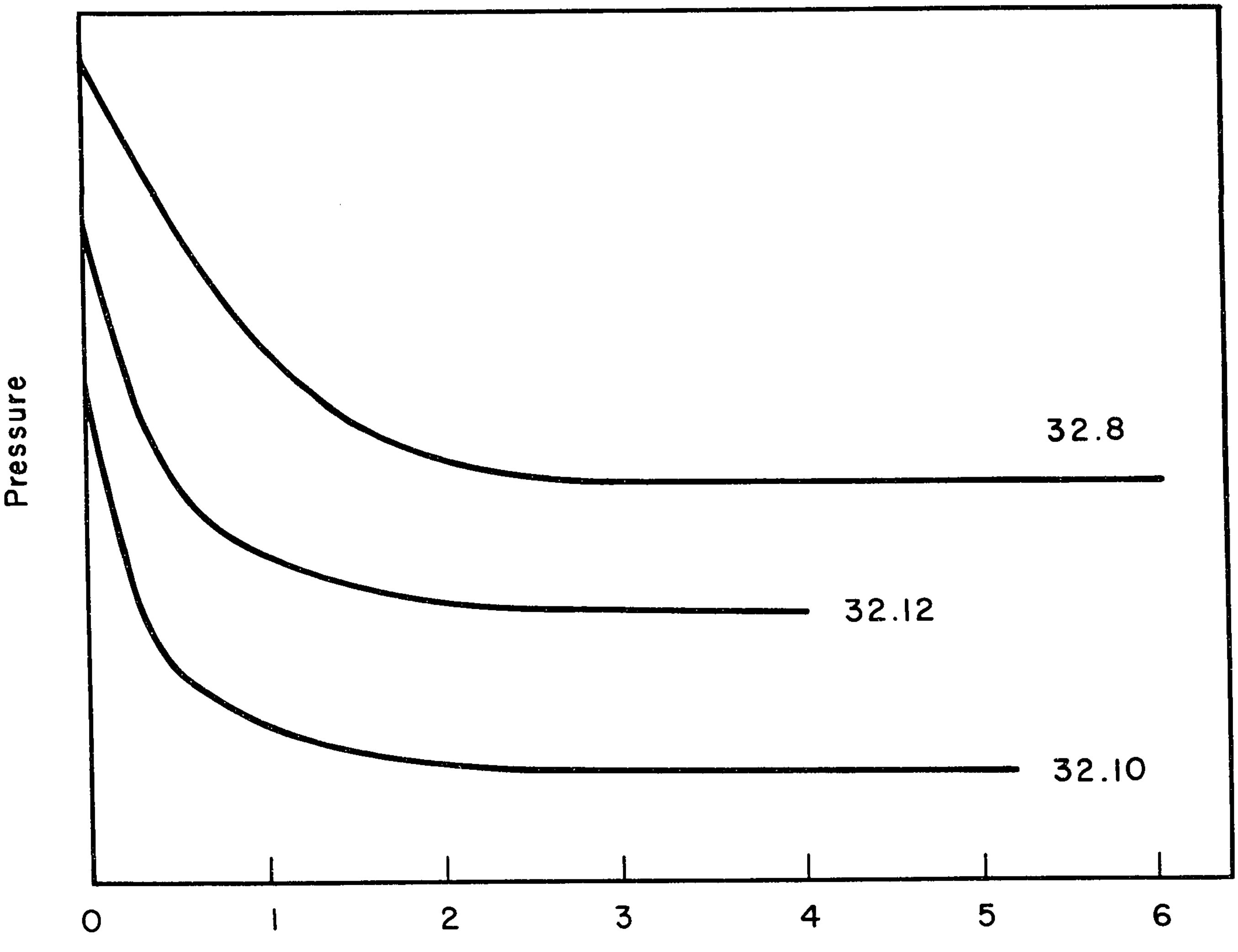


Figure 10 Plot of the decrease in pressure in arbitrary photopen scale units during reaction against the time in minutes. All runs start at the same pressure but they have been displaced down the ordinate for clarity.

slowest reaction was run number 32.8 with an initial rate of 7.8 cm.Hg per minute. Thus the slowest hydrogenation was realized when ethylene was introduced to the reaction vessel first.

Since it was thought that the ethylene hydrogenation reactions in which the ethylene was introduced into the reaction vessel first gave a better indication of the kinetics of the hydrogenation, this technique was used to determine the ethylene pressure dependence of the reaction at 32.3°C and 80°C . These results are shown in Figures 11 and 12. For the 32.3°C study the ethylene pressure was varied from 1.4 cm.Hg to 48.9 cm.Hg with a constant 5.5 cm.Hg initial pressure of hydrogen. As seen from the graph, at high pressures of ethylene the ethylene order was -0.4. At 80°C in the ethylene pressure range from 1.5 cm.Hg to 43.5 cm.Hg (Figure 12), the initial reaction rate depends on the ethylene pressure to the -0.24 power. The hydrogen pressure dependence at 32.3°C for the ethylene hydrogenation reaction in which ethylene was introduced to the film prior to the hydrogen was studied in the pressure range from 1.4 cm.Hg to 26.4 cm.Hg and the results are shown in Figure 13. The slope of the line is 0.7.

TIME COURSE STUDIES

In order to find out still more about the kinetics of the ethylene hydrogenation reaction the time courses of numerous reactions were studied. For these time course reactions a plot was made of the logarithm of the reaction rate at time t against the logarithm of the difference in pressure at time t and the final pressure.

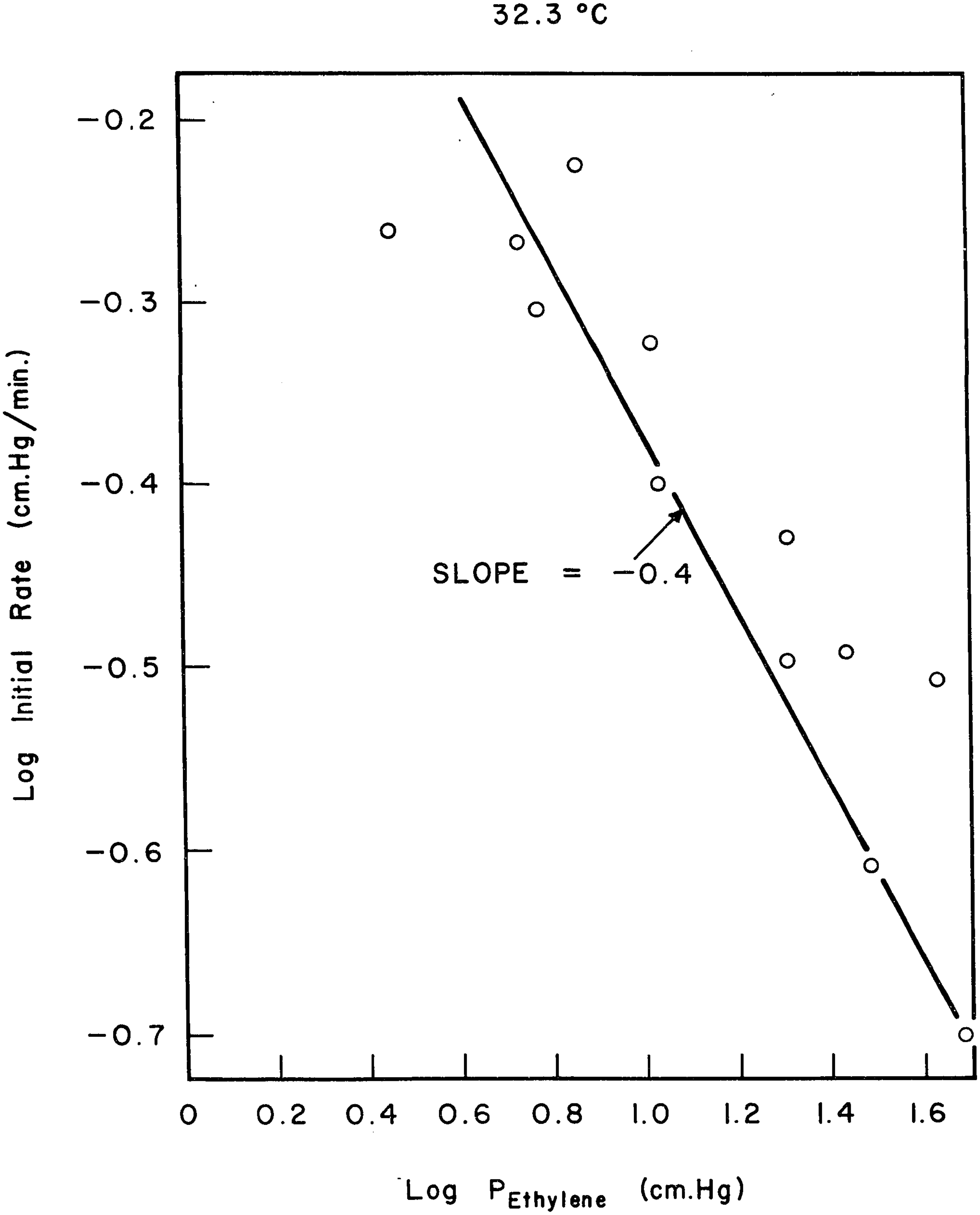


Figure 11 Plot of the logarithm of the initial rate on nickel film in cm. Hg per min. at 32.3°C against the logarithm of initial ethylene pressure. Ethylene introduced to the film prior to the hydrogen. Average initial hydrogen pressure 5.5 cm. Hg.

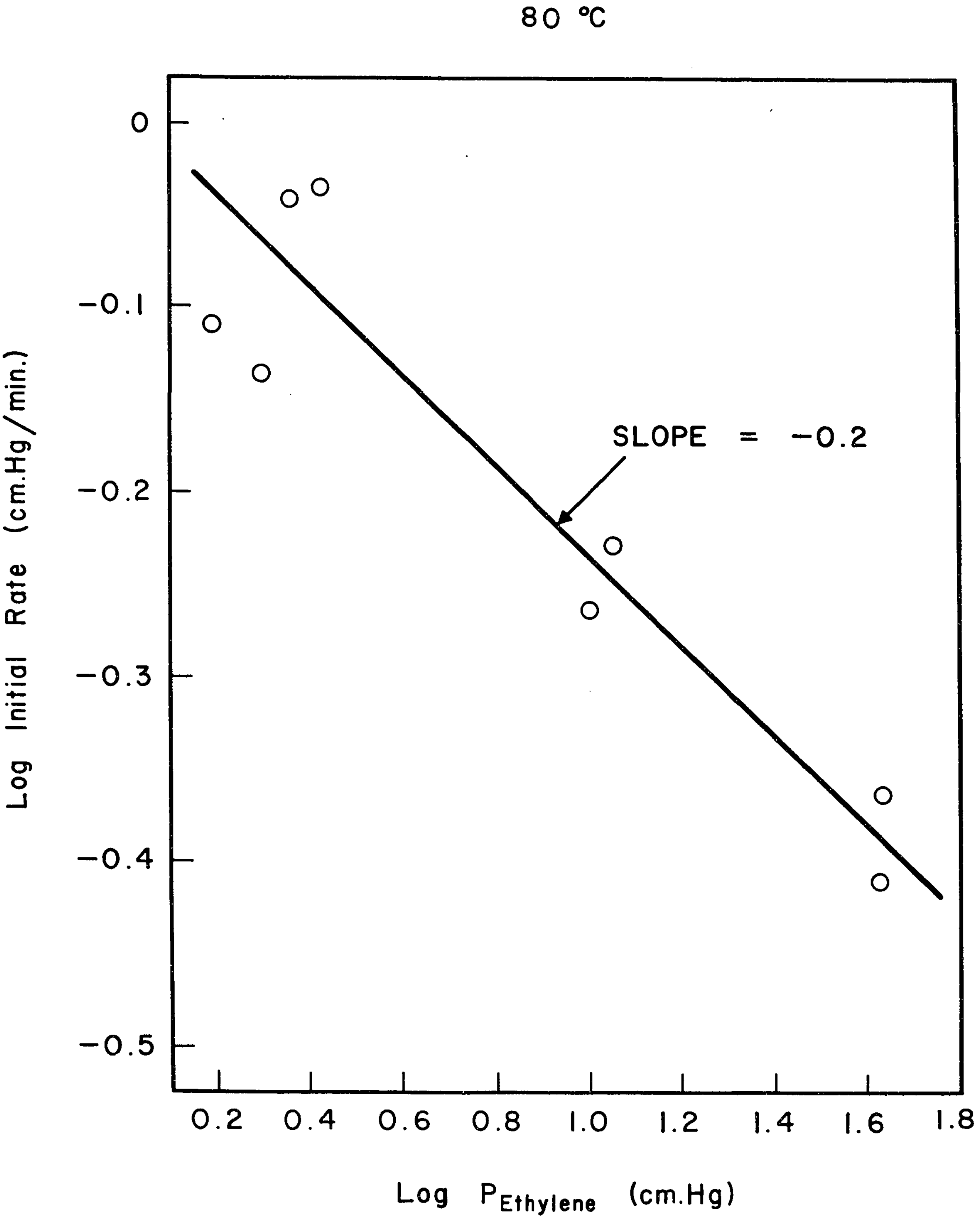


Figure 12 Plot of the logarithm of the initial rate on nickel film in cm. Hg per min. against the logarithm of initial ethylene pressure. Ethylene introduced to the film prior to the hydrogen. Average initial hydrogen pressure 5.5 cm. Hg.

