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THE CATALYTIC EXCHANGE REACTION OF METHANE WITH DEUTERIUM

by

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A thesis submitted to the School of Graduate Studies in partial fulfillment of the requirements for the degree of Ph. D. in the Department of Chemical Engineering.

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ABSTRACT

The kinetics of the catalytic exchange of methane with deuterium over the silica supported nickel, copper and bimetallic nickel-copper powdered catalysts (20 wt % metal loading) was investigated in a static constant volume system at several temperatures for initial deuterium to methane reactant ratios between 0.4 and 2.6.

The orders of reaction with respect to deuterium and methane, the apparent activation energies, and the frequency factors for the various processes of the exchange reaction were determined. The chances of finding a bare site were determined.

The hydrocarbon equilibrium compositions and the equilibrium constants for the exchange reaction with an initial reactant ratio of one were determined.

The activity pattern of the silica supported nickel-copper catalysts showed a maximum at about 20% Cu-80% Ni on silica catalyst. All of the catalysts were highly selective for the stepwise exchange. The most prominent product in the initial stages of the exchange reaction was CH_3D.

A satisfactory compensation effect seems to exist for the methane deuterium exchange reaction over the silica supported catalysts investigated. A possible reaction mechanism has been postulated to explain the formation of different deuterated methanes.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

a	order with respect to deuterium for the initial rate of formation of CH_3D
$a_{j,m}$	constants dependent on the individual component cracking pattern, $C_{m,j}$ and the sensitivity, S_j
A	frequency factor in the Arrhenius equation
A_ϕ	frequency factor for appearance of deuterium in the hydrocarbon, no of D atoms entering 100 methane molecules per min. per gm. catalyst
A_o	frequency factor for the disappearance of methane, % per min. per gm. catalyst
A_s	frequency factor for the formation of CH_3D, % per min. per gm. catalyst
A_m	frequency factor for multiple exchange, % per min. per gm. catalyst
b	order with respect to methane for the initial rate of formation of CH_3D
c	order with respect to deuterium for the total initial rate of production of CH_2D_2, CHD_3 and CD_4
$C_{m,j}$	cracking pattern of jth component at mass m
d	order with respect to methane for the total initial rate of production of CH_2D_2, CHD_3, and CD_4

E	activation energy, kcal/mole
E_ϕ	activation energy for the appearance of deuterium in the hydrocarbon, kcal/mole
E_o	activation energy for the disappearance of methane, kcal/mole
E_s	activation energy for the formation of CH_3D, kcal/mole
E_m	activation energy for multiple exchange, kcal/mole
k	rate constant for CD_4 formation
k_ϕ	rate constant for the appearance of deuterium in the hydrocarbon, no of D atoms entering 100 molecules of hydrocarbon (CH_4) in unit time (min.)
k_o	rate constant for the disappearance of light hydrocarbon (CH_4), % per unit time, %/min.
$\bar{k}_\phi$, k'_ϕ	specific rate constants for the appearance of deuterium in hydrocarbon, no. of D atoms entering 100 methane molecules per min. per gm. catalyst at 160.0°C and no. of D atoms entering 100 methane molecules per min. per gm. metal at 160.0°C respectively.
$\bar{k}_o$, k'_o	specific rate constants for the disappearance of methane, % per min. per gm. catalyst at 160.0°C and % per min. per gm. metal at 160.0 °C respectively
K	equilibrium constant for the reaction of methane with metal

K_i	equilibrium constants for the hydrocarbon interconversion equilibria shown in Eqn. (1)
m	mass m
m	order with respect to deuterium for the initial rate of disappèarance of methane
M	molecular weight
M	a catalyst atom site
M	ratio of two rate constants, k_ϕ/k_o
n	order with respect to methane for the initial rate of disappearance of methane
P_j	partial pressure of jth component in the sample, torr
P_{CH_4} , P_M	initial pressure of methane, torr
P_D, P_{D_2}	initial pressure of deuterium, torr
P_m	mixture peak height in the mass spectrum at mass m
r_{CD_4}	rate of CD_4 formation
R	universal gas constant, 1.987 cal/mole°K
R_o	initial rate of disappearance of methane, %/min., torr/min.
R_s	initial rate of CH_3D formation, %/min., torr/min.
R_m	total initial rate of production of CH_2D_2 , CHD_3 and CD_4, %/min., torr/min.
$\overline{R}_s$, R'_s	specific rate constants for the formation of CH_3D , % per min. per gm. catalyst at 160.0°C and % per min. per gm. metal at 160.0°C respectively.

$\overline{R}_m$, R'_m	specific rate constants for multiple exchange, % per min. per gm. catalyst at 160.0°C and % per min. per gm. metal at 160.0°C respectively
S_j	sensitivity of jth component referred to the base peak of this component, div./torr
t	reaction time, min.
T	reaction temperature, °C, °K
x, x', x''	exponents of P_D in the expressions of θ_F , θ_F, and θ_G respectively
X_i	% of total hydrocarbon present as an isotopic species $C_nH_{m-i}D_i$ at time t
X_j	$= S_j p_j$
X_o	% of C_nH_m (CH_4) present at time t
X_∞	equilibrium value of X_o
y	molar ratio of D_2/C_nH_m
y, y', y''	exponents of P_M in the expressions of θ_F, θ_F, and θ_G respectively
θ_c	fraction of the hydrocarbon radicals adsorbed on the surface
θ_F	fraction of the surface free from adsorbed species, chances of finding a bare site on catalysts(stepwise exchange)
θ_F,	chances of finding a bare site on catalysts (multiple exchange)
θ_G	chances of finding a bare site on catalysts (disappearance of methane)

$\emptyset$	deuterium content of hydrocarbon at any stage of the reaction defined by Eqn. (3)
$\emptyset_0$	initial value of $\emptyset$
$\emptyset_\infty$	equilibrium value of $\emptyset$

I INTRODUCTION

The heterogeneous catalysts, which are solids or solid solutions, have been extensively used by various chemical industries. The activity pattern of these catalysts is of prime importance in the study of various catalytic reactions. The hydrogen isotopes have been rather extensively used since their discovery to elucidate the mechanisms of hydrogenation, hydrogenolysis and exchange reactions and to investigate the activity patterns.

In the earlier studies of the exchange reactions of the hydrocarbons with deuterium, the exchange reaction was followed by measuring the dilution of the deuterium by hydrogen by means of thermal conductivity, examining the hydrocarbons by infrared spectroscopy and determining the total deuterium in hydrocarbon by combustion. The reactions investigated were the exchange of CH_4 and CD_4 and the exchange of a wide range of hydrocarbons, CH_4, C_2H_6, C_3H_8, nC_4H_{10}, nC_6H_{14} and cyclo-C_6H_{12} with deuterium. The following three chief points were established by these early investigations:

(1) The exchange of hydrocarbons occurs much more readily than the cracking of hydrocarbons, despite the fact that C-H bonds are substantially stronger than C-C bonds.

(2) A dissociative mechanism is probably involved.

(3) The ease of exchange depends on the hydrocarbon and the

order of reactivity is roughly.

cyclo-C_6H_{12} = C_6H_{14} = C_4H_{10} > C_3H_8 > C_2H_6 > CH_4.

With the techniques available at that time, it was not possible to determine whether a single hydrogen atom is replaced by a deuterium atom or whether more extensive exchange occurs during the life time of the hydrocarbon molecule on the surface of the catalyst. This type of information became available only after the application of a mass spectrometric technique to follow the course of exchange reactions.

The reaction between methane and deuterium appears to have the advantage of simplicity over more widely used reactions, such as the formic acid decomposition or ethylene hydrogenation, in which the kinetics are often complicated by the competing side reactions and retardation by products. The catalytic exchange of methane with deuterium has been investigated over a series of evaporated metal films. The rate of this exchange reaction has been recently used to investigate the patterns of catalytic activity in binary alloys of the noble metals. These investigations revealed that the reaction mechanism may be a stepwise or a multiple exchange.

Studies on metal alloy catalysts have been of great interest for investigating the relationship between the catalytic activity and the electronic structure of metals. The activity of nickel-copper alloy catalysts for the various reactions, such as hydrogenation, hydrogenolysis, H_2-D_2

equilibrium, has been studied by several investigators and a variety of activity patterns has been observed. For the most part, alloy catalysts have been investigated in such form as films, powders, wires or plates. However, catalytic studies on supported bimetallic systems have received much less attention. In considering such systems one may pose a question:- Will the individual components exist as separate entities on the carrier, or will there be mixing of atoms of the individual metals in the form of heteroatomic groupings on the carrier surface? If the first situation applies, there would be no direct interaction between atoms of different metals and one would expect to find a simple type of additive catalytic behaviour of individual metallic entities. However, if the second situation applies, one might expect to find a different behaviour, especially if the individual metals have very different catalytic activities for the reaction of interest.

In the present study, the catalytic exchange of methane with deuterium over silica supported nickel, copper and nickel-copper bimetallic catalysts (20 wt%metal loading) was followed by a mass spectrometer in a static constant volume system at several temperatures covering a reactant ratio range of 0.4 to 2.6.

The objectives of the present investigation were:

(1) to study the kinetics of the exchange reaction and determine the pressure dependencies of various rates and

compute the apparent activation energies and the frequency factors for various exchange processes.

(2) to determine the hydrocarbon equilibrium compositions and the equilibrium constants for the hydrocarbon interconversion equilibria for the exchange reaction with an initial reactant ratio of 1.

(3) to find whether there is any relationship between

(a) the catalytic activity and the catalyst composition,

(b) the catalytic activity and the electronic structure of the catalyst,

(c) the frequency factors and the activation energies.

(4) to determine whether the reaction mechanism is stepwise exchange or multiple exchange on various catalysts investigated.

II LITERATURE SURVEY

The catalytic exchange of saturated hydrocarbons with deuterium has been investigated by several workers and has been previously reviewed by Anderson (1), Kemball (2) and Bond (3). In this chapter, attention is focussed on the catalytic exchange of methane with deuterium and the reactions over nickel-copper alloy catalysts. The literature is reviewed briefly in two sections:

(A) Exchange of methane with deuterium

(B) Reactions over nickel-copper alloy system

(A) EXCHANGE OF METHANE WITH DEUTERIUM

Morikawa et al. (4) investigated the exchange reaction of methane with deuterium, methane-d_4 and deuterium oxide on active nickel catalysts at temperatures of 138.0°C and higher. The progress of the reaction was followed by the measurements of absorption in the infrared region using a rock salt spectrometer system. The activation energy for the reaction between methane and deuterium, claculated from the rate of change of C-H bonds to C-D bonds at different temperatures, was 28 kcal/mole. In the case of the reaction between CH_4 and CD_4, the activation energy for the rate of conversion from the original CH_4-CD_4 mixture to the equilibrium mixture of the five methanes was 19 kcal/mole. Parravano et al.(5)

studied the reaction between CH_4 and CD_4 over the silica alumina cracking catalysts using a mass spectrometer. The activation energy of 13 kcal/mole was calculated from the straight line plots of the logarithms of the concentrations of masses 20 and 19 as a function of the time at the two temperatures 345.0 and 385.0°C. Wright and Taylor (6) re-examined the interaction of CD_4 and CH_4 on a nickel-chromia catalyst using a mass spectrometer to identify the products of the reaction and reported first order dependence for the disappearance of CD_4 and for the appearance of CHD_3 and CH_2D_2 on the surface. The activation energy for the disappearance of CD_4 was 20.9 kcal/mole between 100.0 and 225.0°C.

In the earliest application of mass spectroscopy to exchange processes, Thompson et al. (7) found that the distribution of exchanged methanes from the reaction over a cobalt-thoria-magnesia-kieselguhr catalyst at 183.0°C after 17 hrs was as follows: 1.7% CD_4, 0.1% CHD_3, 0.0% CH_2D_2, 9% CH_3D and 8.9% CH_4.

It was Kemball (8,9) who thoroughly investigated the exchange reaction of methane with deuterium on evaporated metal films of nickel, palladium, rhodium and tungsten. On all of the catalysts, the production of all four deutero-methanes was observed in the initial stages of the reaction. Kemball (8) classified the exchange reaction into two processes: the stepwise exchange and the multiple exchange. The stepwise exchange is the one in which only a single hydrogen atom is replaced by a deuterium atom in each methane molecule and this process is recognized by the formation of

CH_3D. In the multiple exchange, more than one deuterium atom is introduced into the methane molecule on each interaction on the methane molecule with the catalyst. This process is recognized by the formation of highly deuterated species (CH_2D_2, CHD_3 and CD_4) in the initial stages. The detailed discussion of the classification of the exchange reactions is given in section C of Chapter IV. Over Ni films, the compound CD_4 was the most abundant product in the initial reaction (8). The pressure dependencies of the above mentioned two processes were studied and the reaction orders, the activation energies and the frequency factors were determined. Over Ni films, while the stepwise exchange had an activation energy of 24 kcal/mole and the initial rate of CH_3D formation varied as $P_{CH_4} P_{D_2}^{-1/2}$, the multiple exchange had an activation energy of 32 kcal/mole and the total initial rate of the production of CH_2D_2, CHD_3 and CD_4 was proportional to $P_{CH_4} P_{D_2}^{-1}$. The reaction mechanisms for these two processes were formulated. The equilibrium constants for the interconversion equilibria of five methanes over Ni films were determined at 457 and 465°C and the average values of the experimentally determined equilibrium constants compared well with both the classical values and those determined from quantum mechanical considerations. Mc Kee and Norton (12) have reported the final concentrations after 24 hours for the exchange reaction of methane with deuterium over Pt-Ru alloys. The equilibrium constants calculated from their data showed wide variations and were not in agreement with the classical

values. While the theoretical discussion of the hydrocarbon interconversion equilibria and the equilibrium constants is presented in chapter IV, the experimental findings of the present investigation are discussed in chapter VI.

Laidler et al. (10) have carried out Absolute Rate calculations for the reaction over nickel films, based on the mechanisms outlined by Kemball (8) and have obtained very good agreement with the observed rates by using a value of activation energy of 24.0 kcal/mole for the stepwise exchange and of 33.0 kcal/mole for the multiple exchange. Miyahara (11) has also offered a theoretical discussion of this reaction and suggested that the experimental results of Kemball (8,9) can be satisfactorily interpreted by assuming a single reaction scheme rather than a dual type of mechanism as proposed by Kemball.

Mc Kee and Norton (12-14) have investigated the exchange reaction of methane with deuterium on unsupported platinum, ruthenium, palladium, rhodium, and a series of various binary alloys of these metals. In the platinum-ruthenium series, they observed that the platinum rich alloys were more active than the pure ruthenium and the specific activity of the alloys reached a maximum in the neighbourhood of 10-25% ruthenium. All platinum containing alloys showed a predominance of the stepwise exchange whereas the multiple exchange occurred more readily on pure ruthenium. In the platinum-palladium and the palladium-rhodium alloy series, the stepwise exchange was exhibited by both platinum and palladium. Rhodium showed predominantly the multiple exchange. While

the specific activity of the alloys at 150.0°C decreased with increasing palladium content in both platinum-palladium and palladium-rhodium alloy series, the order of activity of the pure metals followed the sequence Pt > Rh > Pd. In the case of the platinum-rhodium alloy series, it was found that the stepwise exchange occurred on all the alloy catalysts at lower temperatures and the contribution from the multiple exchange increased with increasing temperatures. The specific activity of the alloys reached a maximum at a composition of 60-70 wt % rhodium. Mc Kee (15,16) also investigated the same reaction over a series of unsupported palladium-ruthenium and palladium-gold alloy catalysts. In the palladium-ruthenium series, it was found that the catalysts were homogeneous powders upto a composition of 21 wt% ruthenium. Ruthenium showed a greater tendency to promote the multiple exchange than palladium and the stepwise exchange was predominant over the binary alloy catalysts at lower temperatures. The specific activity of the alloy catalysts showed a pronounced maximum at a composition of about 40 wt% ruthenium and the activation energy fell to a minimum value at this point. In the case of the palladium-gold alloy series, it was observed that the stepwise exchange was the dominant mechanism in every case and while the specific activity of the alloys at 100.0°C showed a small maximum at a composition of about 10 atom % gold, increasing gold concentrations rapidly decreased the exchange rate which

concentrations rapidly decreased the exchange rate which became immeasurably small at about 60 atom % gold. The apparent activation energy for the over all exchange varied between 14 and 23 kcal/mole and showed a shallow minimum at about 20 atom % gold. From this investigation of methane deuterium exchange reaction over various unsupported binary noble metal alloy series, Mc Kee and Norton concluded that the study of the kinetics of the methane deuterium exchange provided a convenient method of investigating the variations in the catalytic activity in alloy systems and the maximum activity for these series was found at alloy compositions corresponding to one unpaired d-electron per metal atom.

Frennet and his co-workers (17-20) studied the chemisorption of methane and the exchange of methane with deuterium in a flow reactor on a series of metal films of rhodium, molybdenum, and rhenium, and obtained some results on tungsten, nickel, tantalum, silver and copper. It was observed that the exchange of methane with deuterium occurs only on those metals in the high temperature range where the chemisorption of methane is accompanied by H_2 evolution. The chemisorption of methane over these films was classified into two categories (a) simple chemisorption-low temperature range and (b) chemisorption with H_2 evolution-high temperature range. These two temperature ranges are separated by the temperature of the appearance of H_2, T_{H_2}, at which,

after one hour, one detects 1% of H_2 in the gaseous methane when latter reacts with the film at a pressure of $2x10^{-2}$ torr. These metals were classified in three groups: (1) no chemisorption occurs on Cu films upto 680.0°C and on Ag films upto 400.0°C in the 10^{-2} torr pressure range and no exchange is measurable; (2) on Mo, W, Ni, Ta and Re, the variation of the catalytic activity is related to the modifications of the surface states with time; (3) on Rh, a quantitative relation between the catalytic activity and the hydrocarbon surface content was developed. On Rh films, CD_4 was the most abundant product formed in the initial stages of the reaction. A mechanism in which the formation of deutero-methanes is constituted by the displacement step was proposed and a rate expression for the formation of CD_4 was developed,

$$r_{CD_4} = kP_{D_2}\theta_C$$

where θ_C is the fraction of the surface covered by the hydrocarbon radicals and is equal to

$$\theta_C = K\,(P_{CH_4}/P_{D_2}^2)\,/\,(1 + K\,(P_{CH_4}/P_{D_2}^2))$$

K is the equilibrium constant for the reaction of methane with the metal. While at low coverages in the hydrocarbon radicals ($1 \gg K\,(P_{CH_4}/P_{D_2}^2)$) the rate expression is $r_{CD_4} = kKP_{CH_4}P_{D_2}^{-1}$, at high coverages ($\theta_C \cong 1$) the rate of formation of CD_4 is directly proportional to the deuterium pressure. This type of pressure dependencies were experimentally observed on Rh film.

While investigating the reaction of saturated hydrocarbons with deuterium over nickel films, Anderson and Macdonald (21)

observed that in the case of exchange of methane with deuterium over (111) and (110) films, the distribution of products did not depend significantly on the film structure and in all cases CH_3D and CD_4 were the main initial products. The reaction had an activation energy of 43 kcal/mole for the total exchange over (111) surface.

In a recent review Kemball (22) points out the structure, stability and role of the hydrocarbon intermediates on the catalyst surface during the exchange reaction. The intermediate for the stepwise exchange of methane is the adsorbed methyl radical CX_3 which is formed by the dissociation of the methane molecule. The multiple exchange of methane is more complex producing CD_4 as the main product and CH_2D_2 and CHD_3 as minor products. This reaction must involve two types of intermediates on the surface, the adsorbed methylene radical CX_2 and probably CX or C (X represents H or D). Of these three types of adsorbed intermediates, while CX_3 is comparatively stable, the other two are relatively more reactive.

Cece and Gonzalez (23) studied the methane deuterium exchange reaction over a series of silica supported nickel catalysts. Measurable rates were observed in the temperature range 220.0-250.0°C on impregnated catalysts which varied from 2 to 50% nickel by weight. The important observations were that (i) the multiple exchange increased with increasing temperature and increasing crystallite size and (ii) while the energy of activation for the stepwise exchange increased from

12 to 27 kcal/mole with increasing crystallite size, the corresponding increase in the activation energy for the multiple exchange was from 20 to 33 kcal/mole.

Sagert and Pouteau (24) investigated the reaction of methane with deuterium over various silica supported platinum catalysts and found that while the particle size had no great effect on the specific activity, the multiple exchange was greater with the smaller particles.

In the exchange of methane with deuterium oxide over finely divided nickel, Metcalfe and Vickers (25) suggested that the exchange reaction proceeds by two distinct mechanisms; by a single atom exchange over clean nickel surfaces and by exchange of two atoms over the surface contaminated by oxygen.

This concludes the review of the literature related to the exchange reaction of methane.

(B) THE REACTIONS OVER NICKEL-COPPER ALLOY SYSTEM

A wide variety of reactions has been investigated over nickel-copper alloys by several workers and the literature pertaining to this subject is briefly reviewed in the following two sections:

(1) The exchange reactions over nickel-copper alloys

(2) Other reactions over nickel-copper alloys.

(1) THE EXCHANGE REACTIONS OVER NICKEL-COPPER ALLOYS

Zhavoronkova et al. (26) studied the catalytic activity of copper-nickel alloy films for the exchange reaction of

deuterium with hydrogen. The activity pattern was temperature dependent and at 20.0°C, the activity exponentially decreased with increased copper content of the alloy.

Byrne et al. (27,28) investigated the rates of equilibration of H_2-D_2 on Cu-Ni alloy films and observed 'broken' Arrhenius plots at several alloy compositions. The activity pattern was similar to that observed by Zhavoronkova (26).

Takasu and Yamashina (29) thoroughly examined the catalytic exchange of hydrogen with deuterium on copper-nickel alloy plates after various surface treatments and found that the catalytic activity pattern at 100.0°C was dependent on the surface treatments of the catalysts. Without any surface treatment, the activity was greatest on pure nickel, decreased gradually as the copper content in the alloys increased and virtually vanished in the alloys containing copper more than 70%. After hydrogen treatment, however, the activity of pure nickel decreased while the catalytic activity appeared in the range of copper rich compositions. The activity of each alloy sample was observed to be extremely enhanced by a slight surface treatment of oxidation-reduction. The activity of the 85% Cu alloy after oxidation-reduction treatment was greatest, one hundred times that of pure nickel. Annealing for a short time in an ultra high vacuum subsequent to oxidation-reduction treatment caused the catalytic activity to decrease abruptly at a critical temperature (425.0°C) and the

activity values were nearly the same regardless of the alloy composition. The nature of active sites on copper-nickel alloys based on the electron microscopic observations and the measurement of the surface roughness changed by the pre-treatments was discussed. The activity for the same reaction on clean surfaces of copper-nickel alloys prepared by argon ion-beam bombardment in an ultra high vacuum apparatus was also studied (30). The surface alloy compositions were determined by means of Auger electron spectroscopy. The activity over these catalysts decreased with the increased copper content.

The catalytic exchange reaction between cyclopentane and deuterium on evaporated nickel-copper alloy films was investigated by Mc Mahon et al. (31) and also by Ponec and Sachtler (32). On all catalysts both groups observed self poisoning of the catalysts. The catalytic effect of alloying was most pronounced on hydrogenolysis and self poisoning, but was rather small with respect to the multiple exchange. It was believed that the doubly bonded surface intermediates $\alpha\alpha\beta\beta$ and $\alpha\alpha\beta\beta\gamma\gamma$, which are strongly adsorbed, are responsible for the self poisoning and the appearance of the even numbered deuteriocyclopentane exchange products.

Ponec et al. (33) investigated the exchange reaction of methylcyclopentane with deuterium on nickel and nickel-copper films and found that Ni film was more active than Ni-Cu films which showed almost constant activity irrespective of Cu content.

(2) OTHER REACTIONS OVER NICKEL-COPPER ALLOYS

The hydrogenation reaction of various hydrocarbons has been extensively studied on nickel-copper alloys which were films, powders or granular catalysts and this has been reviewed thoroughly by Shah (34) and Khulbe (35). The observed activity pattern on nickel-copper alloys has been recently discussed by Mass and Whalley (36). A few other reactions which has been investigated over nickel-copper alloys are briefly reviewed in the following paragraphs.

Sinfelt et al. (37) investigated the hydrogenolysis of ethane to methane and the dehydrogenation of cyclohexane to benzene over a series of copper-nickel alloy powders. The effect of the addition of copper to nickel was very different for the two reactions examined. In the case of the ethane hydrogenolysis, the catalytic activity decreased markedly and continuously with the addition of copper to nickel over the whole range of alloy composition, although much of the activity decline was observed on the addition of first few percent of copper. With cyclohexane dehydrogenation, however, the catalytic activity increased initially with the addition of small amounts of copper to nickel, and then remained insensitive to the alloy composition over a wide range, finally decreased sharply at compositions approaching pure copper. It was concluded that the effects of alloying are clearly very specific to the nature of the reaction.

Hall et al. (38) studied the exchange of deuterium gas with the hydrogen associated with nickel-copper solid catalysts and found that the alloys, but not the pure metals, take up much more hydrogen than their monolayer capacities. While the affinities of the sintered catalysts for hydrogen decreased sharply, the fraction of reversibly held hydrogen on unsintered catalysts increased with increasing nickel content.

In a recent publication Sachtler and Van Der Plank (39) pointed out the role of individual surface atoms in chemisorption and catalysis by nickel-copper alloys and concluded that the chemisorption and catalysis are not determined by the collective properties of the catalyst such as the filling of its d-band but by the chemical properties of its individual surface atoms and the nickel content of the alloy surface can be determined by ' titration ' with chemisorbing hydrogen.

Recently Burton et al. (40) developed a theory for the equilibrium segregation of one component of a binary alloy to its surface and Burton and Hyman (41) have successfully shown the application of this theory to the experimental data obtained by Sinfelt et al. (37) on the hydrogenolysis of ethane to methane over a series of copper-nickel alloys.

Soma-Noto and Sachtler (42) obtained the infrared spectra of carbon monoxide adsorbed on silica supported nickel-copper alloys and found that ratio of the absorbance between the high and low frequency bands assigned to CO adsorbed on nickel atoms increased strongly with increasing copper content in the

alloy but became constant for the alloys above 20% Cu. The adsorbed amount of CO per alloy surface area showed a constant value on alloys with less than 90% Ni. This result suggested that these alloys have a constant composition of the surface. Most of the alloys showed the segregation in two phases.

Takasu and Shimizu (43) investigated the changes in the surface composition of copper-nickel alloy plates with various pre-treatments by means of Auger electron spectroscopy and found that the surface composition was considerably changed from the bulk alloy samples by the pre-treatments, namely the surfaces of the nickel rich alloys were enriched with copper, while those of the copper rich were with nickel. They compared the relations between the activity patterns on nickel-copper alloys observed by several workers and the pre-treatments of the catalysts and classified the observed activity patterns on nickel-copper alloys into 3 types: α_1, α_2 and β. The α_1 type signifies the pattern for which the activity is governed by the nickel content or it obeys the Dowden's forecast (44). The α_2 type has a nearly constant activity region over a wide range of composition, while the β type has a maximum activity in the alloy composition range. From the comparison, they have estimated the original activity pattern of nickel-copper alloy catalysts.

This concludes the literature survey. Most of the investigations of the methane deuterium exchange reaction were carried out over metallic films, unsupported binary noble

metal alloys and silica supported nickel and platinum catalysts. Although very interesting results have been obtained on nickel-copper alloys, very little work is reported on silica supported nickel-copper alloys. So this project was undertaken with the intention of investigating in detail the kinetics of the methane deuterium exchange reaction over a series of silica supported nickel-copper catalysts (20 wt% metal loading).

III EXPERIMENTAL DETAILS

(A) APPARATUS

The experiments were carried out in a constant volume static standard high vacuum system. The schematic diagram of the apparatus is shown in Fig. 1. The following five sections essentially constituted the entire apparatus.

(1) Deuterium Section

This section consisted of a deuterium cylinder, supplied by Matheson Company of Canada Ltd., connected to a cylindrical vessel, which was surrounded by an electrical furnace and contained palladium asbestos catalyst. The cylindrical vessel in turn was connected to a 5-litre deuterium reservoir via a liquid nitrogen trap. This same section was used during the reduction of a catalyst when a hydrogen cylinder supplied by Linde Company, was connected in place of a deuterium cylinder and a 5-litre reservoir was isolated.

(2) Methane Section

This section consisted of a methane cylinder, supplied by Matheson Company of Canada Ltd., connected to the two 3-litre methane reservoirs via a 3 way stopcock. This same section, without the reservoirs, was used during the calibration of the

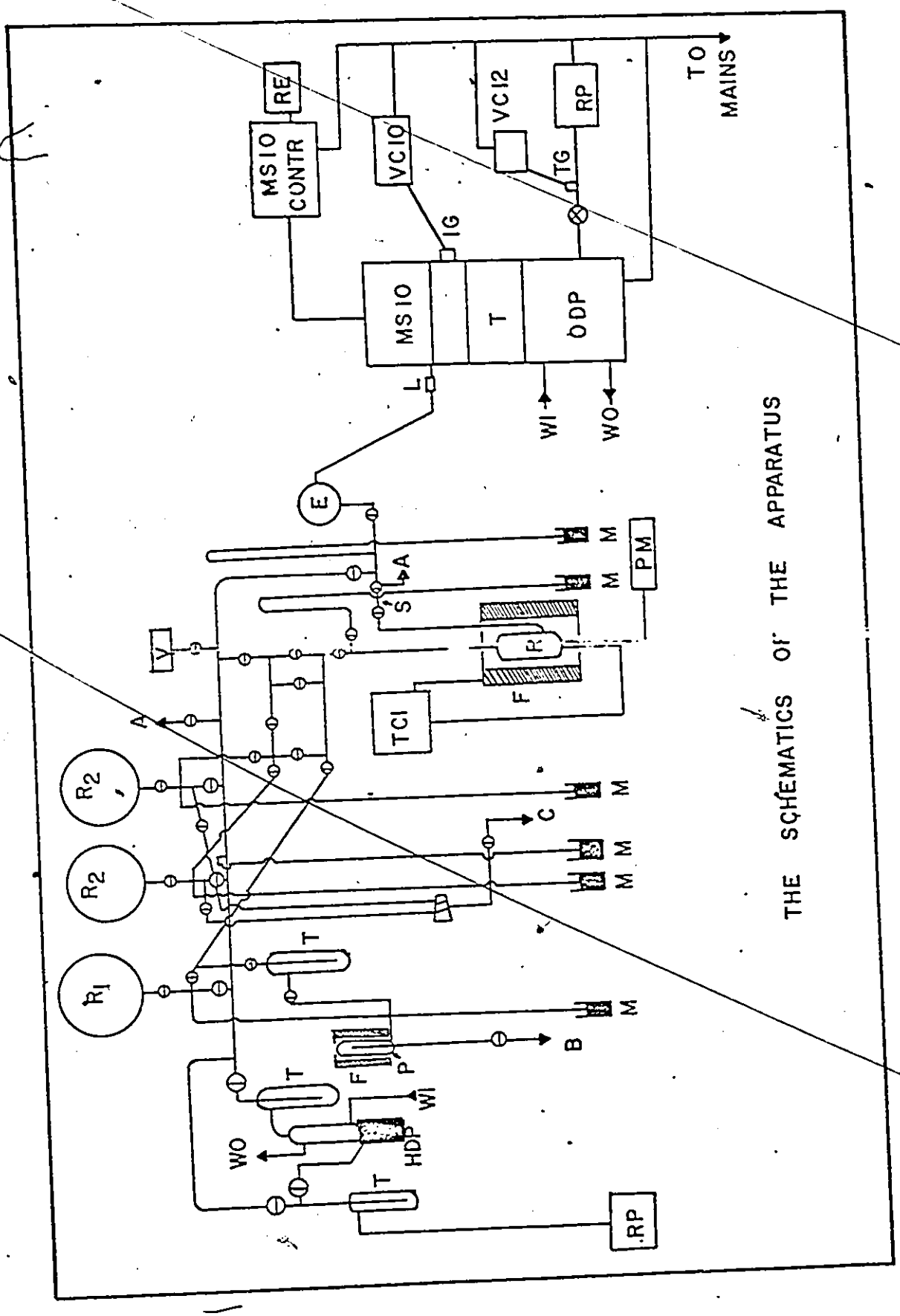

THE SCHEMATICS OF THE APPARATUS
R1
R2
R2'
T
F
P
HDP
WO
WI
RP
A
B
C
M
TCI
R
S
V
E
L
MS10
T
ODP
IG
VC10
VC12
TG
RP
TO MAINS
MS10 CONTR
RE
PM

Fig. 1

LEGEND To Fig. 1

A	to atmosphere
B	connected to deuterium cylinder
C	connected to methane cylinder
E	sample expansion reservoir
F	furnace
HDP	mercury diffusion pump
IG	ion gauge
L	molecular leak
M	mercury manometer
MS 10	mass spectrometer
MS 10 CONTR	mass spectrometer control unit
P	palladium-asbestos thimble
PM	potentiometer
R	reactor
RE	recorder
RP	vacuum pump
R_1	deuterium reservoir
R_2	methane reservoir
S	sample loop
T	liquid nitrogen trap
TC1	temperature controller
TG	thermocouple gauge
V	vacustat
VC 10	ion gauge control unit
VC 12	thermocouple gauge control unit
W1	cooling water flow in
WO	cooling water flow out
ODP	oil diffusion pump

MS10 mass spectrometer with the deuterated methanes.

(3) Reactor Section

This section consisted of a pyrex cylindrical reactor (capacity about 60 ml.) connected through the pyrex tubes and stopcocks to deuterium, methane, and product analysis sections. The reactor was connected to a mercury manometer which facilitated the measurement of the amount of reactants charged. The reactor was surrounded by a furnace which was heated by the nichrome wires wrapped on the outside of the lower section of a ceramic tube. The reactor temperature was controlled by the Honeywell temperature controller (Model 127350A) coupled with a variac and actuated by the chromel alumel thermocouple (Type K) placed inside the furnace near the wall of the reactor. The temperature of the catalyst lying at the bottom of the reactor was measured by placing the iron-constantan thermocouple (Type J) at the bottom of the reactor. The thermocouple in turn was connected to the Honeywell potentiometer (Model 2745) which facilitated the measurement of the temperature.

(4) Product Analysis Section

This section consisted of a small sample loop,S, connected to the reactor and also connected to the sample expansion reservoir,E, which inturn was connected to the sample inlet system of the MS10 mass spectrometer. This section was connected to the high vacuum system which facilitated the evacuation. The high vacuum pumping system of the MS10 mass spectrometer con-

sisted of a cold trap, an oil diffusion pump and a vacuum pump as shown in Fig.1. The schematic arrangement of the MS10 mass spectrometer shown in Fig.2 is self explanatory. The output spectrum was recorded on the Beckmann potentiometric recorder.

(5) High Vacuum System

The main high vacuum system consisted of a Duo-seal vacuum pump, a mercury diffusion pump and two liquid nitrogen traps, before and after the mercury diffusion pump, connected to all the above mentioned four sections. The vacuum was measured by a Vacustat (Model 2G).

(B) PURIFICATION OF THE REACTANTS

(1) Deuterium

The C. P. grade deuterium gas of 99.5% (atom) min. purity was further purified by passing it slowly through a palladium thimble (kept at 200.0-230.0°C). The palladium asbestos catalyst converted the traces of oxygen into water vapour. The deuterium gas was then dried by passing it through a liquid nitrogen trap which removed the water vapour and the condensible impurities. The purified deuterium gas was subsequently stored in the previously evacuated 5-litre reservoir.

(2) Methanes

The Research Grade methane of purity 99.99 mol.% was filled up into the two previously evacuated reservoirs with-

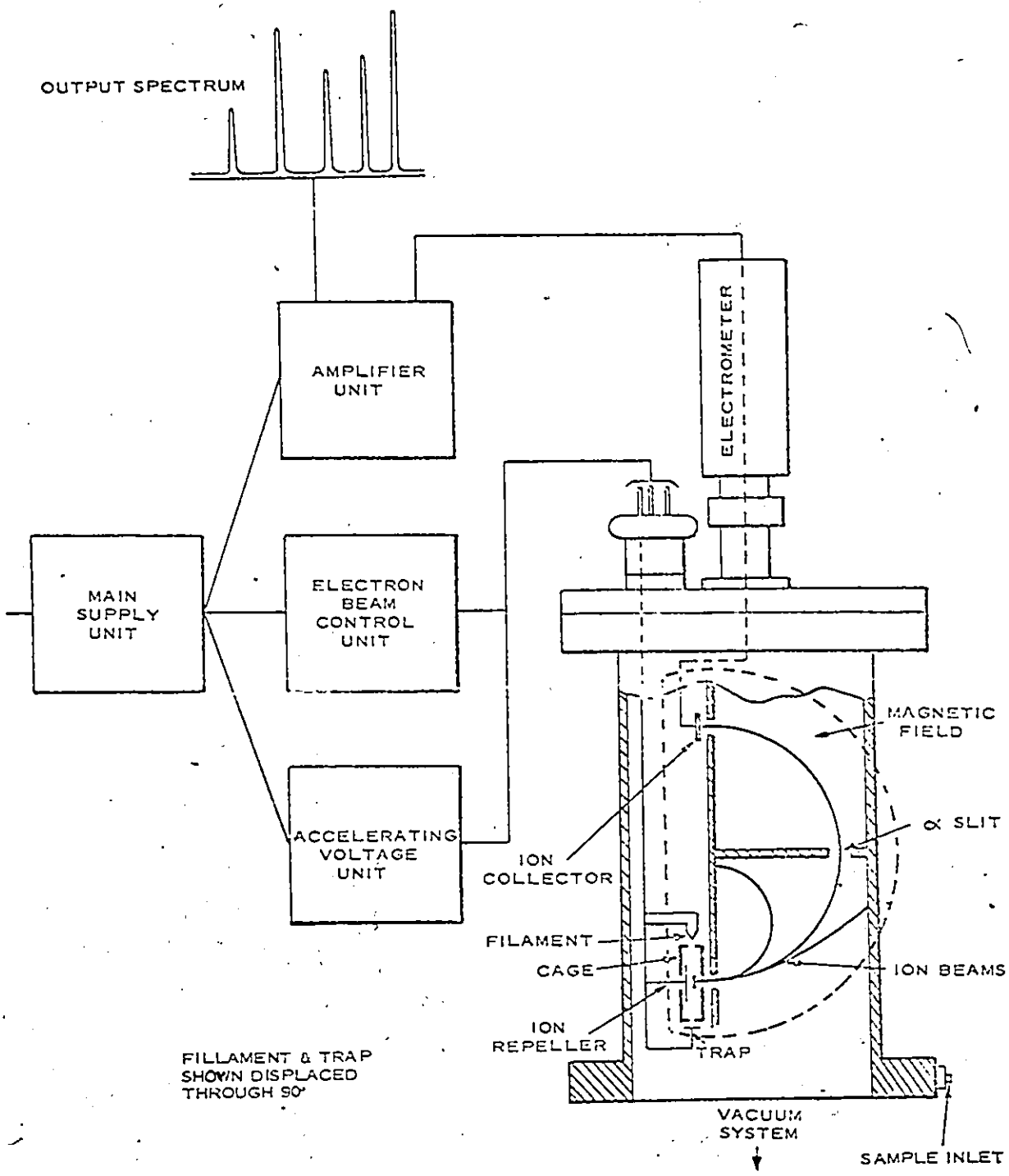


FIG. 2 SCHEMATIC ARRANGEMENT OF THE MS10 MASS SPECTROMETER

out further purification.