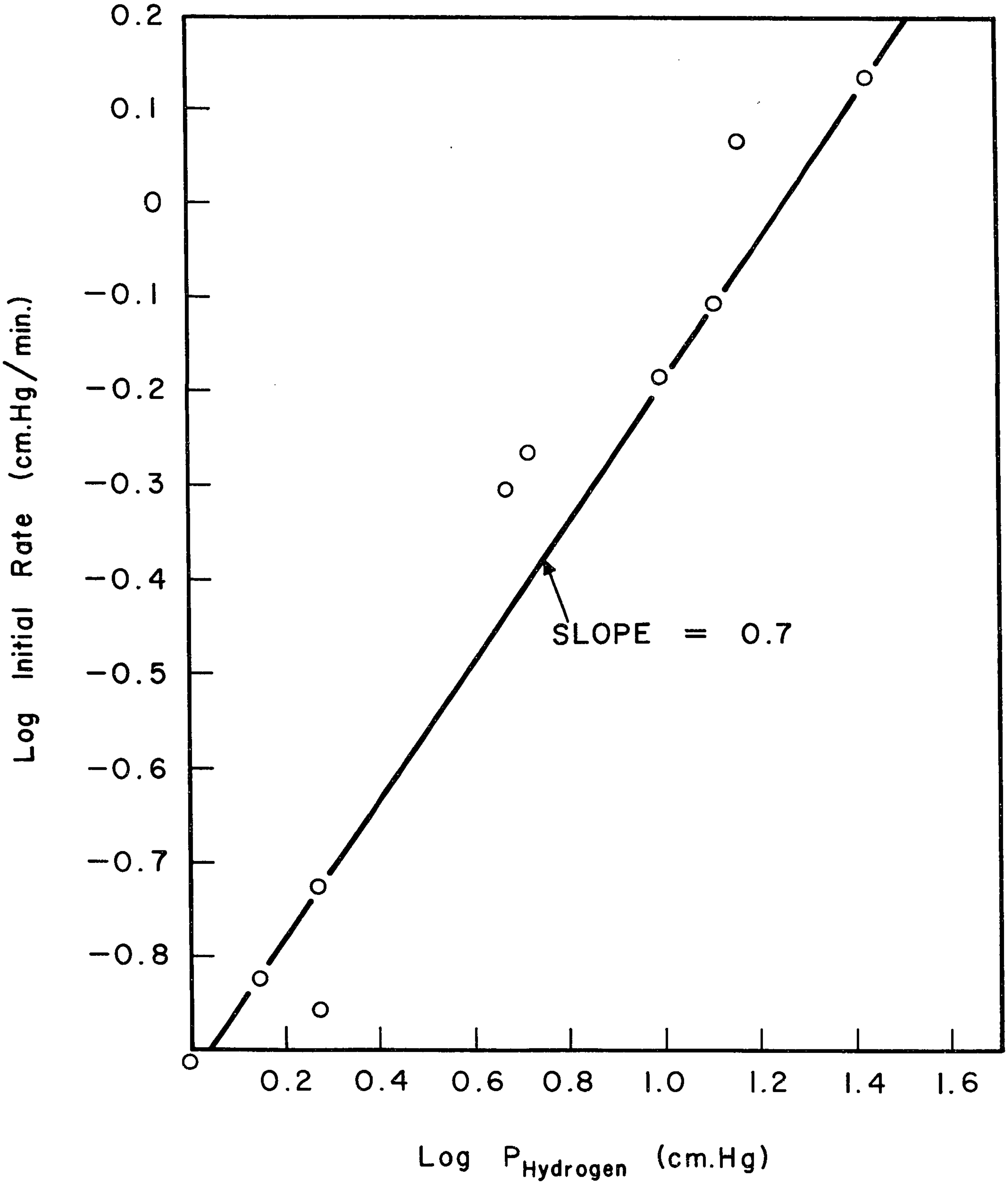


Figure 13 Plot of the logarithm of the initial rate on nickel film at 32.3°C in cm. Hg per min. against the logarithm of the initial hydrogen pressure. Ethylene introduced to the film prior to the hydrogen. Average initial ethylene pressure 6 cm. Hg.

A time course plot was made for run number 31.31 in which the hydrogen and ethylene were introduced on to the film simultaneously but the ethylene was in excess over the hydrogen. This plot is shown in Figure 14. The initial pressure of hydrogen was 7.0 cm.Hg and for ethylene 20.7 cm.Hg. This reaction was initially first order but the order decreased as the reaction progressed so that at a pressure 0.2 cm.Hg from the final pressure the order was 0.67. The time course for a similar hydrogenation reaction but with hydrogen in excess over ethylene (run 31.37) is plotted in Figure 15. The initial pressures of ethylene and hydrogen were 4.9 cm.Hg and 445 cm.Hg respectively. The reaction was initially almost zero order with a rapid change to second order, then a conversion to first order which slowly decreased during the course of the reaction. A second run of this type (run 29.28) was also converted to a time course plot in Figure 16 to confirm the results of the previous run. The ethylene and hydrogen were introduced to the film simultaneously at pressures of 4.4 and 21.3 cm.Hg respectively. This time course plot is initially zero order followed by rapidly increasing order reaching a maximum of second and then decreasing to 0.9 order. For a reaction in which hydrogen and ethylene are introduced to the reaction vessel together in equal quantities, run number 31.32, the time course plot as shown in Figure 17 is 0.67 order for most of the reaction. One time course study was made of a reaction in which the ethylene was introduced first but the pressures of ethylene and hydrogen were 10.8 cm.Hg and 9.4 cm.Hg respectively. These results are given in Figure 18 (number 32.8) and the time course order of reaction is 0.67. The time course plot for run number 31.41, in which the hydrogen was introduced to the film prior to the ethylene,

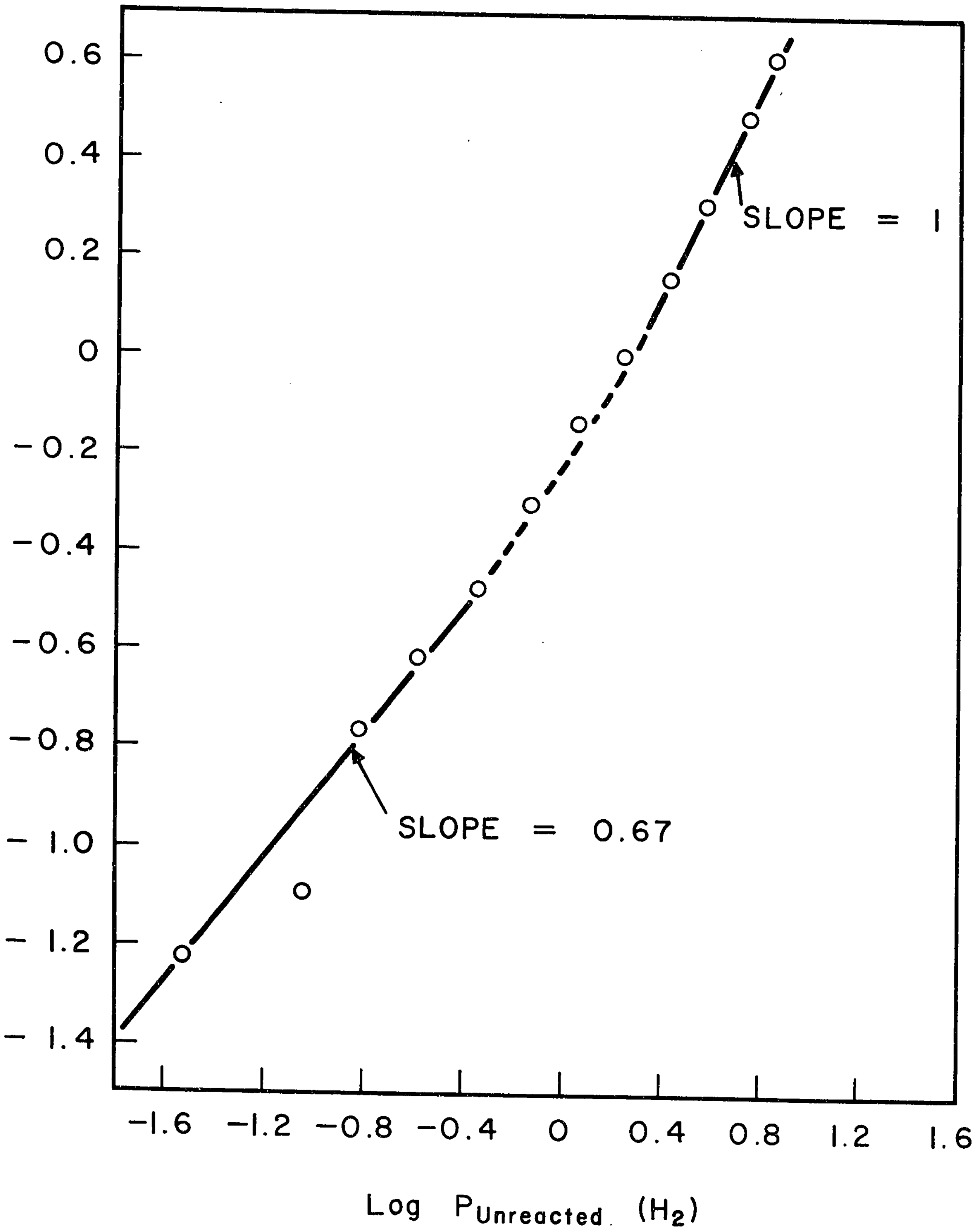


Figure 14 Plot of the logarithm of the rate against the logarithm of the pressure of unreacted hydrogen for run number 31.31. Ethylene and hydrogen introduced together. Nickel film.

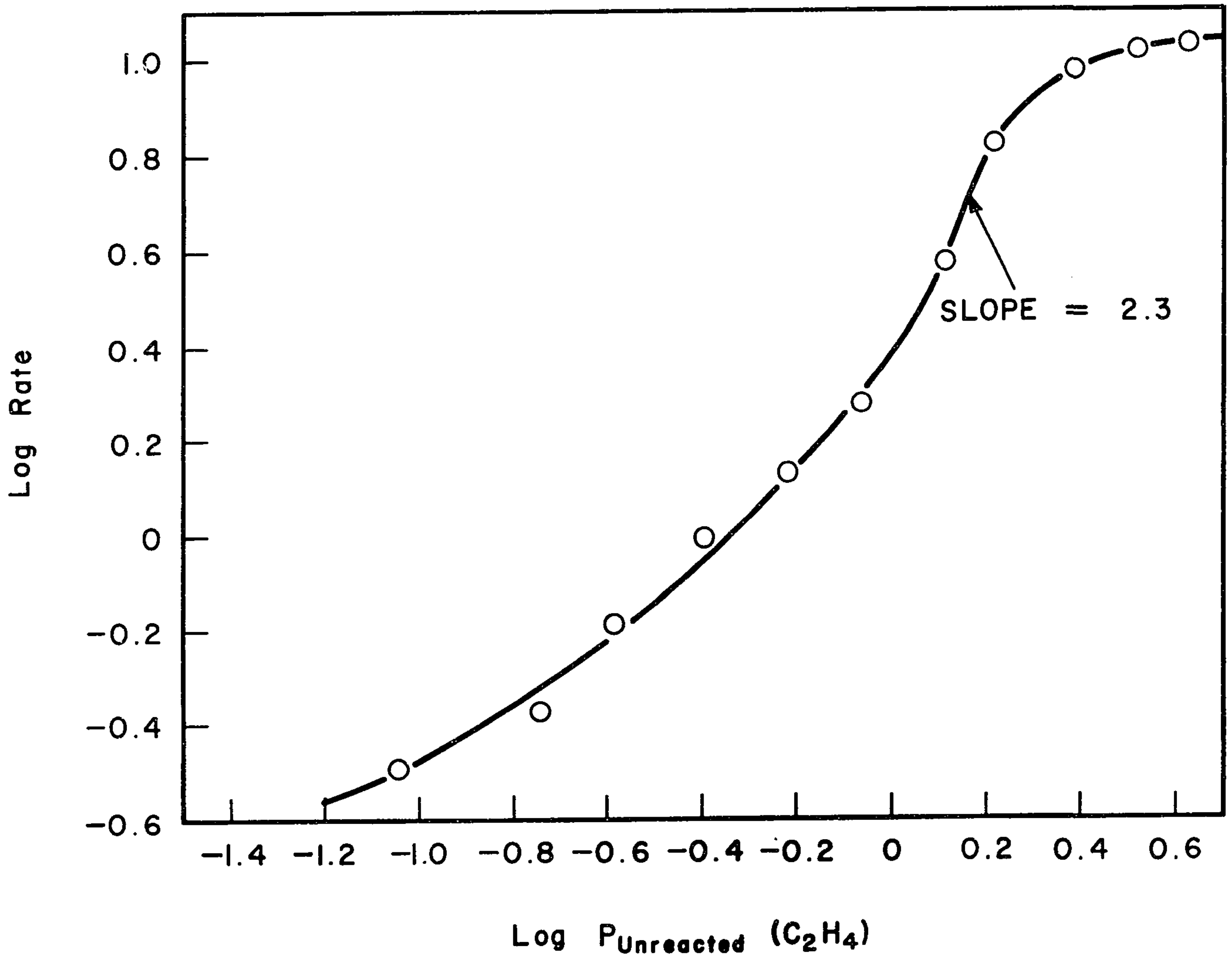


Figure 15 Plot of the logarithm of the rate against the logarithm of the pressure of unreacted ethylene for run number 31.37. Ethylene and hydrogen introduced together. Nickel film.