The deuterated methanes, CH_3D, CH_2D_2, CHD_3 and CD_4, supplied by Merck, Sharp and Dohme Canada Ltd., used for the calibration purpose had minimum isotopic purity of 98 atom% D and were used as such without further purification.

(C) PREPARATION OF THE CATALYSTS

The silica supported nickel, copper, and nickel-copper alloy catalysts (20 wt.% metal loading) were prepared in the following manner. Known amounts, equivalent to 1 gm. metal, of analytical reagent grade $Ni(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$ or both in appropriate ratios, were dissolved in 100-150 ml. acetone. The 4 gm. of Cab-O-Sil (Grade EH5), obtained from Cabot Corp., Boston, a high purity amorphous silica, was impregnated with acetone solution of nitrates. The Cab-O-Sil - nitrate mixture was stirred regularly and dried at room temperature. The resultant dried catalysts were ground and stored until further use.

(D) REDUCTION AND STABILIZATION OF THE CATALYST

The reactor containing the known amount of the catalyst was evacuated until the high vacuum was achieved. The stream of purified hydrogen at the rate of 80 ml. per minute was started through the reactor. The reactor temperature was raised slowly and stepwise such that it reached 400.0°C in 5-6 hrs. The catalyst reduction was continued at 400.0°C for 24 hrs. At the end of the reduction, the flow of hydrogen was stopped, the reactor was evacuated, filled with about

150-200 torr of deuterium, and subsequently cooled to room temperature.

The catalyst was stabilized by conducting several experiments with a fixed initial deuterium to methane ratio at a particular temperature, where measurable exchange occurred, until during the course of two consecutive experiments there was no change in the catalytic activity shown by the constant mass spectrum for the same time interval. Usually four to five experiments were sufficient to stabilize the catalysts. All of the catalysts were active and the activity remained fairly stable over a period of few months.

(E) EXPERIMENTAL PROCEDURE

The experimental technique consisted of evacuating the reactor system when the desired experimental temperature was maintained constant. The required quantity of deuterium was admitted to the reactor and the common interconnecting lines were evacuated. Then the desired amount of methane was introduced and the course of reaction was followed by analyzing the reaction products mass spectrometrically. After a certain time interval, the reaction mixture was transferred to the previously evacuated sample loop. The remaining mixture was evacuated. The sample was then expanded into the 1 litre reservoir which was previously evacuated, admitted to the MS10 mass spectrometer and the mass spectrum was recorded. The same procedure was followed and the reaction products were analyzed at different time intervals for the same initial deuterium to

methane ratio. In this manner several data points were obtained for the course of the exchange reaction for a fixed deuterium to methane ratio. Several experiments were conducted for different initial deuterium to methane ratios and at different temperatures. In all experiments deuterium was always admitted first unless specified otherwise. At the end of the series of experiments, the catalyst was always left in the atmosphere of deuterium. Attempts to study the kinetics by introducing methane first to the reactor followed by deuterium, were not successful.

The single point experimental measurements were carried out to follow the kinetics of the exchange reaction for the following reasons:

(i) In the continuous monitoring of the experiment, the spectral peaks are recorded at certain time intervals but since it takes about 2-3 minutes to record the mass spectrum from mass 14 to mass 20, at the end of analysis (i.e., after 2-3 min.), the peak height at mass 14 must have changed since it was recorded. And the time correction for each peak has to be applied in order to get an accurate analysis of the product composition. In the single point experiments, the analysis at each point gives the correct product composition and the time correction is not required.

(ii) In the semi-continuous monitoring of one reaction mixture, the small samples are collected at different time intervals in the small sample loop, expanded and introduced into the mass spectrometer. This method was found to be

adequate for the slow reactions. The rates determined by this method compared well with the single point experimental determination at low conversion. However, when the exchange rates were higher at high temperatures, the samples had to be analysed at short time intervals in order to obtain the product compositions in the initial stages. And, since it required 10-15 minutes to evacuate the sample reservoir and 2-3 minutes to record a background spectrum, this semi-continuous method of following the exchange experiment was found to be inadequate.

The mass transfer resistance was negligible. To confirm this, single point experiments were done with some initial mixture of the reactants and the products were analysed by introducing small samples (method as applied in present work) at different time intervals. With the same initial mixture, the reaction was followed by analysing large samples at various time intervals. The results of such experiments over 60% Cu-40% Ni on silica catalyst at 193.0°C with $P_D = P_M = 50$ torr showed that the initial rate of disappearance of methane R_o was 0.95 torr/min. with small sample measurements compared to 1.025 torr/min. with the large sample method. The difference was so small as to raise the question of significant mass transfer resistance. Further more, the deuterium is very light compared to methane and it was introduced first into the reactor. The pressure employed was of the order of 0.1 atmosphere and the temperature range was 122.0-440.0°C. Under these experimental conditions the diffusivity of

CH_4-D_2 system is so high ($\sim$6 cm^2/sec at 178.0 C and 100 torr) that these two reactants will be mixed in no time. So the assumption that the mass transfer is negligible is justified. However, if the reaction was mass transfer controlled, the deviation in the Arrhenius plots at high temperatures would have appeared. Since all the Arrhenius plots (Figs. 9-12) were good straight lines, this rules out the possibility of the significant mass transfer resistance or the mass transfer controlled reaction.

(F) MASS SPECTROMETRIC METHOD OF ANALYSIS

The technique of quantitative analysis of the multi-component hydrocarbon mixtures is well established and described in detail elsewhere (45,46). However, the general principles underlying the analysis of gaseous mixtures by mass spectrometry are briefly presented in this section.

Any gas present in the ion source of a mass spectrometer will produce a characteristic mass spectrum which is composed of different ion beams of different masses and different ion currents. The current of an ion beam is referred to as an intensity or a peak height. The relative intensities of the different ion beams depend upon the electron energy, and in the range of energies of 50-100 eV they vary only slightly with electron energy. The mass spectra are usually tabulated after normalization which makes the most intense peak in any spectrum (the so called "base peak") of height 100 units. The complete mass spectrum is referred to as a ' cracking pattern'. Each ion beam is often referred to as a 'peak'.

The sensitivity is usually either given in terms of the height of the most prominent peak per unit pressure, or the relative intensity of this peak to that of a standard compound. The intensity of the ion beam for any ion from one component is directly proportional to the partial pressure of that component in the ion source (except for the ions formed by secondary processes), and to the electron beam current, provided that proper operating conditions are established. When two or more gases are present in the ion source, each gives its own characteristic mass spectrum, and the fundamental basis of the mass spectral method of analysis is that these various mass spectra are linearly additive. The partial pressure of a given gas in the ion source is too small to measure exactly, and the intensity of the ion currents is therefore related to the pressure of the gas in the reservoir or to the sample loop pressure which is proportional to the pressure in the reactor (as in the present case). The reservoir pressure is proportional to the sample loop pressure. The usual practice is to introduce the sample for analysis from a low pressure reservoir through a molecular leak of a mass spectrometer sample inlet system, and the number of molecules of any constituent of molecular weight M passing through per second is proportional to $1/\sqrt{M}$. If the same relation applies to the pumping system which evacuates the ion source, the ratio of pressures in the ion source is equal to the ratio in the reservoir. In the general case when pumping speeds may not be

exactly proportional to $1/\sqrt{M}$, the partial pressure of any gas in the ion source is proportional to its partial pressure in the reservoir provided that the flow of the gas into and out of the ion source proceeds with a rate independent of the other gases present.

While in the case of a binary mixture only two peaks need to be measured for the analysis, the choice of peaks on which to base the analysis of the multicomponent mixtures becomes more difficult. However, for most of the mixtures of light hydrocarbons the analytical procedure is well established. The system of analysis used may be generalized, for such mixtures, for if the mixture peak height at mass m is given by P_m, then

$$P_m = \sum C_{m,j} S_j p_j = \sum C_{m,j} X_j$$

Where C_{mj} is the cracking pattern of the jth component at mass m, S_j is the sensitivity of the detection of the jth component referred to the base peak of this component, and p_j is the partial pressure of jth component in the sample. To find the values of p_j in an n-component mixture from the known values of C_{mj} and S_j, it is necessary to choose n peaks for the measurements of P_m.

In the present investigation of the exchange of methane with deuterium, only the compositions of methanes were required to be determined. The base peaks at mass equal to the molecular weight of the individual methanes were chosen for the purpose of analysis, and the following five simultaneous

equations were formulated.

$$P_{16} = C_{16,0}X_0 + C_{16,1}X_1 + C_{16,2}X_2 + C_{16,3}X_3 + C_{16,4}X_4$$

$$P_{17} = C_{17,0}X_0 + C_{17,1}X_1 + C_{17,2}X_2 + C_{17,3}X_3 + C_{17,4}X_4$$

$$P_{18} = C_{18,0}X_0 + C_{18,1}X_1 + C_{18,2}X_2 + C_{18,3}X_3 + C_{18,4}X_4$$

$$P_{19} = C_{19,0}X_0 + C_{19,1}X_1 + C_{19,2}X_2 + C_{19,3}X_3 + C_{19,4}X_4$$

$$P_{20} = C_{20,0}X_0 + C_{20,1}X_1 + C_{20,2}X_2 + C_{20,3}X_3 + C_{20,4}X_4$$

The subscripts 0, 1, 2, 3, and 4 refer to components CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4 respectively. The other subscripts and symbols have the same meaning as mentioned in the preceding paragraph.

The cracking patterns $C_{m,j}$ and the sensitivities were determined by direct calibration of individual methanes over a wide range of pressures. These calibration experiments were carried out with exactly the same conditions in the ion source as those prevailing during the analysis of the reaction products. The cracking patterns and the sensitivities thus determined are given in Appendix I. Using the calibration data, the above mentioned equations were rearranged so as to express the partial pressures of the individual components in terms of the mixture peak heights observed in the mass spectrum. The rearranged equations are:

$$P_0 = a_{0,16}P_{16} + a_{0,17}P_{17} + a_{0,18}P_{18} + a_{0,19}P_{19} + a_{0,20}P_{20}$$

$$P_1 = a_{1,16}P_{16} + a_{1,17}P_{17} + a_{1,18}P_{18} + a_{1,19}P_{19} + a_{1,20}P_{20}$$

$$P_2 = a_{2,16}P_{16} + a_{2,17}P_{17} + a_{2,18}P_{18} + a_{2,19}P_{19} + a_{2,20}P_{20}$$

$$P_3 = a_{3,16}P_{16} + a_{3,17}P_{17} + a_{3,18}P_{18} + a_{3,19}P_{19} + a_{3,20}P_{20}$$

$$P_4 = a_{4,16}P_{16} + a_{4,17}P_{17} + a_{4,18}P_{18} + a_{4,19}P_{19} + a_{4,20}P_{20}$$

and these can be expressed in the generalized form as $P_j = \sum a_{j,m}P_m$ where $a_{j,m}$s are constants and solely dependent on the individual component cracking pattern, the sensitivity, and the conditions employed in the mass spectrometer.

The computer program CP1, which was developed to solve these simultaneous equations using the mass spectrometer data and to compute the percentage compositions of the hydrocarbon products is given in Appendix I.

The actual conditions employed to obtain the calibration data and to perform the reaction product analysis were as follows. The background spectrum was always taken prior to the analysis and this was subtracted from the sample spectrum to obtain the true sample spectrum. While the mass spectrum of the sample in the mass range 14 to 20 was taken in two minutes, 10-15 minutes were required to evacuate the sample expansion reservoir before another analysis could be performed. The pressure in the ion source was in the range of 10^{-6} - 10^{-7} torr. The spectra were taken at an ionizing voltage of 70 eV, an ion repeller voltage of 1v, a trap current of 50 μA and an amplifier range factor of 250. The recorder chart speed was one inch per minute. The calibration data,

obtained by taking the samples at room temperature, were independent of the temperature and these were frequently checked. The mass spectrometer analyzer tube was baked, after removing the magnet and disconnecting the electronics, for 20-24 hrs after completion of the study over any one catalyst and also when the contribution from the background spectrum was significantly increased. The liquid nitrogen cold trap was replenished twice (morning and evening) except while baking. The operation, the baking and the trouble shooting of the mass spectrometer were carried out according to the procedures outlined in the instruction manual of the MS10 mass spectrometer.

PRECISION OF THE MASS SPECTROMETRIC DETERMINATIONS

With the procedures adopted in the calibrations of the five methanes and the limitations of the MS10 mass spectrometer, the amplifier and the recorder, the sensitivies of the five methanes, (S_j) were determined within $\pm$ 0.03 and the maximum deviations in the relative intensities ($C_{m,j}$) were less than 6%. The individual component concentrations were determined within $\pm$ 5% accuracy. It was not possible to prepare a synthetic mixture of the five methanes to check the accuracy of the final analysis. Typical analyses of the synthetic binary mixtures were as follows:

Mixture as taken	Mixture as analysed	Difference
42.85% CH_4-57.15% CH_3D	39.60% CH_4-60.40% CH_3D	± 3.25
45.22% CHD_3-54.78% CH_2D_2	42.93% CHD_3-57.07% CH_2D_2	± 2.29

Since no analyses were done for the compositions of H_2, D_2 and HD, it was not possible to do a complete mass balance calculations.

IV THEORETICAL ASPECTS OF EXCHANGE REACTIONS

The theory of exchange reactions is well established and discussed elsewhere (2,3,9,47). In this chapter, attention is focussed on the methods of interpretation of experimental data which are relevant to the study of exchange reactions and on the ways in which these may be classified.

(A) THE FINAL EQUILIBRIUM OF AN EXCHANGE REACTION

Consider the reaction between a light hydrocarbon, C_nH_m and D_2. As a result of the exchange reaction, two kinds of equilibria will be established. There will firstly be an equilibrium distribution between the total amount of deuterium in the "hydrocarbon" and the total amount of deuterium in the "hydrogen". Secondly, the relative amounts of the different isotopic species of hydrocarbon will be in equilibrium, and the same will apply to the different isotopic species of the hydrogen. In other words, the following interconversion equilibria for the hydrocarbon will be established,

$$C_nH_m + C_nH_{m-2}D_2 \rightleftharpoons 2C_nH_{m-1}D \qquad (K_1)$$

$$C_nH_{m-1}D + C_nH_{m-3}D_3 \rightleftharpoons 2C_nH_{m-2}D_2 \qquad (K_2)$$

$$- - - - - - - - - - - - - - - - - - \qquad (1)$$

$$C_nH_2D_{m-2} + C_nD_m \rightleftharpoons 2C_nHD_{m-1} \qquad (K_{m-1})$$

In those cases where equilibrium constants for reactions of this type have been measured for hydrocarbons, it is found that the values obtained for the equilibrium constants are fairly close to the values expected for a random or classical distribution of the hydrogen or deuterium atoms between the various isotopic species of the hydrocarbon. This approximation does not apply to the interconversion equilibria between the three isotopic species of "hydrogen," i.e., H_2, HD, and D_2, except at high temperatures because of the effect of the high relative changes in weight as H is replaced by D on the partition functions of the molecules. Likewise, the distribution of the deuterium between the "hydrocarbon" and the "hydrogen" usually differs slightly from the value expected in terms of a random distribution.

The values of the equilibrium constants for the reactions shown in Equation (1) calculated by classical theory correspond to combinations of terms in the appropriate binomial expansion and all the equilibrium constants are given by the general equation

$$K_i = \binom{i}{m}^2 \Big/ \left[\binom{i-1}{m}\binom{i+1}{m}\right] \qquad (2)$$

where the symbol $\binom{i}{m}$ represents the number of ways of selecting i objects from a group of m identical objects.

Kemball has experimentally measured the several equilibrium constants for the deuteromethanes (8), deuteroethanes (49), and deuteropropanes (48) and found that they compared

well with those calculated by Equation (2).

(B) THE RATE CONSTANTS OF AN EXCHANGE REACTION

The course of an exchange reaction may be followed either by mean deuterium content of the hydrocarbon or by some parameter related to this quantity. Let X_i be the percentage of the total "hydrocarbon" present as the isotopic species $C_nH_{m-i}D_i$ at time t. If a parameter $\emptyset$ is defined by

$$\emptyset = X_1 + 2X_2 + 3X_3 + \text{--------} + mX_m \qquad (3)$$

the mean deuterium content at any stage in the reaction is given by $\emptyset/m$. Now provided that all the hydrogen atoms in the molecule are equally susceptible to exchange and provided that the influence of isotopes on the rate of reaction is negligible, the course of the exchange reaction in the initial stages is given by the first order equation, developed by Kemball (8,9),

$$d\emptyset / dt = k_\emptyset (1-\emptyset / \emptyset_\infty) \qquad (4)$$

The theoretical derivation and the validity of Equation (4) have been discussed by Kemball. Here $k_\emptyset$ is a rate constant equivalent to the number of deuterium atoms entering 100 molecules of the hydrocarbon in unit time at the start of the reaction and $\emptyset_\infty$ is the equilibrium value of $\emptyset$. Integration of Equation (4) gives

$$- \log (\emptyset_\infty - \emptyset) = k_\emptyset t/2.303\emptyset_\infty - \log (\emptyset_\infty - \emptyset_o) \qquad (5)$$

where $\emptyset_o$ is the initial value of $\emptyset$. Equations (4) and (5) are equivalent to the general rate equations for exchange kinetics due to Harris (50), and although they are only approximately true because of the assumption that all isotopic species react at the same rate, they are found to be obeyed in a great variety

of exchange reactions.

In order to get a fuller insight into the nature of any exchange reaction, it is necessary to determine a second rate constant k_o, representing the initial rate of disappearance of the light hydrocarbon C_nH_m in percentage per unit time. The disappearance of the light hydrocarbon may be represented by the empirical first-order equation,

$$-\log (X_o - X_\infty) = k_o t / 2.303 (100 - X_\infty) - \log (100 - X_\infty) \quad (6)$$

where X_o is the percentage of C_nH_m present at time t and 100 and X_∞ are the initial and final percentages of this species.

The parameter M, defined by

$$M = k_\phi / k_o \quad (7)$$

is an important quantity representing the average number of hydrogen atoms replaced by deuterium atoms in each molecule of the hydrocarbon under initial exchange conditions, and M may obviously also be evaluated from the initial product distributions themselves.

Values for ϕ_∞ and X_∞ can be easily calculated assuming that at equilibrium there is a random isotopic distribution between hydrocarbon and "hydrogen". For instance, with a mixture in which the initial molar ratio of D_2 / C_nH_m equalled y, ϕ would be given by

$$\phi_\infty = (100m \times 2y / (m + 2y)) \quad (8)$$

Gault and Kemball (51), as a matter of fact, observed that the measured values of $\emptyset_\infty$ differ appreciably from those calculated by classical statistics, with the ratio of $\emptyset_\infty$ obs / $\emptyset_\infty$ cal ranging from 1.14 to 1.28 for some lower hydrocarbons. For work of any accuracy, particularly for the use of Equation (5) at high conversions, $\emptyset_\infty$ should, if possible, be measured experimentally. While working with reaction mixtures containing a substantial excess of deuterium, typically D_2 / $C_nH_m > 5$, the value of X_∞ is so small that negligible error is introduced by using the statistically calculated rather than the experimental value: under these conditions X_∞ can often be set equal to zero without appreciable error.

The rate constants $k_\emptyset$ and k_o differ from the rate constants of an ordinary chemical reaction. They are constant only for the course of an exchange reaction with a single mixture of reacting gases, but they are dependent on pressure and assume different values if the initial pressures of the reactants are altered. The true kinetics of an exchange reaction can be determined only by means of a series of experiments with different mixture of reactants because the course of a reaction with a single mixture follows the apparent first-order Equation (5).

The kinetics of hydrocarbon exchange reactions are more complicated than those of the hydrogen equilibration reactions, in as much as two species rather than one take part; they are,

however, uncomplicated by the formation of a chemically different product. Hydrogen is more strongly adsorbed than saturated hydrocarbons, and so one expects to find positive orders up to unity for the hydrocarbons and zero or negative orders for hydrogen. The study of the kinetics of exchange reactions has focussed attention on the way in which the surface concentrations of various kinds of adsorbed species depend on the pressure of the reacting gases. Now consider a situation where the adsorption of species is weak; i.e., the extent of surface is large compared with the fraction covered by adsorbed species. Assume that the strength of adsorption is constant, which is true for small variations in surface coverages. Under these conditions and over a limited range of pressure, it can be shown that for the adsorption of mixtures of hydrocarbon and deuterium, the fraction of the surface, θ_F, free from adsorbed species may be expressed as

$$\theta_F \propto P_D^x P_{C_nH_m}^y \qquad (9)$$

(C) CLASSIFICATION

The exchange reactions are classified in the following two categories:

(1) Simple or Stepwise Exchange Reactions

In this class of exchange reaction, only a single hydrogen atom is replaced by a deuterium atom in each molecule which reacts on the surface of the catalyst. Isotopic species con-

taining two or more deuterium atoms are formed only by successive reactions. This class of reaction can be recognized in three ways:

(a) The value of M (= k_{ϕ} / k_0) will be unity.

(b) Only the monodeuterated species, $C_nH_{m-1}D$, will be observed initially.

(c) The interconversion equilibria, Equations (1) and (2), will be satisfied throughout the course of reaction, provided that the isotopic species of the hydrocarbon used as reactants are in equilibrium and provided that all hydrogen atoms in the molecule are equally susceptible to exchange.

(2) Multiple Exchange Reactions

An exchange reaction in which more than one deuterium atom is introduced into the hydrocarbon molecule on each interaction of the molecule with the catalyst is classified as a multiple exchange reaction. The existence of such a process may be recognized in three ways, exactly analogous to those described above for simple exchange reactions:

(a) The value of M will be greater than unity and will give the average number of deuterium atoms introduced to each hydrocarbon molecule reacting at the beginning of the reaction.

(b) The initial products will contain species having more than one deuterium atom; and the initial product distribution will be important as a means of deciding the type of process occurring.

(c) The distribution of isotopic species during the course of the reaction will be richer in more highly deuterated species than calculated distributions based on Equation (2).

(D) PRESENT PROJECT

In the present investigation of the exchange reaction of methane with deuterium, in addition to $k_\emptyset$ and k_0, the initial rate of formation of CH_3D, R_s, and the total initial rate of production of CH_2D_2, CHP_3 and CD_4, R_m, were also determined from the plot of the percentage of CH_3D against time and by a direct plot of the sum of percentages of CH_2D_2, CHD_3 and CD_4 against time respectively. Thus

$$R_s = d\ (\ \%\ CH_3D\ )\ /\ dt \qquad (10)$$

and

$$R_m = d\ (\%\ CH_2D_2 + \%\ CHD_3 + \%\ CD_4)\ /\ dt \qquad (11)$$

where R_s and R_m are in percent per unit time. The initial rate of disappearance of methane, R_0, was also determined from the plot of the percentage of CH_4 against time. Since any methane molecule reacted appeared as one of the four deuteromethanes,

$$k_0 = R_0 = R_s + R_m \qquad (12)$$

The various initial rates were satisfactorily expressed by the 'Power Rate Law' due to Schuit and Reijen (52) as follows,

The initial rate of disappearance of methane = $R_0 \propto P_D^m\ P_M^n$

The initial rate of formation of $CH_3D = R_s \propto P_D^a P_M^b$ (13)

and

The total initial rate of production of CH_2D_2, CHD_3 and $CD_4 = R_m \propto P_D^c P_M^d$

where P_D and P_M are the initial pressures of deuterium and methane in torr respectively, and m, a, and c, and n, b and d are the orders of reaction with respect to deuterium and methane respectively. The initial rates are in torr per unit time.

The dependence of the initial rates on the initial pressure of deuterium was studied by carrying out several experiments keeping an initial pressure of methane constant at 50 torr and varying the initial deuterium pressure (20-130 torr). From the log-log plots of the initial rates against the initial pressures of deuterium, the exponents m, a, and c were determined from the slopes. Similarly the effect of methane pressure on the initial rates was studied by varying the initial methane pressure (20-130 torr) while the initial deuterium pressure was kept constant at 50 torr and the exponents n, b, and d were determined. This procedure was always adopted for the evaluation of the exponents unless specified otherwise.

The various specific rate constants were determined from the exchange experiments conducted with an initial reactant ratio of 1 ($P_D = P_M = 50$ torr) at different temperatures. The rate constants k_ϕ and k_0 were evaluated from Equations

(5) and (6) by the application of the least square method. The computer program CP2 for the least square fit is given in Appendix I. The initial rates for the stepwise exchange, R_s, and the multiple exchange, R_m, determined from the composition-time plot for the course of exchange reaction with an initial reactant ratio of 1 ($P_D = P_M = 50$ torr) were taken as the specific rate constants.

The influence of the temperature on the specific rate constants, $k_\emptyset$, k_0, R_s and R_m, was satisfactorily expressed by the well known Arrhenius equation,

$$k = A\, e^{-(E / RT)} \qquad (14)$$

Taking logarithm,

$$\log k = \log A - E/(2.303\ RT) \qquad (15)$$

The computer program CP3 was used for the evaluation of the apparent activation energies, $E_\emptyset$, E_0, E_s and E_m, and the frequency factors, $\log A_\emptyset$, $\log A_0$, $\log A_s$ and $\log A_m$, from Equation (15) by the least square method. The computer program CP3 is given in Appendix I.

V RESULTS OF INVESTIGATION

The present investigation of the exchange reaction of methane with deuterium over silica supported nickel, copper and nickel-copper alloy catalysts consisted of studying the kinetics of the exchange reaction by analyzing the reaction products using the MSIO mass spectrometer.

The hydrocarbon equilibrium compositions for a reaction with an initial reactant ratio of 1 ($P_D = P_M = 50$ torr) were determined by analyzing the reaction products after 70 hrs. The equilibrium values, ϕ_∞ and X_∞, observed at high temperature, which showed a maximum methane conversion and a maximum value of ϕ_∞, were utilized to calculate the specific reaction rate constants k_ϕ and k_0 at all temperatures. These values of ϕ_∞ and X_∞ were dependent on the catalyst investigated.

Over all of the catalysts, the reaction mechanism was stepwise exchange and the contribution from the multiple exchange increased at high temperatures as shown by the corresponding increase in the value of M, the ratio of two rate constants.

The pressure dependencies of the various initial reaction rates were determined by studying the reaction over a wide

range of the initial reactant pressures. Thus while studying the effect of deuterium pressures, the initial methane pressure was always kept constant at 50 torr, the dependence on the initial methane pressure was investigated by maintaining the initial deuterium pressure constant at 50 torr unless specified otherwise. From these experiments the orders of reaction with respect to deuterium and methane were determined for the different processes of the exchange reaction.

The experimental results of the methane deuterium exchange reaction over the silica supported nickel, copper and nickel-copper alloy catalysts are given in Appendix II.

(A) REACTION OVER SILICA SUPPORTED NICKEL CATALYST

The experimental results of the kinetic study of the reaction of methane with deuterium over a known amount of silica supported nickel catalyst are given in Table 1.

The reaction proceeded with a measurable rate at 130.0°C after the stabilization of the catalyst at this temperature. The catalyst was stabilized by conducting several experiments with an initial reactant ratio of 1 ($P_D = P_M = 50$ torr). The product distribution, for the reaction with an equimolar mixture of the reactants ($P_D = P_M = 50$ torr), observed at 171.0°C is shown in Fig. 3A. The effects of the deuterium pressure and the methane pressure on the initial rates of disappearance of methane and of formation of CH_3D are shown in Fig. 4 and 5 respectively. The dependence of the initial

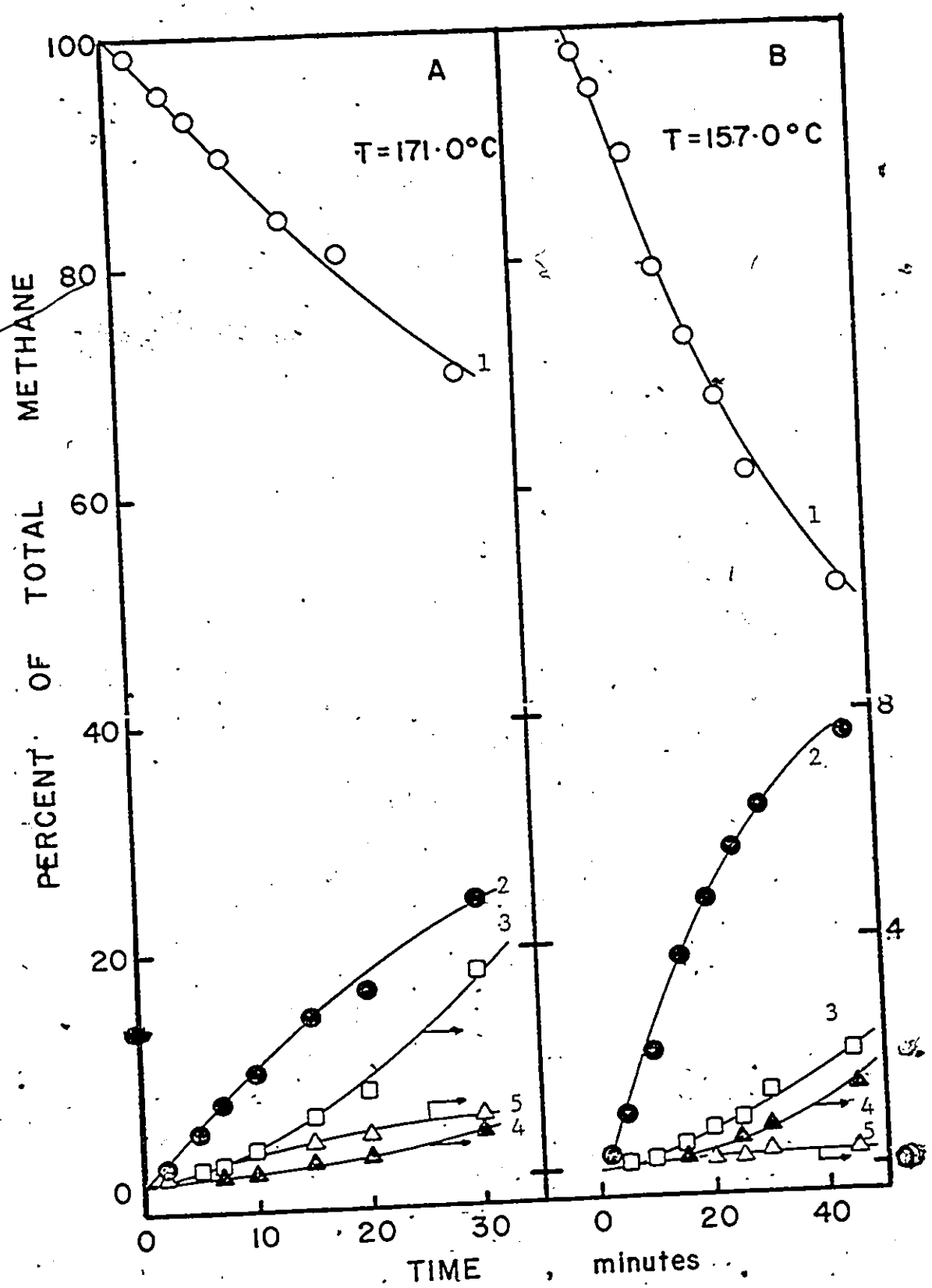


Fig. 3 The course of reaction with $P_D = P_M = 50$ torr over (A) Ni on Silica and (B) 20% Cu-80% Ni on Silica catalysts.

1. CH_4 ; 2. CH_3D ; 3. CH_2D_2 ; 4. CHD_3 ; 5. CD_4

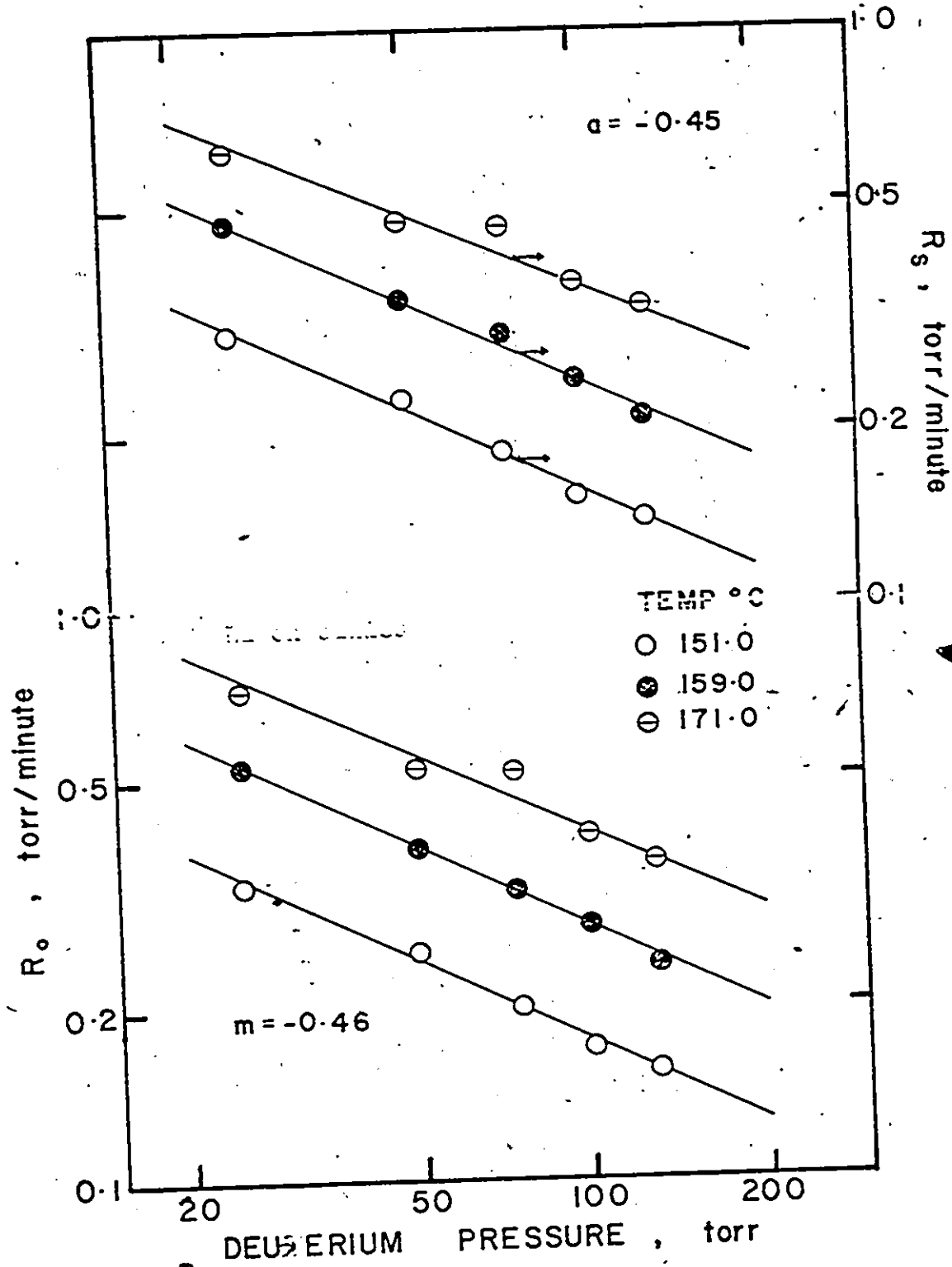


Fig. 4 The effects of the deuterium pressure on R_o and R_s (P_M = 50 torr) over Ni on silica catalyst.