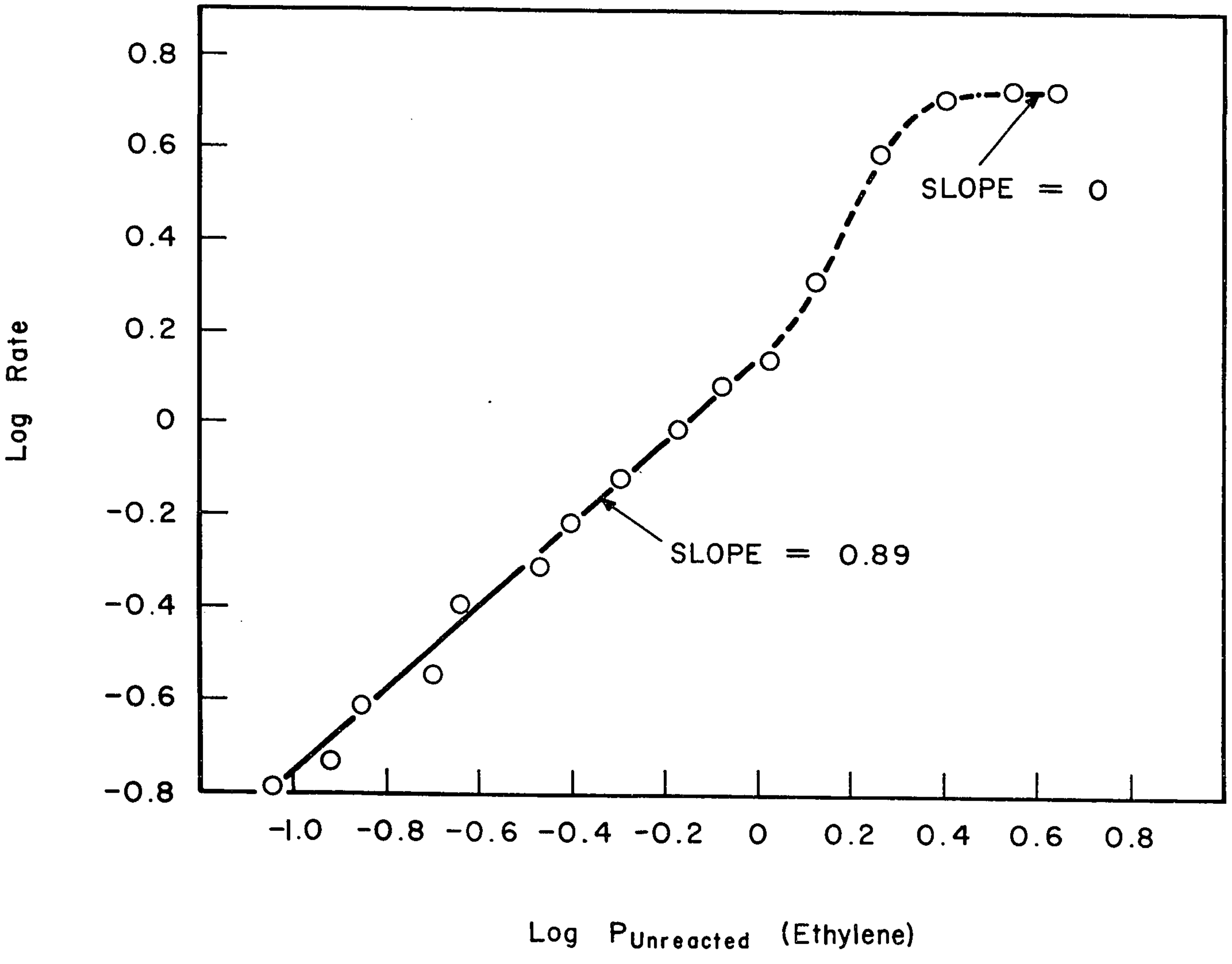


Figure 16 Plot of the logarithm of the rate against the logarithm of the pressure of unreacted ethylene for run number 29.28. Ethylene and hydrogen introduced together. Nickel film.

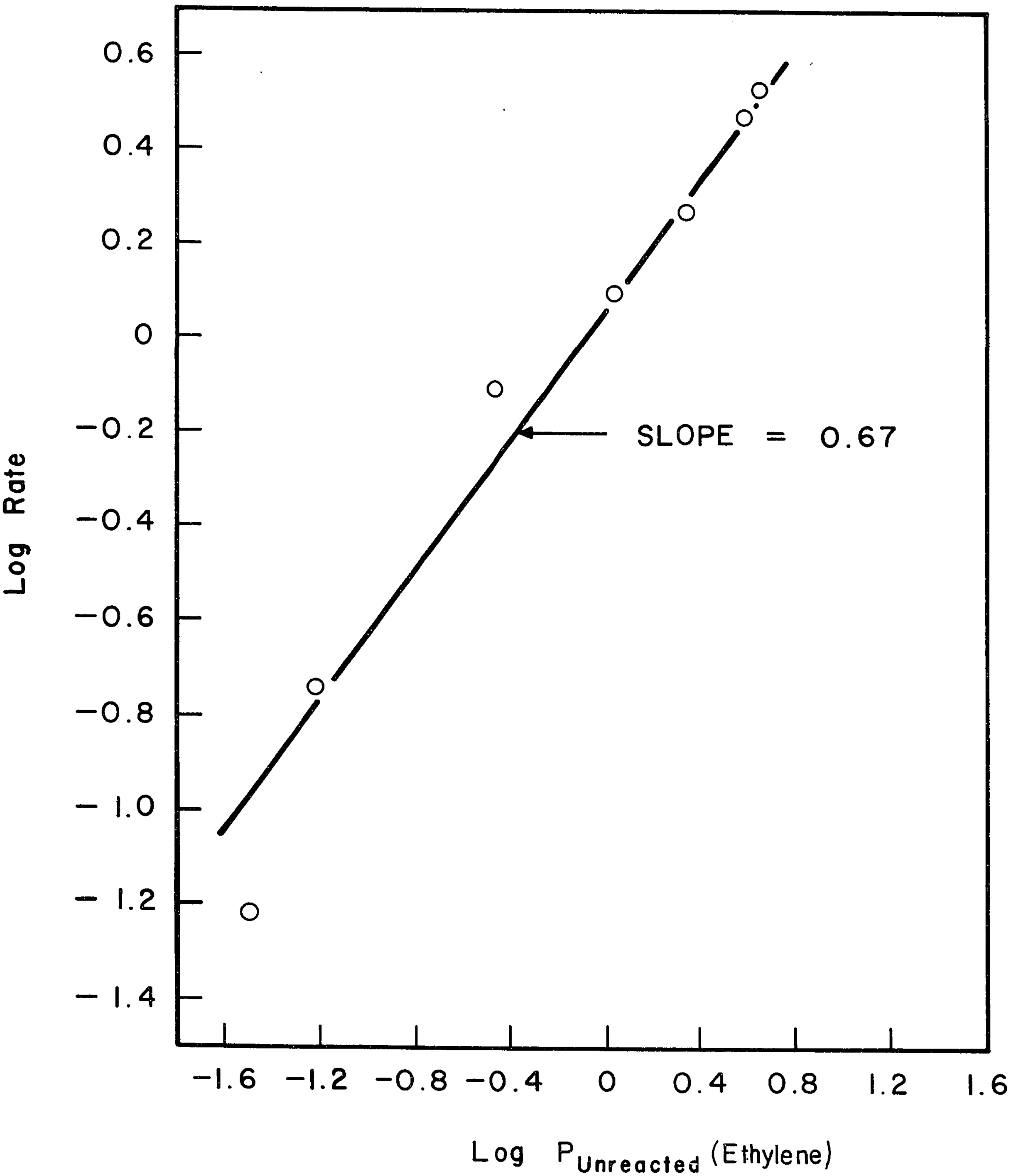


Figure 17 Plot of the logarithm of the rate against the logarithm of the pressure of unreacted ethylene for run number 31.32. Ethylene and hydrogen introduced together. Nickel film.

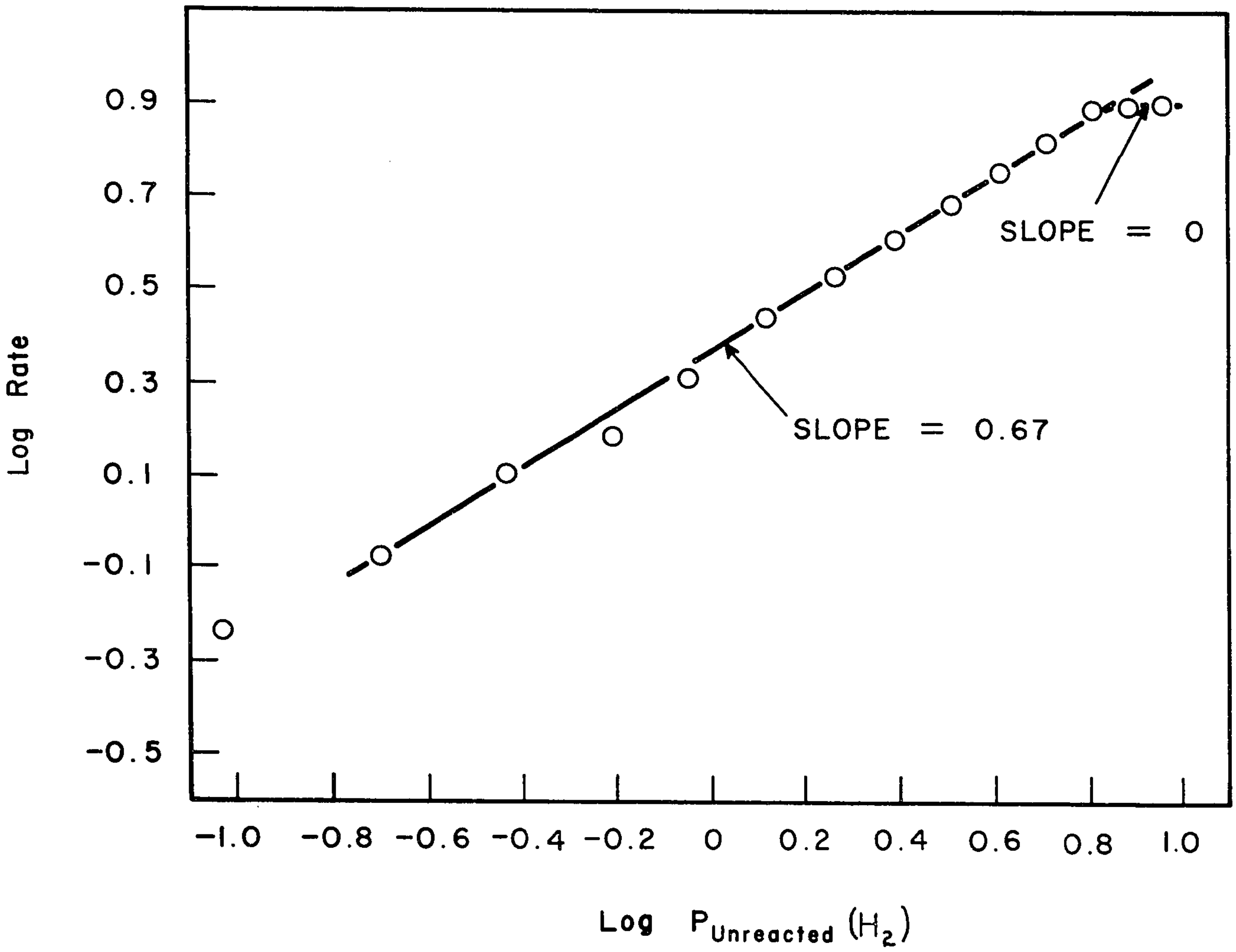


Figure 18 Plot of the logarithm of the rate against the logarithm of the pressure of unreacted hydrogen for run number 32.8. Ethylene introduced first. Nickel film.

is given in Figure 19. The initial pressures of hydrogen and ethylene were 8.6 and 4.5 cm.Hg respectively. This plot has a slope of 0.81 and therefore the time course order is 0.81.

PALLADIUM FILM REACTIONS

The ethylene hydrogenation reactions carried out on metallic palladium films could not be measured accurately because there was a very rapid absorption of the hydrogen into the palladium film. For example, one run in which the ethylene was introduced first and the initial pressures of ethylene and hydrogen were equal, had a very rapid initial rate followed by a very slow rate. The initial rapid rate must have been the rate of solution of the hydrogen in the palladium. The following slow rate may have been hydrogenation. Another run was carried out in which the hydrogen was introduced to the film first. In this case 9.3 cm.Hg of hydrogen were introduced to the reaction vessel and the pressure rapidly fell to 2.2 cm.Hg as the hydrogen was dissolved. Upon the addition of a mixture of equal quantities of ethylene and hydrogen to this 2.2 cm.Hg of hydrogen in the reaction vessel, the pressure decreased from 10.49 cm.Hg to 10.40 cm.Hg in 4.0 minutes. An examination of the palladium film after these reactions revealed that the film which was originally smooth and well adhered to the reaction vessel walls was now very badly flaked and peeled from the walls. Because of this deterioration of the palladium film, which was observed in the case of two films, it was not deemed expedient to continue the ethylene hydrogenation studies on evaporated palladium films.