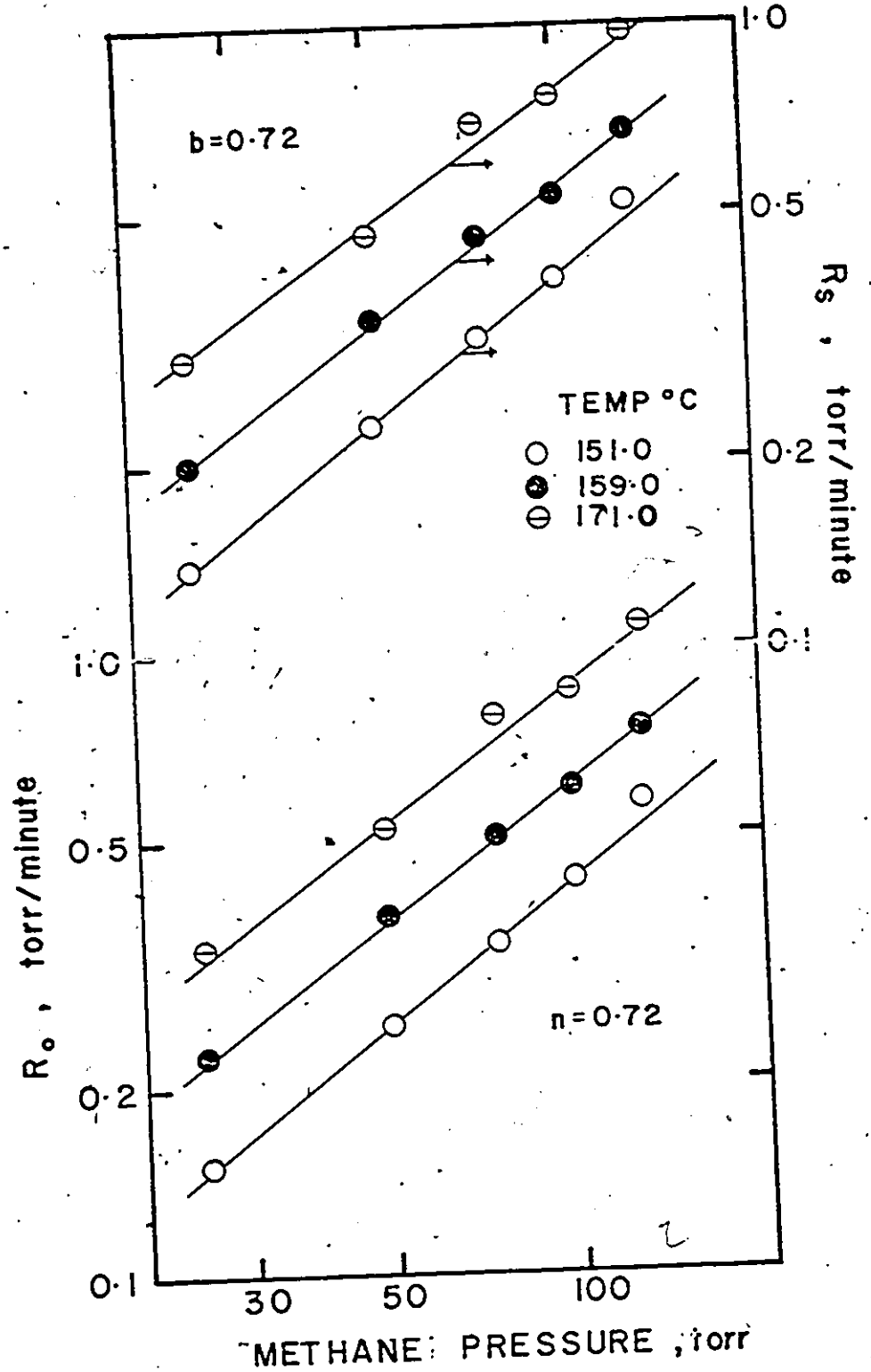


Fig. 5 The effects of the methane pressure on R_o and R_s. (P_D = 50 torr) over Ni on silica catalyst.

rate of formation of CH_2D_2, CHD_3, and CD_4 upon the initial pressures of the reactants is shown in Fig. 6. The dependence of the initial rate of the disappearance of methane at 171.0°C, upon the initial pressures of deuterium, when methane pressure is kept constant at 25 and 100 torr, and upon the initial methane pressures, when the initial deuterium pressure is kept constant at 25 and 100 torr, is shown in Fig. 7.

The compositions of the reaction products, for the exchange reaction with an equimolar mixture of reactants ($P_D = P_M = 50$ torr), after 20 and 70 hrs are given in Table 1B1. The effect of the initial pressures of the reactants on the product composition at 178.0°C after 20 hrs is shown in Table 1B2. The values ϕ_∞ and X_∞ observed at 171.0°C after 70 hrs were utilized for the computation of k_ϕ and k_0 from the plots of log ($\phi_\infty - \phi$) and log ($X_0 - X_\infty$) against time which are shown in Fig. 8.

The Arrhenius plots, showing the dependence of the various specific rate constants upon the temperature, are presented in Figures 9-12. The derived apparent activation energies for the appearance of deuterium in the hydrocarbon products E_ϕ, for the disappearance of methane, E_0, for the formation of CH_3D, E_s, and for the formation of CH_2D_2, CHD_3 and CD_4, E_m, were 17.4, 16.3, 14.5, and 21.4 kcal/mole respectively. The kinetic parameters are given in Table 1C.

(B) REACTION OVER 20% Cu - 80% Ni ON SILICA CATALYST

The experimental data observed for the exchange reaction

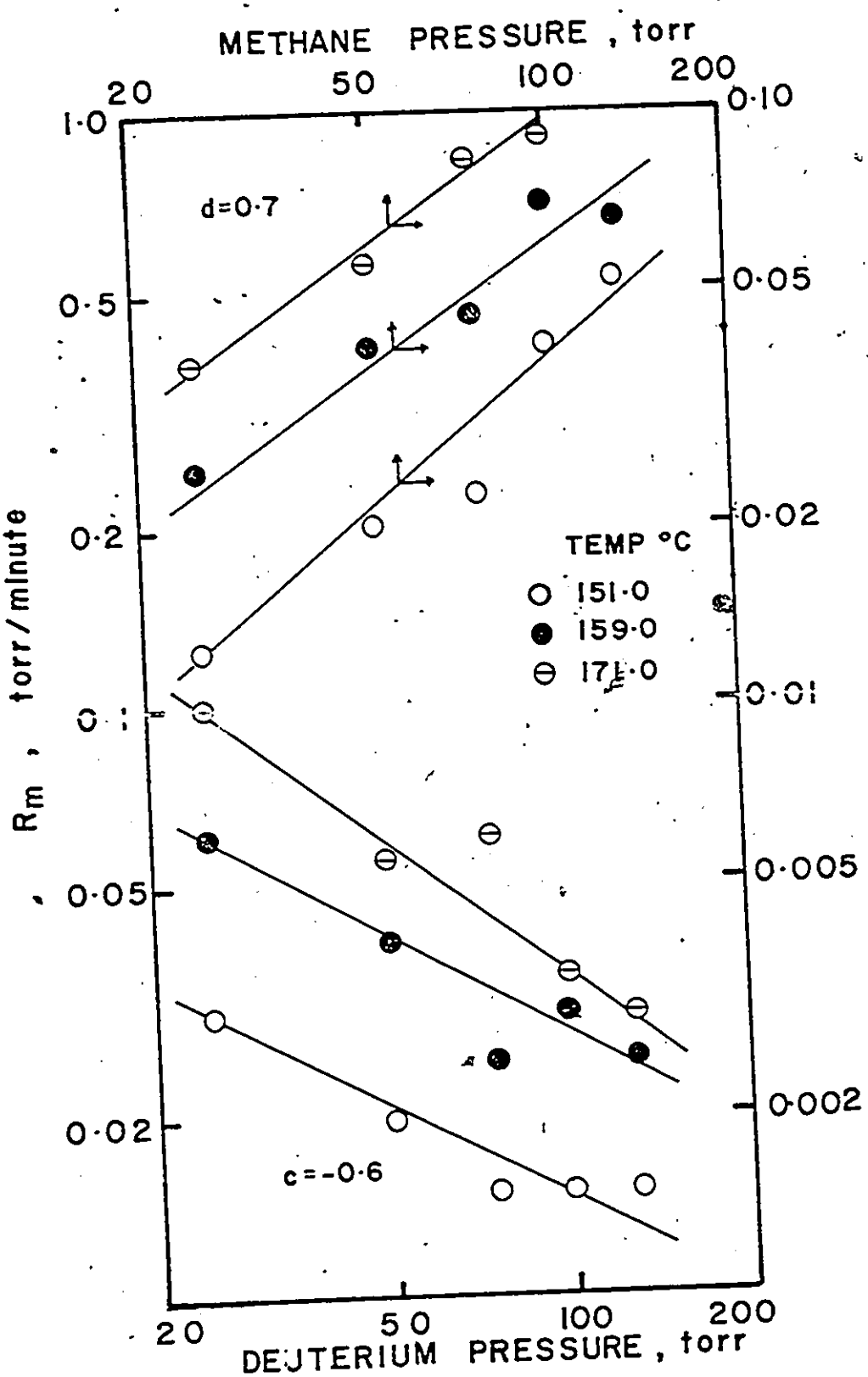


Fig. 6 The dependence of R_m upon the initial pressures of the reactants over Ni on silica catalyst.

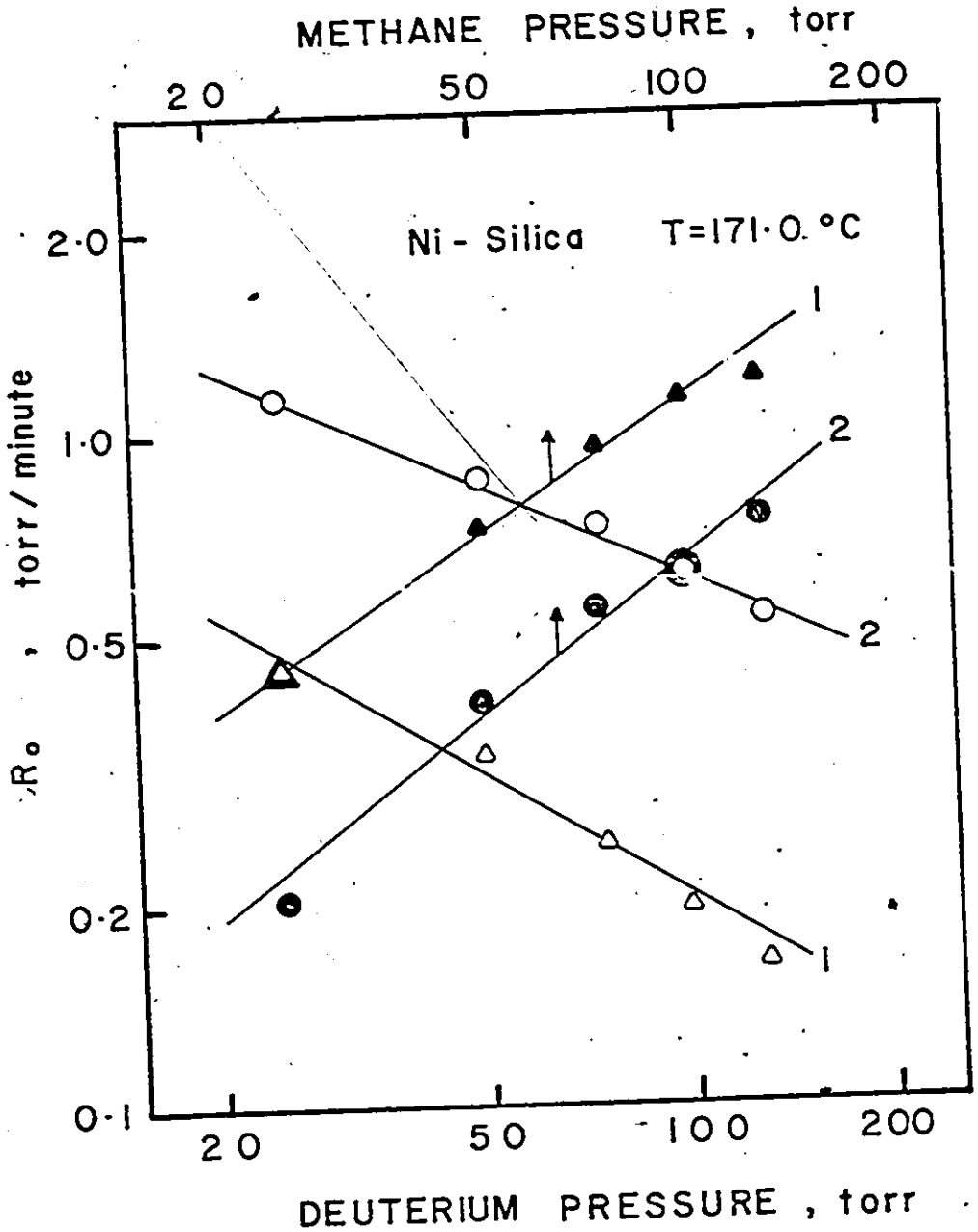


Fig. 7 The dependence of R_0 upon the initial pressures of
(a) deuterium when (1) P_M = 75 torr and (2) P_M = 100 torr
(b) methane when (1) P_D = 25 torr and (2) P_D = 100 torr

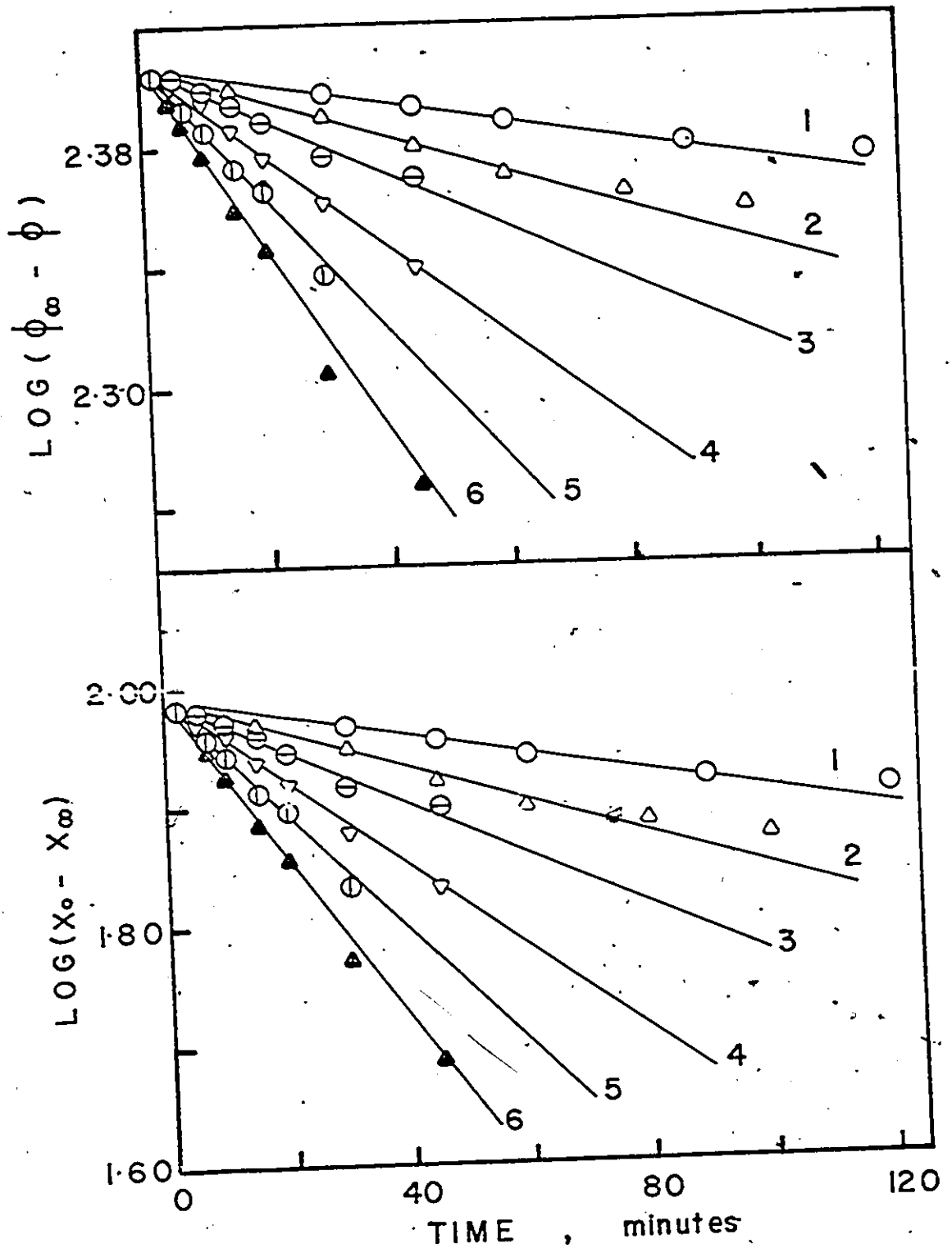


Fig. 8 The plots of log (ϕ_∞ - ϕ) and log (X_0-X_∞) against time at (1) 130.0°C, (2) 140.0°C, (3) 151.0°C, (4) 159.0°C, (5) 171.0°C, and (6) 178.0°C over Ni on silica catalyst.

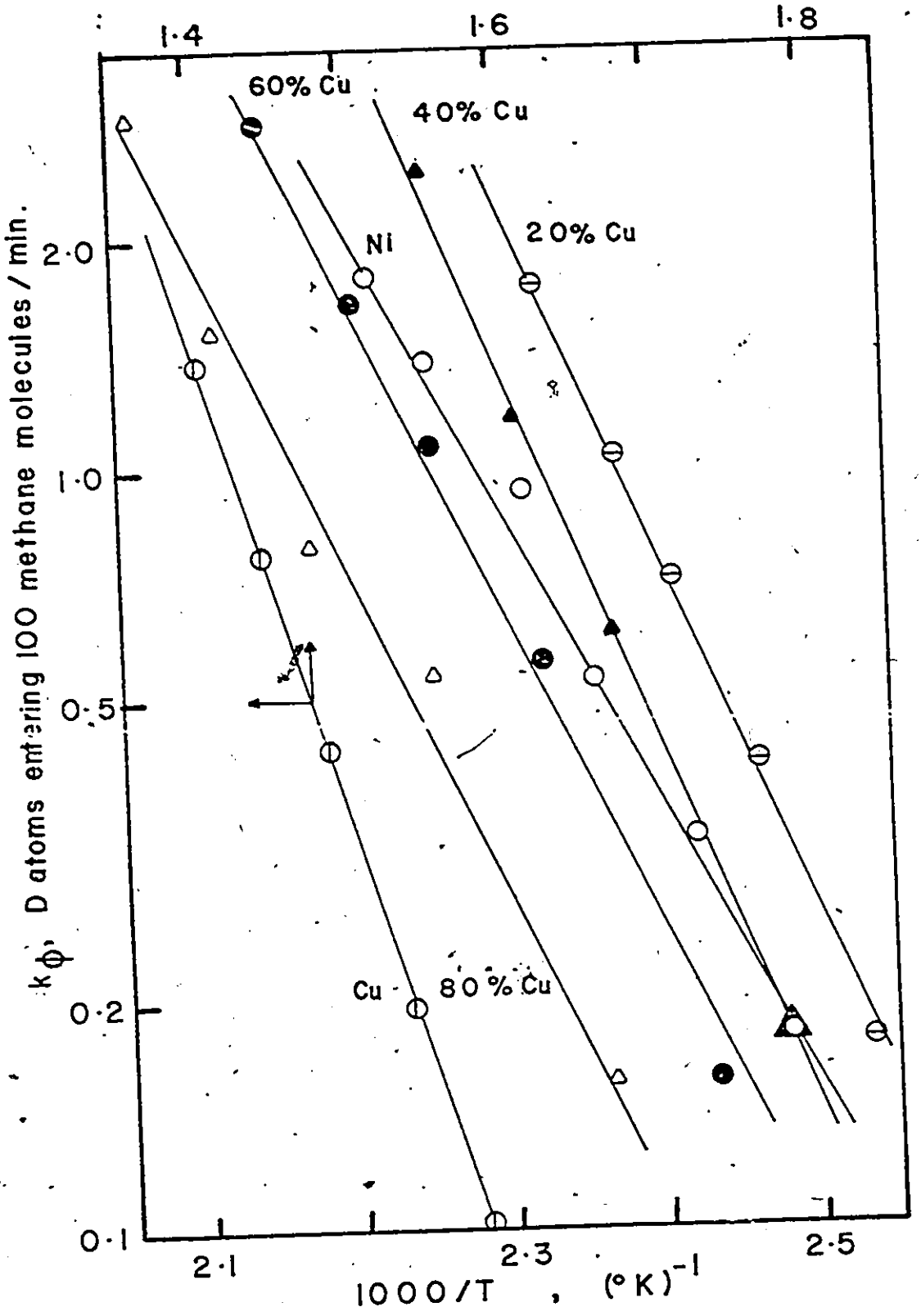


Fig. 9 The dependence of k_{ϕ} upon the temperature.

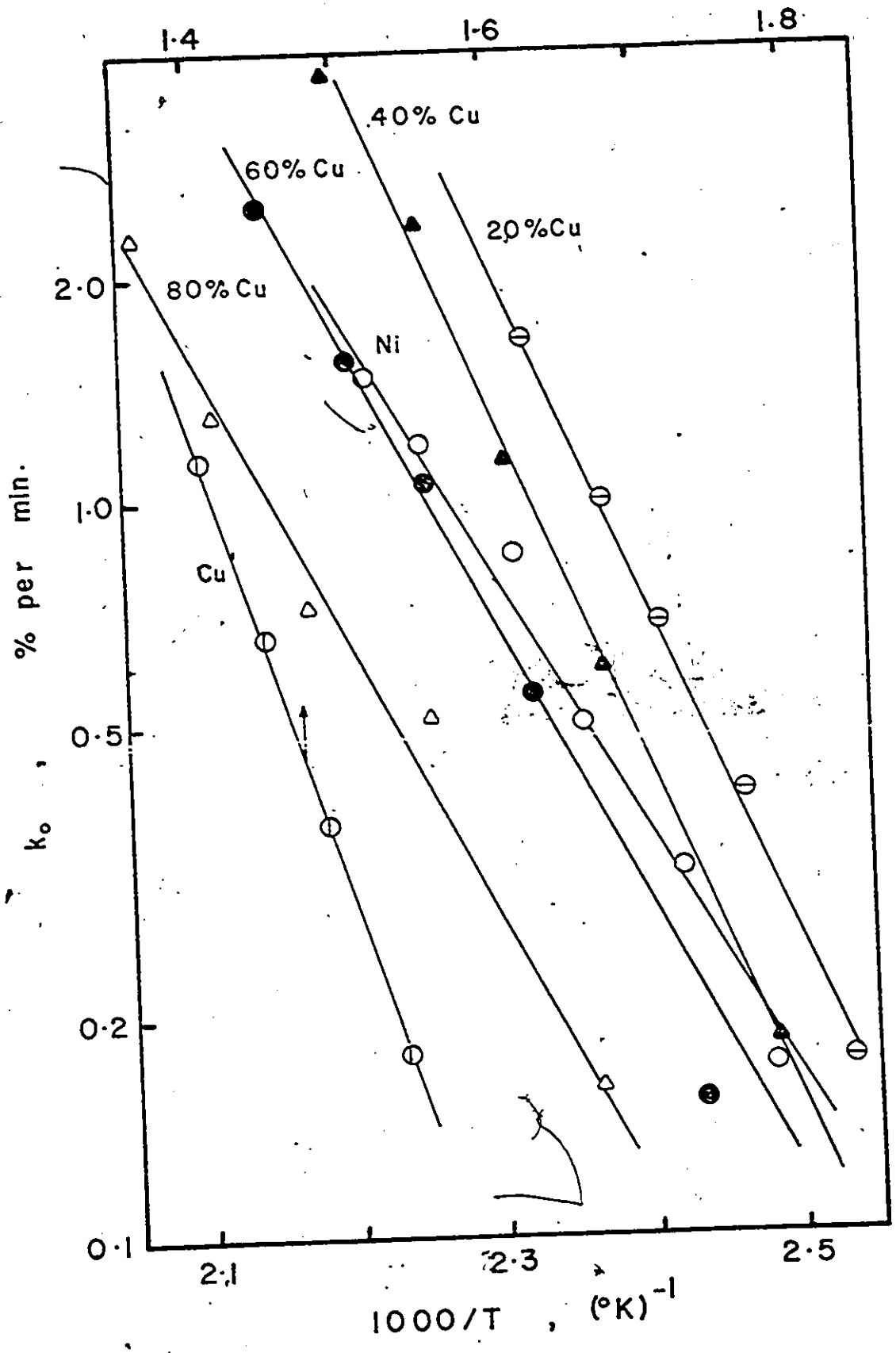


Fig. 10 The dependence of k_0 upon the temperature.

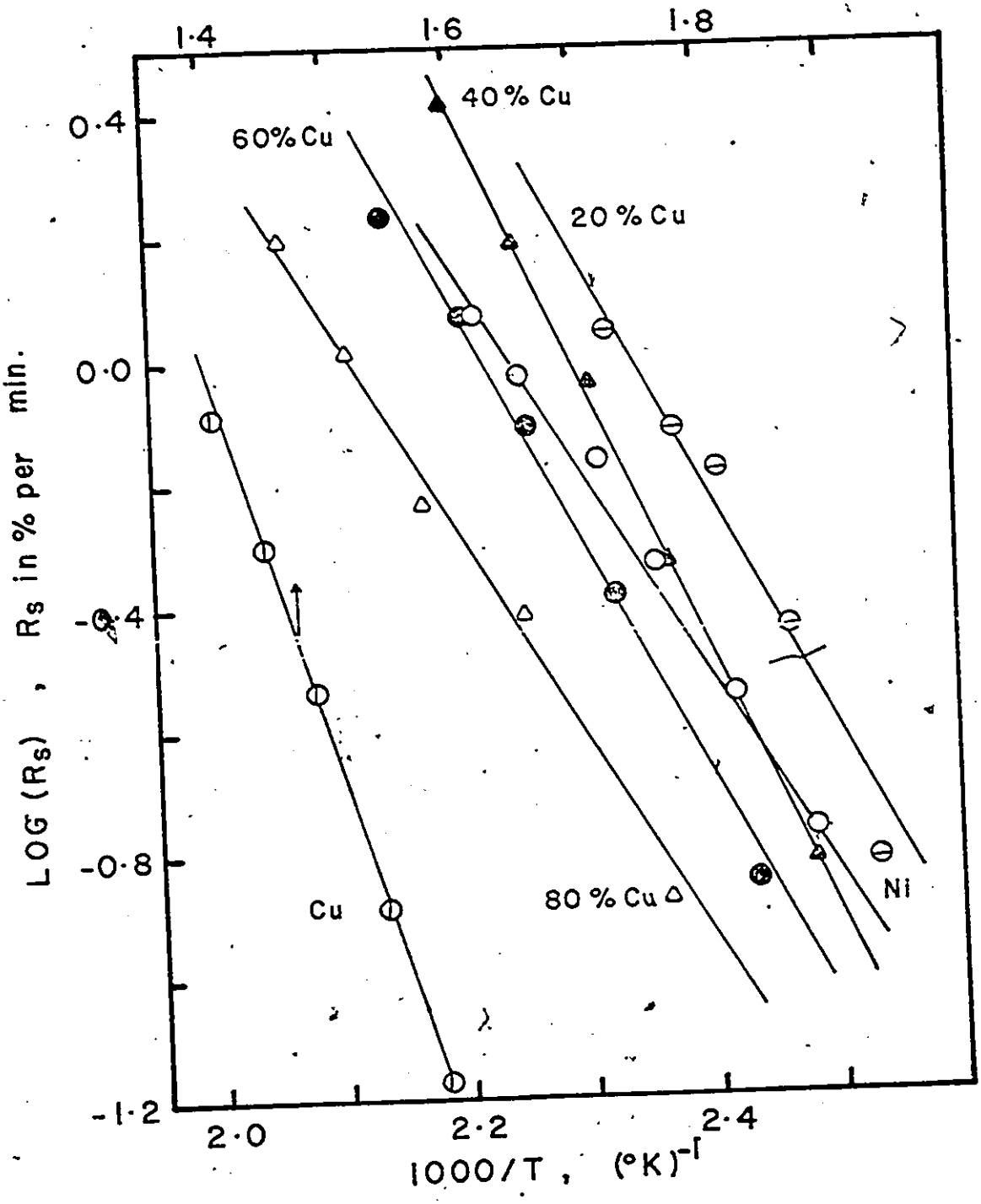


Fig. 11 The dependence of R_s upon the temperature.

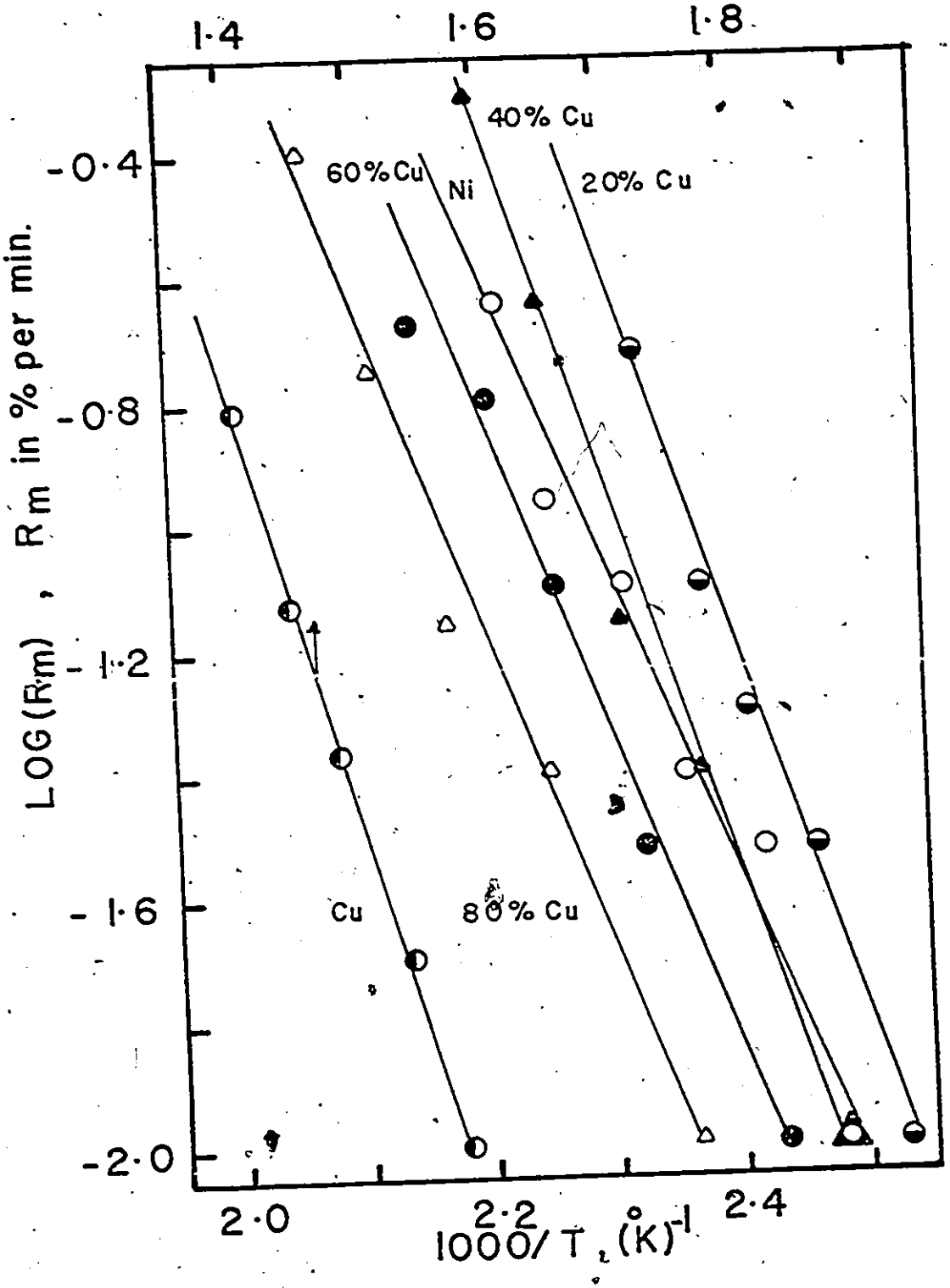


Fig. 12 The dependence of R_m upon the temperature.

over the known amount of 20% Cu-80% Ni on silica catalyst in the temperature range 122.0 - 157.0°C are given in Table: 2.

The catalyst was stabilized using an initial reactant ratio of 1 ($P_D = P_M = 50$ torr) at 122.0°C at which temperature measurable reaction rates were observed. The course of reaction at 157.0°C for an equimolar mixture of reactants shows the predominance of the stepwise exchange in the initial stages of the reaction (Fig. 3B). The dependance of the initial rate of disappearance of methane upon the initial pressures of deuterium and methane is shown in Fig. 13. While the effects of the initial pressures of deuterium and methane upon the initial rate of formation of CH_3D are shown in Fig.14, the variation of the initial rates of formation of CH_2D_2, CHD_3 and CD_4 with the initial deuterium and methane pressures is represented in Fig. 15.

The observed product compositions for the reaction with an equimolar mixture of reactants ($P_D = P_M = 50$ torr) after 70 hrs are given in Table: 2B. The equilibrium values, ϕ_∞ and X_∞, observed at 142.0°C were used to determine k_ϕ and k_0. Fig. 16 shows the plots of log ($\phi_\infty - \phi$) and log ($X_0 - X_\infty$) against time at different temperatures.

The dependence of various specific rate constants upon the temperature is shown in Figures 9-12. These Arrhenius plots were good straight lines and the derived apparent activation energies for the various processes are $E_\phi = 22.0$, $E_0 = 21.6$, $E_s = 19.2$, and $E_m = 27.3$ kcal/mole. The value of M increased

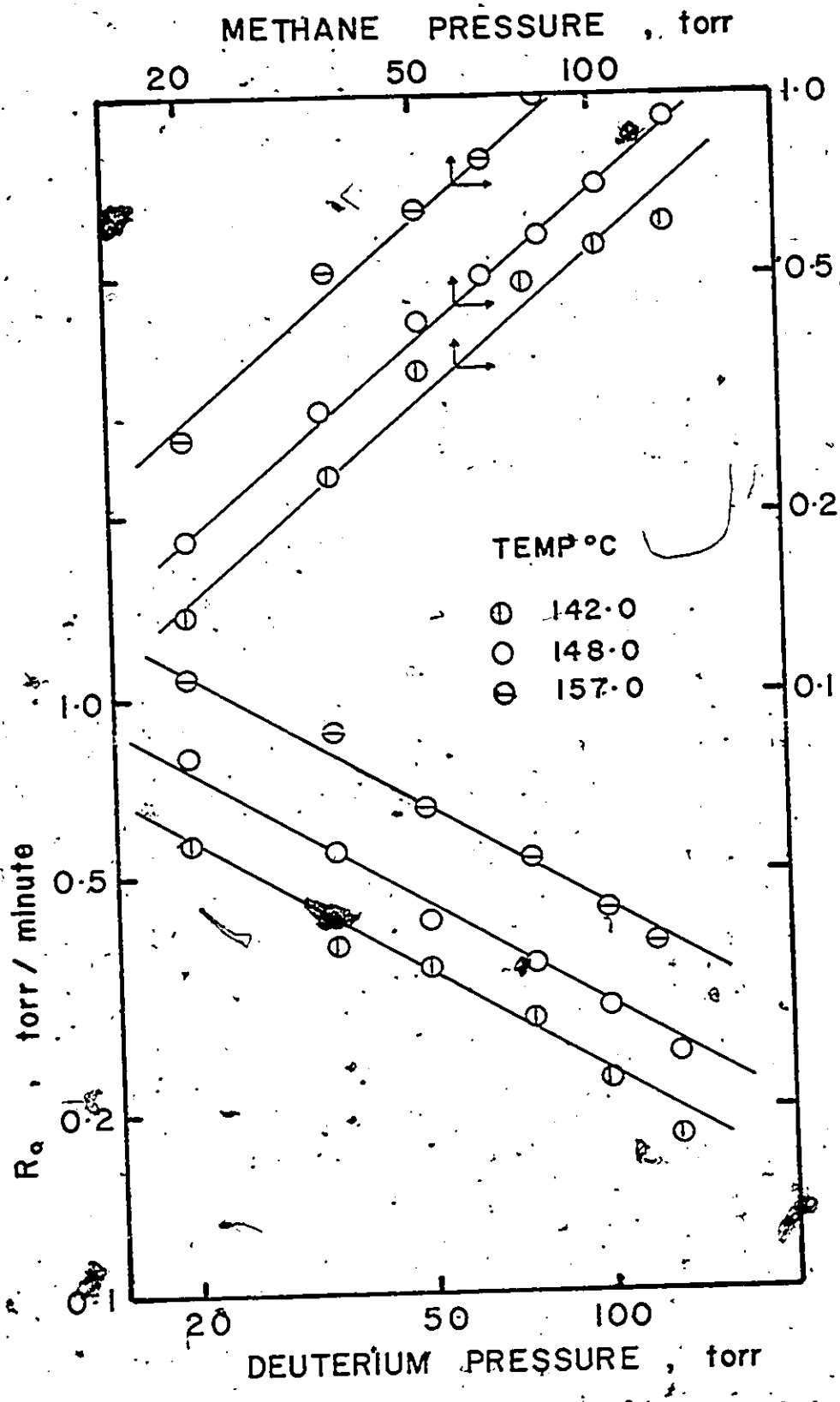


Fig. 13 The dependence of R_0 upon the initial pressures of the reactants over 20% Cu-80% Ni on silica catalyst.

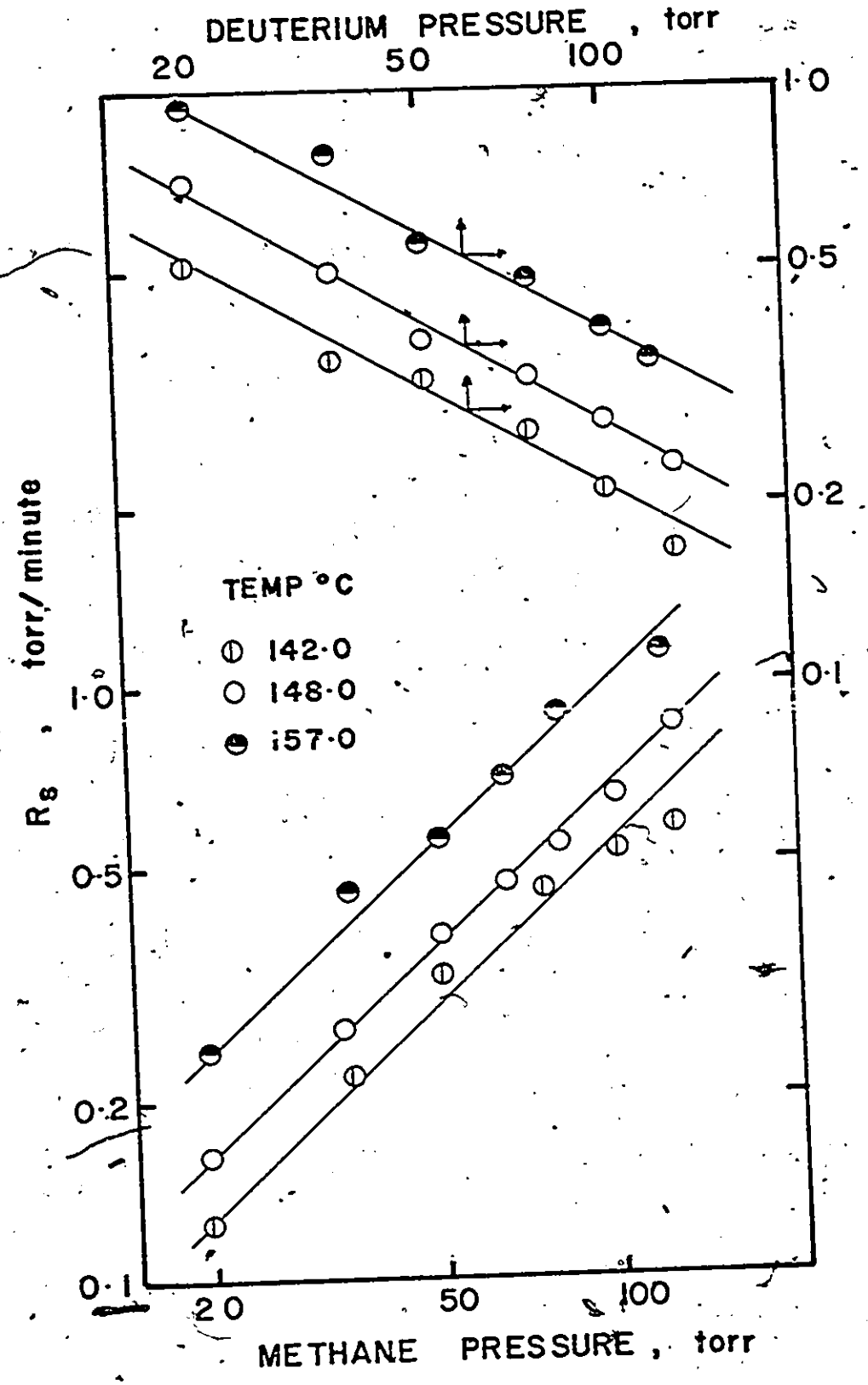


Fig. 14 The dependence of R_s upon the initial pressures of the reactants over 20% Cu-80% Ni on silica catalyst.

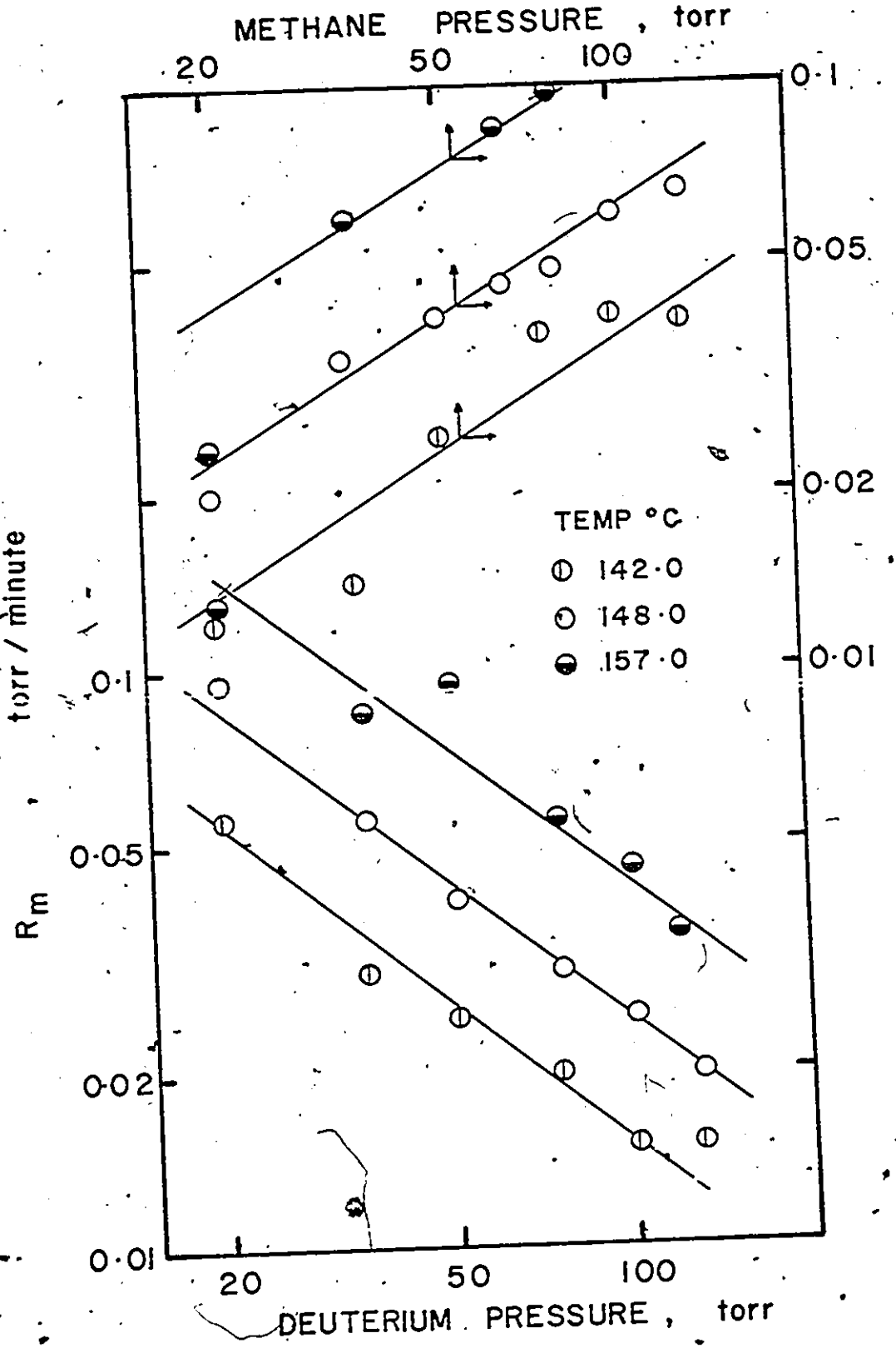


Fig. 15 The dependence of R_m upon the initial pressures of the reactants over 20% Cu-80% Ni on silica catalyst.

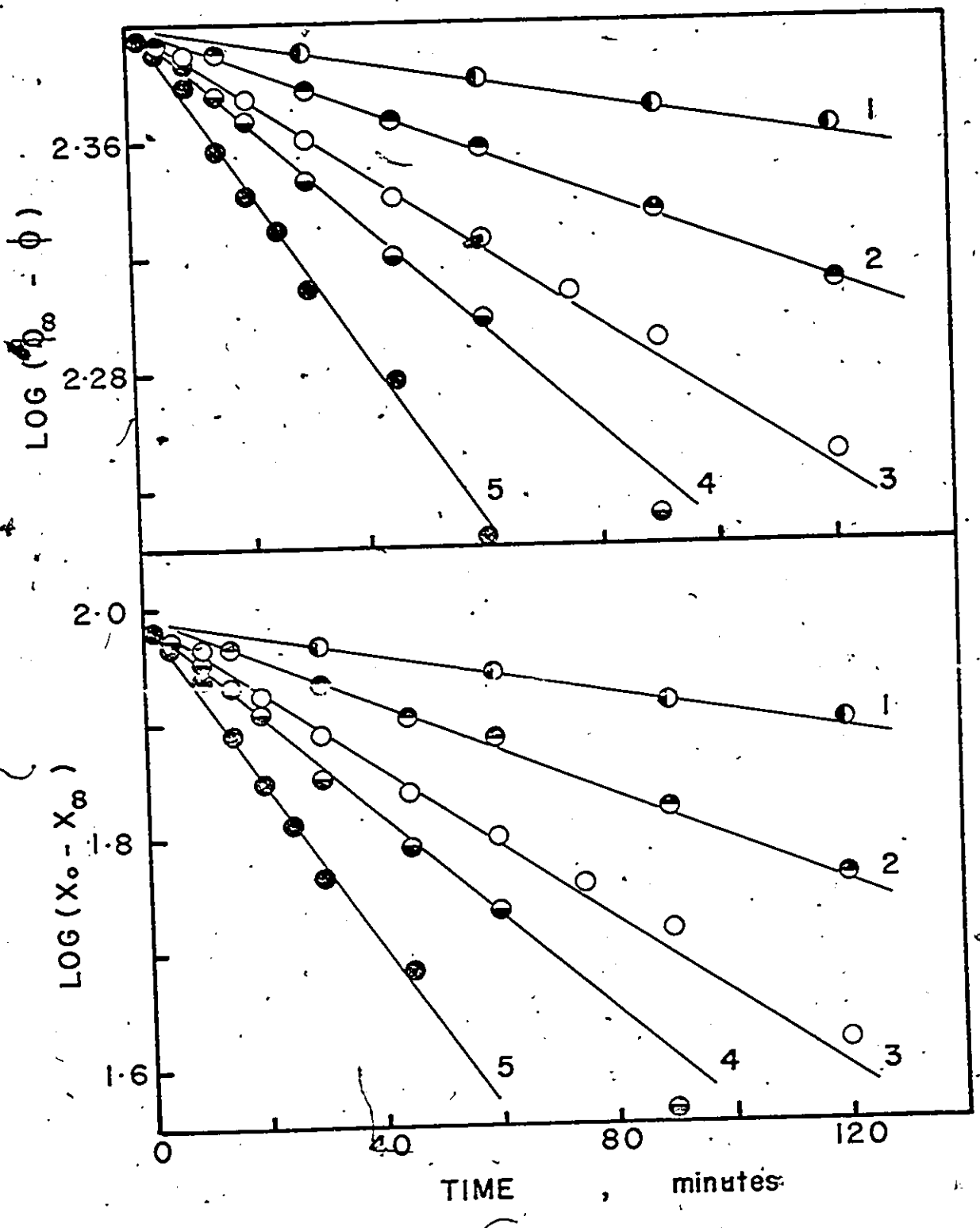


Fig. 16 The plots of log (ϕ_∞ - ϕ) and log (X_0 - X_∞) against time over 20% Cu-80% Ni on silica catalyst at (1) 122.0°C, (2) 133.0°C, (3) 142.0°C, (4) 148.0°C, and (5) 157.0°C.

with increasing temperatures. The kinetic parameters are given in Table: 2C.

(C) REACTION OVER 40% Cu - 60% Ni ON SILICA CATALYST

The results of the investigation of the exchange reaction over the silica supported 40% Cu - 60% Ni catalyst in the temperature range of 130.0 - 182.0°C are given in Table: 3.

The catalyst was stabilized at 130.0°C by conducting several experiments with an initial reactant ratio of 1. The product distribution for the exchange reaction at 182.0°C with an equimolar mixture of the reactants ($P_D = P_M = 50$ torr) is shown in Fig. 17A. The dependence of the initial rate of disappearance of methane upon the initial pressures of deuterium and methane is shown in Figs. 18 and 19 respectively. While the effects of the initial deuterium pressures on the initial rates of the stepwise and the multiple exchange are shown in Figs. 20 and 21 respectively, the dependence of these two rates on the initial methane pressures is represented in Figs. 22 and 23 respectively. The stepwise exchange was the most prominent reaction mechanism in the initial stages of the reaction and the contribution from the multiple exchange increased at high temperatures (Table 3C).

The compositions of the reaction products after 20 and 70 hrs for the exchange reaction with an initial reactant ratio of 1 ($P_D = P_M = 50$ torr) at various temperatures are given in Table: 3B. The equilibrium values $\emptyset_\infty$ and X_∞ observed at 182.0°C were used to compute the rate constants $k_\emptyset$ and

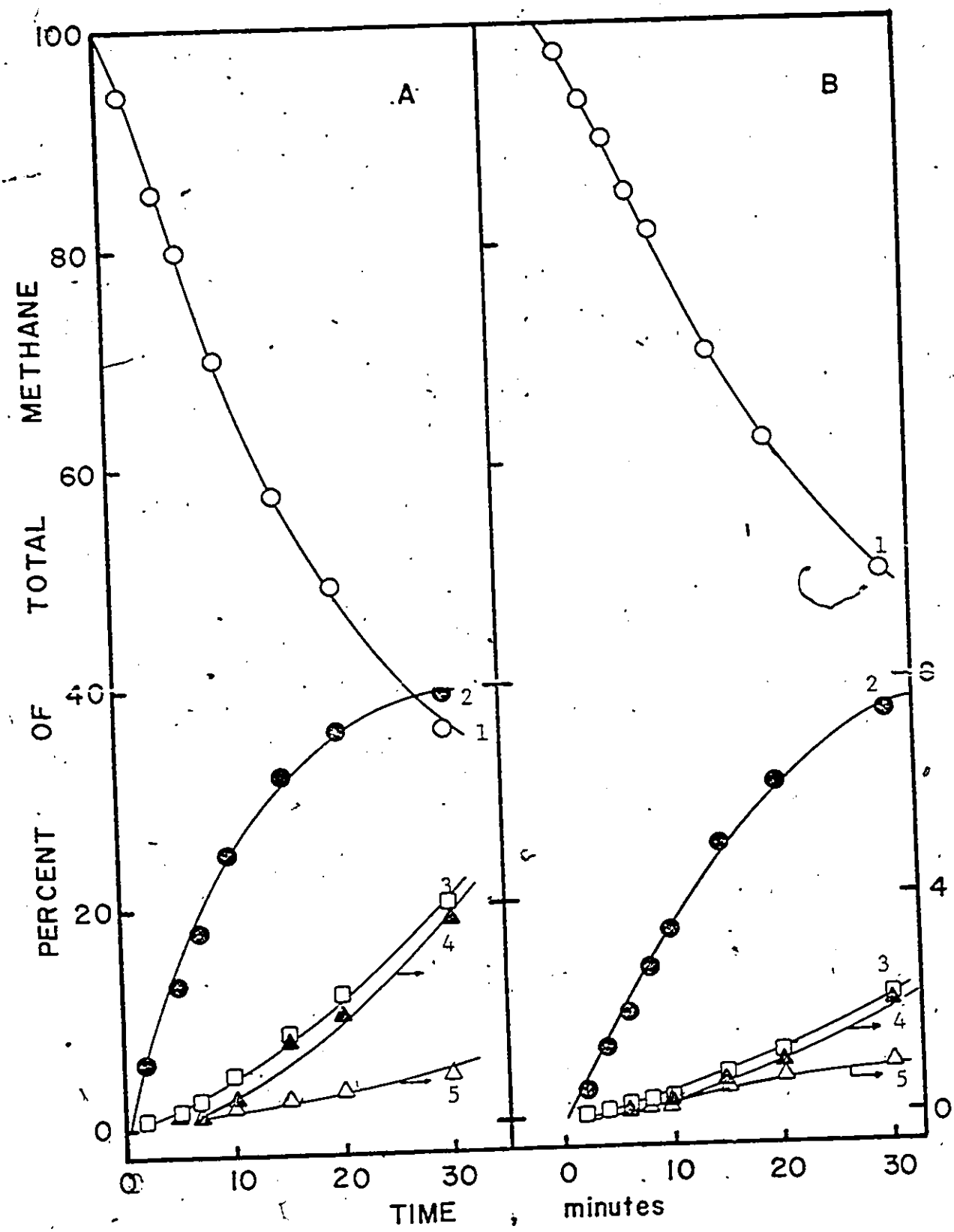


Fig. 17 The course of reaction ($P_D = P_M = 50$ torr) over
(A) 40% Cu-60% Ni on silica catalyst at 182.0°C
(B) 60% Cu-40% Ni on silica catalyst at 193.0°C.
1. CH_4; 2. CH_3D; 3. CH_2D_2; 4. CHD_3; 5. CD_4.

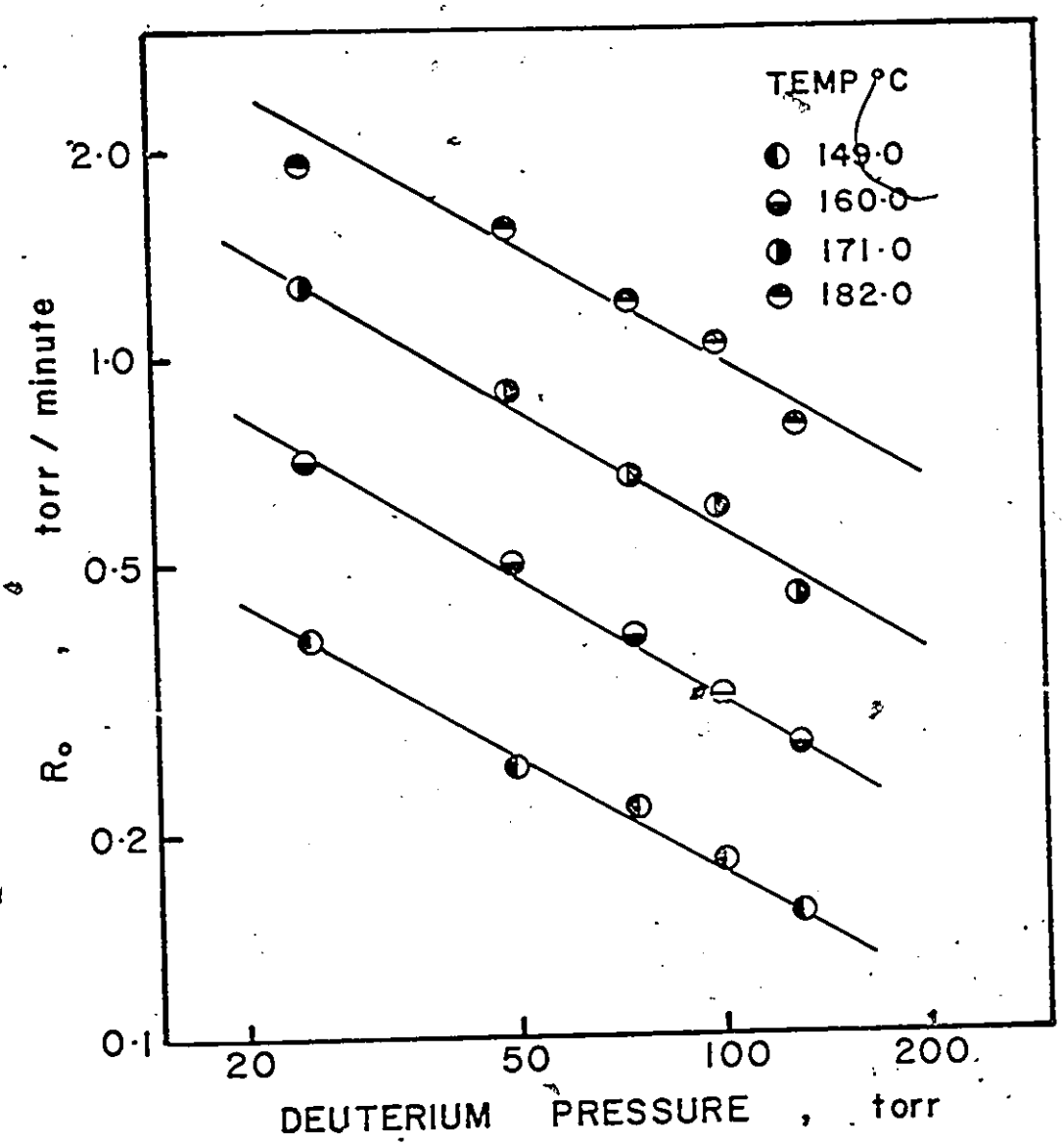


Fig. 18 The dependence of R_0 upon the initial pressure of deuterium over 40% Cu-60% Ni on silica catalyst (P_M = 50 torr).

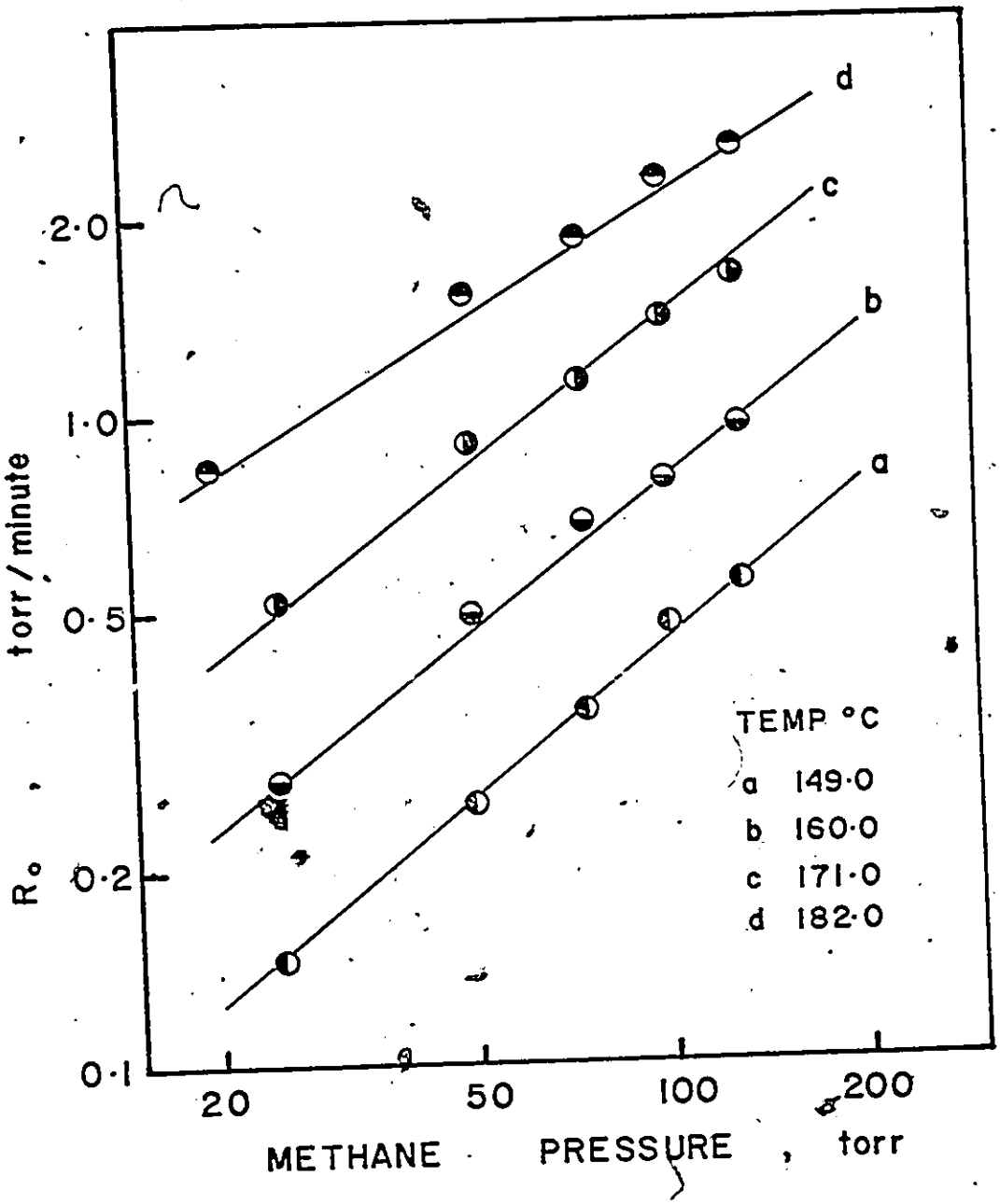


Fig. 19 The dependence of R_O upon the initial methane pressure over 40% Cu-60% Ni on silica catalyst (P_D = 50 torr).

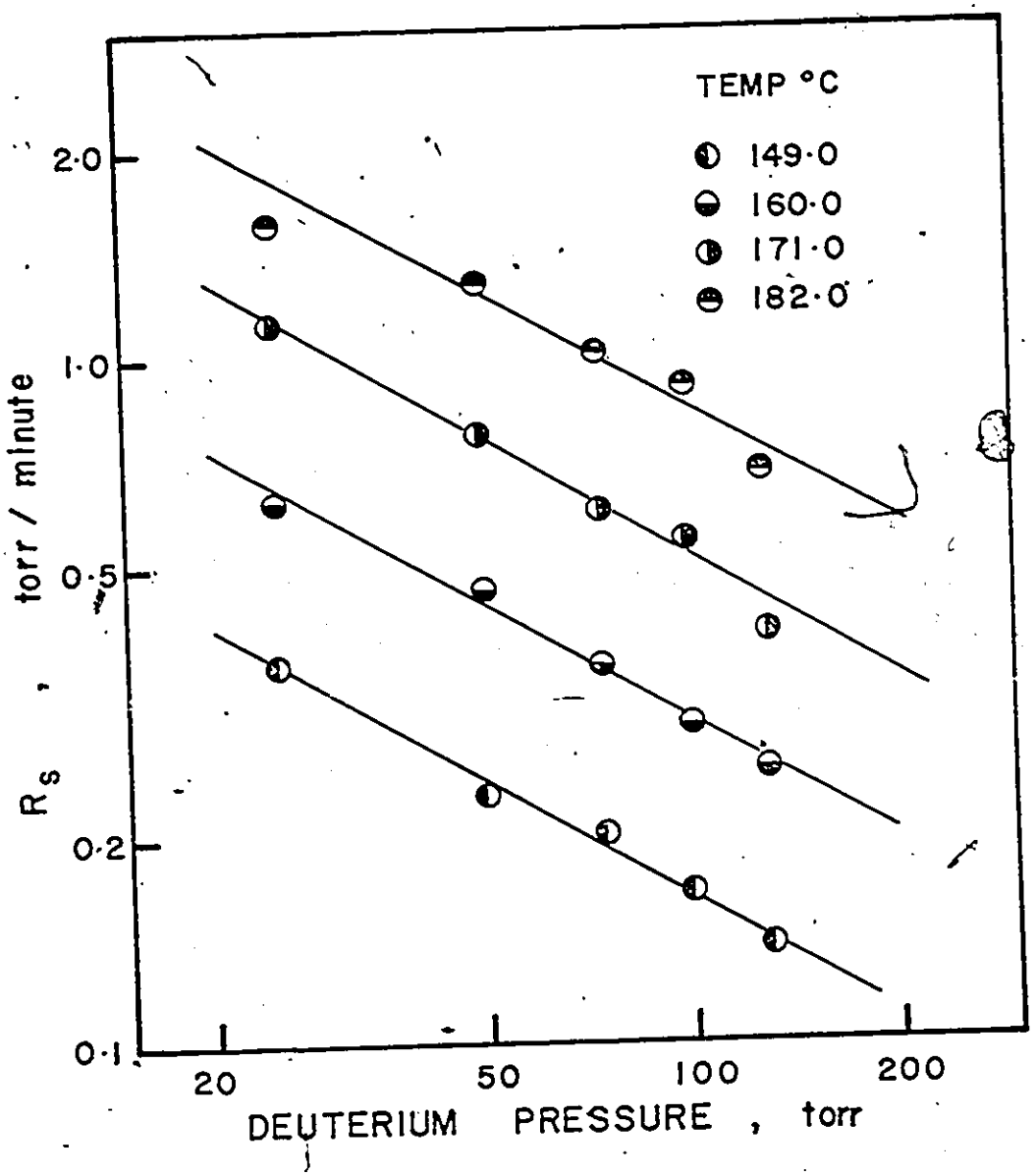


Fig. 20 The dependence of R_s upon the initial deuterium pressure over 40% Cu-60% Ni on silica catalyst (P_M = 50 torr).

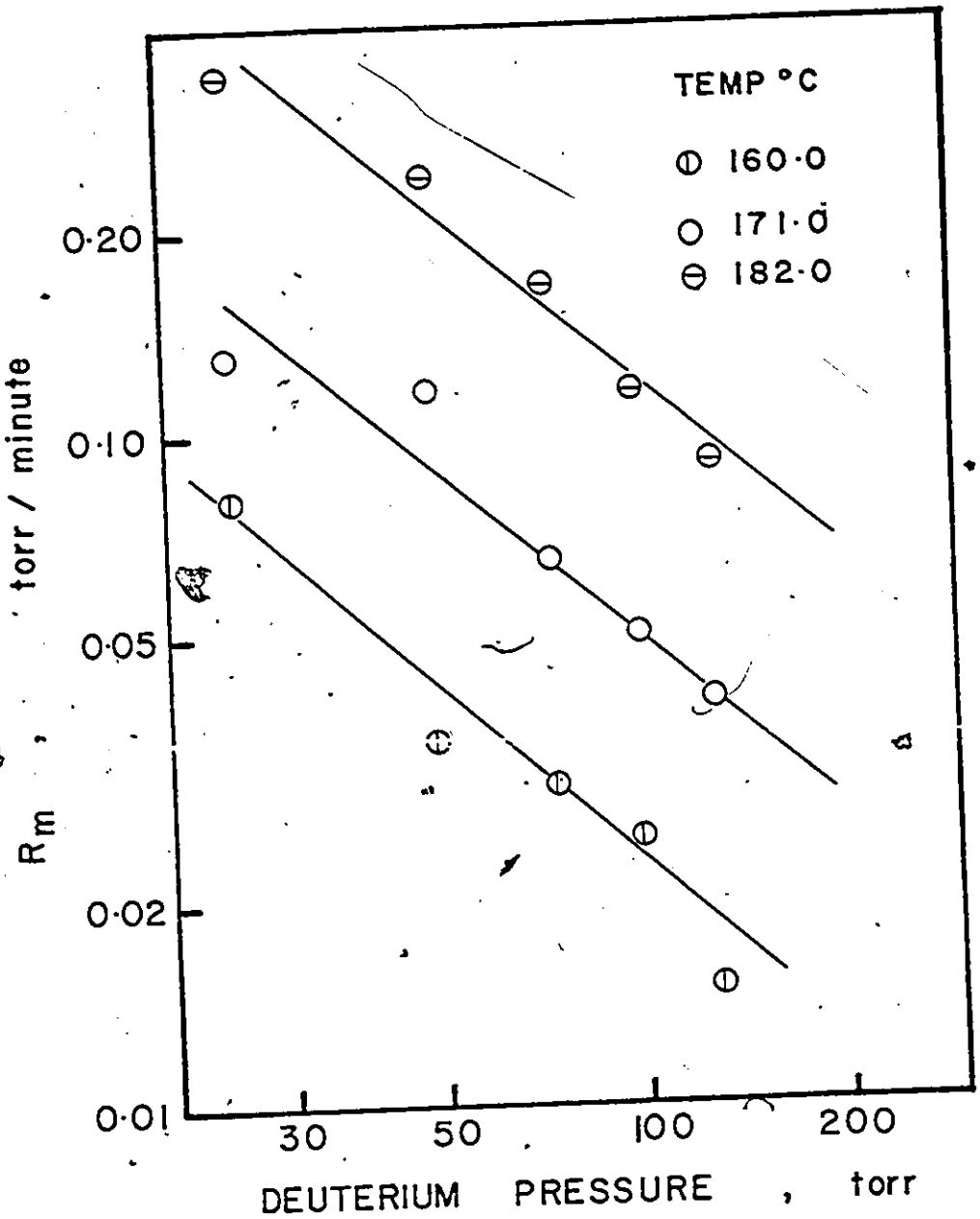


Fig. 21 The dependence of R_m upon the initial deuterium pressure over 40% Cu-60% Ni on silica catalyst (P_M = 50 torr).

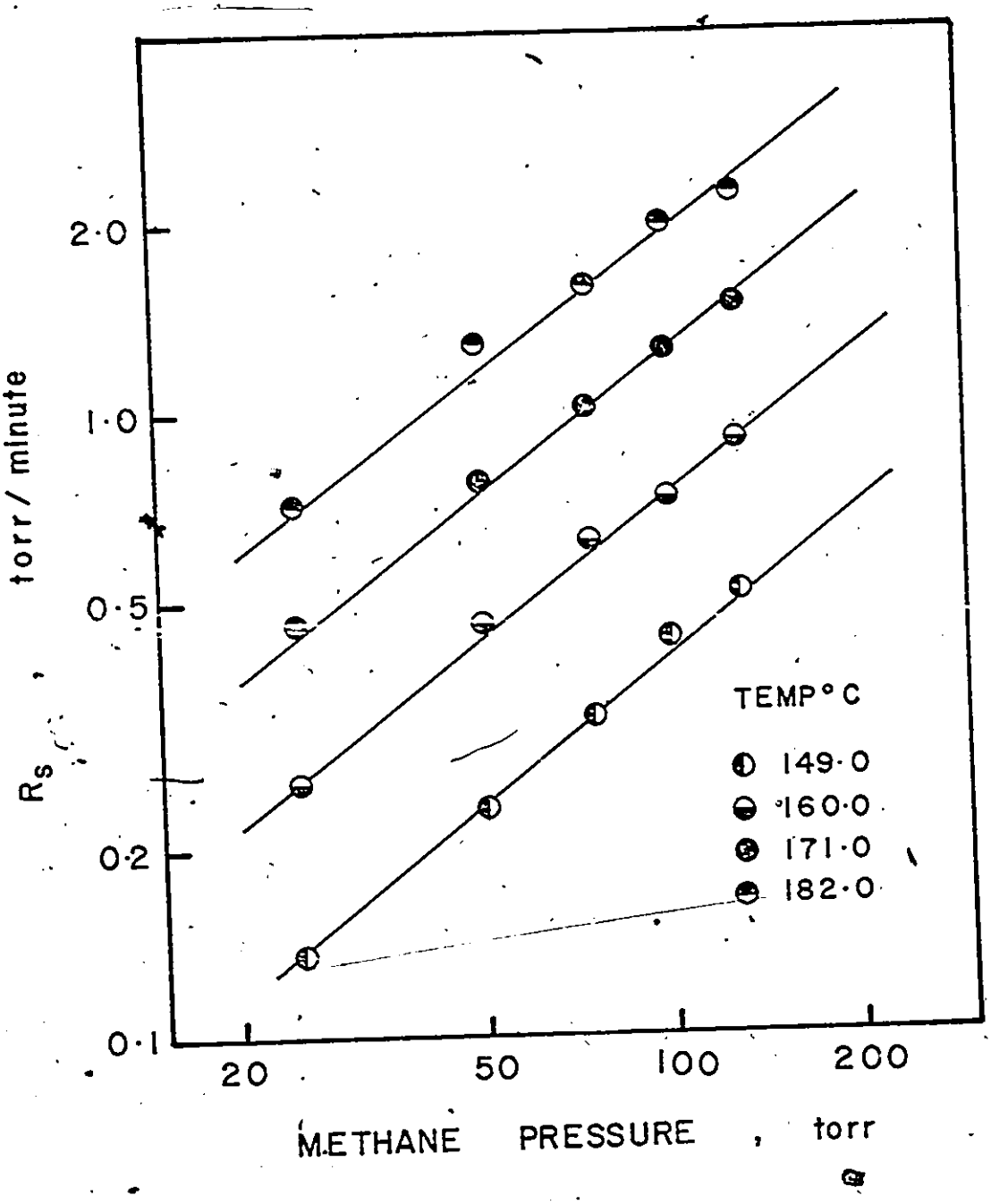


Fig. 22 The dependence of R_s upon the initial methane pressure over 40% Cu-60% Ni on silica catalyst (P_D = 50 torr)).

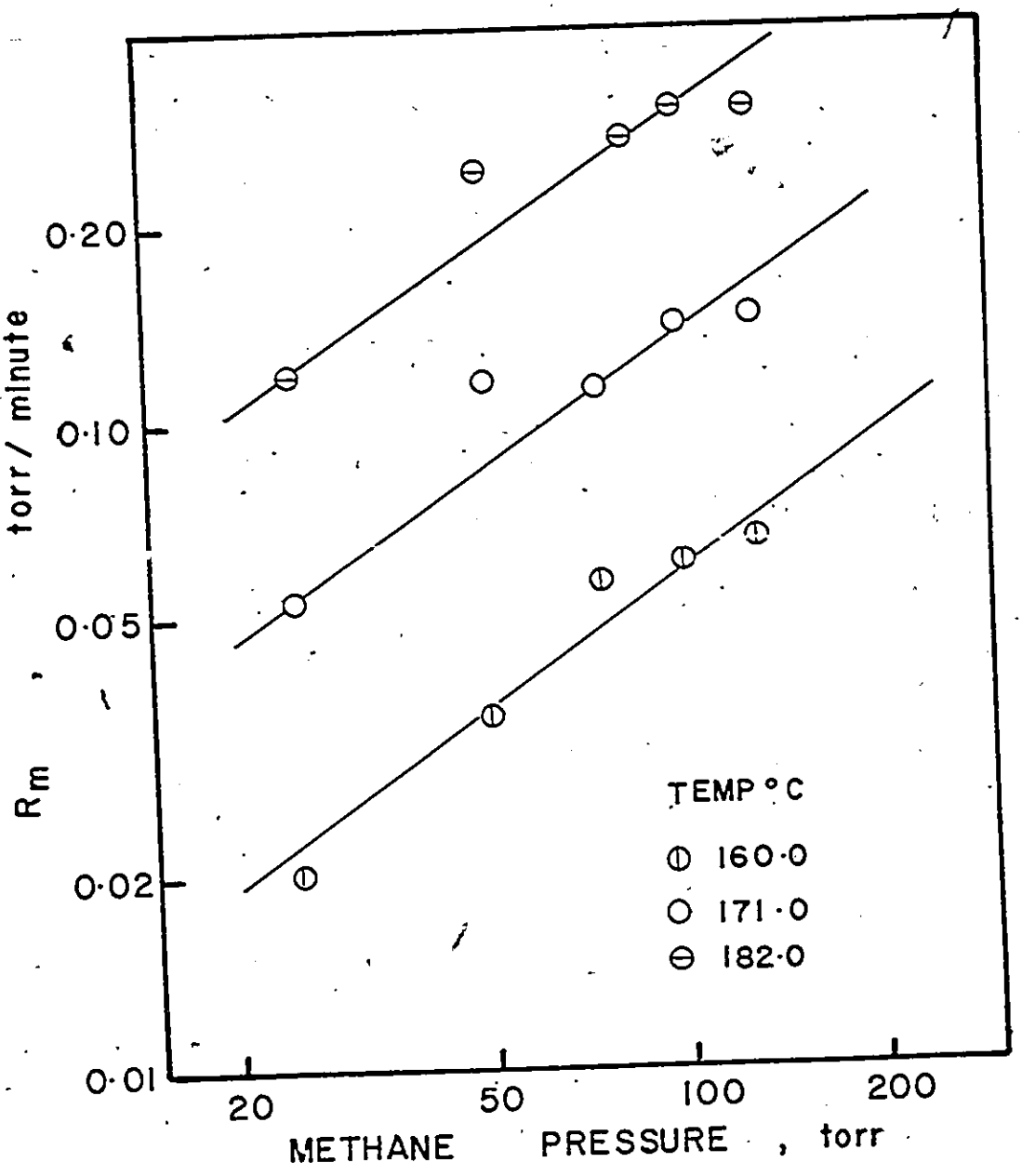


Fig. 23 The dependence of R_m upon the initial methane pressure over 40% Cu-60% Ni on catalyst (P_D = 50 torr).

k_0 from the plots of log ($\phi_\infty - \phi$) and log ($X_0 - X_\infty$) against time which were good straight lines in the initial stages of the reaction as shown in Fig. 24.