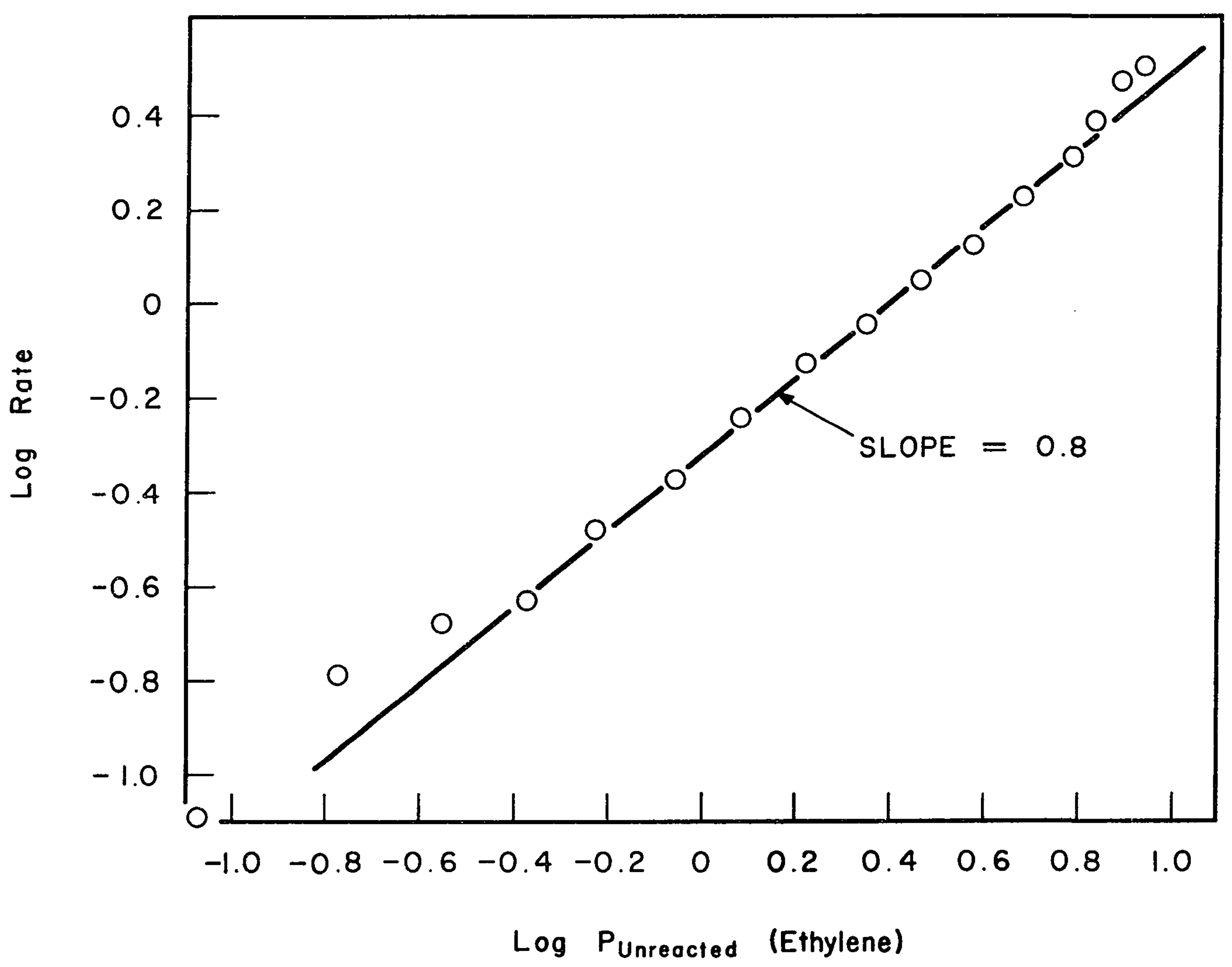


Figure 19 Plot of the logarithm of the rate against the logarithm of the pressure of unreacted ethylene for run number 31.41. Hydrogen introduced first. Nickel film.

IRON FILM REACTIONS

The activation energy for the iron film ethylene hydrogenations was determined in the temperature range from 32.3°C to 80°C. The average initial ethylene pressure was 5.5 cm.Hg and the average initial hydrogen pressure was 5.2 cm.Hg. The ethylene was introduced into the reaction vessel prior to the hydrogen. Figure 20 gives the actual plot which has a slope of 1.6×10^3 which gives an activation energy of 7.3 kcal. per mole.

A series of reactions with the introduction of ethylene prior to the hydrogen was carried out at 32.3°C and another series at 80°C to determine how the initial rate of the hydrogenation of ethylene catalyzed by iron films depended upon the initial pressure of ethylene. In the series at 32.3°C the ethylene pressures varied from 2.5 cm.Hg to 39.4 cm.Hg while the initial hydrogen pressure for each run was approximately 4.9 cm.Hg. The results of these runs are plotted in Figure 21, from which it is seen that the ethylene pressure dependence is of the order - 0.61. In Figure 22 a plot of logarithm of ethylene pressure against logarithm of the initial hydrogenation rate is given for the series carried out at 80°C. In this series the ethylene pressure range was from 2.3 cm.Hg to 47.2 cm.Hg with a value of 5.2 cm.Hg for the initial hydrogen pressure for each run. The slope of the graph gives the ethylene pressure dependence as - 0.22.

To determine the hydrogen pressure dependence of the ethylene hydrogenation reaction on iron films, the technique by which ethylene was introduced to the reaction vessel first was also used. At a temperature of 32.3°C the hydrogen pressure was varied from 1.1 cm.Hg

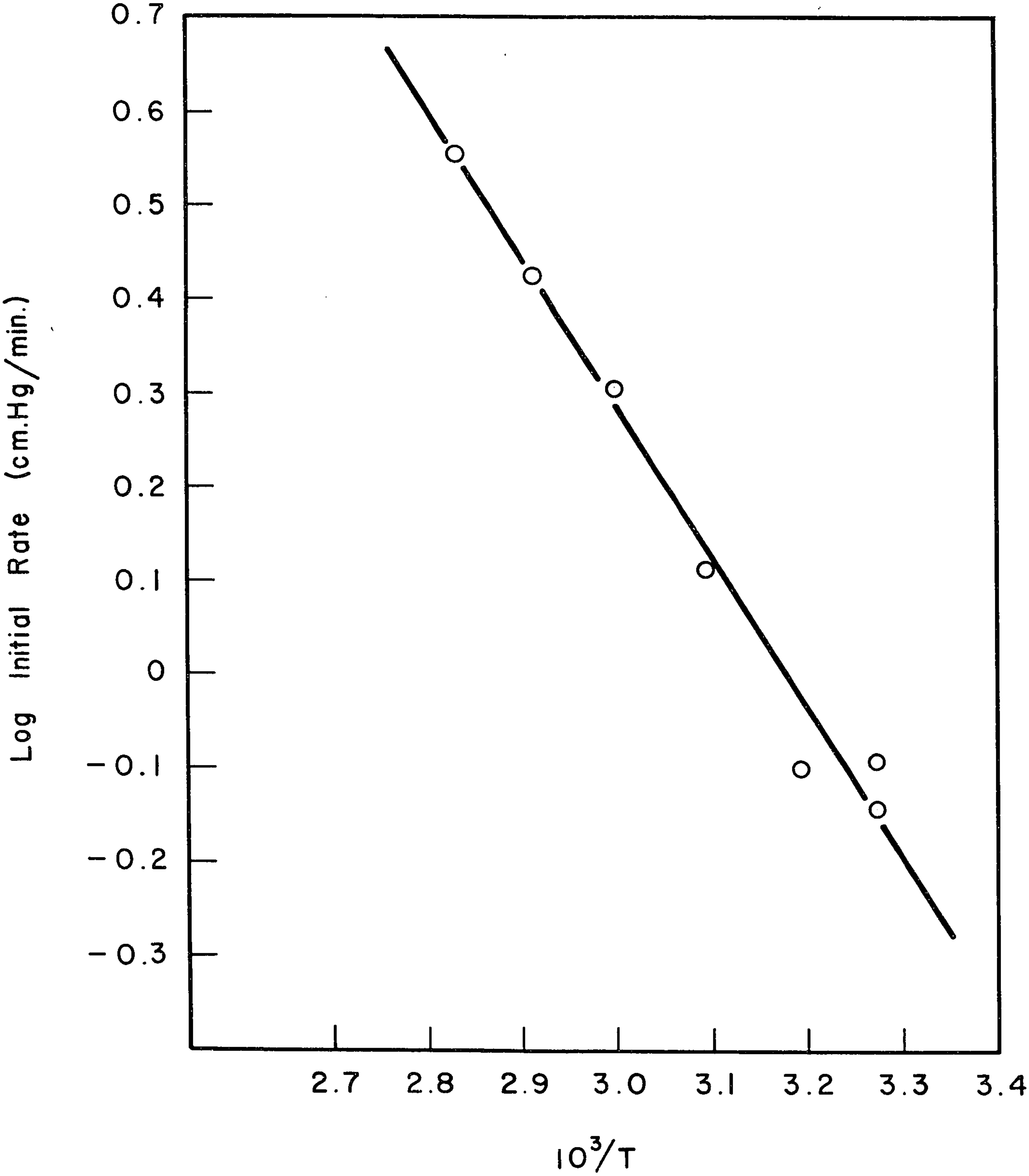


Figure 20 Plot of the logarithm of the initial rate on iron film against 1/T. Ethylene introduced first.

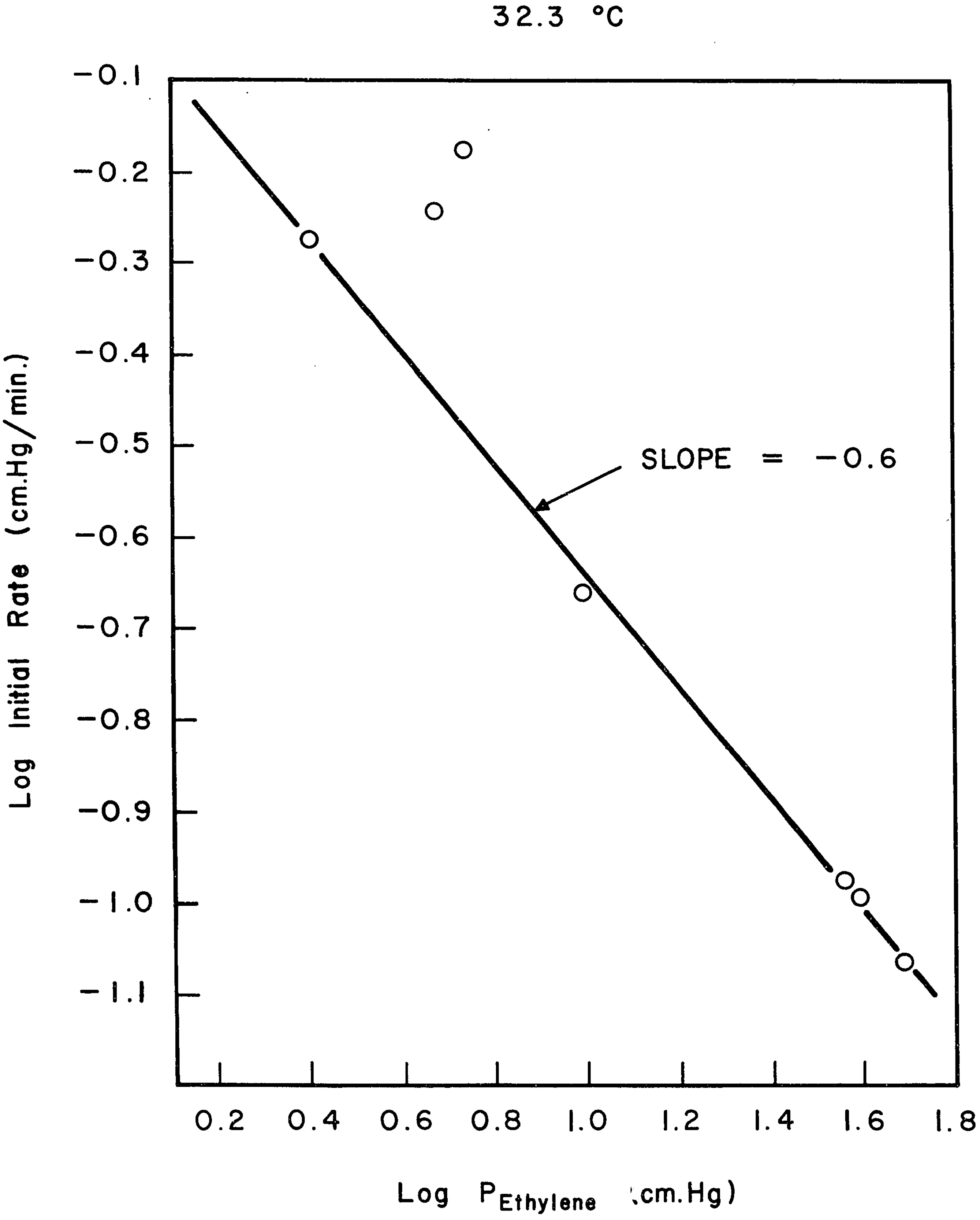


Figure 21 Plot of the logarithm of the initial rate on iron film in cm. Hg per min. against the initial pressure of ethylene in cm. Hg. Ethylene introduced first. Average initial hydrogen pressure 5 cm. Hg.