The various apparent activation energies for the different rate processes were determined from the straight line plots of log (specific rate constant) against the reciprocal of the absolute temperature (Figs. 9-12). The activation energies for the appearance of deuterium in the hydrocarbon products, E_ϕ, the disappearance of methane, E_0, the stepwise exchange, E_s, and the multiple exchange, E_m, were 22.4, 21.7, 20.0, and 27.2, kcal/mole respectively. The kinetic parameters are given in Table: 3C.

(D) REACTION OVER 60% Cu - 40% Ni ON SILICA CATALYST

The experimental results of the kinetic study of the methane deuterium exchange reaction over the known amount of silica supported 60% Cu - 40% Ni catalyst in the temperature range 138.0 - 193.0°C are given in Table: 4.

The catalyst was stabilized at 138.0 C by carrying out experiments with an initial reactant ratio of 1 ($P_D = P_M = 50$ torr). The observed product distribution during the course of the reaction at 193.0°C with an initial reactant ratio of 1 is presented in Fig. 17B. The stepwise exchange was the dominant mechanism in the initial stages. While the dependence of the initial rate of disappearance of methane and the initial rate of formation of CH_3D upon the initial pressures of deuterium is shown in Fig. 25, the effects of the initial

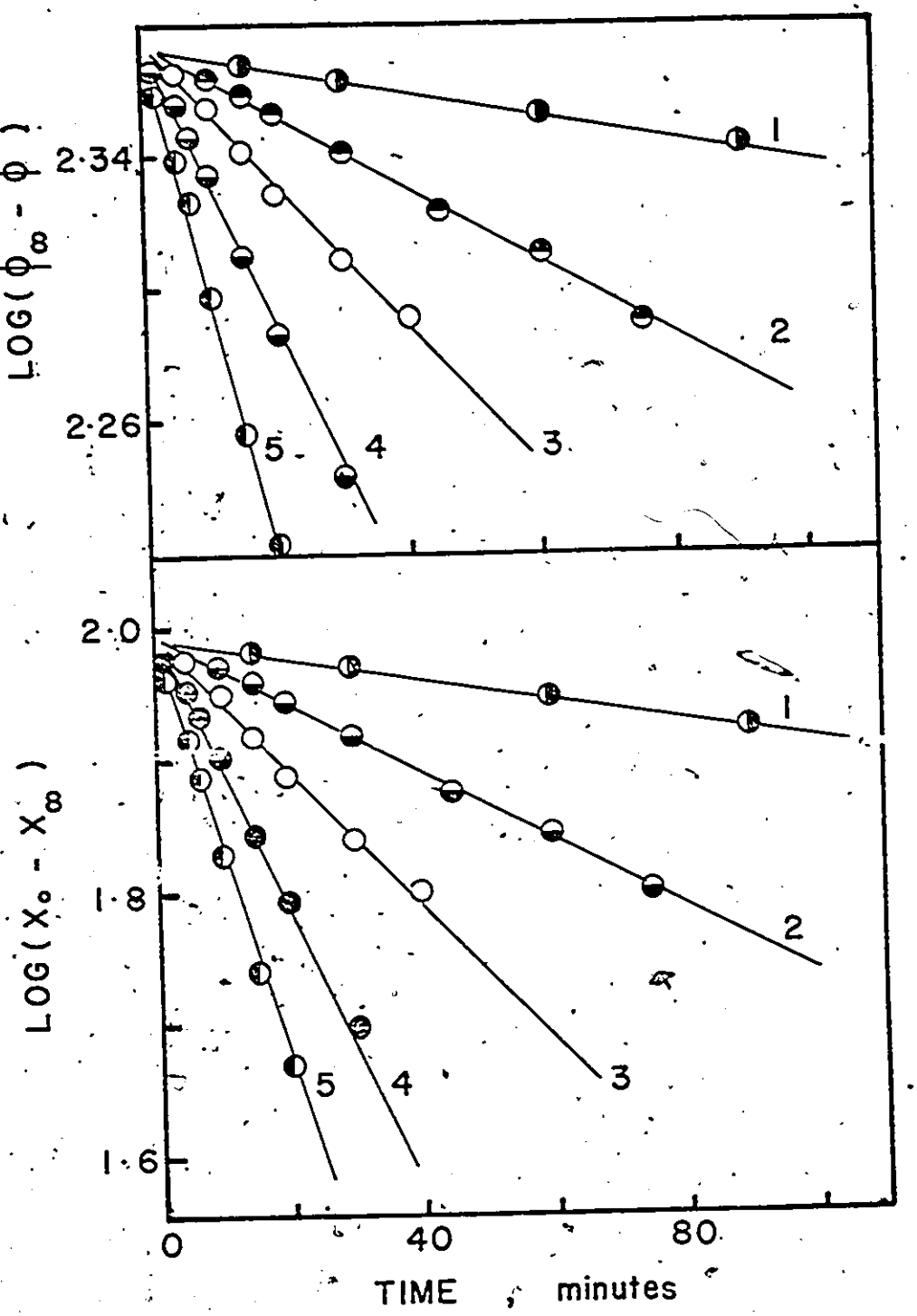


Fig. 24 The plots of log (ϕ_∞ - ϕ) and log (X_0 - X_∞) against time over 40% Cu-60% Ni on silica catalyst at (1) 130.0, (2) 149.0, (3) 160.0, (4) 171.0, and (5) 182.0°C.

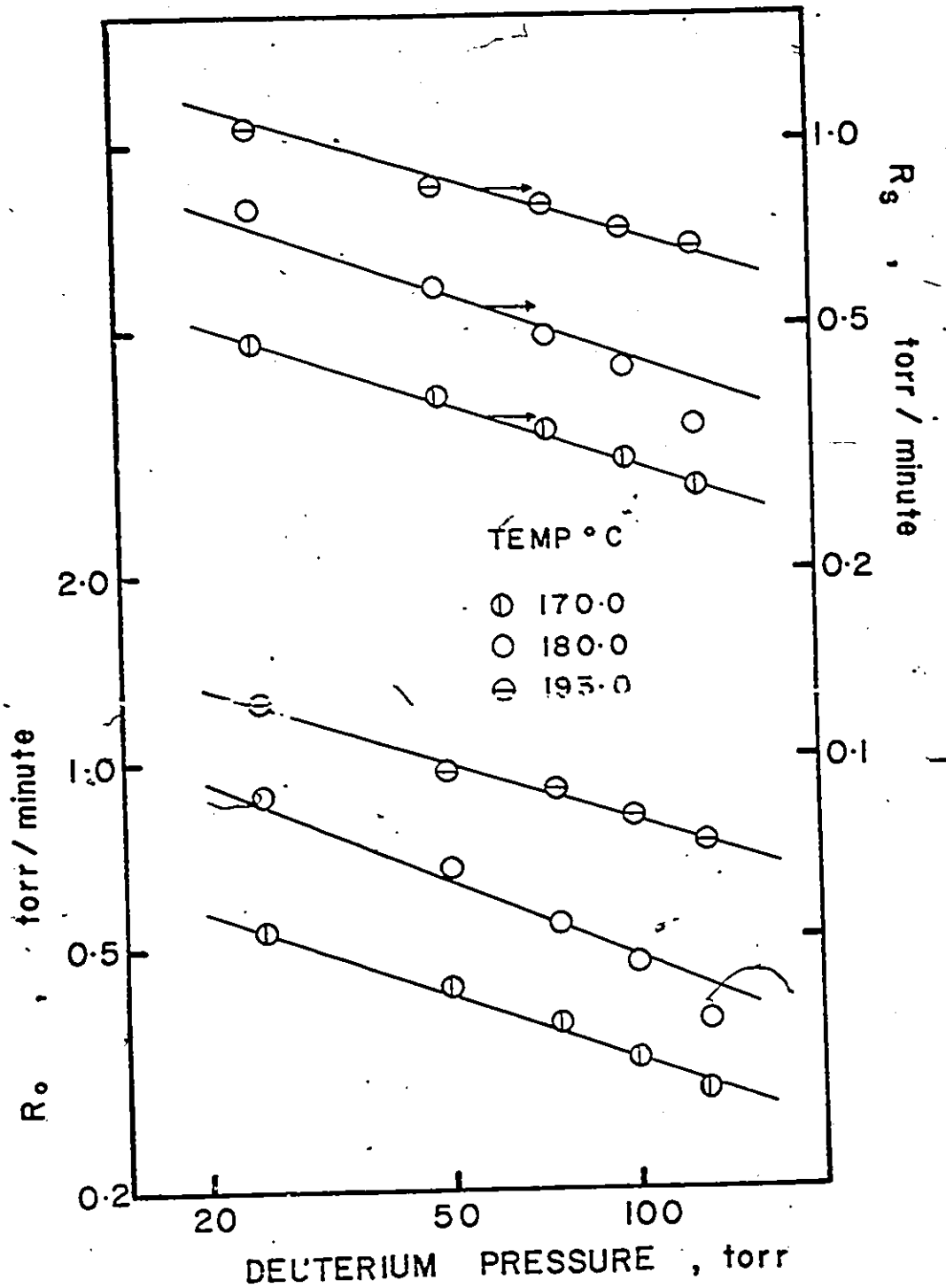


Fig. 25 The dependence of R_0 and R_s upon the initial deuterium pressure over 60% Cu-40% Ni catalyst (P_M = 50 torr).

pressures of methane upon R_o and R_s are represented in Fig. 26. The dependence of the initial rate of formation of CH_2D_2, CHD_3 and CD_4 upon the initial reactant pressures is shown in Fig. 27.

The product compositions for the exchange reaction with an equimolar quantity of the reactants, after 20 and 70 Hrs are given in Table: 4B. The values of $\emptyset_\infty$ and X_∞ observed at 180.0°C after 70 hrs were used to compute the rate constants $k_\emptyset$ and k_o from the plots of log ($\emptyset_\infty - \emptyset$) and log ($X_o - X_\infty$) against time which are shown in Fig. 28.

The Arrhenius plots, showing the dependence of the various specific rate constants upon the temperature, were good straight lines (Figs. 9-12). The derived apparent activation energies were $E_\emptyset$ = 19.9, E_o = 19.3, E_s = 17.5, and E_m = 22.3 kcal/mole. The kinetic parameters are given in Table: 4C.

(E) REACTION OVER 80% Cu - 20% Ni ON SILICA CATALYST

The experimental results of the exchange reaction of methane with deuterium over a weighed amount of silica supported 80% Cu - 20% Ni catalyst in the temperature range 150.0 - 212.0°C are given in Table: 5.

The measurable exchange rates were observed after the stabilization of the catalyst at 150.0°C by conducting exchange experiments with an initial reactant ratio of 1 ($P_D = P_M$ = 50 torr). Fig. 29A shows the product distribution during the course of the reaction at 212.0°C with an equimolar quantity

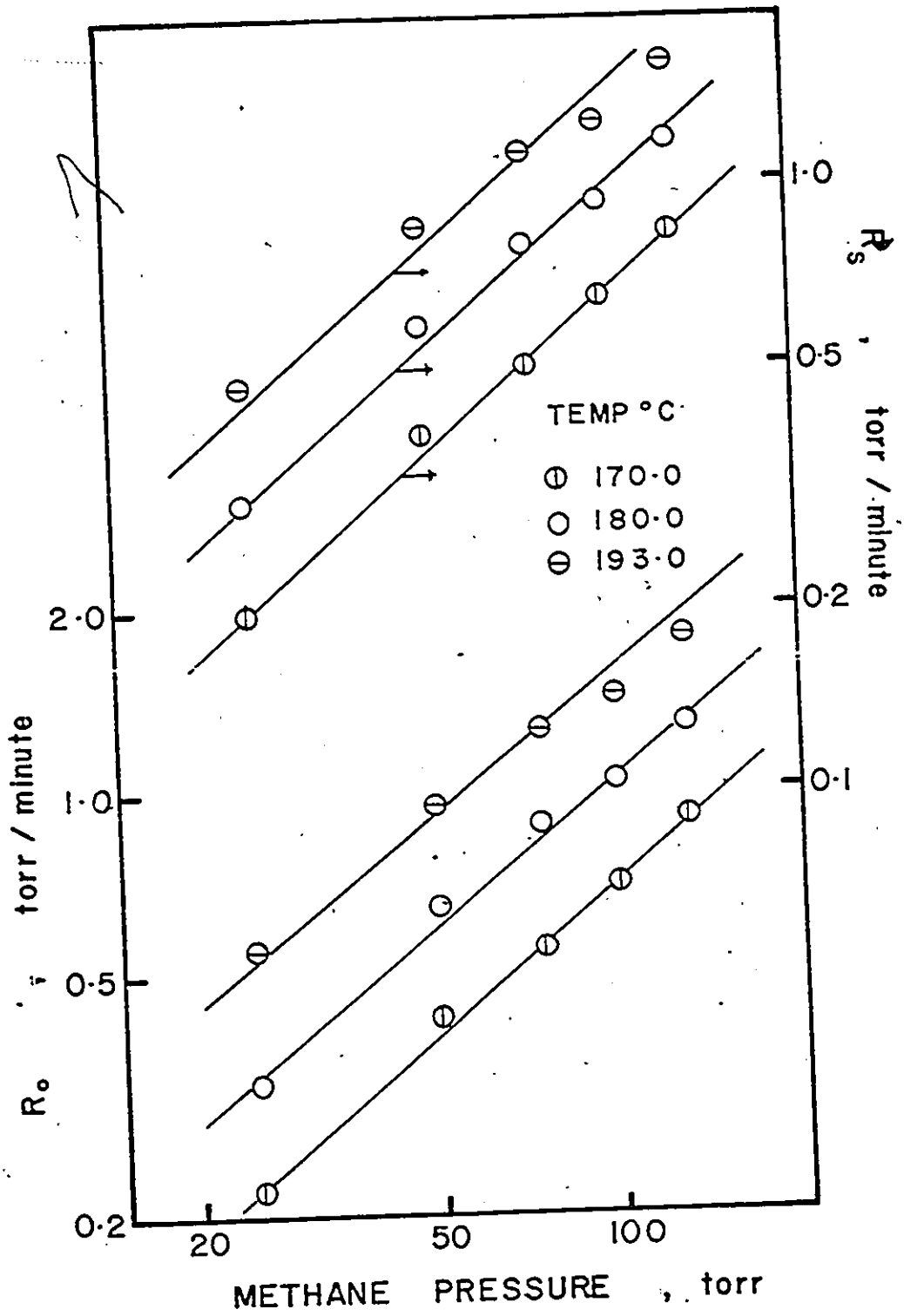


Fig. 26 The dependence of R_0 and R_s upon the initial methane pressure over 60% Cu-40% Ni on silica catalyst (P_D = 50 torr).

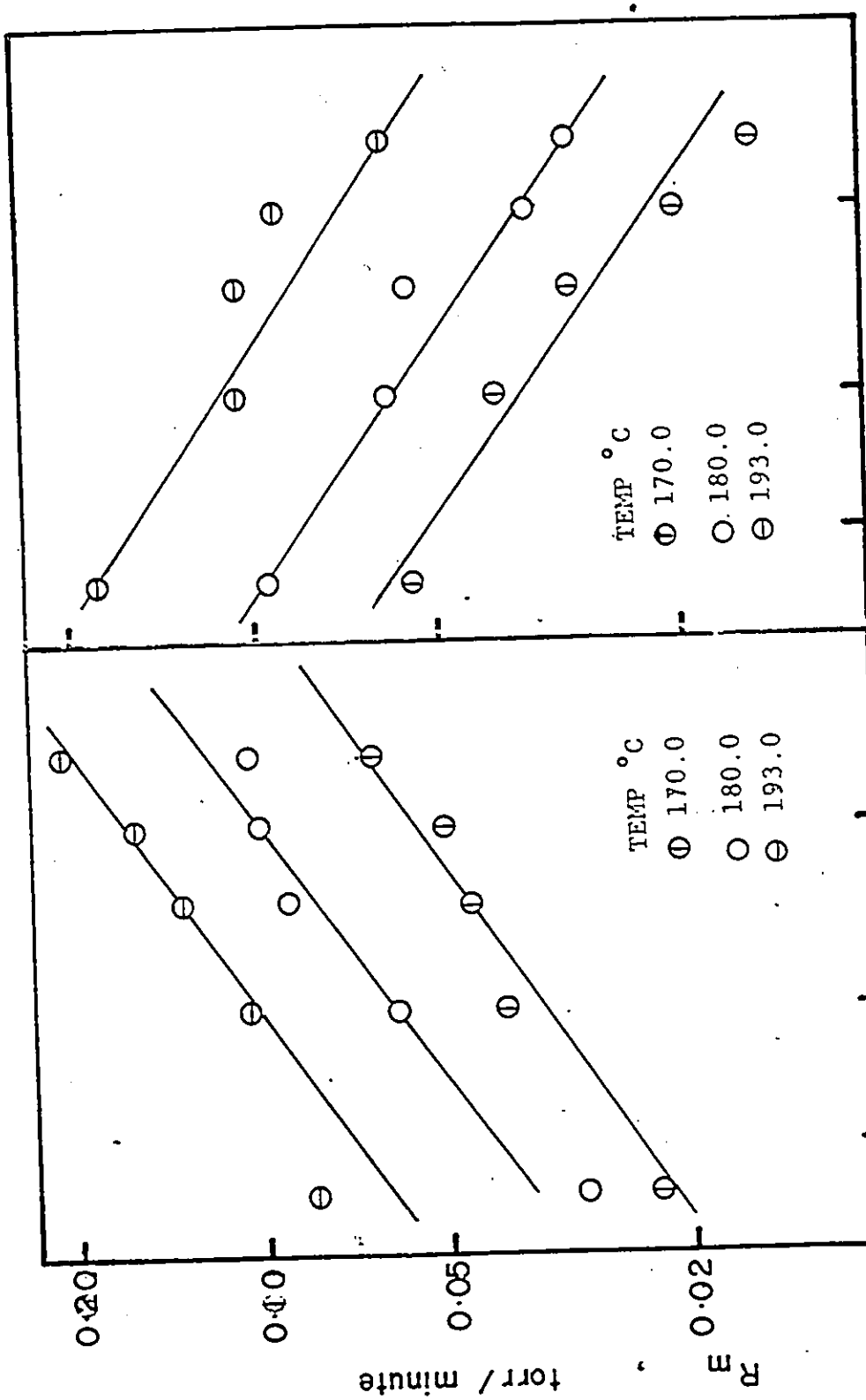


Fig. 27 The dependence of R_m upon the initial pressures of the reactants over 60% Cu-40% Ni on silica catalyst.

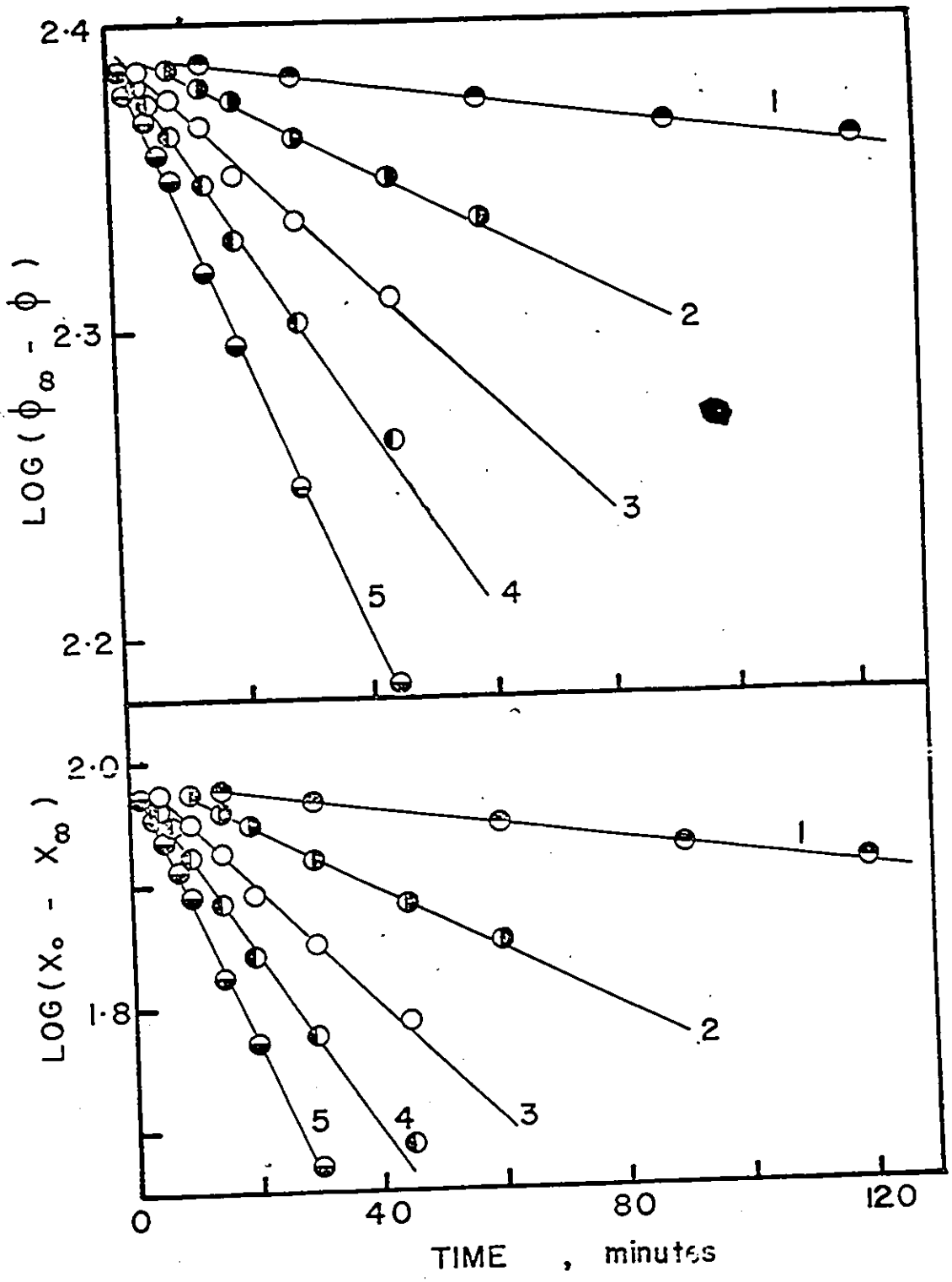


Fig. 28 The plots of log (ϕ_∞ - ϕ) and log (X_0 - X_∞) against time over 60% Cu-40% Ni on silica catalyst at (1) 138.0, (2) 157.0, (3) 170.0, (4) 180.0, and (5) 193.0°C.

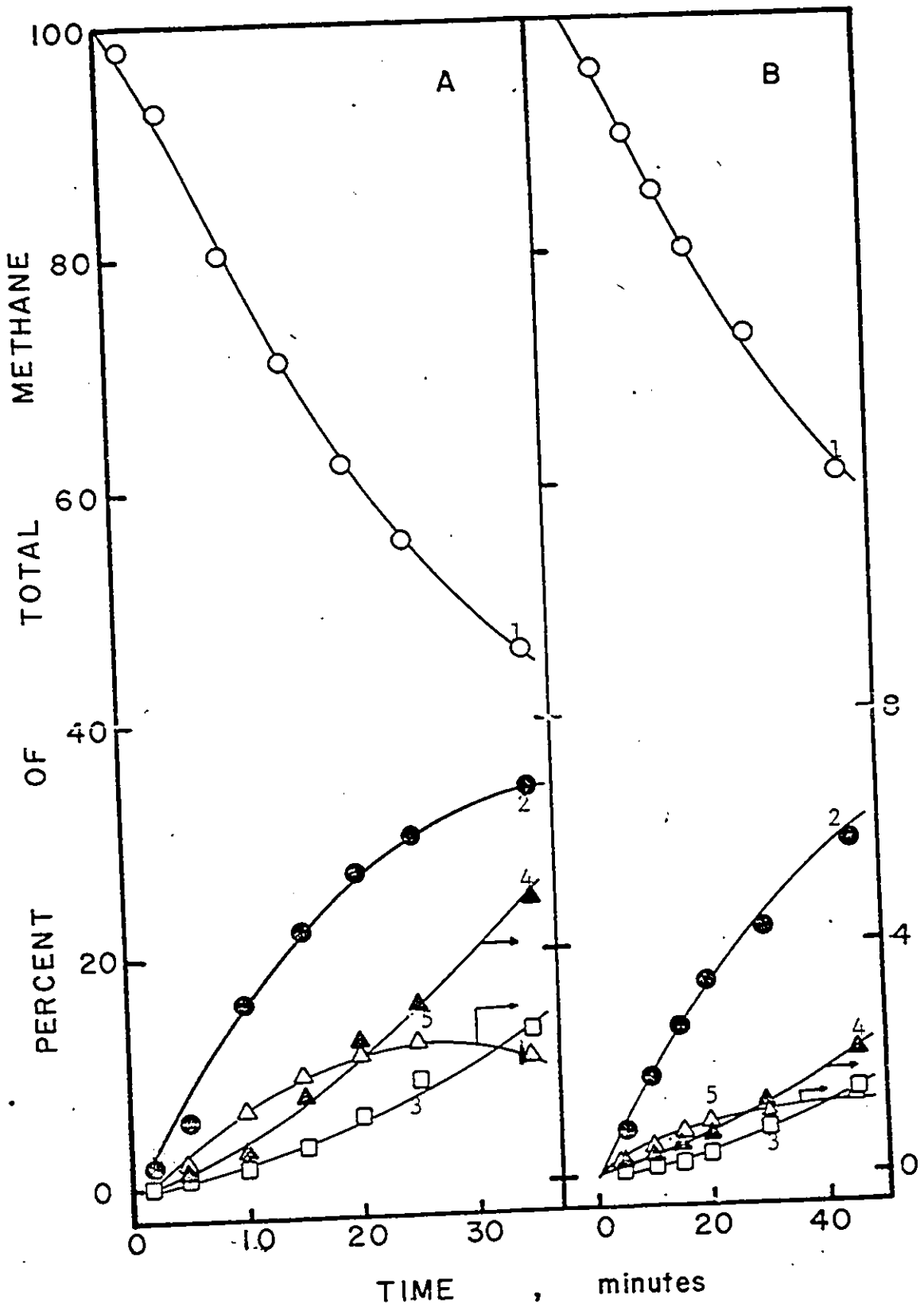


Fig. 29 The course of reaction with $P_D = P_M = 50$ torr over (A) 80% Cu-20% Ni on silica catalyst at 212.0°C; (B) silica supported Cu catalyst at 440.0°C.
1. CH_4, 2. CH_3D, 3. CH_2D_2, 4. CHD_3, 5. CD_4

of the reactants. The dependence of the initial rate of disappearance of methane upon the initial deuterium and methane pressures is shown in Fig. 30. While the effects of the initial pressures of deuterium and methane on the initial rate of formation of CH_3D are shown in Fig. 31, the dependence of the initial rate of multiple exchange upon the initial pressures of the reactants is represented in Fig. 32. The dependence of the initial rate of disappearance of methane upon the initial pressures of the reactants at 212.0°C, when the initial pressure of one of the reactant is kept constant at 25 and 100 torr while that of the other reactant is varied, is shown in Fig. 33.

The observed product distributions for the reaction with an initial reactant ratio of 1 after 20 and 70 hrs at different temperatures are given in Table:5B. The values of ϕ_∞ and X_∞ observed at 200.0°C after 70 hrs were utilized to calculate k_ϕ and k_0. Fig. 34 shows the plots of log ($\phi_\infty - \phi$) and log ($X_o - X_\infty$) against time.

The influence of the temperature on the various rate constants is shown in Figs. 9-12. From the straight line Arrhenius plots, the apparent activation energies were calculated for the appearance of deuterium in the hydrocarbon products, the disappearance of methane, the stepwise exchange and the multiple exchange which were 18.3, 16.7, 16.0, and 23.5 kcal/mole respectively. The kinetic parameters are given in Table: 5C.

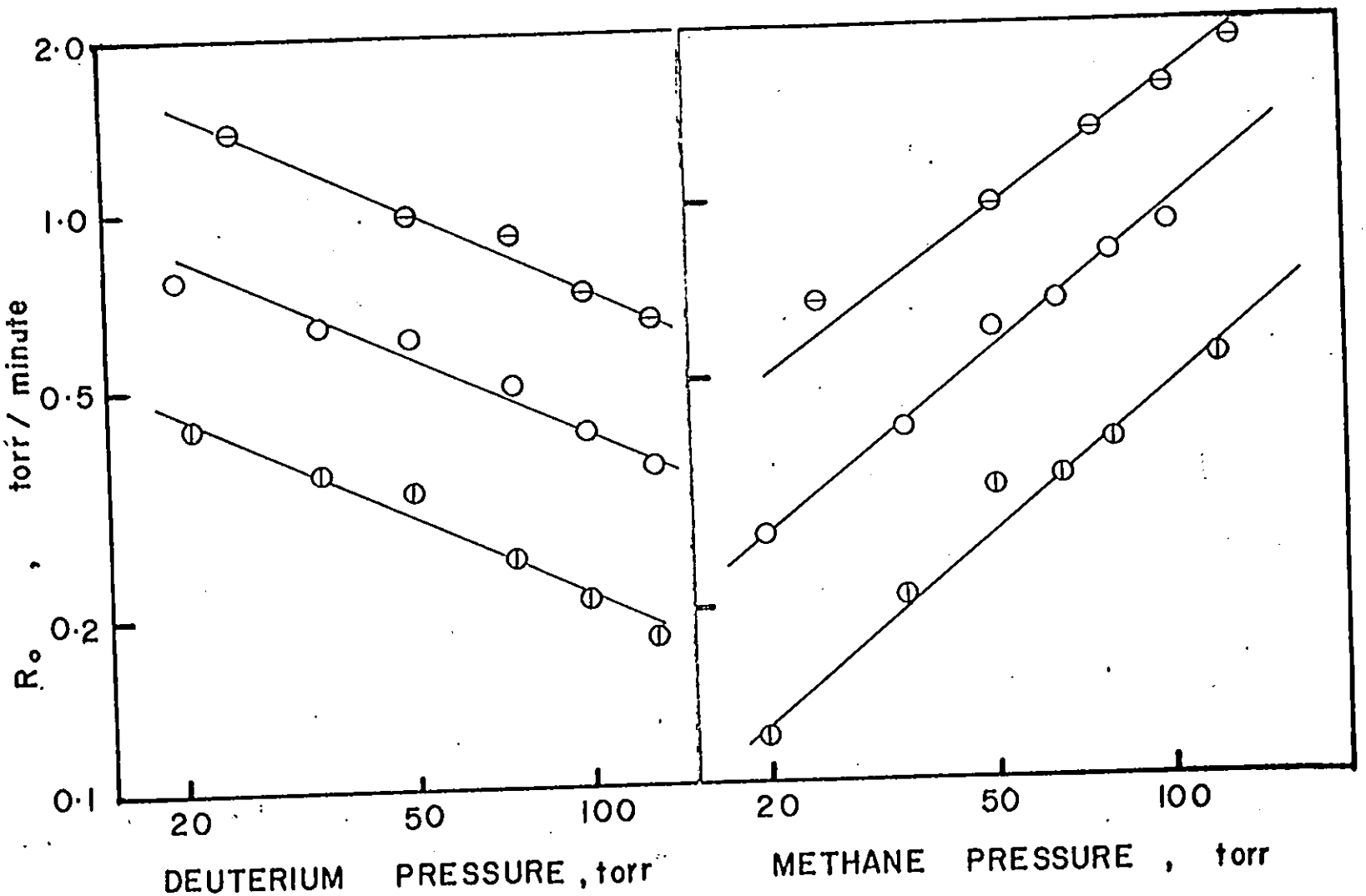


Fig. 30 The dependence of R_0 upon the initial pressures of the reactants over 80% Cu-20% Ni on silica catalyst at 187.0 ◐ ; 200.0 ○ ; and 212.0°C.⊖

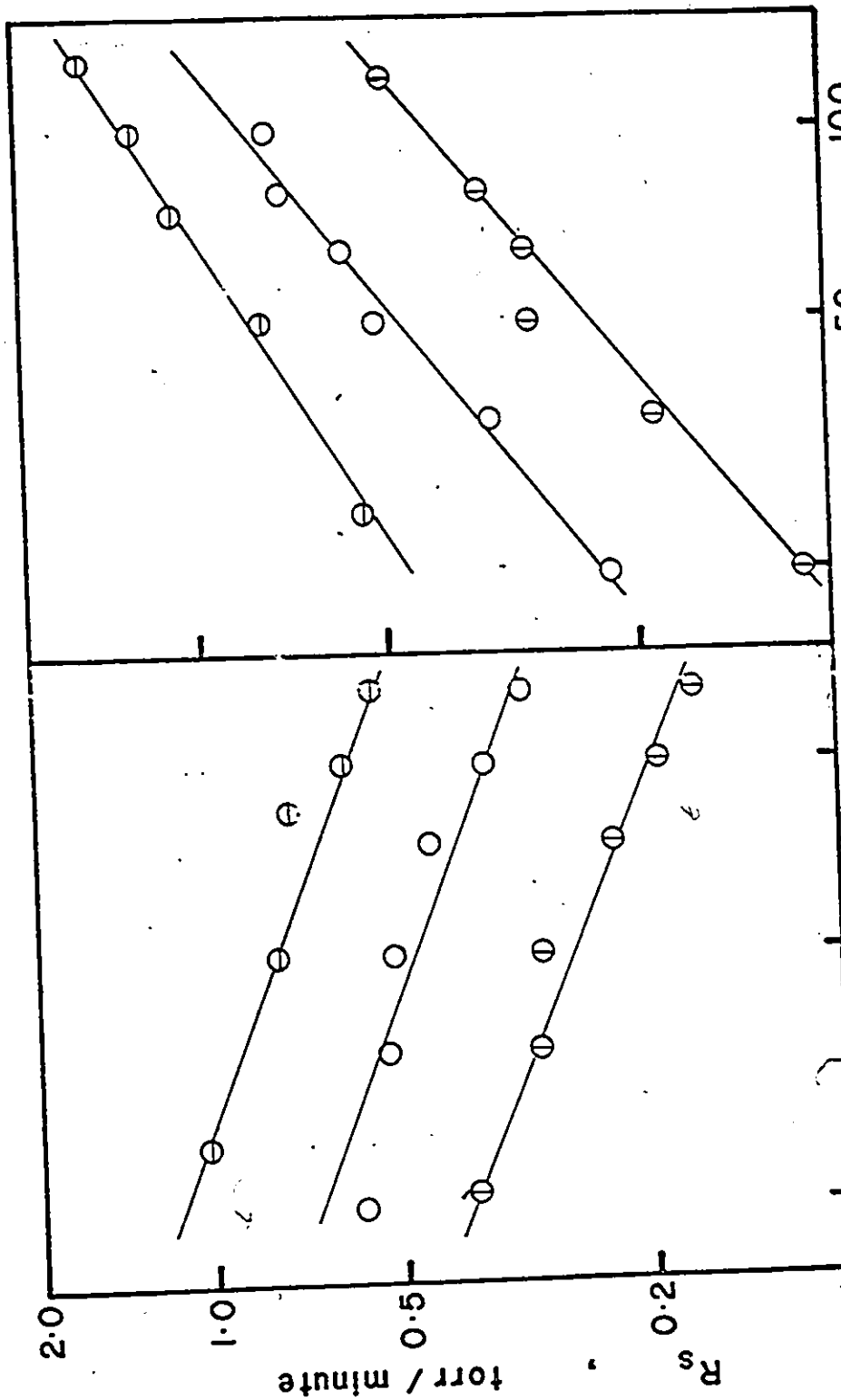


Fig. 31 The dependence of R_s upon the initial pressures of the reactants over 80% Cu-20% Ni on silica catalyst at 187.0 Φ; 200.0 O; and 212.0°C Θ

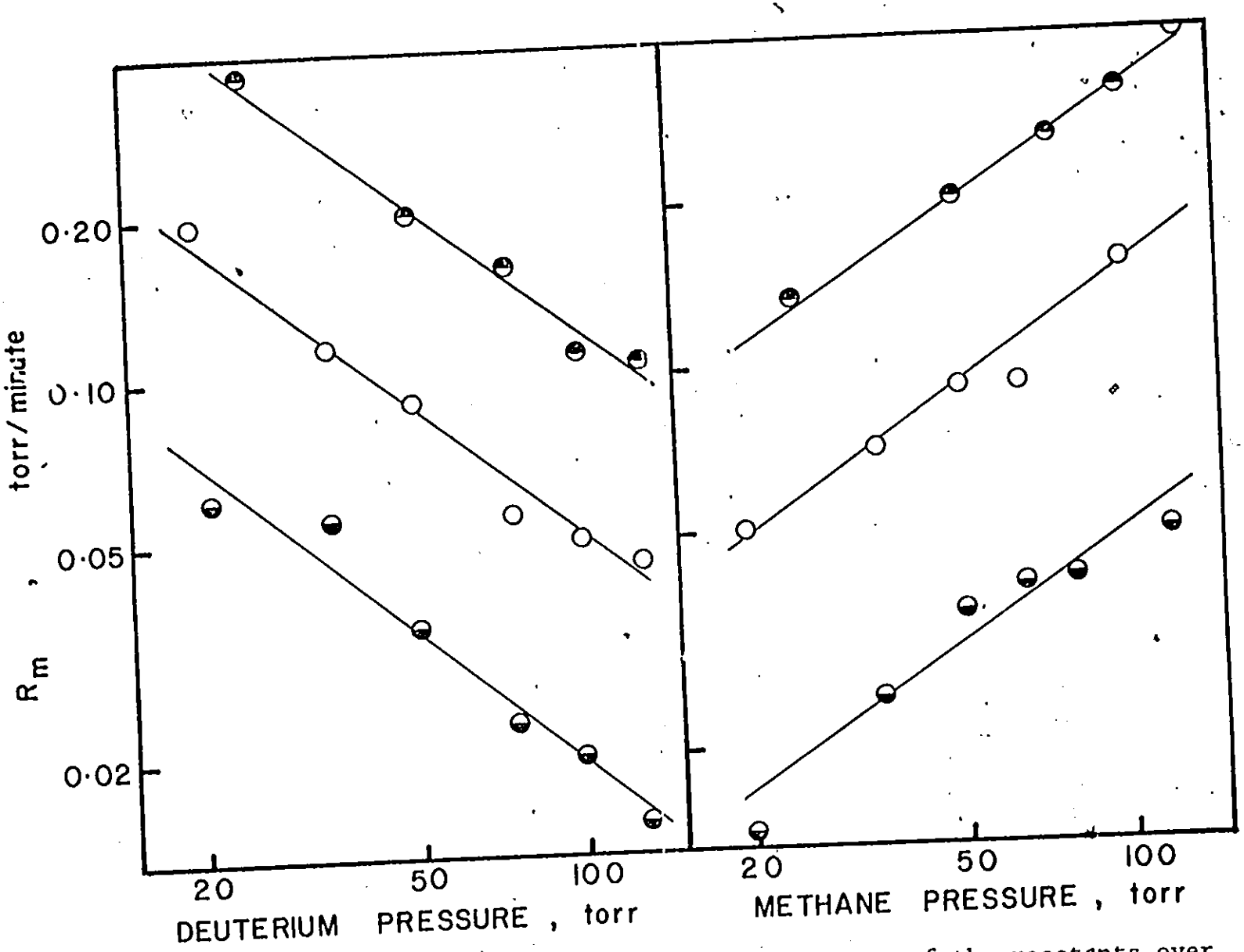


Fig. 32 The dependence of R_m upon the initial pressures of the reactants over 80% Cu-20% Ni on silica catalyst at (i) 187.0 ◒; (ii) 200.0 ○; and (iii) 212.0°C ◓.