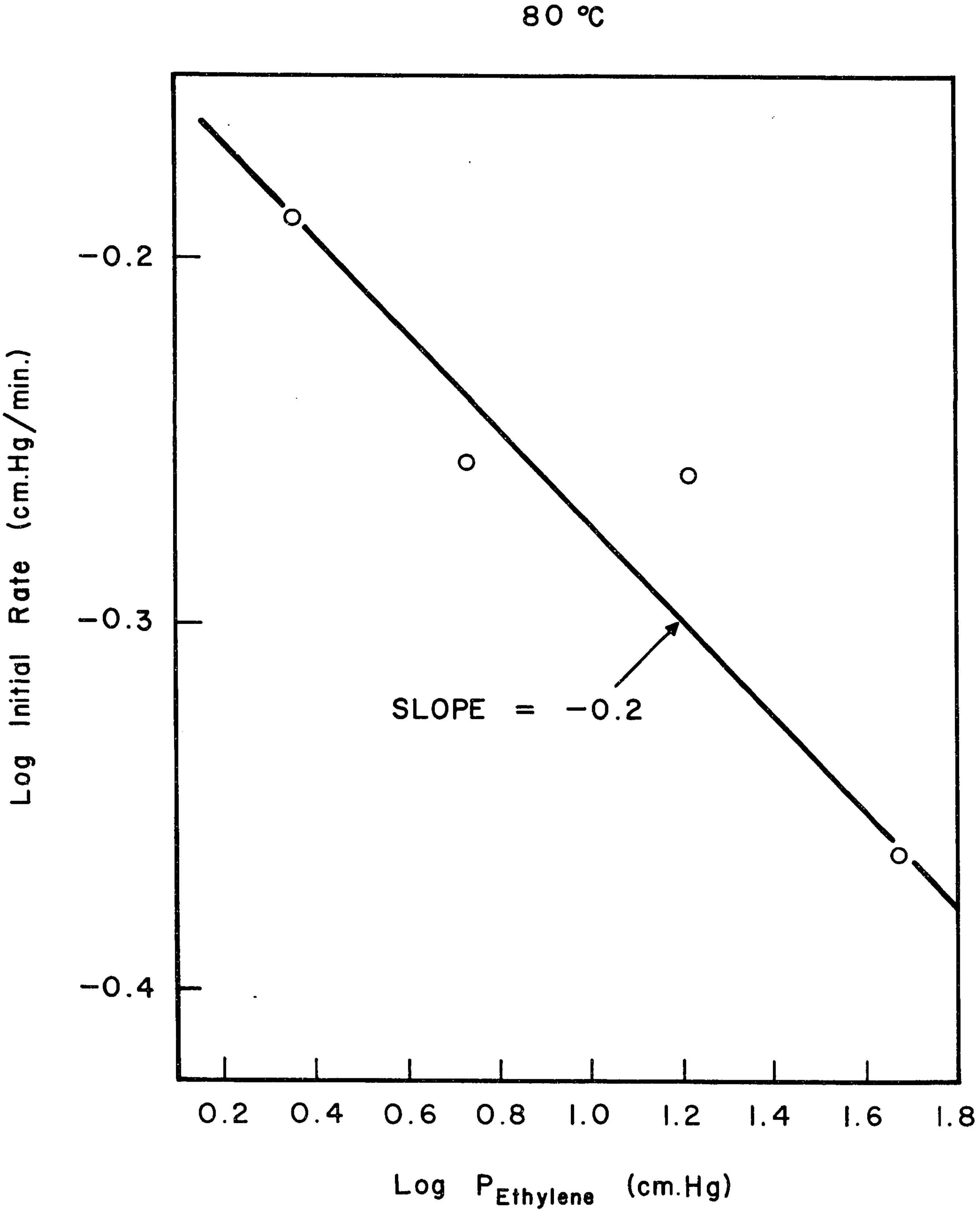


Figure 22 Plot of the logarithm of the initial rate on iron film in cm. Hg per min. against the initial pressure of ethylene in cm. Hg. Ethylene introduced first. Average initial hydrogen pressure 5.5 cm. Hg.

to 18.2 cm.Hg for a series of runs each of which had an initial ethylene pressure of approximately 5.4 cm.Hg. This series is plotted in Figure 23 from which it can be seen that the hydrogen pressure dependence was 0.87 for the ethylene hydrogenation. For a series of runs at 80°C the maximum hydrogen pressure was 21.2 cm.Hg and the minimum 1.8 cm.Hg with an initial ethylene pressure of approximately 5.6 cm.Hg for each of these runs. The slope of the line in Figure 24 gives the hydrogen pressure dependence at 80°C as 0.74.

A series of ethylene hydrogenations on iron films was carried out in order to study the time course of each reaction. The logarithm of the rate at time t was plotted against the logarithm of the difference between the final pressure and the pressure at any time t.

In run number 39.5 the hydrogen was introduced to the reaction vessel prior to the addition of the ethylene and the initial pressures of hydrogen and ethylene were 10.7 and 8.6 cm.Hg respectively. The time course plot for this reaction is given in Figure 25, and from this plot it is seen that the reaction is 0.94 order throughout its course.

The following series of runs was carried out with the ethylene being introduced to the reaction vessel before the hydrogen; the temperature of the reaction vessel bath was 32.3°C.

In run number 41.6 the initial pressures of hydrogen and ethylene were 11.7 and 12.4 cm.Hg respectively and the time course is plotted in Figure 26. The reaction was 0.48 order for most of the course but as it reached completion the order increased. The time

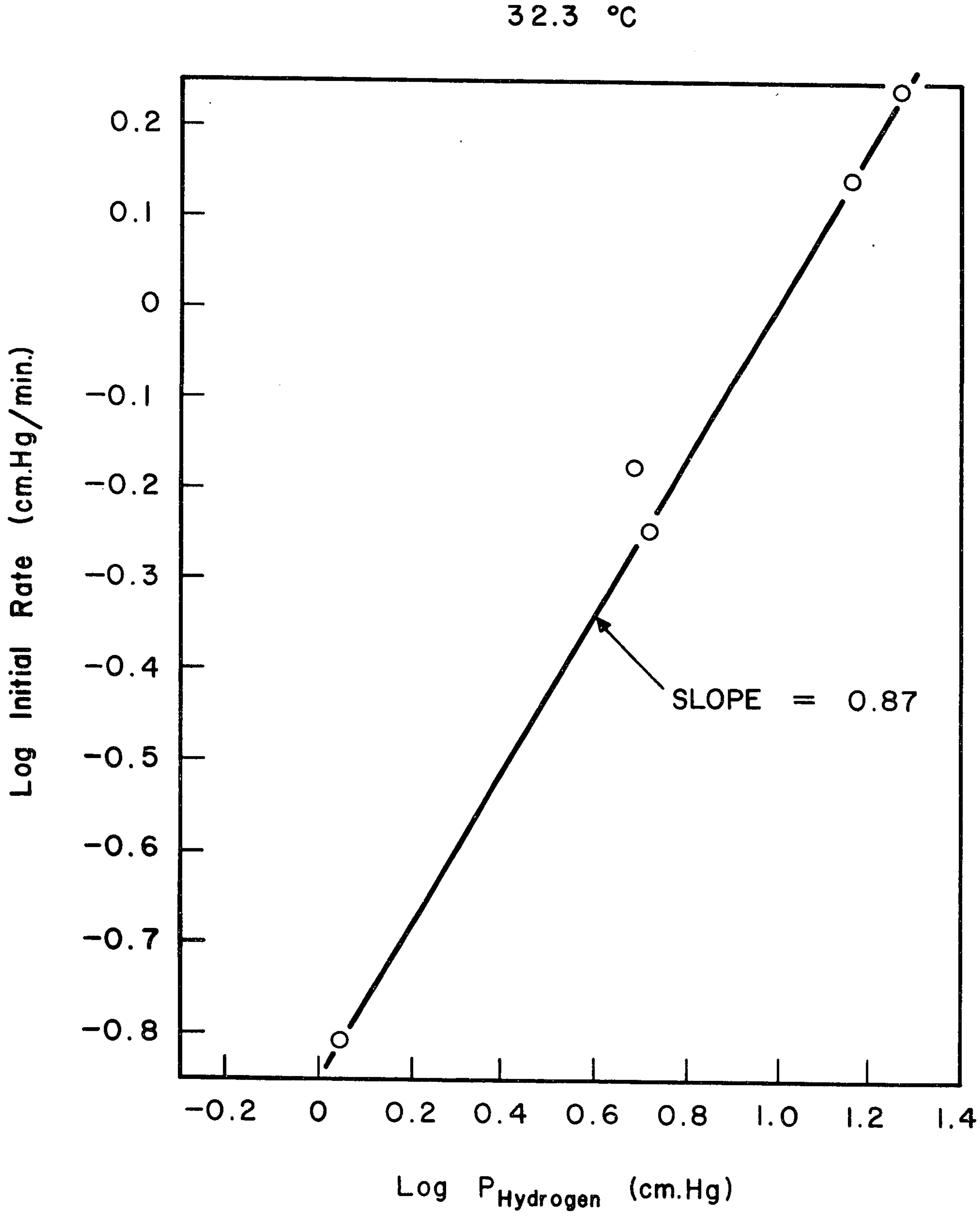


Figure 23 Plot of the logarithm of the initial rate on iron film in cm. Hg per min. against the initial pressure of hydrogen in cm. Hg. Ethylene introduced to the film prior to the hydrogen. Average initial ethylene pressure 5.5 cm. Hg.

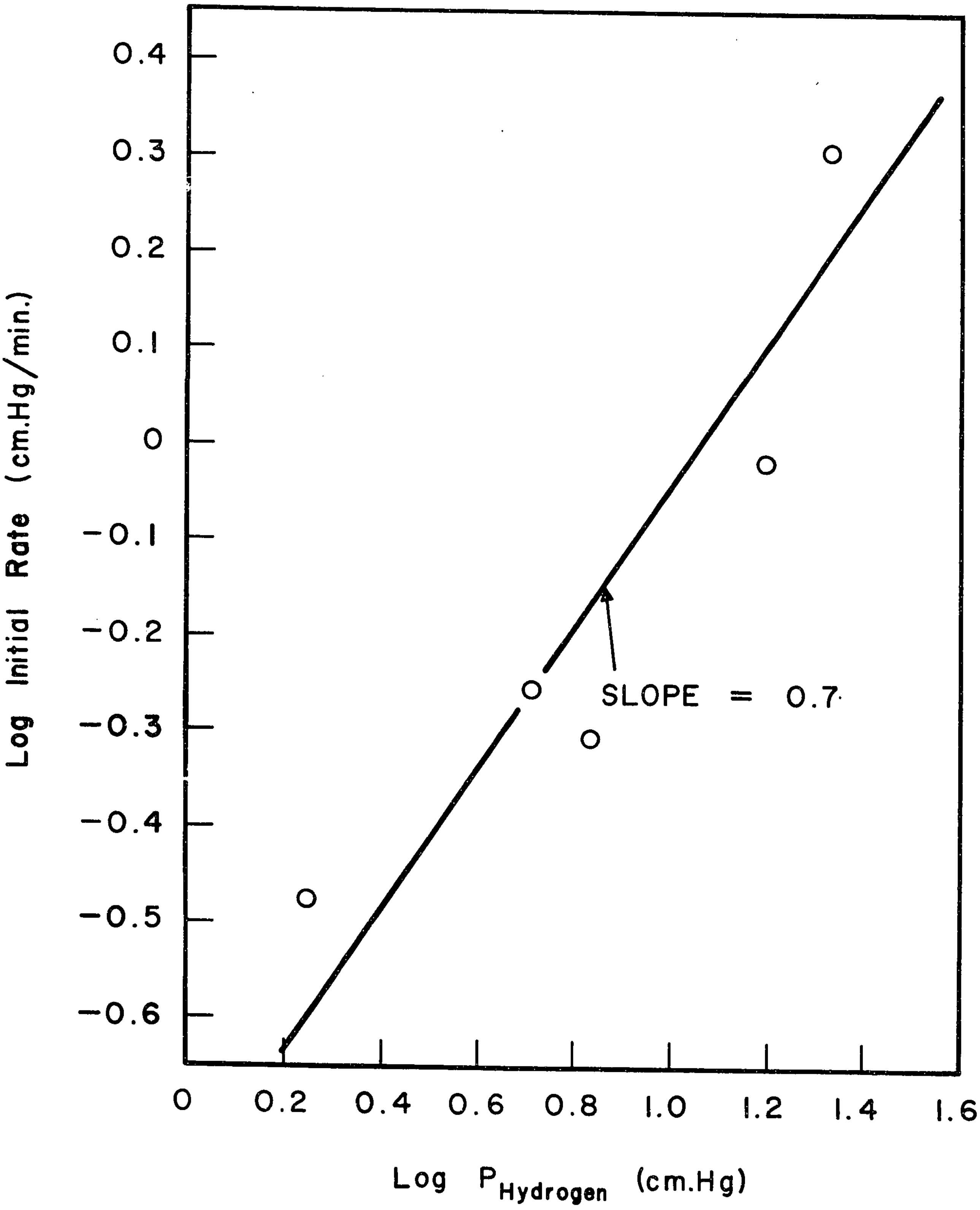


Figure 24 Plot of the logarithm of the initial rate on iron film at 80°C in cm. Hg per min. against the initial pressure of hydrogen in cm. Hg. Ethylene introduced to the film prior to the hydrogen. Average initial ethylene pressure 5.7 cm. Hg.