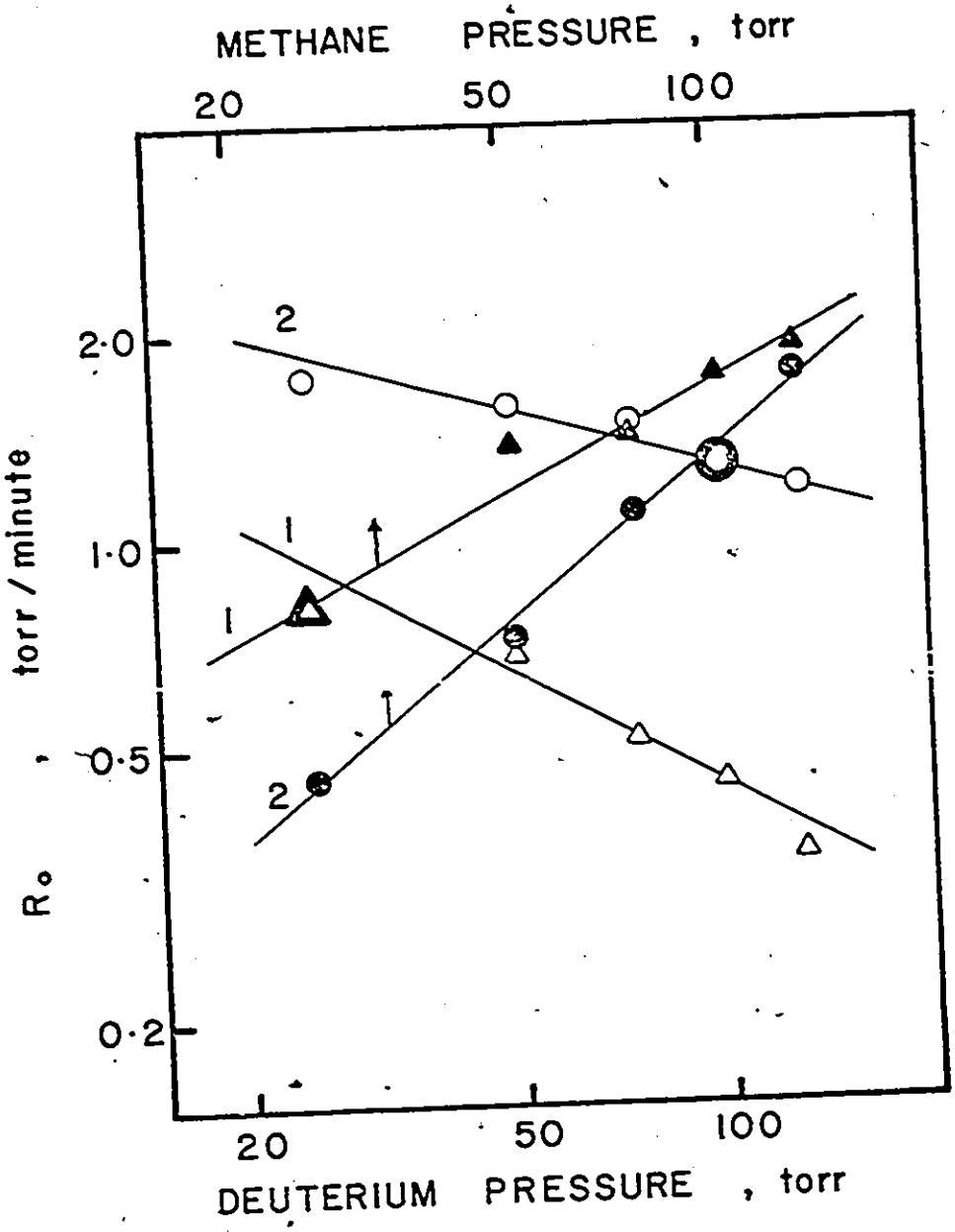


Fig. 33 The dependence of R_O upon the initial pressures of (a) deuterium when (1) P_M = 25 torr and (2) P_M = 100 torr; (b) methane when (1) P_D = 25 torr and (2) P_D = 100 torr over 80% Cu-20% Ni on silica catalyst at 212.0°C.

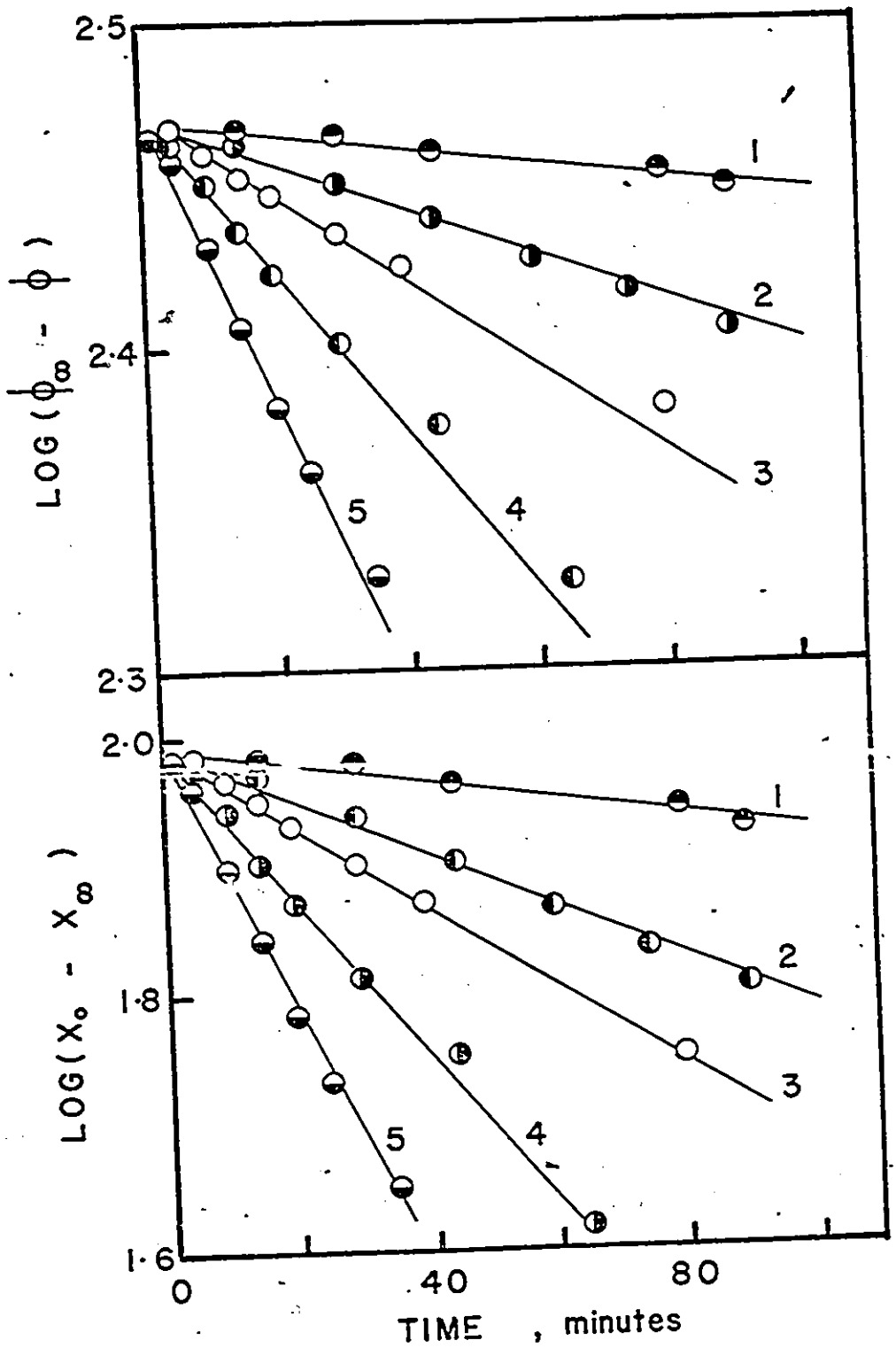


Fig. 34 The plots of log (ϕ_∞ - ϕ) and log (X_0 - X_∞) against time over 80% Cu-20% Ni on silica catalyst at (1) 150.0, (2) 171.0, (3) 187.0, (4) 200.0, and (5) 212.0°C.

(F) REACTION OVER Cu ON SILICA

This catalyst was not very active and the experimental results obtained at high temperatures after the stabilization of the catalyst at 360.0°C by performing experiments with an initial reactant ratio of 1 ($P_D = P_M = 50$ torr) are given in Table: 6.

While Fig. 29B shows the product distribution during the course of reaction at 440.0°C with an initial reactant ratio of 1. Fig. 35 represents the dependence of the initial rate of disappearance of methane upon the initial pressures of the reactants. The effects of the initial pressures of the reactants on the initial rates of stepwise and multiple exchange are shown in Figs. 36 and 37 respectively.

The observed product compositions for the exchange reaction with an equimolar mixture of the reactants ($P_D = P_M =$ 50 torr) after 20 and 70 hrs at various temperatures are given in Table: 6B. The values of ϕ_∞ and X_∞ observed at 420.0°C after 70 hrs were used to compute the rate constants k_ϕ and k_0 from the plots of log ($\phi_\infty - \phi$) and log ($X_0 - X_\infty$) against time which are shown in Figs. 38 and 39 respectively.

The Arrhenius plots, showing the influence of the temperature on the various specific rate constants, were good straight lines (Figs. 9-12). The derived activation energies for different processes were $E_\phi = 29.3$, $E_0 = 29.0$, $E_s = 28.4$ and $E_m = 30.3$ kcal/mole. The stepwise exchange was the dominant mechanism and the value of M increased at high tempera-

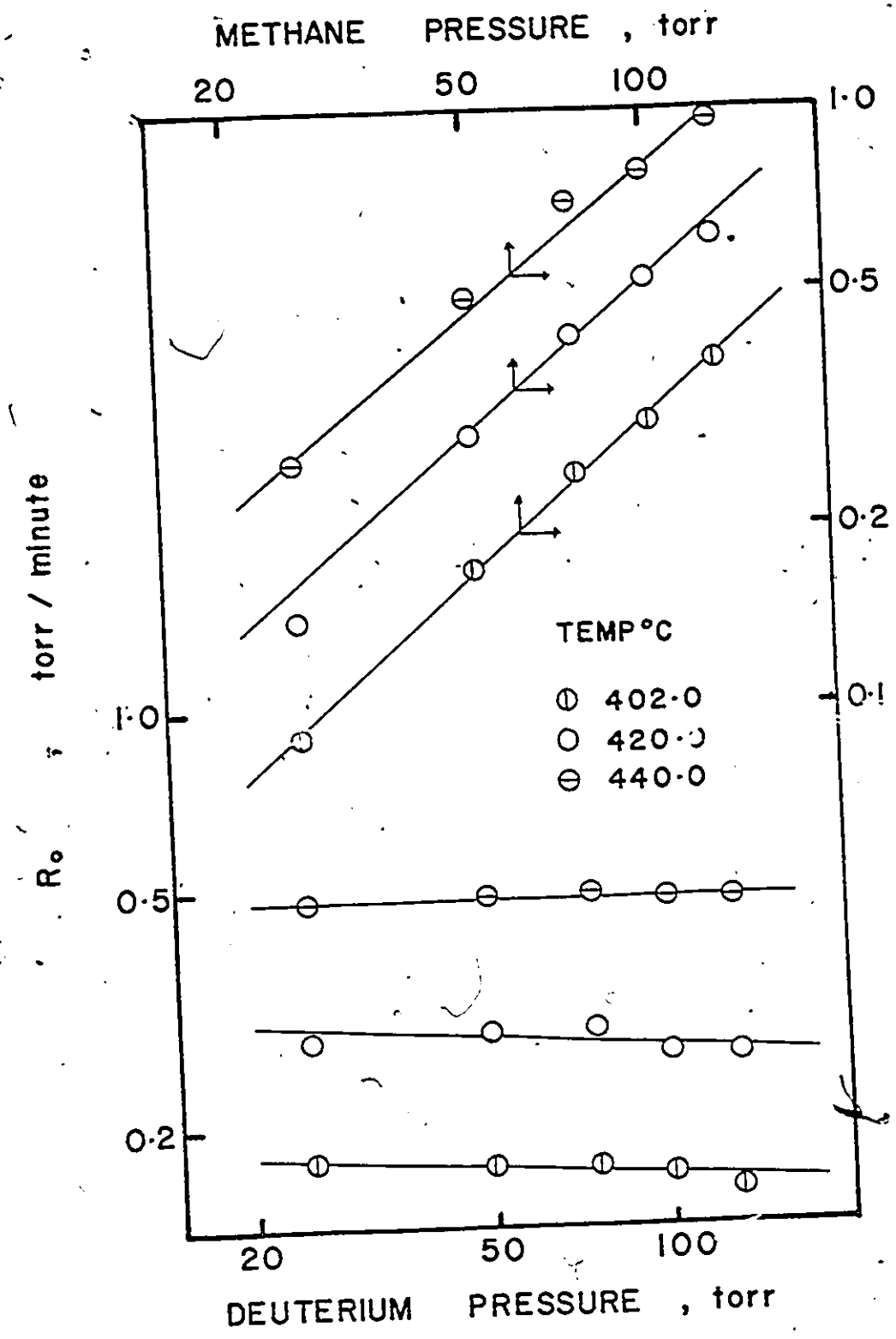


Fig. 35 The dependence of R_0 upon the initial pressures of the reactants over silica supported Cu catalyst.

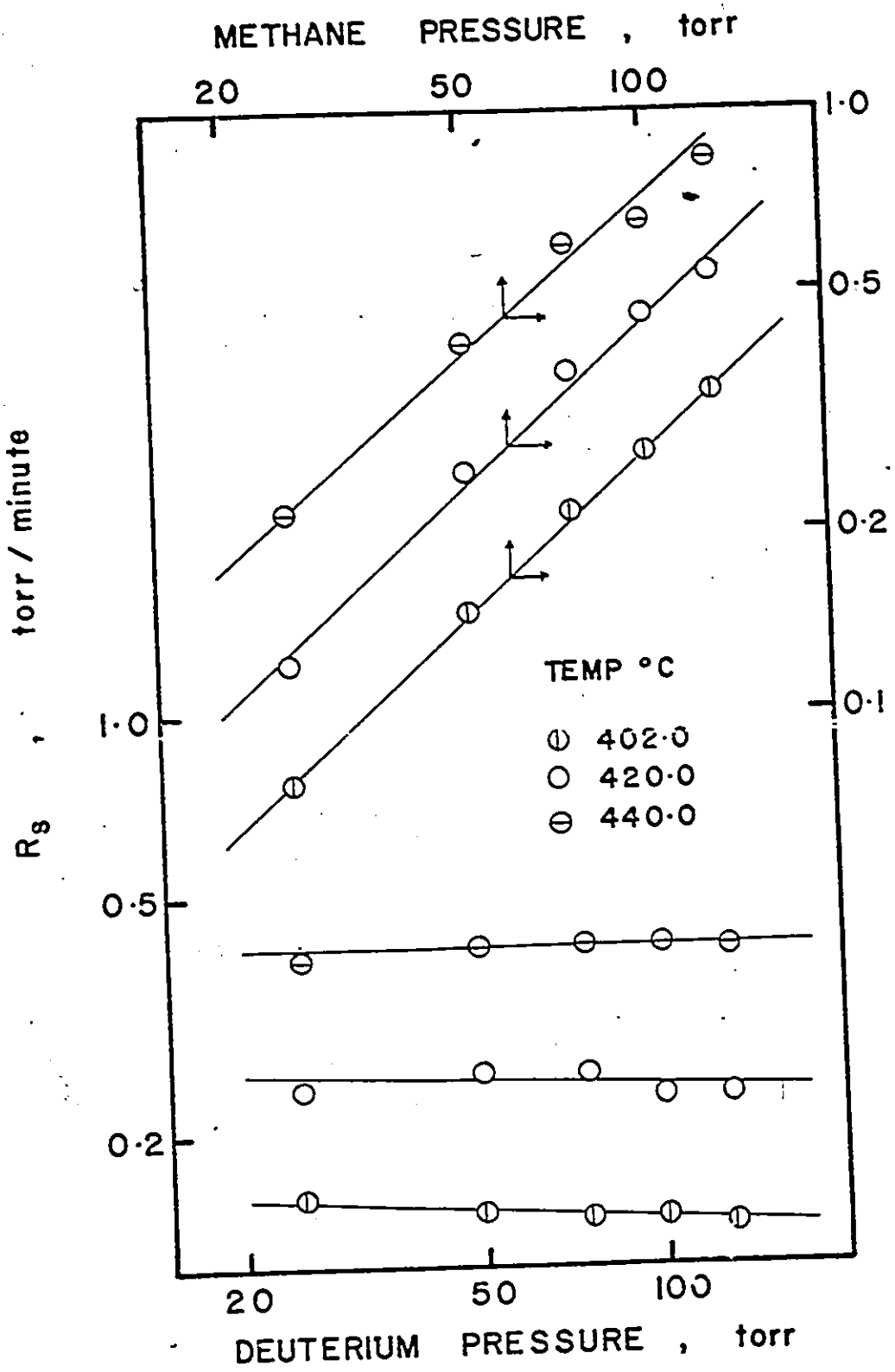


Fig. 36 The dependence of R_s upon the initial pressures of the reactants over Cu on silica catalyst.

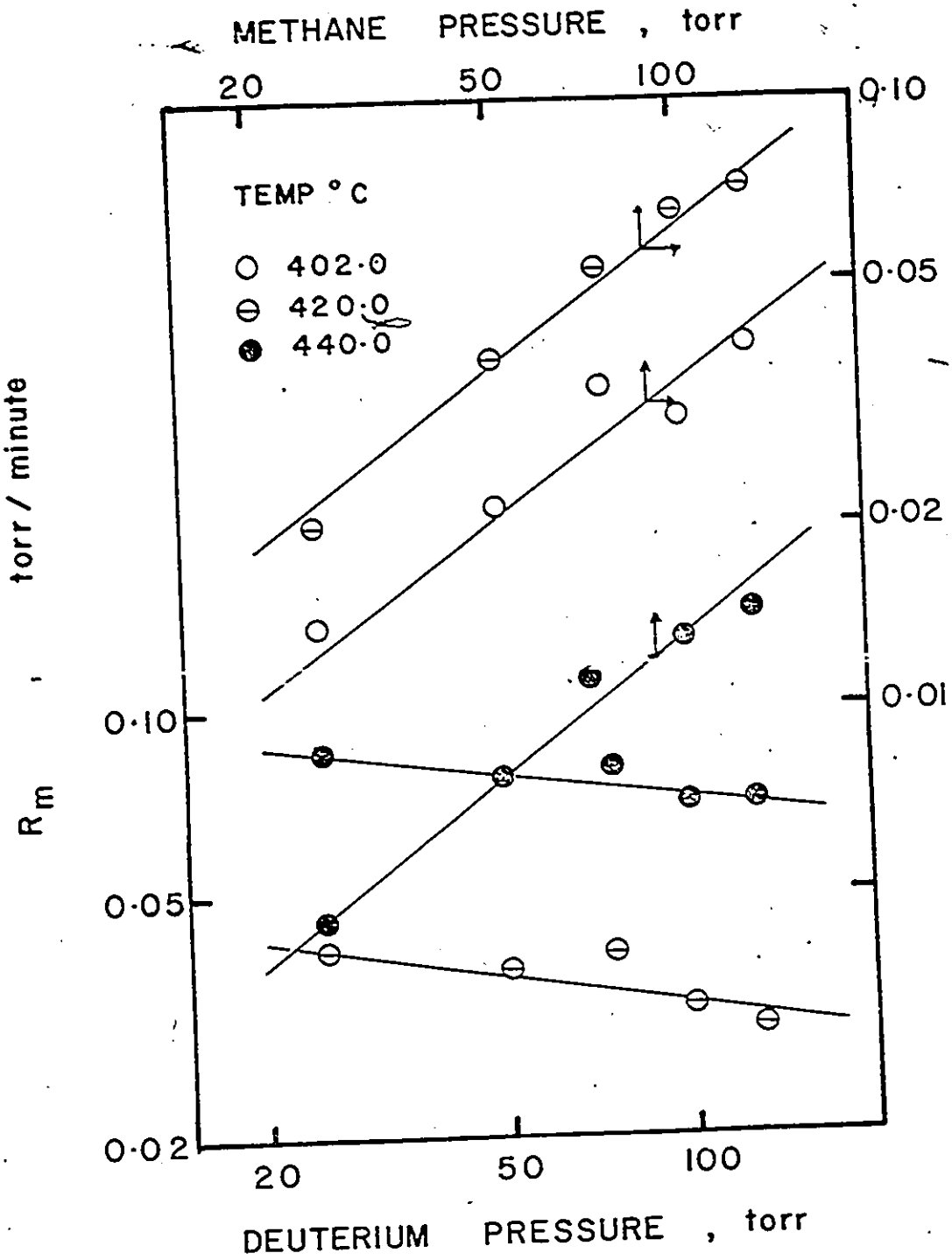


Fig. 37 The dependence of R_m upon the initial pressures of the reactants over silica supported Cu catalyst.

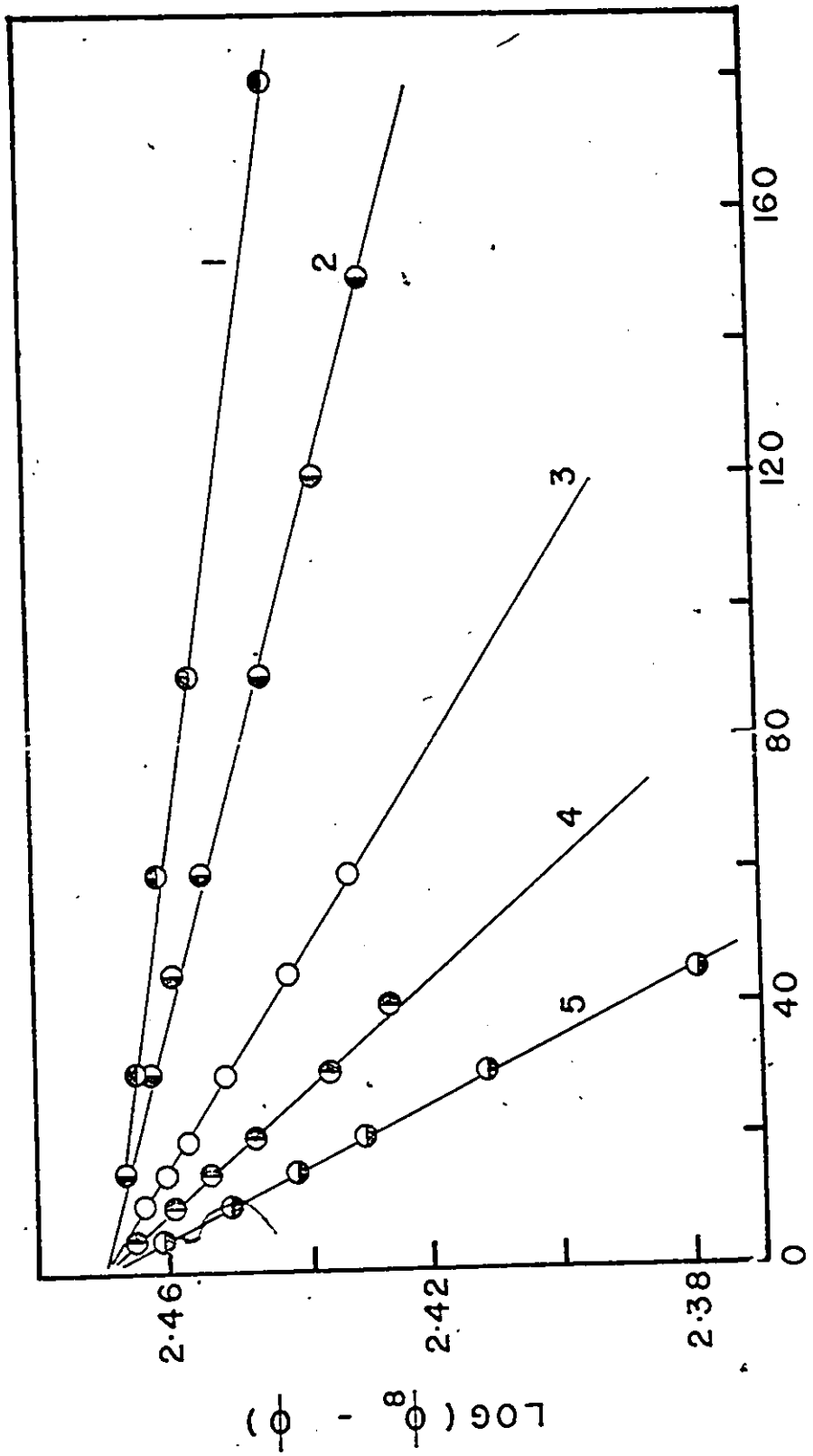


Fig. 38 The plots of log (ϕ_∞ - ϕ) against time over Cu on silica catalyst at (1) 360.0, (2) 379.0, (3) 402.0, (4) 420.0, and (5) 440.0°C.

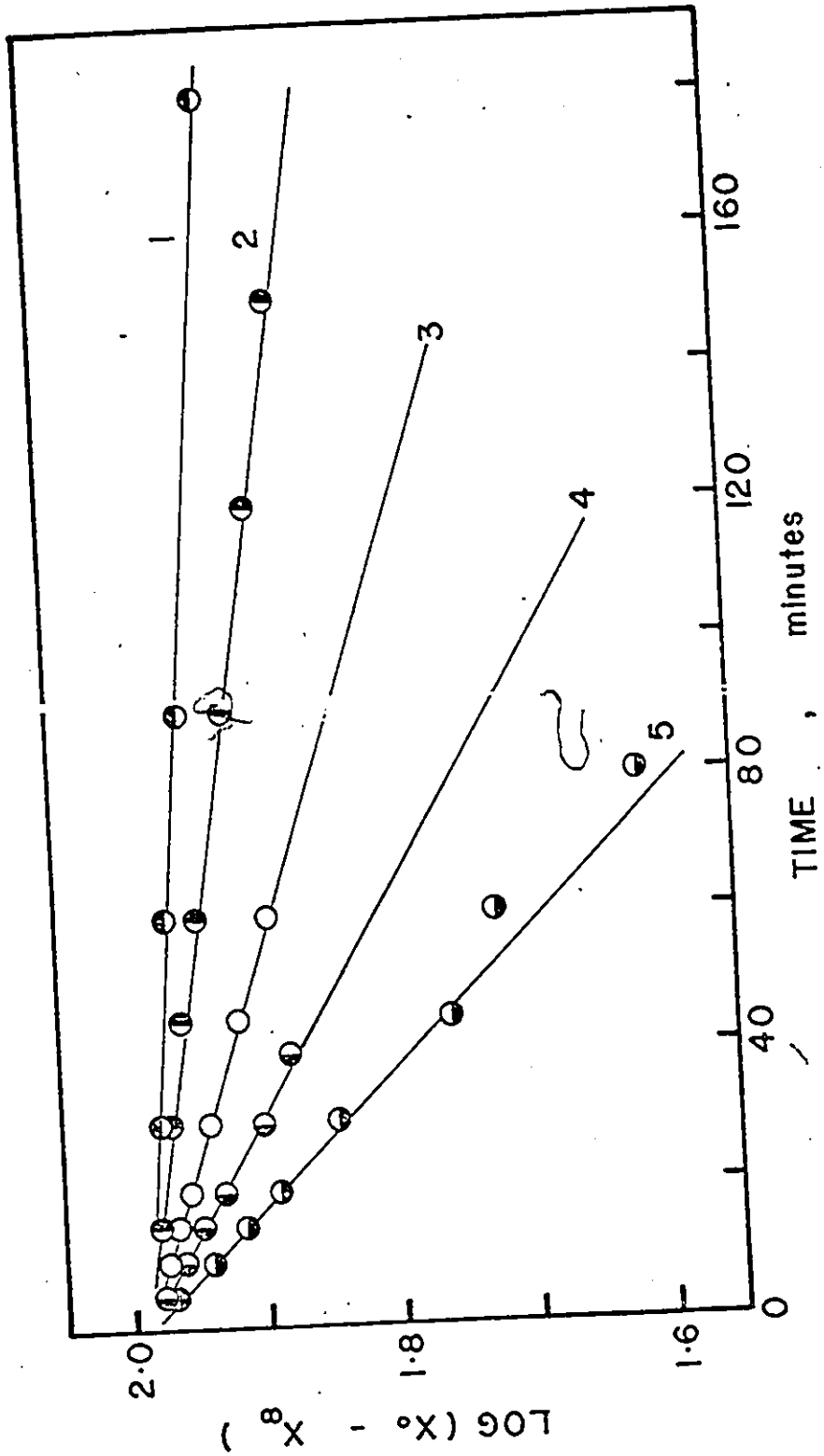


Fig. 39 The plots of log (X_0 - X_∞) against time over Cu on silica catalyst at (1) 360.0, (2) 379.0, (3) 402.0, (4) 420.0, and (5) 440.0°C.

tures. The kinetic parameters are given in Table: 6C.

EXPERIMENTAL ERRORS

The estimated errors in the measured quantities were as follows:

Temp. ^{o}C	$\Delta T = \pm 0.5\,^{o}C$
Time	$\Delta t = \pm 3$ seconds
Deuterium pressure	$\Delta P_D = \pm 1$ torr
Methane pressure	$\Delta P_M = \pm 1$ torr

The initial rates for the various exchange processes were determined within the accuracy mentioned below:

ΔR_o (%/min) $= \pm 0.05$ (%/min)

ΔR_s (%/min) $= \pm 0.05$ (%/min)

ΔR_m (%/min) $= \pm 0.005$ (%/min)

The maximum errors in the experimentally determined kinetic parameters and the equilibrium constants were as follows:

The orders of reaction

$$\Delta a = \Delta b = \Delta m = \Delta n = \pm 0.05$$

$$\Delta c = \Delta d = \pm 0.1$$

The activation energies

$$\Delta E_{\phi} = \Delta E_o = \Delta E_s = \Delta E_m = \pm 1 \text{ kcal/mole}$$

The frequency factors

$$\Delta \log A_{\emptyset} = \Delta \log A_{o} = \Delta \log A_{s} = \pm 0.5$$

$$\Delta \log A_{m} = \pm 0.8$$

The hydrocarbon inter conversion equilibrium constants

$$\Delta K_1 = \pm 0.4$$

$$\Delta K_2 = \pm 0.6$$

$$\Delta K_3 = \pm 0.3$$

VI DISCUSSION

(A) CATALYSTS

The Cab-O-Sil supported nickel, copper and bimetallic nickel-copper catalysts (20 wt % metal loading) employed in the present study were examined by Debye-Scherrer X-ray diffraction camera. The x-ray lines were too diffuse to permit the calculation of the lattice parameters and to determine the homogeneity of the alloys. Phase segregation in the case of nickel-copper films, unsupported nickel-copper alloys and nickel-copper plates has been reported elsewhere (53, 54, 26-30, 39-43). The unsupported nickel-copper alloys prepared in the laboratory and used in the hydrogenation of ethylene (55-56), acetylene (57), methylacetylene (58), dimethyl acetylene (59), and allene (60) were homogeneous preparations. The nature of the alloy catalysts, whether they are homogeneous alloys or consist of two phases, depends upon the method of preparation. Studies using nickel-copper alloys supported on kieselghur (61) and alumina (62,63) have been reported. Swift et. al (64) examined impregnated nickel and nickel-copper silica alumina catalysts and found that a nickel-copper alloy phase is formed when impregnated nickel-copper silica alumina catalysts are reduced with hydrogen. Silica

(Aerosil) supported nickel-copper alloys (42) prepared by the impregnation of silica with mixed aqueous solution of nickel and copper nitrates showed the existence of two phases in alloys with less than 50% Cu. Very recently Robertson et al. (65) studied the reducibility and alloying in silica (Davison 70) supported nickel-copper catalysts for various metal loadings by the Temperature-Programmed Reduction (TPR) technique and suggested that the direct reduction of the dried nickel-copper silica gives rise to a more concomitant creation of the metals implying the formation of alloys. Based on their findings, and the present observation that the catalytic activity is not the simple function of the catalyst composition (fig. 40), it can be safely assumed that the silica supported nickel-copper catalysts used in the present study were homogeneous alloys. These catalysts were very active and did not get poisoned during the course of investigation over a period of few months. Since the surface area of the catalysts were not determined, it was not possible to express the activity as per surface area.

(B) EQUILIBRIUM COMPOSITIONS AND EQUILIBRIUM CONSTANTS

As a result of the exchange reaction of methane with deuterium, the following hydrocarbon interconversion equilibria are established

$$CH_4 + CH_2D_2 \rightleftharpoons 2\ CH_3D \qquad (K_1)$$

$$CH_3D + CHD_3 \rightleftharpoons 2\ CH_2D_2 \qquad (K_2)$$

$$CH_2D_2 + CD_4 \rightleftharpoons 2\ CHD_3 \qquad (K_3)$$

and the average equilibrium constants calculated from the observed product compositions after 70 hrs at high temperatures (Tables: 1B, 2B...6B) are given in Table :I. They differ greatly from the classical values calculated by Eqn. (2) of chapter IV and appear to depend upon the catalyst investigated. Kemball (8) determined the equilibrium compositions of the five methanes over Ni films with P_D=16.1 torr and P_M=7.50 torr at 457.0°C and with P_D=12.9 torr and P_M=6.66 torr at 475.0°C. The mean equilibrium constants

Table I

Hydrocarbon Interconversion Equilibrium Constants
($P_D = P_M = 50$ torr)

Silica Supported Catalysts % Cu of Metal Loading	K_1	K_2	K_3	Temp. °C
0	0.87	3.68	2.42	151.0-178.0
20	0.92	4.06	2.34	142.0-157.0
40	1.26	3.28	2.50	149.0-182.0
60	1.08	3.33	2.59	170.0-193.0
80	0.33	3.88	2.38	200.0
100	0.11	5.83	2.37	402.0-420.0
Ni films (8)	2.40	2.20	2.17	466.0
Classical	2.67	2.25	2.67	
Quantum-mechanical(8)	2.35	2.48	2.27	466.0

determined from these measurements were in good agreement with both the classical and the quantum mechanical values (Table I). The values observed in the present investigation were determined from the product distributions observed after 70 hours over all of the catalysts with the initial reactant ratio of 1. They do represent the equilibrium values because no great change was observed in the product compositions after 20 and 70 hours at high temperatures, (Tables 1B...6B). It is emphasized that these constants are functions of the initial reactant pressures. In order to investigate the effect of the initial reactant pressures on the final compositions and the equilibrium constants, a series of exchange experiments were performed on a silica supported nickel catalyst at 178.0°C with different initial reactant ratios and the observed product distributions after 20 hours are given in Table 1B2. Assuming that these compositions do represent the equilibrium compositions, the equilibrium constants were determined from the data and are given in Table II. It is seen (Table 1B) that the final product compositions greatly depended on the initial reactant pressures. Similar observations were made by Mc Kee and Norton(12), while studying the exchange reaction of methane with deuterium over unsupported Pt-Ru alloys. The observed product distributions after 24 hours are shown in Table IIA along with the equilibrium constants calculated from these data on the assumption that the equilibrium was reached. It is found that the final compositions show wide variation with temperature and the initial

Table: II

The effects of the initial pressures of the reactants on the equilibrium constants over Ni-Silica at 178.0°C

P_D, torr	P_M, torr	K_1	K_2	K_3
25.0	25.0	0.067	7.68	2.20
100.0	100:0	1.93	3.09	2.44
50.0	50.0	1.37	3.35	2.36
50.0	100.0	2.61	2.74	2.12
25.0	50.0	1.65	3.87	3.15
100.0	50.0	0.30	6.42	2.12

reactant pressures, but an excess of deuterium favoured the formation of the more highly deuterated species. Kemball (48) determined the equilibrium compositions for the exchange reaction of propane with deuterium on tungsten films at 45.0°C (Table IIB). These results show that the final compositions are a function of the initial reactant ratios and as the initial deuterium to methane ratio increases, the formation of the highly deuterated species also increases. As shown in Tables II and IIA, the equilibrium constants are a function of the initial reactant pressure and do not agree with the classical values. The values observed by Mc Kee and Norton (12) (Table IIA) do not show any trend since

TABLE : IIA

DISTRIBUTIONS AFTER 24 HRS CONTACT WITH CATALYSTS

McKee - Norton (12)

CATALYST	Temp. °C	P_D / P_M	Final Concentrations, % of Total CH_4					Equil. Consts.		
			CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	K_1	K_2	K_3
Pt- 8% Ru	84	200/107	1.3	15.1	41.5	30.8	11.3	4.23	3.7	2.02
Pt- 8% Ru	80	45/83	7.5	16.0	36.4	29.6	10.4	0.93	2.8	2.3
Pt- 8% Ru	96	120/59	4.1	7.2	15.4	29.8	43.4	0.82	1.1	1.33
Pt- 8% Ru	99	139/65	--	--	32.6	25.9	41.5	indet.	∞	0.5
100 % Ru	154	78/40	--	6.6	24.2	37.7	31.5	∞	2.35	1.86
Pt-58% Ru	90	41/78	1.1	10.9	29.2	36.7	22.1	3.7	2.13	2.09

Table: IIB

Equilibrium percentages of propanes at 45.0°C over tungsten films. Kemball (48)

$P_{D_2}/P_{C_3H_8}$	0.5	2.0	8.0
percentages			
d_0	39.4	1.8	—
d_1	38.3	7.8	—
d_2	16.7	19.3	—
d_3	4.7	29.2	0.8
d_4	0.8	23.6	2.7
d_5	0.07	12.7	12.1
d_6	—	4.5	29.3
d_7	—	1.0	36.3
d_8	—	0.1	18.8

they were taken at different temperatures. The present results over a nickel silica catalyst (Table II) show a reasonable trend. It is found that

(i) with the initial reactant ratio of 1, while K_1 increased with the increased total pressure, K_2 decreased and K_3 slightly increased;

(ii) with a constant initial deuterium pressure of 50.0 torr, while K_3 slightly decreased with methane pressure, K_1 increased and K_2 decreased with the increased methane pressure; and

(iii) when the initial methane pressure was kept constant at 50.0 torr, K_1 and K_3 decreased with the increased deuterium pressure and K_2 first decreased and then increased with the corresponding increase in the deuterium pressure.