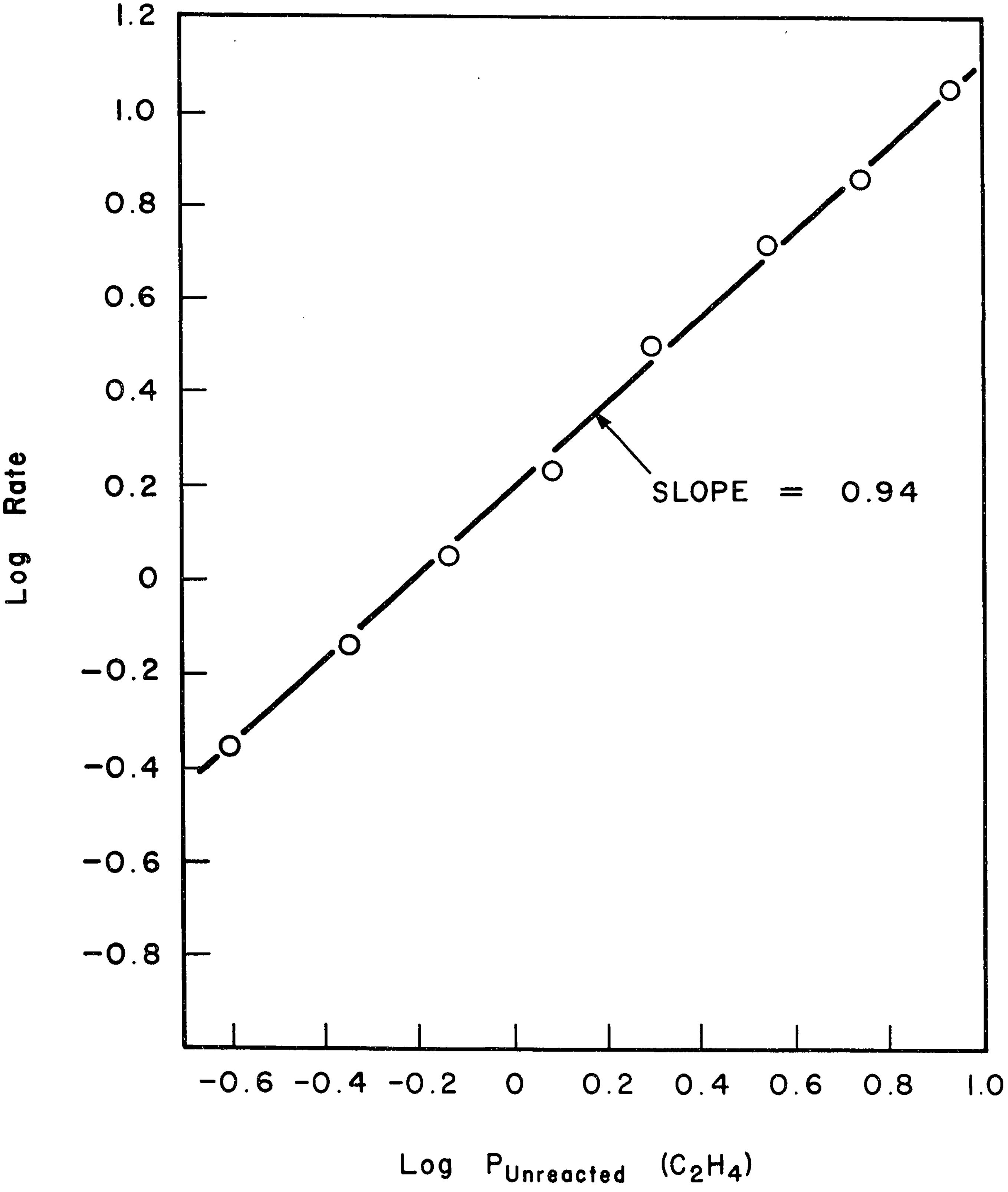


Figure 25 Plot of the logarithm of the rate against the logarithm of the pressure of unreacted ethylene for run number 39.5. Hydrogen introduced first. Iron film.

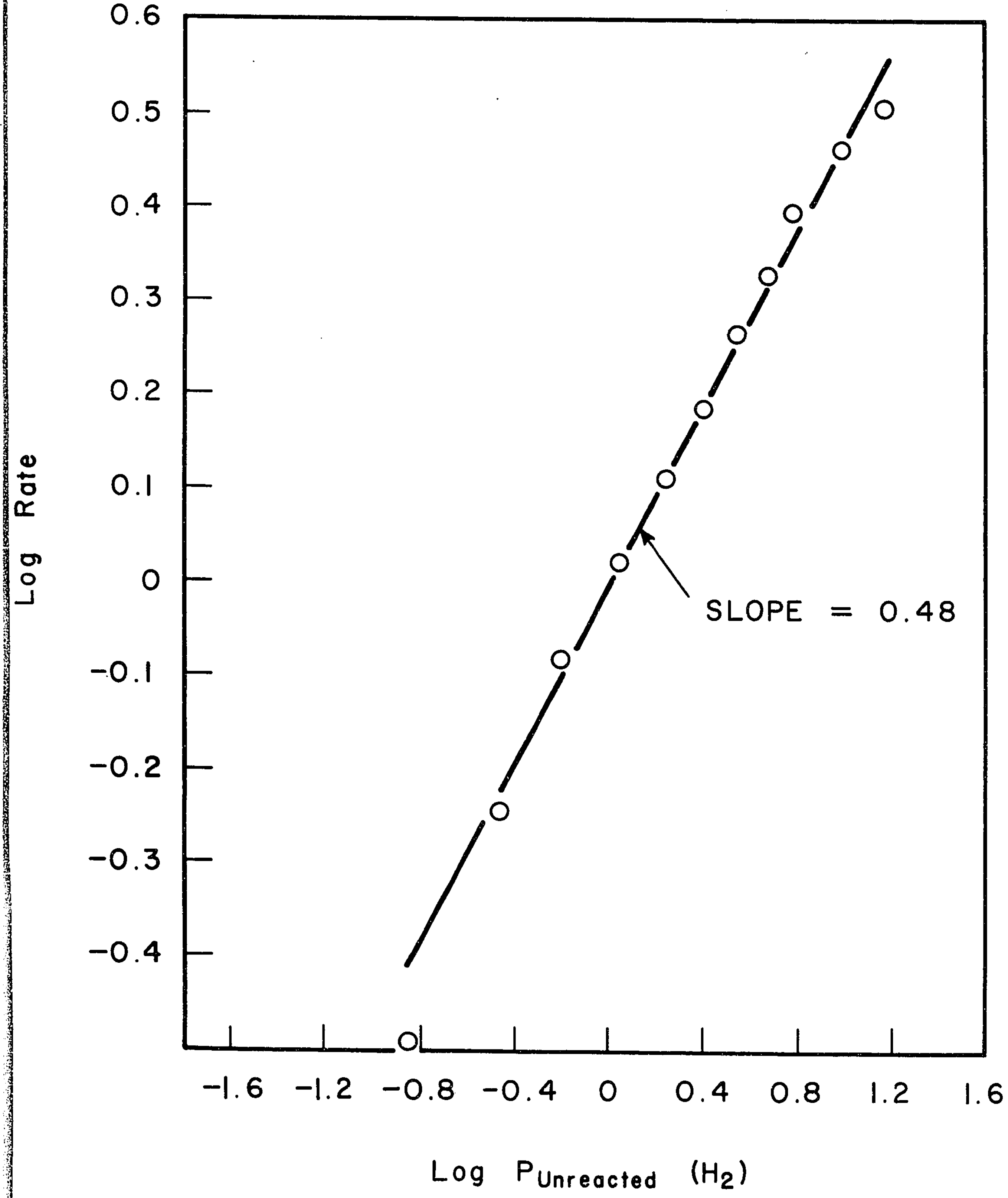


Figure 26 Plot of the logarithm of the rate against the logarithm of the pressure of unreacted hydrogen for run number 41.6. Ethylene introduced first. Iron film.

course for run number 39.4 which had an initial pressure of 10.4 cm. of ethylene and 8.8 cm.Hg of hydrogen is given in Figure 27. The time course was initially of 0.57 order but towards completion the order increased to 0.8.

The courses of two hydrogenations in which the hydrogen was in excess over the ethylene were converted to time-course plots in Figure 28 and 29. In run number 39.18 the initial pressures of hydrogen and ethylene were 18.2 cm.Hg and 5.9 cm.Hg respectively and the reaction was initially of 0.19 order with a break to 0.85 order after the pressure of ethylene had fallen to a value of 0.54 cm.Hg. The other run, number 41.8, in which the initial pressures of hydrogen and ethylene were 17.5 cm.Hg and 11.0 cm.Hg respectively started out initially as 0.29 order but fell sharply to 0.78 order after the ethylene pressure had fallen to 1.6 cm.Hg.

Hydrogenations with large excesses of ethylene were carried out and the results converted to time-course plots. Typical behaviour was exhibited by run number 41.2 which went from low order to 0.75 order as shown in Figure 30. In run 41.2 the initial ethylene pressure was 39.4 cm.Hg whereas the initial hydrogen pressure was 5.9 cm.Hg.

CHROMATOGRAPHIC RESULTS

The C.P. grade ethylene from Matheson was found to contain from 1.0% to 1.2% ethane as an impurity. All other impurities were of such minute quantities that they did not show up in chromatographic analysis.

The ethylene hydrogenation reaction products were

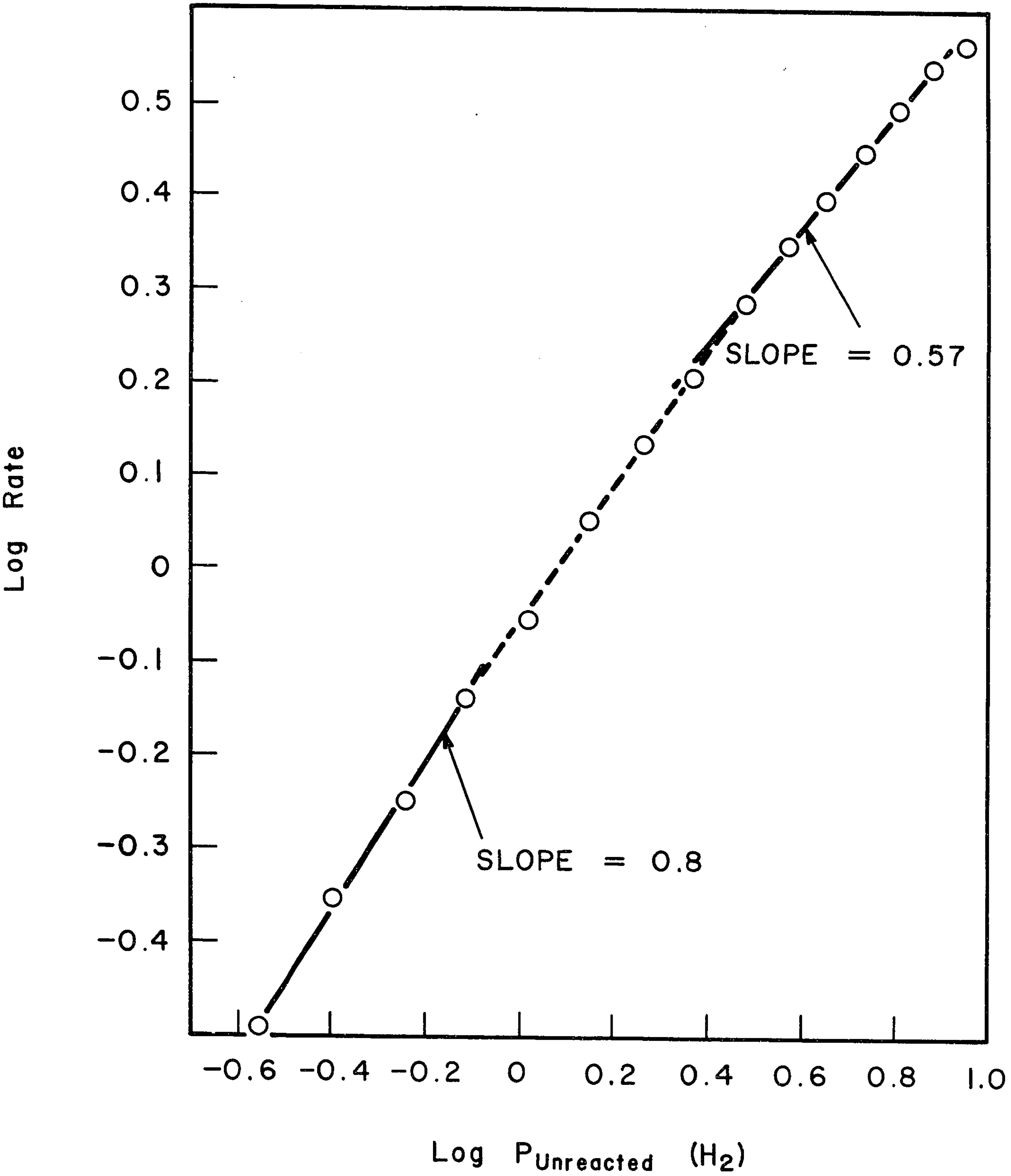


Figure 27 Plot of the logarithm of the rate against the logarithm of the pressure of unreacted hydrogen for run number 39.4. Ethylene introduced first. Iron film.

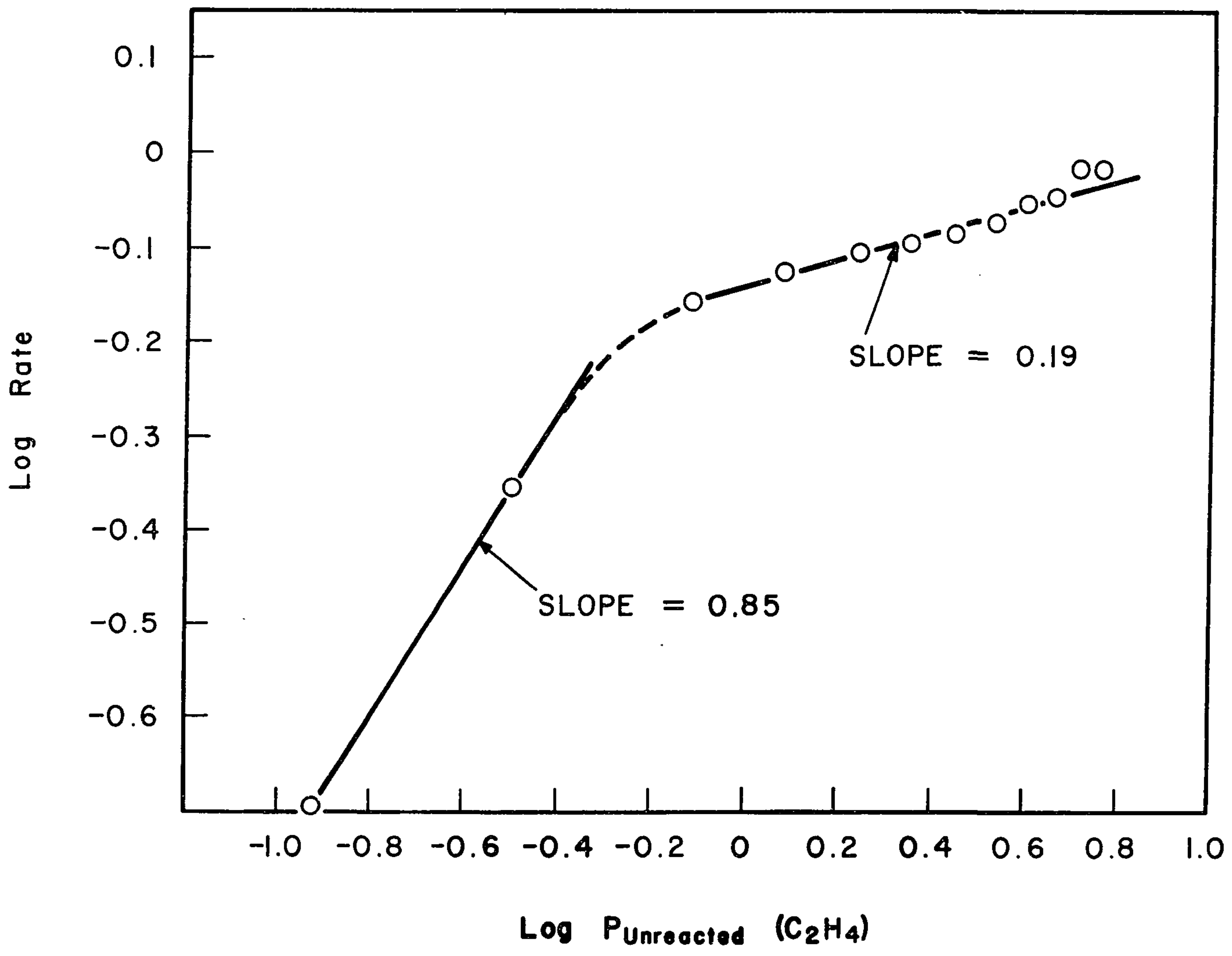


Figure 28 **Plot of the logarithm of the rate against the logarithm of the pressure of unreacted ethylene for run number 39.18. Ethylene introduced first. Iron film.**

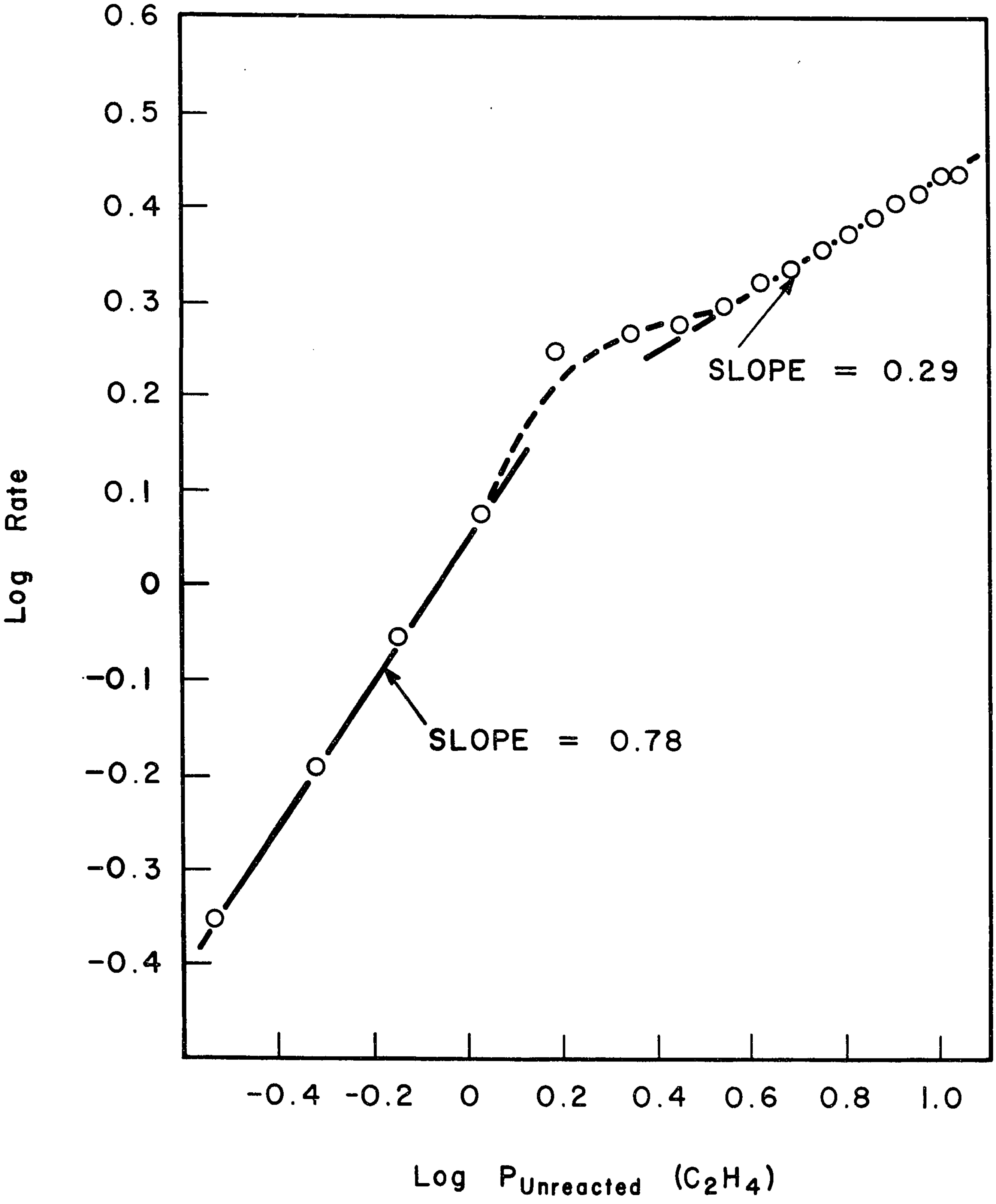


Figure 29 Plot of the logarithm of the rate against the logarithm of the pressure of unreacted ethylene for run number 41.8. Ethylene introduced first. Iron film.

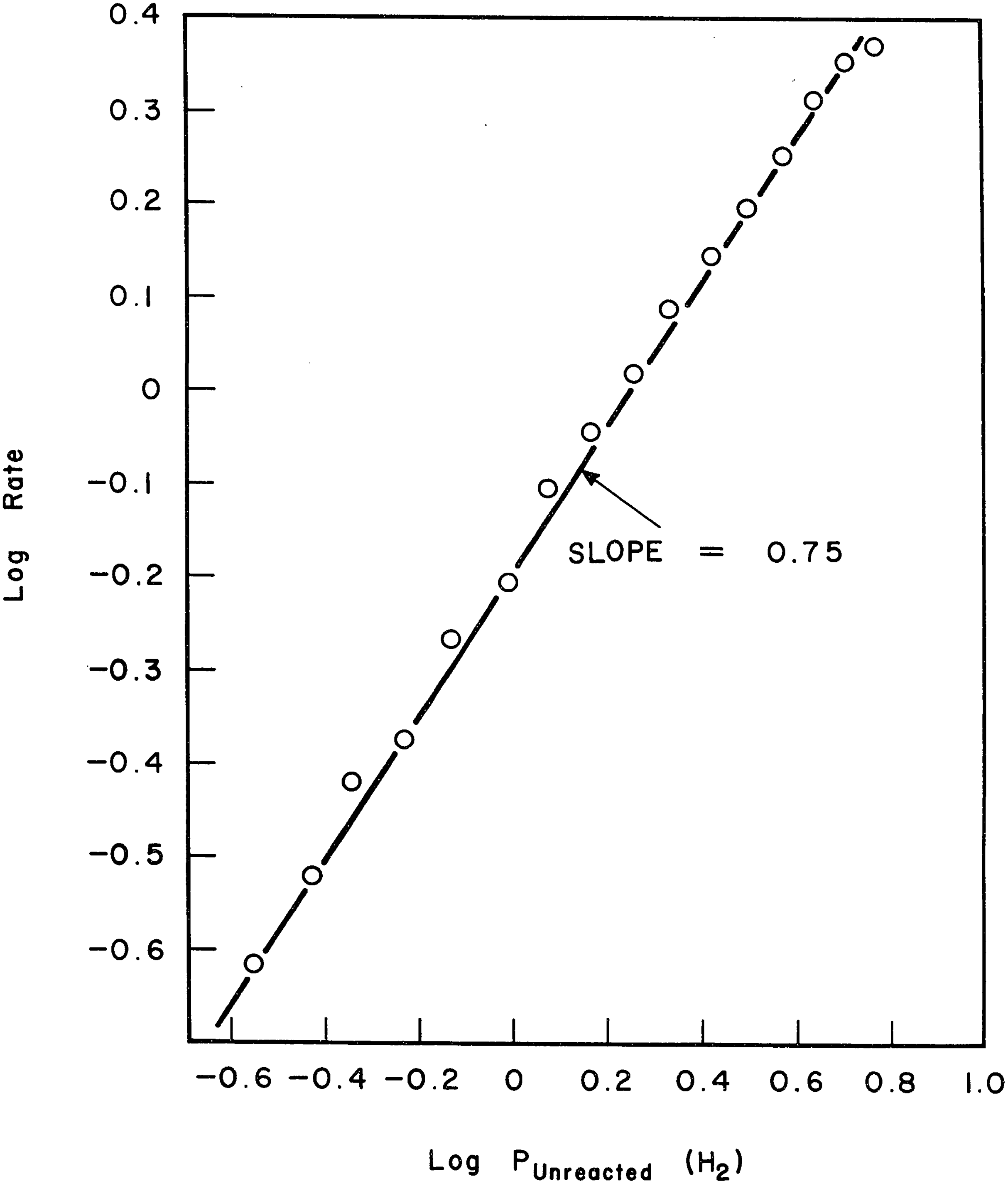


Figure 30. Plot of the logarithm of the rate against the logarithm of the pressure of unreacted hydrogen for run number 41.2. Ethylene introduced first. Iron film.

analyzed chromatographically for ethane, ethylene, and hydrogen. At a flow rate of 8 cc per minute the hydrogen came out in 3/4 of a minute, ethane in 3.4 minutes and ethylene in 7.2 minutes. Hydrogen could not be analyzed quantitatively because it passed through the column rapidly giving a very sharp peak soon after the sample was put into the chromatograph. Also the thermal conductivity of hydrogen is very close to the value of the thermal conductivity of helium thus rendering the detector insensitive to hydrogen in a flow of helium.

For the eight ethylene hydrogenation reactions, of which four were on a nickel film and four were on an iron film, the only product which could be detected by the chromatograph was ethane regardless of whether the ethylene was introduced to the reaction vessel prior to the hydrogen or whether the ethylene and hydrogen were added to the reaction vessel simultaneously.

Four of the eight ethylene hydrogenations were carried out using a definite excess of hydrogen for which no ethylene would be expected to remain on completion of the reaction. However in all four runs some ethylene was left in the reaction vessel upon completion of the reaction. These reactions, which were normally considered to be complete after 5 minutes, were allowed to react for 30 minutes. Thus there must be a measurable equilibrium set up at 32.3°C for the ethylene hydrogenation reaction. The results for the calculation of an equilibrium constant K_p, for these four reactions are 6, 20, 10 and 32 $(\text{cm.Hg})^{-1}$.

The other four of the eight ethylene hydrogenations were carried out using an excess of ethylene. In the chromatographic analysis of the gas in the reaction vessel upon completion of the reaction, it was found that the ratio of ethylene to ethane was much lower than that which would be expected from a calculation considering only the simple addition of hydrogen to ethylene to form ethane. In an extreme case for which the ethylene pressure of 12.6 cm.Hg was twice the hydrogen pressure of 6.5 cm.Hg, the chromatographic ratio of ethylene to ethane was 0.073, whereas from calculations the value of this ratio should have been 0.93. From these results it is concluded that upon depletion of the hydrogen a self hydrogenation of ethylene may become important.

CHAPTER IV

GENERAL CONCLUSIONS

FILM ACTIVITY

The low activity of one series of nickel films must have been due to the presence of some impurity during the evaporation process. An extremely high vacuum is necessary during evaporation in order to insure high film activity. The series of high activity nickel films must have resulted from some unknown improvement in the technique of evaporation or in the vacuum.

Since it is generally found that an increase in the number of holes in the d band usually results in increased activity, iron films with seven 3d electrons per atom would have been expected to be more active than nickel films with nine 3d electrons per nickel atom. However, it was found experimentally that iron films had an activity per mole which was equal to the activity per mole of nickel films. Thus it is expected that the crystal lattice spacings in iron films are not as favourable for the ethylene hydrogenation reaction as the spacings in nickel films.

The double bond distance for ethylene is given as 1.32Å and the carbon - carbon single bond distance in ethane is 1.54Å. In nickel the interatomic distances in the 100, 110, and 111 planes are 3.52, 2.47 and 3.50, and 2.47 Å respectively. However, in iron the interatomic distances are 2.87 Å in the 100 plane, 2.48 and 2.87 Å in the 110 plane, and 4.06 Å in the 111 plane. Beeck (19) attempted to classify the activity of the transition metals for ethylene hydrogenation in purely geometric terms. His plot of the logarithm of the specific activity of a number of metal films for ethylene hydrogenation at 0°C against the lattice spacings gave a maximum activity for lattice spacings in the range 3.5 to 4.0 Å. Nickel has two spacings in this range and iron has only one. Thus it can be concluded that the greater number of large interatomic distances found in nickel, which are more favourable for the adsorption of ethylene, compensates for the fewer number of d-band holes.

The activation energy for the hydrogenation of ethylene reaction on nickel films is 10.0 kcal. per mole as compared to a value of 7.3 kcal. per mole for the reaction on iron films. Therefore, since both iron and nickel films have similar activities per mole for the ethylene hydrogenation reaction, the frequency factor for nickel must be larger than that for iron. This compensating effect between the activation energy and the frequency factor is quite often found in catalytic reactions.