(C) COURSE OF REACTION

The product distributions during the course of exchange reaction over several silica supported catalysts are shown in Figs. 3, 17 and 29. It is quite clear that the stepwise exchange, leading to the formation of CH_3D, is initially dominant with only trace amounts of CD_4, CHD_3 and CH_2D_2 being formed. The M values were 1.0-1.2 and slightly temperature dependent. The product distributions over the silica supported nickel catalyst compare well with the observations made by Cece and Gonzalez (23). While the M values at 225.0-250.0°C observed by them were 2.0 to 3.0, the M value at 178.0°C in the present case was 1.21. Since the M value increases with increasing temperatures due to the increased contribution from the multiple exchange, the differences in the M values is understandable. However, the

present observations over the silica supported nickel catalyst do not compare with the results over nickel films (8,21) where CD_4 was the most abundantly formed initial product. From the observed product distributions over a series of silica supported catalysts in the present investigation it is concluded that the stepwise exchange is the dominant mechanism in the initial stages of the reaction.

Mc Kee and Norton (12) observed that over pt-8% Ru catalyst the stepwise exchange was predominant in the initial stages. Over this catalysts, the simultaneous exchange of H_2 and D_2 was followed and it was found that the ratio of the initial rate of formation of HD and the rate of disappearance of D_2 was close to unity, and the ratio of the initial rate of HD formation to that of the disappearance of methane was almost proportional to M, the mean number of hydrogen atoms displaced by deuterium in each molecule of methane. It was suggested that for the catalysts for which one type of exchange mechanism predominates, a relative measure of the rate of exchange as a function of temperature or pressure can be made by comparing the initial rate of formation of HD.

(D) PRESSURE DEPENDENCIES OF THE INITIAL RATES

The results of the exchange experiments at several temperatures over the initial reactant ratio range of 0.4 to 2.6 are given in Appendix II (Tables: 1 to 6). The computed

orders of reaction with respect to deuterium and methane for various initial rates over different catalysts are summarized in Table III. The positive orders up to unity for the hydrocarbon and negative orders for deuterium are explained by the fact that deuterium is more strongly adsorbed than the hydrocarbon. As stressed by Trapnell (66) the kinetic orders of the reaction indicate that deuterium covers an important part of the surface. One has to consider also that the order may be zero with respect to methane (18) as well as with respect to deuterium (67). Examining Table III, it is found that while deuterium is more strongly adsorbed on 20% Cu-80% Ni on silica and 40% Cu-60% Ni on silica catalysts, it is least strongly adsorbed on Cu-silica catalyst. Methane is weakly adsorbed and the strength of adsorption is more or less the same over all of the catalysts.

Table III

THE ORDERS OF REACTION

% Cu of Metal Loading	$R_s \propto P_D^a P_M^b$		$R_m \propto P_D^c P_M^d$		$R_o \propto P_D^m P_M^n$	
	a	b	c	d	m	n
0	-0.45	0.72	-0.6	0.7	-0.46	0.72
20	-0.56	0.88	-0.8	0.6	-0.56	0.84
40	-0.56	0.75	-0.8	0.7	-0.58	0.76
60	-0.33	0.85	-0.7	0.7	-0.35	0.81
80	-0.39	0.75	-0.8	0.7	-0.45	0.75
100	-0.03	0.86	-0.1	0.7	-0.03	0.82

In order to determine the effect of the initial reactant pressures on the orders of reaction, several exchange experiments were performed over silica supported nickel catalyst at 171.0°C and 80% Cu-20% Ni on silica catalyst at 212.0°C by keeping the initial pressure of one of the reactants constant at 25 or 100 torr while the pressure of the other reactant was varied. The orders of reaction for the initial rate of the disappearance of methane, R_0, determined from such experiments are given in Table IV. It is seen from this table that the orders of reaction are dependent on the

Table IV

The Orders of Reaction For Disappearance of Methane, R_0

Catalyst	Order w. r. t. D_2, m			Order w. r. t. CH_4, n		
	P_M=25 torr	P_M=50 torr	P_M=100 torr	P_D=25 torr	P_D=50 torr	P_D=100 torr
Ni - Silica T = 171.0°C	-0.60	-0.46	-0.43	0.66	0.72	0.74
80% Cu-20% Ni on silica T = 212.0°C	-0.55	-0.45	-0.27	0.52	0.75	0.80

initial reactant pressures. These orders increased with the increased amount of the reactant pressure that was kept constant. Frennet et al. (18-20) also observed that the reaction orders were quite dependent on the surface concentration of the

hydrocarbon radicals, which is a simple function of the partial pressures of methane and deuterium. This shows the importance of the conditions under which the orders are determined and also shows that the reaction mechanism is modified or the kinetic equation is complex. The kinetic orders (Table III) for the reaction over all of the catalysts were determined by the same procedure in all cases. Attempts to find a rate expression of the Langmuir-Hinshelwood or Langmuir-Rideal type were not successful. The power rate law was found to represent the observed kinetics adequately.

(E) ACTIVITY

The specific activity of the catalyst can be defined in several ways. For comparison of the activities of a series of catalysts, a certain reference temperature must be chosen. In the present investigation the rate constants for the various processes of the exchange reaction were determined from the exchange experiments performed with an initial reactant ratio of 1 ($P_D=P_M=50$ torr). The specific activity was then defined as follows:

(1) $\bar{k}_{\phi}$, the specific rate constant for the appearance of deuterium in the hydrocarbon expressed as the number of deuterium atoms entering 100 molecules of methane per minute per gm. of catalyst at 160.0°C.

(2) $\bar{k}_o$, the specific rate constant for the disappearance of methane expressed as % methane reacted per minute per gm. of catalyst at 160.0°C.

(3) $\bar{R}_s$, the specific rate constant for the stepwise exchange expressed as % CH_3D formed per minute per gm. of catalyst at 160.0°C, and

(4) $\bar{R}_m$, the specific rate constant for the multiple exchange

expressed as total % of CH_2D_2, CHD_3 and CD_4 produced per minute per gm. of catalyst at 160.0°C.

In the past, several attempts have been made to correlate the catalytic activity of the metals and alloy catalysts with the geometric and electronic properties of the catalysts. Metals which catalyze dehydrogenation and exchange of hydrocarbons are also generally active for the hydrogenation of unsaturated hydrocarbons.

Balandin (68) suggested that the catalytic activity depended on the presence of correctly spaced groups of atoms to accomodate the various reactant molecules. Only face centered cubic metals were active for hydrogenation and these same metals were also found to be active for the exchange reaction of saturated hydrocarbons. Beeck (69) found a bell shaped curve when the activity for ethylene hydrogenation was plotted against the lattice spacing, Rh with a lattice spacing 3.75 Å having a maximum activity. Kemball (2,9) also found that Rh had the maximum activity for the stepwise as well as the multiple exchange of methane with deuterium.

Beeck (69), following the suggestion of Boudart (77), obtained a smooth curve on the plot of the Pauling's percentage d-character (70) against the logarithm of the activity of the metals for ethylene hydrogenation with Rh having the highest activity. Kemball (9) found that the activity of metals for the methane deuterium exchange reaction increased roughly in proportion to the percentage d-character. Accord-

ingly nickel should be more active than copper and the activity of Ni-Cu alloy should decrease as Cu is alloyed with Ni.

Frennet (20) classified the metals according to the value of the ratio of the rate of CD_4 formation to the rate of CH_3D formation when the total rate of CH_4 disappearance was around 1% per second and obtained the sequence Rh > Ni > Re > Mo > W > Ta. While Kemball (9) in the investigation of methane deuterium exchange reaction over metal films observed the activity sequence Rh > W > Pt > Pd > Ni, McKee and Norton (13) found that the activity of the unsupported metals followed the sequence Pt > Rh > Ir > Ru > Pd for the same reaction.

Fig. 40 shows the plots of specific activity for the disappearance of methane, $\overline{k}_0$, the stepwise exchange, $\overline{R}_s$, and the multiple exchange, $\overline{R}_m$, against the catalyst composition. The most striking and interesting feature of the activity pattern observed in the present investigation is that the activity of silica supported nickel catalyst increases on addition of small amounts of copper, passes through a maximum at about 20% Cu-80% Ni on silica, decreases on further addition of copper and virtually vanishes for silica supported copper catalyst. According to the theory of Dowden (44) the activity of transition metals is due to holes in d-band. Dowden and Reynolds (71) regulated the concentration of d-holes of nickel by alloying it with copper and studied styrene hydrogenation. It was suggested that the activity of pure nickel (0.6 d-holes)

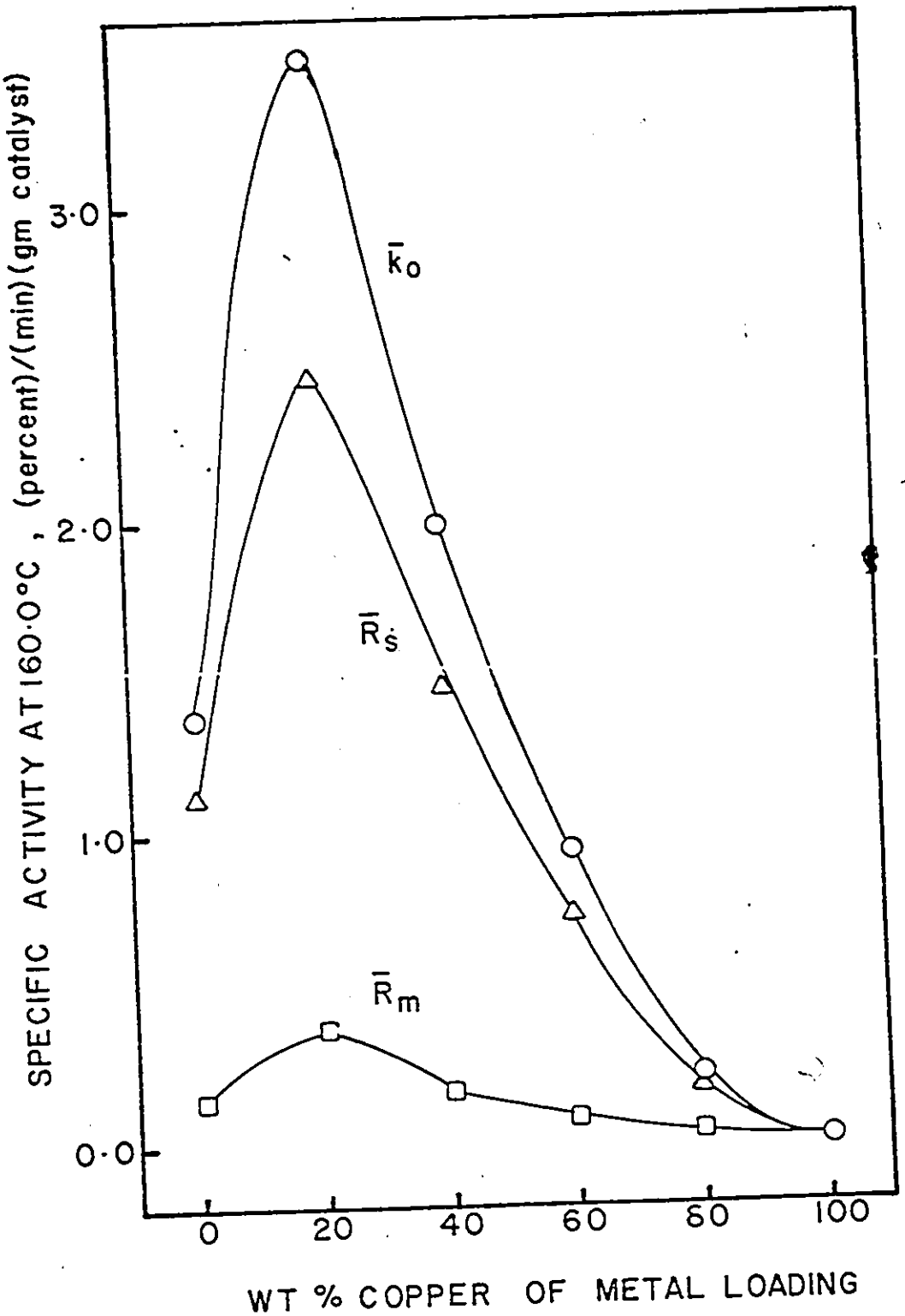


Fig. 40 The specific activity as a function of the catalyst composition.

should decrease as copper (no d-holes) is alloyed due to the filling of the holes in d-band and that at about 60% Cu it should fall to zero at which composition the d-band holes are completely filled. This is suppose to occur from s-electrons from copper atoms which enter the d-band of the nickel. The various reactions over nickel-copper alloys which were either films, plates, powders or granular alloys have been investigated and a variety of activity patterns has been observed (chapter II). However, since no work has been reported on the activity patterns of the silica supported nickel-copper catalysts for the methane deuterium exchange reaction, no comparision of the present results is possible.

Theoretically, there can be three idealized possible forms for the dependence of activity on composition for nickel-copper alloys as suggested by Bond and Mann (57) and recently by Takasu and Shimizu (43). The form A or α_1 type signifies the pattern for which the activity is governed by the content of nickel or it obeys the Dowden's forecast, i.e. the activity decreases progressively as the concentration of holes in d-band falls until it reaches zero at 60% copper. This type of the activity pattern has been observed in the hydrogenation of styrene (71) over nickel-copper alloys, in the H_2-D_2 equilibrium reaction on Cu-Ni alloy plates (29,30) and on Ni-Cu alloy films (26-28), and in ethane hydrogenolysis over unsupported nickel-copper alloys (37). In the case of the B or β type there is a maximum activity in the alloy composition range. For the

B type, it is suggested that as the d-band is filled the binding strength decreases and the activity increases, reaching a maximum before the d-band is completely filled. In the β type a maximum activity may be observed in the nickel rich or copper rich region. This type of pattern has been observed in H_2-D_2 equilibrium reaction over nickel-copper alloy plates (29), in several hydrogenation reactions (56-60, 72) over nickel-copper alloys and in the present investigation of methane deuterium exchange reaction over the silica supported nickel-copper catalysts. The activity-composition pattern C or α_2 type has a constant activity region over a wide range of composition. This type of pattern is observed in the cases where either the electron level density n (E) determines the activity or the activity is independent of the hole concentrations so long as there are some holes in the d-band. The results of Rienacker and Bommer (73) for the hydrogenation of ethylene over nickel-copper foils, of Ponec and Sachtler (32,33) for the exchange reactions of cyclopentane and methylcyclopentane with deuterium over nickel-copper alloy films, of Sinfelt et al. (37) for the dehydrogenation of cyclohexane over copper-nickel alloys and of Sachtler and Van Der Plank (39) for the benzene hydrogenation over copper-nickel alloys conform to this pattern.

Since no work has been reported on the exchange reactions of saturated hydrocarbons with deuterium over the silica supported nickel-copper catalysts, it is impossible to compare the present results of methane deuterium exchange reaction with

other known results. Over most of nickel-copper alloys where the existence of phase segregation has been confirmed the observed activity patterns were either of α_1 (A) or α_2 (C) type. Over most of the homogeneous nickel-copper alloys, the activity pattern of type β (B) has been observed. Furthermore, the pattern of the amount of hydrogen adsorbed, where determined, was similar to the activity pattern. So it can be safely assumed that the pattern of the amount of deuterium adsorbed over the silica supported nickel-copper catalysts of the present investigation would be of B type. Comparison of the observed activity pattern for the methane deuterium exchange reaction reveals a similarity in the activity patterns for the exchange reactions and the hydrogenation reactions. Bond and Webster (74) have reported the hydrogenation behaviour of the platinum-ruthenium alloys which closely parallels the activity patterns of these alloys in the methane-deuterium exchange reaction (12), and a similar parallelism (14) has been observed for the hydrogenation over platinum-rhodium alloys (75).

(F) ACTIVATION ENERGY

The variation of the activation energies, E_o, E_s, and E_m for the disappearance of methane, for the stepwise exchange and for the multiple exchange respectively with the catalyst composition is represented in Fig.41. The activation energies for the appearance of deuterium in the hydrocarbons, E_ϕ, and for the disappearance of methane, E_o, are quite similar, so

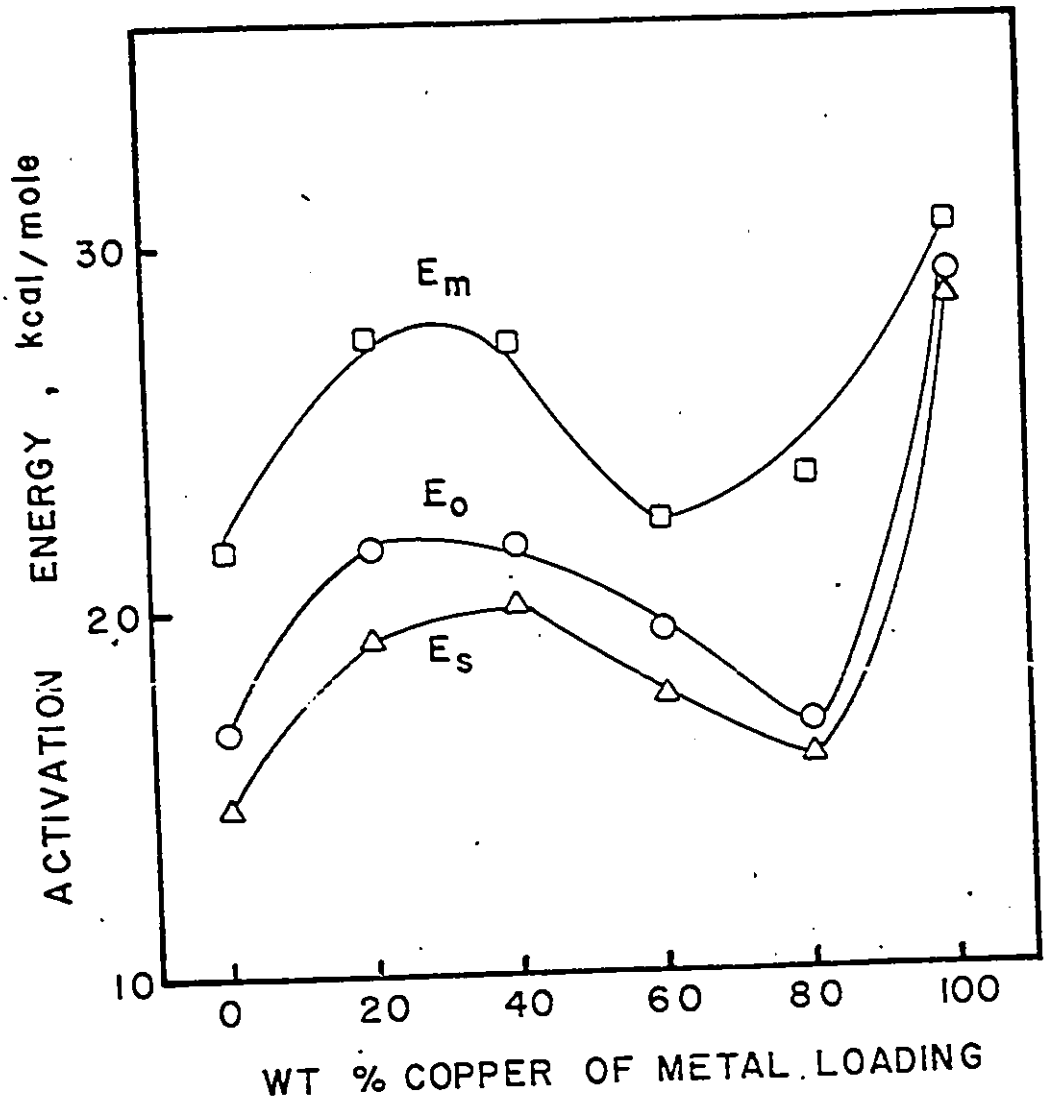


Fig. 41 The activation energy as a function of the catalyst composition.

only E_O is shown Fig. 41 and this is understandable because of the predominance of the stepwise exchange and the M values being close to unity. Though there is no specific trend for the variation of the activation energy with the catalyst composition, the sequence $E_m > E_\emptyset \cong E_O > E_s$ is observed for all of the catalysts investigated. At higher temperatures contribution from multiple exchange is of increasing importance and since further dissociation of chemisorbed methyl radicals to methylene radicals or other multiply bonded surface radicals requires an activation energy, E_m being greater than E_s is understandable. E_m is 6-8 kcal/mole greater than E_s in every case except for the silica supported copper catalyst where the difference is of 2 kcal/mole. Similar results have been observed for the methane deuterium exchange reaction over noble metal alloys (12-16).

The values of the activation energies and the logarithm of frequency factors tend to increase together indicating that these kinetic parameters exhibit a compensation effect. A well-defined compensation effect was observed in the present investigation as shown in Fig.42. While the logarithm of frequency factors and the activation energies for the appearance of deuterium in hydrocarbon, for the disappearance of methane and for the stepwise exchange followed the relation,

$$\log A_i = 0.61\ E_i - 1.8 \qquad i = \emptyset,\ O,\ s.$$

those for the multiple exchange obeyed,

$$\log A_m = 0.58\ E_m - 2.6,$$

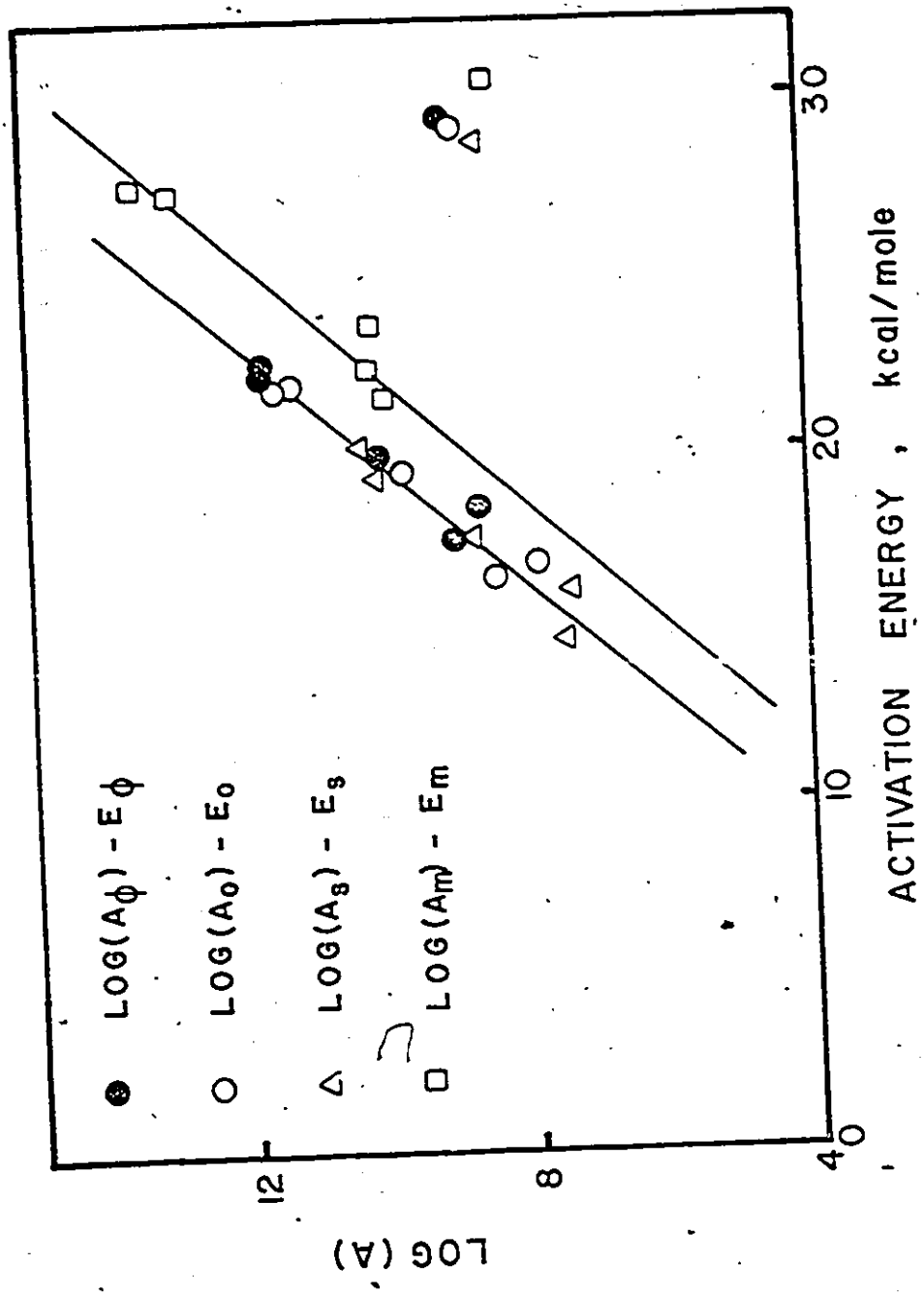


Fig. 42 The compensation effect for the exchange reaction of methane with deuterium.

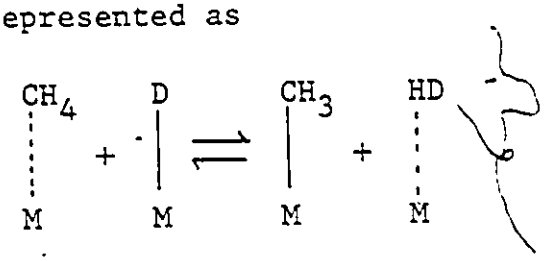
with the exception of the silica supported copper catalyst in both cases.

(G) MECHANISM

The experimental results show the predominance of stepwise exchange in the methane-deuterium exchange reaction over silica supported catalysts.

According to Kemball (2) " the exchange reaction is governed by an adsorption-desorption process and the main factor governing the reactivity on different metals is the ease of chemisorption of the hydrocarbon on the catalyst". Bond (76) considers that the rates of adsorption and desorption are much more rapid for hydrogen than for the hydrocarbon, so that the released hydrogen atom is rapidly replaced by a deuterium atom and the rate of exchange is thus limited by the rates of adsorption and desorption of the hydrocarbon. In the exchange of methane with deuterium two processes namely the stepwise and the multiple exchange are involved. According to Kemball (22), the intermediate responsible for the stepwise exchange leading to the formation of CH_3D is the adsorbed methyl radical formed by the dissociative chemisorption of methane. The multiple exchange must involve two more types of intermediates, adsorbed methylene radical, CH_2 and CH radical. Kemball suggested two sets of mechanisms. In the first set, it is assumed that the two mechanisms are independent processes and in the second set, the possibility that the second mechanism involves the first mechanism as an interme-

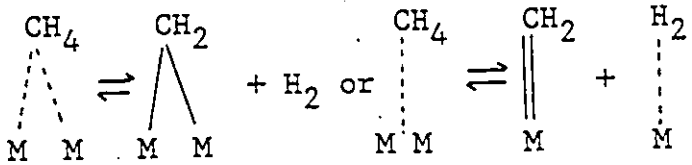
diate process was considered. In the first set, it was suggested that the observed results for stepwise exchange R_s and multiple exchange R_m are explicable if the rate determining step of the first mechanism is the adsorption of methane as methyl radical which is equal to the rate of desorption of methyl radicals as methane molecules. The mechanism may be represented as



(I)

where ..... M represents a catalyst atom-site .

The second mechanism will be governed by the rate of adsorption or desorption of methylene radicals which involves one less hydrogen or deuterium atom than the first mechanism and it may be represented as



(II)

Assuming these two mechanisms and using the experimentally determined orders of reaction for stepwise exchange and multiple exchange (Table III), the chances of finding one bare site on each catalyst θ_F (for stepwise exchange) and θ_F' (for multiple exchange) were calculated, which are given in Table V.For a given catalyst θ_F and θ_F' should be same. Since in the present study $R_s \gg R_m$ and there was much scattering

Table V

The Chances of Finding a Bare Site on Catalysts

Catalyst	$\theta_F \propto P_D^x P_M^y$		$\theta_{F'} \propto P_D^{x'} P_M^{y'}$	
% Cu of Metal Loading	x	y	x'	y'
0	-0.475	-0.14	-0.3	-0.15
20	-0.53	-0.06	-0.4	-0.20
40	-0.53	-0.125	-0.4	-0.15
60	-0.415	-0.075	-0.35	-0.15
80	-0.445	-0.125	-0.4	-0.15
100	-0.265	-0.07	-0.05	-0.15

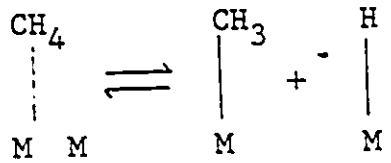
in data for the dependence of R_m on P_D and P_M, the orders for R_m are less accurate than those for R_s. R_m was much smaller. Contributions from R_m was less than 8% at lower temperatures and at high temperatures the maximum contribution was about 12%. So it is suggested that θ_F more appropriately represents the chances of finding a free surface site on each catalyst.

In the second set Kemball expressed the initial rates of the two slow steps, i.e. adsorption or desorption of methyl radicals and dissociation of methyl radicals to methylene radicals as

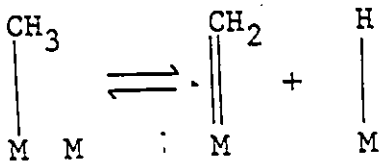
$$R_0 = R_s + R_m \quad \text{and} \quad R_{0'} = \frac{R_m}{R_s} (R_s + R_m) .$$

The orders of reaction are now slightly different as shown in

Table: III for R_0. The mechanisms may be represented as



(III)



(IV)

Assuming these mechanisms, and using the experimental orders for the disappearance of methane, R_0, the chances of finding a bare site on catalysts θ_G were calculated which are given in Table VI. θ_G is quite different from θ_F or θ_F, because of different mechanisms that were assumed. In the present study, deuterium was always admitted first to the reactor

Table VI

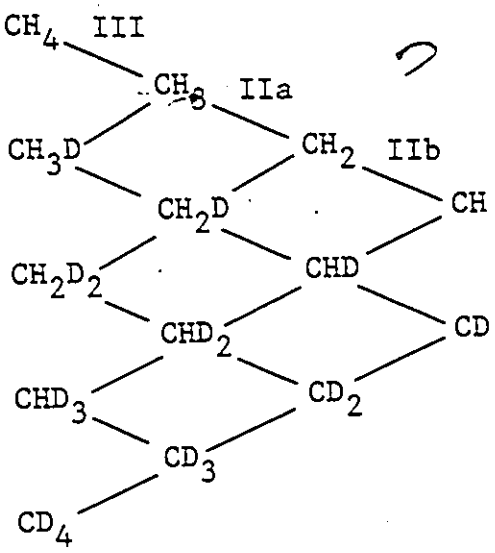
The Chances of Finding

a Bare Site on Catalysts

Catalyst % Cu of Metal Loading	$\theta_G \propto P_D^{x''} P_M^{y''}$	
	x''	y''
0	-0.23	-0.14
20	-0.28	-0.08
40	-0.29	-0.12
60	-0.175	-0.095
80	-0.225	-0.113
100	-0.015	-0.09

so it is more likely that the methyl radicals are formed by mechanism I and not by mechanism III. Hence, it is suggested that θ_F more appropriately represents the chances of finding a free surface site on the catalyst.

Miyahara (11) suggested that the experimental results of Kemball (8,9) can be satisfactorily interpreted by assuming a single reaction scheme as shown below.



In this scheme, Rate IIb has to be fast enough as compared to Rate IIa so that all methyl radicals that dissociate to give methylene radicals give back a methyl radical that is completely deuterated under initial conditions. This, of course, implies fast exchange between the hydrogen atoms directly chemisorbed on the metal and the gaseous D_2. The ratio of the rates of formation of CH_3D and CD_4 is then a function of the ratio of the Rates III and IIa.

Based on the study of methane-deuterium exchange re-

action on Rh film, where CD_4 was the most abundantly formed initial product, Frennet et al. (18-20) proposed as an alternative to the ideas of Bond and Kemball, that the rate determining step for the formation of CD_4 should be the displacement of a hydrocarbon radical by D_2 . It was proposed that the formation of CD_4 takes place through a displacement reaction of the type

$$H_2 + CH_3^* \rightleftharpoons CH_4 + H^*$$

corresponding to the first step following which methane interacts with metal. In that case, the formation of CD_4 by the displacement of CH_3 is explained, if first, all surface radicals are in rapid equilibrium with gaseous hydrogen with respect to isotopic distribution. Thus all CH_3 radicals are perdeuterated at initial conditions. Second assumption was that the concentration of CH_3 radical is very small and, at each temperature, proportional to the degree of coverage in hydrocarbon radicals θ_c. The rate expression for the formation of CD_4 was developed which explained observed kinetics.

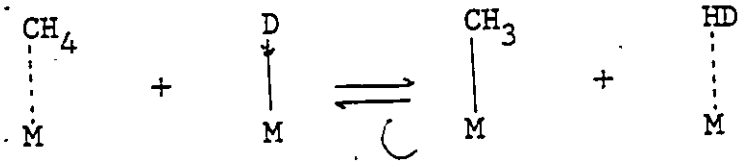
$$r_{CD_4} = k P_{D_2} \frac{K (P_{CH_4} / P_{D_2}^2)}{1 + K (P_{CH_4} / P_{D_2}^2)}$$

Where k is a rate constant and K is an equilibrium constant for the reaction between methane and metal surface.

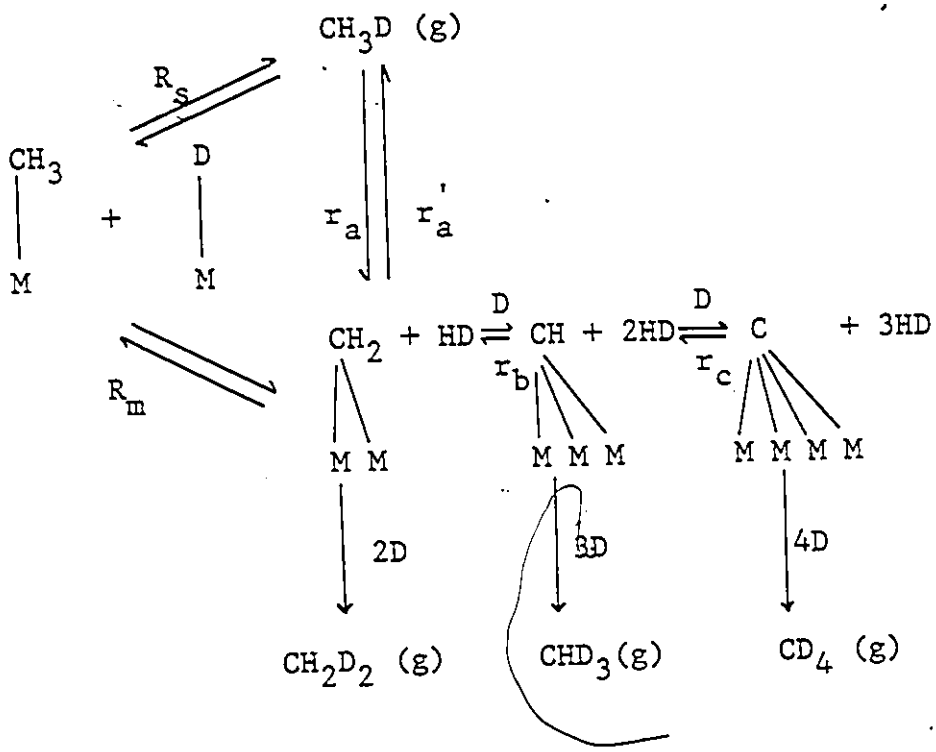
McKee and Norton (12-16) found a rough correlation between the type of mechanism and the lattice parameters of the noble metals. While metals having smaller atomic radii

(Ru-1.32 Å, Rh-1.34 Å, Ir-1.35 Å, Ni-1.24 Å) favor the multiple exchange, those having larger atomic radii (Pt-1.38 Å, Pd-1.37 Å) are good for the stepwise exchange. Over the noble metal alloys, it was found that a maximum in the activity-composition plot was observed at an alloy composition corresponding to one unpaired d electron per metal atom. However, as observed by Cece and Gonzalez (23) and in the present investigation, the silica supported nickel catalyst favoured the stepwise exchange and CH_3D was the most abundant initial product. Thus nickel can promote both the stepwise and the multiple exchange and so the role of the lattice parameters is somewhat less than as suggested by Mc Kee and Norton.