The lack of correlation between the quantity of hydrogen chemisorbed at 0°C and the activity of a nickel film for films of low activity may be due to the increasing importance of physical adsorption. If only very small quantities of hydrogen are chemisorbed on low activity films, the quantity of hydrogen physically adsorbed, though very small, may become significant in relation to the quantity chemisorbed,

It is interesting to compare the areas of the films in this work with the areas of those prepared by Beeck and co-workers. On one 5 mg. nickel film used in this work approximately 10^{-5} moles of hydrogen were chemisorbed and this amount of chemisorption gives an area of 4,000 $cm.^2$, the average area per nickel atom being assumed to be 6.72 $Å^2$. The geometrical area was 200$cm.^2$. The surface area of a 50 mg. oriented nickel film was 10^4 $cm.^2$ in Beeck's work (26). Beeck claimed that in this range the weight is proportional to the surface area; thus a 5 mg. nickel film would have an area of 10^3 $cm.^2$ by Beeck's preparation which is a fourth of the area obtained in this research. In the present work the nickel may have been evaporated on to a larger geometrical area than in Beeck's work; however Beeck did not report the geometrical area.

The decrease in the activity of a film during a series of reactions may be due to very small quantities of oxygen or to dehydrogenated forms of ethylene, that is acetylenic complexes or carbide complexes, which are very strongly attached to the film. It was found that the activity of a film was greatly reduced after a hydrogenation reaction carried out with a large excess of ethylene, whereas after a hydrogenation reaction carried out with a large excess of hydrogen there was an increase in film activity. Thus hydrogen can, to a limited extent, remove the deactivating material.

MECHANISMS

When hydrogen was introduced to the film prior to the ethylene, or when hydrogen and ethylene were introduced to the film simultaneously, the rate of hydrogenation was greater than when ethylene was introduced into the reaction vessel first. It is concluded that in the first two cases the concentration of hydrogen on the film surface was much greater than in the third case. But, since ethylene is much more strongly chemisorbed on metallic films than hydrogen, the hydrogen is rapidly displaced by the ethylene until an equilibrium situation is reached, or, as Rideal and Jenkins have suggested, until all the positions of four point contact are covered by ethylene, a coverage which they have found to be 80% of the surface.

When the concentration of hydrogen on the surface is great there is a possibility that the Rideal mechanism may contribute the greatest part of the initial rate; this is probably true initially in the first case. However as ethylene is strongly adsorbed it will displace the hydrogen from the surface and greatly reduce the contribution to the rate of hydrogenation by the Rideal mechanism. As the concentration of ethylene on the surface becomes greater the Langmuir-Hinshelwood mechanism will probably take over as the greater contributor to the rate. In the third case, when ethylene was introduced to the film prior to the hydrogen, the ethylene was probably hydrogenated almost entirely by the Langmuir-Hinshelwood mechanism with only a very small contribution by the Rideal mechanism.

ACTIVATION ENERGY FOR NICKEL FILMS

The foregoing explanation could account for the difference in activation energies between the value of 7.8 kcal. per mole determined for the hydrogenation reaction in which hydrogen and ethylene were introduced to the reaction vessel simultaneously and the value of 10.0

kcal. per mole measured for the ethylene hydrogenation reaction in which ethylene is introduced prior to the hydrogen.

The 7.8 kcal. per mole activation energy is probably the activation energy for the hydrogenation of ethylene by the Rideal mechanism since the hydrogen was in slight excess over the ethylene for the reactions used to measure this activation energy. The 10.0 kcal. per mole value will be the activation energy for the hydrogenation of ethylene by the Langmuir-Hinshelwood mechanism. It is difficult to explain why the activation energy is greater for the Langmuir-Hinshelwood mechanism than for the Rideal mechanism because so many complicating factors are involved. However one possible postulate is that, since ethylene is so strongly chemisorbed, the reaction between chemisorbed ethylene and chemisorbed hydrogen will require a greater activation energy than the reaction between gaseous ethylene and chemisorbed hydrogen. It is of interest to note that Beeck, and Jenkins and Rideal, reported activation energies of 10.7 and 10.2 kcal. per mole respectively while Foss and Eyring gave a value of 8 kcal. per mole; unfortunately little is reported about the methods used in the introduction of the gases to the films.

PRESSURE DEPENDENCIES ON NICKEL FILMS

For the ethylene hydrogenations in which ethylene and hydrogen were introduced simultaneously the initial rate depended upon the first power of the hydrogen pressure at low hydrogen pressures, but at higher pressures as the reaction reached hydrogen saturation the rate became more independent of the hydrogen pressure and the order had fallen to 0.67 at a hydrogen pressure of 55 cm.Hg. For the hydrogenation reaction in which ethylene was introduced prior to the hydrogen, the rate depended upon the hydrogen pressure to the 0.7 power.

Before considering the ethylene pressure dependence a restatement of the equations which result from the Langmuir-Hinshelwood and the Rideal mechanismswill be given. Langmuir-Hinshelwood:

$$\text{Rate} = \frac{k_2 KK' pp'}{(1 + Kp + K'p')^2}$$

where p is the ethylene pressure and p' the hydrogen pressure.
Rideal:

$$\text{Rate} = \frac{kK' pp'}{1 + Kp + K'p'}$$

The rate in the Langmuir-Hinshelwood expression passes through a maximum as the ethylene pressure is increased. In the Rideal expression the rate reaches an upper limit as the ethylene pressure is increased but the rate can never have a negative order with respect to the ethylene pressure.

For the ethylene hydrogenation reactions with simultaneous introduction of ethylene and hydrogen to the nickel film, at high ethylene pressures the rate was -0.6 order in ethylene with an indication of zero order at low ethylene pressures. At high initial ethylene pressures and with simultaneous addition of ethylene and hydrogen to a film, it is expected that the hydrogen atom concentration on the surface will be small. Under these conditions the rate of reaction must be due primarily to the Langmuir-Hinshelwood mechanism and thus the order in ethylene is negative. However at low initial ethylene pressures the hydrogen is in excess and a greater contribution by the Rideal mechanism is expected. Therefore the approach to zero order in ethylene at low ethylene pressures may be due to a greater contribution to the rate by the Rideal mechanism or to the approach to the maximum in the Langmuir-Hinshelwood mechanism.

The rate of ethylene hydrogenation with the addition of the ethylene to the nickel film prior to the hydrogen addition was dependent upon the -0.4 power of the ethylene pressures at 32.3°C and upon the -0.2 power at 80°C. The more positive ethylene pressure order of -0.2 obtained at 80°C is due to ethylene being less strongly chemisorbed at higher temperatures, and therefore having a smaller inhibiting effect. In this case the Langmuir-Hinshelwood mechanism is initially the primary contributor.

TIME COURSE STUDIES ON NICKEL FILMS

The time course study for run number 31.31, Figure 14, showed that the reaction was initially first order, which was due to the fact that the ethylene was in large excess over the hydrogen and thus did not change significantly throughout the course of the reaction. The ethylene could be considered to be roughly constant so that the time course would show only the first order dependence on hydrogen. When both ethylene and hydrogen were introduced simultaneously in equal proportions as in run number 31.32, Figure 17, the time course shows a 0.67 order dependence which is roughly the sum of a hydrogen pressure dependence of 1.0 and a negative ethylene pressure dependence of 0.6. The time course was initially zero when the hydrogen was in large excess over ethylene as in runs number 31.37, Figure 15, and 29.28, Figure 16. Since the hydrogen was in excess over the ethylene, the concentration of hydrogen atoms on the surface will be large and the Rideal mechanism is expected to make the major contribution to the reaction rate initially. The initial order will be zero since the hydrogen pressure can be considered to be roughly constant. As the reaction proceeds the hydrogen atoms will be displaced from the surface by ethylene molecules and the Langmuir-Hinshelwood mechanism will begin to make a larger contribution. The rapid change in order is probably due to the change in mechanism. It is expected that towards the end of the reaction when the ethylene has been largely depleted the mechanism would revert again to the Rideal type. Since there are so many variable factors involved it is difficult to fit a theoretical rate expression to the experimental curve. The Langmuir-Hinshelwood mechanism, the Rideal mechanism, the rate of displacement of hydrogen atoms on the surface by ethylene molecules, and the rate of depletion of the reactants must all be considered when attempting to write a theoretical rate expression.

The time course plot for the ethylene hydrogenation in which ethylene was added to the nickel film first and at a pressure equal to the hydrogen pressure, run number 32.8, Figure 18, was 0.67 order which is approximately the sum of a first order hydrogen dependence and a -0.4 order ethylene dependence.

Since a negative ethylene pressure dependence is necessary to explain the experimental results obtained for the ethylene hydrogenation catalyzed by a nickel film, the Langmuir-Hinshelwood mechanism must be the most important mechanism taking part in a reaction when the ethylene is introduced prior to the hydrogen or when ethylene is in excess over hydrogen.

In run number 31.41, Figure 19, the hydrogen was in excess over the ethylene and introduced to the film prior to the ethylene. This reaction probably takes place to a great extent through the Rideal mechanism, and the order of 0.8 found is in keeping with this assumption. This is the hydrogen pressure order with a zero order ethylene dependence.

PRESSURE DEPENDENCIES ON IRON FILMS

The ethylene hydrogenation reaction rate with the prior addition of ethylene catalyzed by iron films was dependent on the ethylene pressure to the -0.6 power at 32.3°C and to the -0.22 power at 80°C. Once again the more positive order at higher temperatures is due to the fact that ethylene is more weakly chemisorbed as the temperature is raised. These negative ethylene pressure orders are compatible only with the Langmuir-Hinshelwood mechanism. For the same reaction the hydrogen pressure dependence was 0.87 order at 32.3°C and 0.7 order at 80°C.

TIME COURSE STUDIES ON IRON FILMS

In run number 39.5, Figure 25, the hydrogen was introduced to the reaction vessel prior to the ethylene and the time course order was 0.94 which is compatible with the Rideal mechanism.

When ethylene is introduced to the film prior to the hydrogen and in approximately equal amount, as in runs number 41.6, Figure 26, and 39.4, Figure 27, the reaction should take place primarily by the Langmuir-Hinshelwood mechanism. The time course orders which are 0.48 and 0.57 respectively confirm this assumption since these orders are approximately the sum of first order in hydrogen and -0.6 order in ethylene.

However in runs number 39.18, Figure 28 and 41.8, Figure 29, the ethylene was introduced to the film prior to the hydrogen and the reaction was initially primarily Langmuir-Hinshelwood with time course orders of 0.19 and 0.29 which are approximately the sum of a first order hydrogen dependence and a -0.6 order ethylene dependence. But since in both these runs the hydrogen was in excess, as the ethylene is depleted the mechanism will change over to Rideal and this change over will explain the change over from 0.19 order to 0.85 order for run number 39.18 and from 0.29 order to 0.78 order for run number 41.8.

The results found in this research confirm the presence of a hydrogenation of ethylene reaction taking place by both the Langmuir-Hinshelwood and the Rideal mechanisms. The conditions of the reaction will determine which mechanism makes a greater contribution to the reaction rate. The Langmuir-Hinshelwood mechanism is the principal one when the ethylene is introduced to the film prior to the hydrogen if the ethylene pressure is not much smaller than the hydrogen pressure, or when the ethylene and the hydrogen are introduced simultaneously to the film with the ethylene in excess. The Rideal mechanism is the primary mechanism when hydrogen is in excess over ethylene or when hydrogen is introduced to the film prior to the ethylene. All intermediate conditions will result in simultaneous reactions, one going by the Rideal mechanism, and the other by the Langmuir-Hinshelwood mechanism.

ABSOLUTE RATE CALCULATIONS

The initial reaction rate as calculated by absolute rate theory is in satisfactory agreement with the experimental rate. The expression for the maximum rate of hydrogenation by either the Rideal or the Langmuir-Hinshelwood mechanisms is the same and is

$$v_{max.} = 1/2 \quad L \, c_g^! \frac{kT}{h} \, \frac{1}{F_g^!} \, e^{-\epsilon_o/kT}$$

where L is the total number of sites per cm.^{2} of surface area, $c_g^!$ is the concentration of hydrogen molecules in the gas phase, $F_g^!$ is the partition function for gaseous hydrogen, and ϵ_o is the activation energy. From hydrogen chemisorption studies the area of the nickel films was approximately 4000 cm.^{2} For run number 36.1 the hydrogen pressure was 5.7 cm.Hg and the activation energy was 7.7 kcal. per mole. The partition function for hydrogen at 32.3°C is 5.7×10^{24} as calculated from data in the National Bureau of Standards Tables (83). L is taken as 10^{15} sites per cm.^{2} of nickel surface. Thus

$$v_{cal.} = 4.6 \times 10^{14} \text{ molecules per second per square cm.}$$

The experimental value of the rate is

$$v_{exp.} = 10.9 \times 10^{14} \text{ molecules per second per square cm.}$$

The agreement is very satisfactory.

CONCLUSION

The conclusions reached in this research explain why in the past there has been so much controversy over which of the two mechanisms is correct. In the past different workers have found different ethylene pressure dependencies and it is now concluded that some must have been working under conditions where the reaction proceeds primarily by the Rideal mechanism and others must have been working under conditions where the reaction proceeds primarily by the Langmuir-Hinshelwood mechanism.

CLAIMS TO ORIGINAL RESEARCH

1. The catalyzed ethylene hydrogenation has been studied using apparatus which gives a continuous record of the rate of the reaction.

2. The ethylene hydrogenation reaction catalyzed by nickel has been studied using three methods of reactant introduction.

3. The ethylene and hydrogen pressure ranges have been extended up to 50 cm.Hg for the catalyzed ethylene hydrogenation.

4. Time course studies have been made for the nickel catalyzed ethylene hydrogenation.

5. On the basis of these studies conclusions have been drawn about the reaction mechanisms under different conditions.

6. The ethylene hydrogenation reaction catalyzed by iron films has been studied from the point of view of activation energy, reactant pressure dependencies, and time course.

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