Following Kemball (8,9) and Mc Kee et al. (12-16), the reaction scheme for the methane-deuterium exchange reaction over the silica supported nickel-copper catalysts is formulated as follows. In the present investigation, the stepwise exchange was predominant over all of the catalysts investigated. It seems reasonably certain that the stepwise exchange proceeds via the initial dissociation of C-H bond and the formation of the chemisorbed methyl radicals on the catalyst surface. Since, in the present experiments, deuterium was always admitted first, the catalyst surface is initially covered with strongly adsorbed deuterium atoms and it is likely that the dissociation of methane arises from an interaction between weakly adsorbed methane and surface D atoms.



The details of the multiple exchange mechanism are, however, less clear but the initially formed methyl radicals probably dissociate further into methylene or more highly dissociated fragments. A possible reaction scheme in which both mechanisms can take place simultaneously is shown below.



In the present investigation, the stepwise exchange was predominant with $R_s \gg R_m$, the higher deuterated species would have been formed during the course of reaction by readsorption and dissociation of CH_3D via steps r_a, r_b, and r_c. The rapid removal of methyl radicals from the surface as CH_3D would tend to suppress the initial appearance of the highly deuterated products by the R_m mechanism. The tendency to form highly dissociated fragments will be expected to be favoured by an increase in the temperature, leading to a greater participation

of R_m reaction. This scheme satisfactorily explains the observed results of the methane-deuterium exchange reaction over silica supported nickel-copper catalysts.

(H) SIGNIFICANT CONTRIBUTION

The study of the catalytic exchange of methane with deuterium over silica supported nickel-copper catalysts (20 wt % metal loading) has made the following contributions to the field of heterogeneous catalysis:

(1) Silica supported copper catalyst was found to be active for methane-deuterium exchange reaction in the temperature range 360.0 - 440.0°C as opposed to Cu films where no exchange was observed in the past even at 700.0°C (18-20).

(2) Silica supported nickel catalyst was quite active and the exchange was observed at comparatively lower temperatures (130.0-178.0°C) than those for Ni-films (206.0 - 255.0°C). Furthermore this catalyst was highly selective for stepwise exchange as opposed to Ni-films (8,9) where multiple exchange was predominant.

(3) It was found that the activity of silica supported nickel catalyst can be increased by an addition of small amounts of copper without affecting the selectivity.

(4) Silica supported nickel-copper catalysts were quite active for the exchange reaction and did not get poisoned as compared to unsupported nickel copper alloys where

severe self poisoning has been observed in the past in the exchange reactions of cyclopentane and methylcyclopentane with deuterium (31-32) and in some H_2-D_2 equilibrium reactions (27-28).

(5) The hydrocarbon equilibrium compositions and the equilibrium constants for the hydrocarbon interconversion equilibria were determined for the exchange reaction with an initial reactant ratio of 1. Knowledge of these equilibrium constants is necessary in the separation of isotopic species by chemical process.

(6) Nickel catalyst has been widely used by chemical industries in the hydrogenation of olefins, acetylenes and aromatic hydrocarbons and in dehydrogenation and hydrogenolysis reactions. Knowledge gained by the present investigation over silica supported catalysts can be successfully applied to these other reactions.

VII CONCLUSION

The catalytic exchange reaction of methane with deuterium over silica supported nickel, copper and nickel-copper catalysts was investigated at several temperatures for initial reactant ratios between 0.4 and 2.6 in a static constant volume system.

The orders of reaction for the stepwise exchange were -0.03 to -0.56 and 0.72 to 0.88 with respect to deuterium and methane respectively. While the orders of the reaction with respect to deuterium and methane for the multiple exchange were -0.1 to -0.8 and 0.6 to 0.7 respectively, those for the disappearance of methane were -0.03 to -0.58 and 0.72 to 0.82 respectively. Though these orders were independent of the temperature, they were quite dependent on the initial pressures of the reactants. While deuterium is more strongly adsorbed on 20% Cu and 40% Cu on silica catalysts and least strongly adsorbed on silica supported copper catalyst, methane is weakly adsorbed and the strength of adsorption is more or less same over all of the catalysts investigated. The chances of finding a bare metal site were determined.

The hydrocarbon equilibrium compositions and the equilibrium constants for the hydrocarbon interconversion equilibria

for the exchange reaction with an initial reactant ratio of 1 were determined. The effects of the initial pressures of the reactants on the hydrocarbon equilibrium compositions and equilibrium constants over silica supported nickel catalyst at 178.0°C were investigated.

While the apparent activation energies for the appearance of deuterium in hydrocarbon and for the disappearance of methane were 17.4 to 29.3 and 16.3 to 29.0 kcal/mole respectively, those for the stepwise exchange and for the multiple exchange were 14.5 to 28.4 and 21.4 to 30.3 kcal/mole respectively. A well defined satisfactory " compensation effect " appears to exist for the exchange of methane with deuterium over the silica supported catalysts investigated.

The study of the kinetics of methane deuterium exchange provided a convenient method for the investigation of the catalytic activity pattern of the silica supported nickel-copper catalysts. A maximum activity was observed at about 20% Cu-80% Ni on silica in the activity-composition plot. The activity of the catalysts could not be satisfactorily explained in terms of % d-character or the lattice parameter. An attempt was made to explain the activity in terms of the concentration of holes in the d-band. The dependence of the catalytic activity for the exchange reaction on the electronic factors is not yet well established. The H_2-D_2 equilibration reaction over nickel-copper films and the exchange of propane with deuterium over nickel-copper alloys followed pattern A.

The exchange of cyclopropane and methylcyclopropane with deuterium over nickel-copper films exhibited pattern C. The activity pattern in the present investigation was of B type. Although a theoretical interpretation of the results has not been completely established; it seems certain that the changes observed in the activities of the silica supported nickel-copper catalysts in the present investigation might be related to the deuterium preadsorbed (or dissolved) on them.

All of the silica supported catalysts were active and highly selective for the stepwise exchange leading to the formation of CH_3D. A reaction scheme, based on the results of the investigation, was postulated which satisfactorily explains the formation of different deuterated methanes.

VIII RECOMMENDATIONS

A detailed study of some factors such as the configuration of alloys, the method of preparation and the chemisorption of methane and deuterium on the silica supported nickel-copper catalysts must be carried out in order to establish any firm interpretation for the maximum activity being at 20% Cu-80% Ni on silica catalyst in the present investigation.

Further kinetic study must be made on other light hydrocarbons such as propane, ethane for the better understanding of the exchange reaction over the silica supported nickel-copper catalysts. An additional work must be carried out before the dependence of the catalytic activity on the geometric and electronic factors is well established.

For the catalytic exchange of methane with deuterium, following recommendations are made:

(1) The exchange reaction over other alloys such as Pt-Cu, Pd-Cu, Rh-Cu, Ru-Cu, Ir-Cu, Os-Cu, Ni-Fe, and Ni-Co should be studied to understand the significance of the role played by the holes in the d-band in the heterogeneous catalysis.

(2) The exchange reaction over the unsupported nickel-copper catalysts and over nickel-copper catalysts supported on

different carriers should be investigated in order to understand the effect of the carriers on the activity pattern.

(3) The surface area of the silica supported catalysts employed in the present investigation must be determined in order to get a correct activity pattern for the methane deuterium exchange reaction.

(4) The rate expression of the Langmuir-Hinshelwood type must be developed, if possible.

(5) The detailed study of the equilibrium constants for the various initial reactant ratios must be carried out to confirm the non-classical nature of these constants.

(6) The exchange reaction over supported bimetallic nickel-copper catalysts with various metal loadings should be investigated to see how they affect the activity pattern and the exchange mechanism.

(7) The effect of admitting methane first, followed by deuterium, on the kinetics of the reaction must be investigated.

(8) The various bimetallic catalysts, supported or unsupported, should be examined by X-ray and the electron microscope to find out the surface homogeneity, and the chemisorption of methane and deuterium over these catalysts should be studied to correlate the activity pattern with the catalyst surface composition and to understand the kinetics of the exchange reaction.

(9) Attempts should be made to study the reaction between

CD_4 and H_2 over the silica supported bimetallic nickel-copper catalysts and to compare the results with the present findings. Simultaneous exchange of hydrogen and deuterium must also be investigated.

(10) The exchange reaction over the same catalysts should be studied in a batch reactor and a flow reactor to see whether the kinetic parameters and the activity pattern are the same or different.

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X APPENDICES

APPENDIX I

CRACKING PATTERNS OF METHANES AND COMPUTER PROGRAMS

The cracking patterns of interest obtained from the calibration data of the individual methanes over a range of pressures are given in Table A.

Table A

The Cracking Patterns of Methanes

I. V. = 70 eV Trap Current = 50 μA

I. R. = + 1 v Amplifier Range = 250

Component j / Mass, m	0 CH_4	1 CH_3D	2 CH_2D_2	3 CHD_3	4 CD_4
16	100.00	77.78	33.88	5.93	7.29
17	0.89	100.00	69.86	53.33	1.23
18		0.77	100.00	44.00	82.58
19			0.91	100.00	2.79
20				0.65	100.00
Sensitivity S_j, div./torr	0.89	0.81	0.71	0.75	0.775

I. V. = Ionization voltage. I. R. = Ion repeller voltage.

From these cracking patterns, five equations of the form, $P_m = \sum C_{m,j} S_j p_j = \sum C_{m,j} X_j$, were formulated as follows:

$$P_{16} = X_o + 0.7778X_1 + 0.3380X_2 + 0.0593X_3 + 0.0729X_4$$

$$P_{17} = 0.0089X_o + X_1 + 0.6986X_2 + 0.5333X_3 + 0.0123X_4$$

$$P_{18} = 0.0077X_1 + X_2 + 0.4400X_3 + 0.8258X_4$$

$$P_{19} = 0.0091X_2 + X_3 + 0.0279X_4$$

$$P_{20} = 0.0065X_3 + X_4$$

These equations were rearranged, the values of sensitivity of individual methanes, S_j, were substituted and the partial pressures of individual methanes were expressed in terms of the observed peak heights, P_m, in the sample spectrum. The rearranged equations are:

$$P_o = 1.1314P_{16} - 0.8818P_{17} + 0.2308P_{18} + 0.3034P_{19} - 0.2707P_{20}$$

$$P_1 = - 0.0111P_{16} + 1.2498P_{17} - 0.8668P_{18} - 0.2894P_{19} + 0.7093P_{20}$$

$$P_2 = - 0.011P_{17} + 1.4216P_{18} - 0.6121P_{19} - 1.1568P_{20}$$

$$P_3 = - 0.0123P_{18} + 1.3389P_{19} - 0.0272P_{20}$$

$$P_4 = - 0.0085P_{19} + 1.2905P_{20}$$

These equations were solved using a computer program CP1 and the compositions of the individual methanes as percent of total methane were determined.

COMPUTER PROGRAM CP1

Calculation of the compositions of the individual methanes from the observed peak heights in the sample mass spectrum.

Nomenclature

D/M = P_D/P_M	Initial ratio of the reactants
NR = RN	Observation no.
NTIME = TIME	Time in minutes
P0, P1,....P4	Partial pressures of CH_4, CH_3D...CD_4 respectively, torr
P16, P17...P20	Peak heights at mass 16, 17...20 respectively, div.
PD0, PD1...PD4	Compositions of CH_4, CH_3D....CD_4 respectively, % of total methane
PDS	Sum of percentages of CH_2D_2, CHD_3 and CD_4
PHI = ϕ	Deuterium content of the hydrocarbon at time t

```
$JOB  ACCT=VON,A.N.SHAH,TIME=30,PAGES=20
      DIMENSION HEAD(20),SUBH(9),RATIO(8)
      IIN=5
      IOUT=6
      READ(IIN,3)(HEAD(N),N=1,20),(SUBH(J),J=1,9)
    3 FORMAT((20A4),/,(9A4))
    8 K1=0
      WRITE(IOUT,35)
   35 FORMAT('1')
    9 READ(IIN,20)(RATIO(N),N=1,8)
   20 FORMAT(5X,8A4)
      WRITE(IOUT,4)(HEAD(N),N=1,15),(RATIO(N),N=1,8),(SUBH(J),J=1,9)
    4 FORMAT(//////,1X,15A4,2X,8A4,///,1X,A4,8(6X,A4))
    5 READ(IIN,10)NR,NTIME,P16,P17,P18,P19,P20
   10 FORMAT(I3,7X,I5,5F10.5)
   30 FORMAT(/,1X,I3,6X,I5,7F10.2)
      IF(NR.EQ.0) GO TO100
      IF(NR.EQ.999) GO TO 200
      P0=1.1310*P16-0.8010*P17+0.2308*P18+0.3034*P19-0.2707*P20
      P1=-0.0111*P16+1.2498*P17-0.3668*P18-0.2894*P19+0.7093*P20
      P2=-0.011*P17+1.4216*P18-0.6121*P19-1.1568*P20
      P3=-0.0123*P18+1.3389*P19-0.0272*P20
      P4=-0.0085*P19+1.2905*P20
      PT=P0+P1+P2+P3+P4
      PD0=(P0/PT)*100.0
      PD1=(P1/PT)*100.0
      PD2=(P2/PT)*100.0
      PD3=(P3/PT)*100.0
      PD4=(P4/PT)*100.0
      PHI=PD1+2.0*PD2+3.0*PD3+4.0*PD4
      PDS=PD2+PD3+PD4
      WRITE(IOUT,30)NR,NTIME,PD0,PD1,PD2,PD3,PD4,PHI,PDS
      GO TO 5
  100 CONTINUE
      K1=K1+1
      IF(K1.EQ.1)GO TO 9
      GO TO 8
  200 WRITE(IOUT,35)
      STOP
      END
$ENTRY
```

TYPICAL OUTPUT OF CP1

METHANE DEUTERIUM EXCHANGE OVER NI ON SILICA D/H=50/50 TEMP=171,0C

NRI	TIME	PD0	PD1	PD2	PD3	PD4	PHI	PD8
203	2	98,52	1,26	0,05	0,07	0,11	1,99	0,22
204	5	95,33	4,27	0,16	0,04	0,19	5,49	0,39
205	7	92,78	6,54	0,24	0,10	0,35	8,71	0,69
206	10	89,63	9,32	0,53	0,12	0,41	12,36	1,05
207	15	83,97	14,10	1,11	0,22	0,60	19,39	1,93
208	20	81,02	16,36	1,50	0,36	0,76	23,50	2,63
209	30	70,35	24,28	3,58	0,76	1,03	37,85	5,37
210	1200	2,48	11,54	38,20	35,12	12,66	243,94	85,98
210	4200	2,32	9,04	36,09	36,24	16,31	255,18	88,64
210	4215	2,48	8,70	35,39	36,04	16,49	256,26	88,82

COMPUTER PROGRAM CP2

Calculation of the rate constants, k_ϕ and k_o, by the method of least square fit from the mass spectrometer data obtained for the exchange experiments with initial reactant ratio of 1. ($P_D = P_M = 50$ torr).

NOMENCLATURE

APHD = $\log (\phi_\infty - \phi_o)$

APDO = $\log (100 - X_\infty)$

BPHD = $k_\phi / (2.303\ \phi_\infty)$

BPDO = $k_o / (2.303\ (100 - X_\infty))$

PHEQ = ϕ_∞

PDOINF = X_∞

PKHI = k_ϕ

PKDO = k_o

PM = M

COMPUTER PROGRAM CP2

```
      $JOB  ACC1-NUM,A.M.SHAH,TIME=3 ,PAGES=20
    1       DIMENSION HEAD(20),SUBH(8),RATIO(8)
    2       IIN=5
    3       IOUT=6
    4       READ(IIN,3)(HEAD(N),N=1,20),(SUBH(J),J=1,8)
    5     3 FORMAT((20A4),/,(8A4))
    6       WRITE(IOUT,35)
    7    35 FORMAT('1')
    8       WRITE(IOUT,4)(HEAD(N),N=1,20),(SUBH(J),J=1,8)
    9     4 FORMAT(//////,1X,20A4,//,9X,A4,19X,2(6X,A4,2X),5(6X,A4))
   10     9 READ(IIN,20)(RATIO(N),N=1,8)
   11    20 FORMAT(5X,8A4)
   12       WRITE(IOUT,30)(RATIO(J),J=1,8)
   13    30 FORMAT(///,1X,8A4)
      C       READ NUMBER OF DATA POINTS,N
   14       READ(IIN,25)N
   15    25 FORMAT(I3)
   16       IF(N.EQ.999)GO TO 200
      C       DEFINE FLOATING POINT VARIABLE AN EQUAL TO N
   17       AN=N
      C       INITIALIZE ALL SUMS TO ZERO
   18       SUMX=0.0
   19       SUMY=0.0
   20       SUMZ=0.0
   21       SUMXY=0.0
   22       SUMXZ=0.0
   23       SUMXX=0.0
      C       THE FOLLOWING DO LOOP  CALCULATES X, Y,Z VALUES  FROM INPUT DAT
      C       AND CALCULATES SUMS
   24       DO 2 I=1,N
   25     5 READ(IIN,10)NR,NTIME,P16,P17,P18,P19,P20
   26    10 FORMAT(I3,7X,I5,5F10.5)
   27       P0=1.1314*P16-0.8816*P17+0.2308*P18+0.3034*P19-0.2707*P20
   28       P1=-0.0111*P16+1.2496*P17-0.6668*P18-0.2894*P19+0.7093*P20
   29       P2=-0.011*P17+1.4216*P18-0.6121*P19-1.1568*P20
   30       P3=-0.0125*P18+1.3389*P19-0.0272*P20
   31       P4=-0.0085*P19+1.2905*P20
   32       PT=P0+P1+P2+P3+P4
   33       PD0=(P0/PT)*100.0
   34       PD1=(P1/PT)*100.0
   35       PD2=(P2/PT)*100.0
   36       PD3=(P3/PT)*100.0
   37       PD4=(P4/PT)*100.0
   38       PHI=PD1+2.0*PD2+3.0*PD3+4.0*PD4
   39       PHEQ=255.18
   40       PDOINF=2.32
   41       PHID=PHEQ-PHI
   42       PHDL=ALOG10(PHID)
   43       PDOD=PD0-PDOINF
   44       PDOL=ALOG10(PDOD)
   45       X=NTIME
   46       Y=PHDL
   47       Z=PDOL
   48       SUMX=SUMX+X
   49       SUMY=SUMY+Y
   50       SUMZ=SUMZ+Z
   51       SUMXY=SUMXY+X*Y
   52       SUMXZ=SUMXZ+X*Z
   53     2 SUMXX=SUMXX+X**2
      C       COMPUTE AVERAGES
```

```
      XAV=SUMX/AN
      YAV=SUMY/AN
      ZAV=SUMZ/AN
      CPXY=SUMXY-SUMX*SUMY/AN
      CPXZ=SUMXZ-SUMX*SUMZ/AN
      CSS=SUMXX-SUMX**2/AN
C     CALCULATE FIT PARAMETERS
      BPHD=CPXY/CSS
      BPDO=CPXZ/CSS
      APHD=YAV-BPHD*XAV
      APDO=ZAV-BPDO*ZAV
C      CALCULATE RATE CONSTANT
      PDOO=100.0-PDOINF
      PKHI=-2.303*PHEQ*BPHD
      PKDO=-2.303*PDOQ*BPDO
      PM=PKHI/PKDO
      WRITE(IOUT,40)BPHD,BPDO,APHD,APDO,PKHI,PKDO,PM
   40 FORMAT(33X,2F12.7,5F10.3)
      GO TO 9
  200 WRITE(IOUT,33)
      STOP
      END
SENTRY
```

TYPICAL OUTPUT OF CP2

METHANE DEUTERIUM EXCHANGE OVER NI ON SILICA

TEMP	BPHD	BPDC	APHD	APDO	PKHI	PKDO	PH
D/H=50/50 TEMP=130,0C	=0,00 3826	=0,0007612	2,406	1,947	0,178	0,171	1,038
D/H=50/50 TEMP=140,0C	=0,00 5502	=0,0013659	2,406	1,927	0,328	0,307	1,068
D/H=50/50 TEMP=151,0C	=0,00 8953	=0,0028885	2,407	1,949	0,526	0,497	1,059
D/H=50/50 TEMP=159,0C	=0,00 5898	=0,0037318	2,408	1,923	0,934	0,839	1,113
D/H=50/50 TEMP=171,0C	=0,00 3366	=0,0052849	2,409	1,937	1,373	1,189	1,155
D/H=50/50 TEMP=178,0C	=0,00 8162	=0,0065359	2,406	1,859	1,773	1,470	1,206

END OF DATA

COMPUTER PROGRAM CP3

Calculation of the activation energies and the frequency factors by the least square fit method from the rate constants determined at several temperatures from the exchange experiments with initial reactant ratio of 1 ($P_D = P_M = 30$ torr), and the determination of the specific activity.

NOMENCLATURE

A1 = log A_ϕ

A2 = log A_o

A3 = log A_s

A4 = log A_m

AKPH16 = KP16 = log (k_ϕ at 160.0°C)

AKDO16 = KD16 = log (k_o at 160.0°C)

ARS16 = RS16 = log (R_s at 160.0°C)

ARM16 = RM16 = log (R_m at 160.0°C)

B1 = $E_\phi/(2.303\ R)$

B2 = $E_o/(2.303R)$

B3 = $E_s/(2.303\ R)$

B4 = $E_m/(2.303\ R)$

EPHI = E_ϕ

EDO = E_o

ES = E_s

EM = E_m

PR1 = R_s

PR2 = R_m

COMPUTER PROGRAM CP3

```
      $JOB  ACCT-NUM,A.M.SHAH,TIME=30,PAGES=20
      C     PROGRAM TO CALCULATE ACTIVATION ENERGIES BY LEAST SQUARE FIT
      C     DIMENSION HEAD(20),SUBH(14),CATAL(4)
    1       READ(5,30)(HEAD(N),N=1,20),(SUBH(J),J=1,14)
    2    30 FORMAT((20A4),/,(14A4))
    3       WRITE(6,35)
    4    35 FORMAT('1')
    5       WRITE(6,40)(HEAD(N),N=1,20),(SUBH(J),J=1,14)
    6    40 FORMAT(/////,20X,20A4,///,6X,2A4,6X,12(2X,A4,2X))
    7    50 READ(5,20)(CATAL(N),N=1,4)
    8    20 FORMAT(4X,4A4)
    9    C  READ NUMBER OF DATA POINTS,N
   10       READ(5,1)N
   11     1 FORMAT(I3)
   12       IF(N.EQ.999)GO TO 200
   13    C  DEFINE FLOATING POINT VARIABLE AN EQUAL TO N
            AN=N
   14    C  INITIALIZE ALL SUMS TO ZERO
   15       SUMX=0.0
   16       SUMY=0.0
   17       SUMZ=0.0
   18       SUMY1=0.0
   19       SUMZ1=0.0
   20       SUMXY=0.0
   21       SUMXZ=0.0
   22       SUMXY1=0.0
   23       SUMXZ1=0.0
   24       SUMXX=0.0
   25    C  THE FOLLOWING DO LOOP READS THE INPUT VALUES AND CALCULATES SUMS
   26       DO2I=1,N
   27       READ(5,3)PTEM,PKHI,PKDO,PR1,PR2
   28     3 FORMAT(5F10.5)
   29       X=1/(PTEM+273.0)
   30       Y=ALOG10(PKHI)
   31       Z=ALOG10(PKDO)
   32       Y1=ALOG10(PR1)
   33       Z1=ALOG10(PR2)
   34       SUMX=SUMX+X
   35       SUMY=SUMY+Y
   36       SUMZ=SUMZ+Z
   37       SUMY1=SUMY1+Y1
   38       SUMZ1=SUMZ1+Z1
   39       SUMXY=SUMXY+X*Y
   40       SUMXZ=SUMXZ+X*Z
   41       SUMXY1=SUMXY1+X*Y1
   42       SUMXZ1=SUMXZ1+X*Z1
   43       SUMXX=SUMXX+X**2
   44    C  COMPUTE AVERAGES
   45       XAV=SUMX/AN
   46       YAV=SUMY/AN
   47       ZAV=SUMZ/AN
   48       Y1AV=SUMY1/AN
   49       Z1AV=SUMZ1/AN
   50    C  COMPUTE CORRECTED SUMS AND CROSS PRODUCTS
   51       CPXY=SUMXY-SUMX*SUMY/AN
            CPXZ=SUMXZ-SUMX*SUMZ/AN
            CPXY1=SUMXY1-SUMX*SUMY1/AN
            CPXZ1=SUMXZ1-SUMX*SUMZ1/AN
         2  CSS=SUMXX-SUMX**2/AN
    C     CALCULATE FIT PARAMETERS
```

```
      B1=CPXY/CSS
      B2=CPXZ/CSS
      B3=CPXY1/CSS
      B4=CPXZ1/CSS
      A1=YAV-B1*XAV
      A2=ZAV-B2*XAV
      A3=Y1AV-B3*XAV
      A4=Z1AV-B4*XAV
C       COMPUTE ACTIVATION ENERGIES
      PM=1000.0
      EPHI=-4.5761*B1/PM
      EDO=-4.5761*B2/PM
      ES=-4.5761*B3/PM
      EM=-4.5761*B4/PM
C     CALCULATE SPECIFIC RATE CONSTANTS AT 100.0C
      PD=PM/(4.5761*433.0)
      AKPH16=A1-PD*EPHI
      AKDO16=A2-PD*EDO
      ARS16=A3-PD*ES
      ARM16=A4-PD*EM
C     WRITE ACTIVATION ENERGIES,FREQUENCY FACTORS,AND SPECIFIC RATE CONSTANTS
      WRITE(6,60)(CATAL(N),N=1,4),EPHI,EDO,ES,EM,A1,A2,A3,A4,AKPH16,AKDO
     116,ARS16,ARM16
   60 FORMAT(/,4X,4A4,12F8.3)
      GO TO 50
  200 WRITE(6,35)
      STOP
      END
$ENTRY
```

OUTPUT OF CP3

METHANE DEUTERIUM EXCHANGE OVER SILICA SUPPORTED CATALYSTS

CATALYST	EPHI	EDO	ES	EH	A1	A2	A3	A4	KP16	KD16	RS16	RH16
NICKEL	17,381	16,324	14.512	21,384	8,699	8,114	7,125	9,670	-0,073	-0,124	-0,199	-1,122
20XCU 80XNI	21,991	21,641	19.160	27,317	11,425	11,220	9,838	13,124	0,327	0,385	0,161	-0,662
40XCU 60XNI	22,413	21,658	20.030	27,208	11,395	10,992	10,027	12,785	0,084	0,062	-0,066	-1,027
60XCU 40XNI	19,929	19,313	17.531	22,315	9,828	9,533	8,500	9,870	-0,229	-0,244	-0,348	-1,392
80XCU 20XNI	18,328	16,737	15.959	23,510	8,672	7,805	7,388	10,129	-0,573	-0,578	-0,674	-1,736
COPPER	29,306	29,009	28.354	30,298	9,122	8,956	8,624	8,452	-5,669	-5,684	-5,686	-6,838

APPENDIX II

EXPERIMENTAL RESULTS

Table 1

Results Over Silica Supported Nickel Catalyst

Weight of catalyst = 0.98157 gm. Ni-nitrate silica.

Weight of reduced catalyst = 0.5482 gm. Ni-silica.

Equivalent amount of metal = 0.1096 gm. Ni.

1A1 Dependence of initial rates on initial pressures of the reactants.

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
151.0	100	50	0.155	0.015	0.170
	130	50	0.140	0.015	0.155
	50	130	0.520	0.052	0.572
	50	100	0.390	0.040	0.430
	50	75	0.315	0.023	0.338
	75	50	0.185	0.015	0.200
	50	25	0.137	0.013	0.150
	25	50	0.300	0.030	0.330
	50	50	0.230	0.020	0.250
159.0	100	50	0.245	0.030	0.275
	130	50	0.210	0.025	0.235
	50	130	0.676	0.065	0.741
	50	100	0.530	0.070	0.600
	50	75	0.458	0.045	0.503

Table 1. (continued)

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
159.0	75	50	0.295	0.025	0.320
	50	25	0.200	0.025	0.225
	25	50	0.465	0.060	0.525
	50	50	0.340	0.040	0.380
171.0	100	50	0.365	0.035	0.400
	130	50	0.330	0.030	0.360
	75	50	0.455	0.060	0.515
	50	75	0.698	0.082	0.780
	50	130	0.975	0.117	1.092
	50	100	0.770	0.090	0.860
	50	25	0.298	0.037	0.335
	130	25	0.145	0.017	0.162
	100	25	0.179	0.021	0.200
	75	25	0.218	0.027	0.245
	25	25	0.385	0.062	0.447
	25	50	0.620	0.100	0.720
	50	50	0.465	0.055	0.520
	130	100	0.480	0.050	0.530
	100	130	0.689	0.065	0.754
	100	100	0.570	0.050	0.620
	100	75	0.488	0.060	0.548
	75	100	0.660	0.070	0.730
	25	100	0.930	0.200	1.130

Table 1. (continued)

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
171.0	25	75	0.788	0.165	0.953
	25	130	0.988	0.208	1.196

1A2 The Orders of Reaction

Temp. °C	Order w.r.t. Deuterium			Order w.r.t. Methane		
	a	c	m	b	d	n
151.0	-0.47	-0.5	-0.47	0.76	0.8	0.73
159.0	-0.45	-0.5	-0.46	0.71	0.7	0.72
171.0	-0.42	-0.7	-0.45	0.69	0.7	0.71
avg. order	-0.45	-0.6	-0.46	0.72	0.7	0.72

Table 1. (continued)

1B1 Hydrocarbon Compositions after 20 and 70 hrs., $P_D = P_M = 50$ torr.

Temp. °C	After 20 hrs. Percent of Total Methane					After 70 hrs. Percent of Total Methane				
	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
130.0	24.27	43.34	25.47	6.16	0.76					
140.0	11.53	33.80	36.22	15.66	2.79	1.46	16.39	41.68	29.11	11.36
151.0	5.42	25.51	41.03	22.09	5.95	3.23	10.28	35.62	36.28	14.58
159.0	3.68	14.23	37.73	32.94	11.42	3.33	8.58	36.32	36.92	14.84
171.0	2.48	11.54	38.20	35.12	12.66	2.32	9.04	36.09	36.24	16.31
178.0	3.36	13.24	38.25	33.04	12.10	3.73	11.22	35.25	35.09	14.71

At 171.0°C after 70 hrs., $X_\infty = 2.32$, $\phi_\infty = 255.18$.

Table 1. (continued)

1B2 The effect of the initial pressures of the reactants on the hydrocarbon compositions after 20 hrs at 178.0°C.

P_D torr	P_M torr	% of Total Methane				
		CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
50	50	3.36	13.24	38.25	33.04	12.10
100	50	1.69	4.06	32.05	39.40	22.80
50	100	9.67	31.07	38.32	17.27	3.67
100	100	5.25	20.31	40.82	26.55	7.07
25	25	2.46	2.03	25.15	40.57	29.79
25	50	5.80	20.65	44.46	24.72	4.37

1C1 The Rate Constants. ($P_D = P_M = 50$ torr)

Temp. °C	k_ϕ	k_o %/min.	R_s %/min.	R_m %/min.	$M = k_\phi/k_o$
130.0	0.178	0.171	0.17	0.01	1.04
140.0	0.328	0.307	0.28	0.03	1.07
151.0	0.526	0.497	0.46	0.04	1.06
159.0	0.934	0.839	0.68	0.08	1.11
171.0	1.373	1.189	0.93	0.11	1.56
178.0	1.773	1.470	1.17	0.23	1.21

k_ϕ in D atoms entering 100 methane molecules/min.

Table 1. (continued)

1C2 Activation Energy, Frequency Factor, and Specific Activity.

Exchange Process	E kcal/mole	Log A	Specific Activity at 160.0°C
Appearance of Deuterium in hydrocarbon	17.4	8.96	1.54
Disappearance of Methane	16.3	8.38	1.37
Stepwise Exchange	14.5	7.39	1.15
Multiple Exchange	21.4	9.93	0.138

A_ϕ , $\overline{k}_\phi$ in D atoms entering 100 methane molecules per min. per gm. catalyst.

A_o, A_s, A_m, $\overline{K}_o$, $\overline{R}_s$, $\overline{R}_n$, in % per min., per gm. catalyst.

Table 2

Results Over 20% Cu-80% Ni on Silica Catalyst

Weight of catalyst = 1.01475 gm. metal-nitrate silica.

Weight of reduced catalyst = 0.5816 gm. metal silica.

Equivalent amount of metal = 0.1164 gm. metal.

2A1 Dependence of the initial rates on the initial pressures of the reactants.

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
142.0	50	50	0.325	0.025	0.350
	20	50	0.510	0.055	0.565
	100	50	0.210	0.015	0.225
	75	50	0.265	0.020	0.285
	35	50	0.350	0.030	0.380
	130	50	0.165	0.015	0.180
	50	75	0.450	0.038	0.488
	50	20	0.124	0.012	0.136
	50	100	0.520	0.040	0.560
	50	131	0.572	0.039	0.611
	50	35	0.221	0.014	0.235
148.0	50	50	0.380	0.040	0.420
	100	50	0.275	0.025	0.300
	130	50	0.230	0.020	0.250
	20	50	0.700	0.095	0.795

Table 2 (continued)

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
148.0	75	50	0.325	0.030	0.355
	35	50	0.495	0.055	0.550
	50	131	0.845	0.065	0.910
	50	20	0.162	0.020	0.182
	50	100	0.65	0.060	0.710
	50	34	0.265	0.034	0.299
	50	65	0.462	0.046	0.508
	50	80	0.536	0.048	0.584
157.0	50	50	0.550	0.095	0.645
	100	50	0.390	0.045	0.435
	35	50	0.780	0.085	0.865
	75	50	0.475	0.055	0.530
	20	50	0.945	0.130	1.075
	50	65	0.696	0.085	0.781
	50	35	0.452	0.059	0.511
	50	20	0.244	0.024	0.268
	120	50	0.345	0.035	0.380
	50	80	0.888	0.096	0.984
	50	120	1.128	0.120	1.248

Table 2. (continued)

2A2 The Orders of Reaction

Temp. °C	Order w.r.t. Deuterium			Order w.r.t. Methane		
	a	c	m	b	d	n
142.0	-0.56	-0.8	-0.56	0.89	0.6	0.84
148.0	-0.57	-0.8	-0.56	0.88	0.6	0.85
157.0	-0.54	-0.8	-0.55	0.88	0.6	0.84
avg. order.	-0.56	-0.8	-0.56	0.88	0.6	0.84

2B Hydrocarbon Compositions after 70 hrs., $P_D = P_M = 50$ torr.

Temp. °C	Percent of Total Methane				
	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
122.0	4.77	17.65	41.65	28.63	7.30
133.0	4.76	15.70	38.80	31.03	9.70
142.0	2.74	9.42	37.20	35.42	15.23
148.0	2.47	11.50	37.17	34.98	13.89
157.0	5.28	9.61	38.80	34.02	12.26

At 142.0°C. $X_\infty = 2.74$, $\phi_\infty = 250.97$.

Table 2. (continued)

2C The Rate Constants, ($P_D = P_M = 50$ torr).

Temp. °C	k_ϕ	k_o %/min.	R_s %/min.	R_m %/min.	$M = k_\phi/k_o$
122.0	0.174	0.172	0.15	0.01	1.01
133.0	0.408	0.399	0.36	0.03	1.02
142.0	0.716	0.684	0.65	0.05	1.05
148.0	1.021	0.994	0.76	0.08	1.03
157.0	1.729	1.642	1.10	0.19	1.05

k_ϕ in D atoms entering 100 methane molecules/min.

2C2 Activation Energy, Frequency Factor, and Specific Activity.

Exchange Process	E kcal/mole	Log A	Specific Activity at 160.0°C
Appearance of Deuterium in hydrocarbon	22.0	11.66	3.65
Disappearance of Methane	21.6	11.46	3.47
Stepwise Exchange	19.2	10.07	2.49
Multiple Exchange	27.3	13.36	0.37

A in same units as that of specific activity.

Table 3

Results Over 40% Cu-60% Ni on Silica Catalyst

Weight of catalyst = 0.99191 gm. metal-nitrate silica.

Weight of reduced catalyst = 0.5838 gm. metal silica.

Equivalent amount of metal = 0.1168 gm. metal.

3A1 Dependence of the initial rates on the initial pressures of the reactants.

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
149.0	50	50	0.230	0.020	0.250
	25	50	0.355	0.025	0.380
	75	50	0.200	0.015	0.215
	100	50	0.165	0.015	0.180
	130	50	0.138	0.012	0.150
	50	130	0.507	0.039	0.546
	50	100	0.430	0.040	0.470
	50	75	0.323	0.023	0.346
	50	25	0.135	0.010	0.145
160.0	50	50	0.455	0.035	0.490
	100	50	0.290	0.025	0.315
	75	50	0.355	0.030	0.385
	25	50	0.620	0.080	0.700
	130	50	0.250	0.015	0.265
	50	130	0.884	0.065	0.949

Table 3. (continued)

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
160.0	50	100	0.720	0.060	0.780
	50	25	0.255	0.020	0.275
	50	75	0.619	0.056	0.675
171.0	50	50	0.770	0.115	0.885
	50	25	0.460	0.053	0.513
	25	50	1.125	0.130	1.255
	130	50	0.395	0.040	0.435
	50	130	1.469	0.143	1.612
	50	100	1.240	0.140	1.380
	100	50	0.540	0.050	0.590
	75	50	0.595	0.065	0.660
	50	75	1.005	0.113	1.118
182.0	50	50	1.275	0.240	1.515
	130	50	0.680	0.090	0.770
	100	50	0.905	0.115	1.020
	75	50	1.015	0.165	1.180
	25	50	1.565	0.340	1.905
	50	130	2.223	0.299	2.522
	50	100	1.960	0.300	2.260
	50	75	1.575	0.270	1.845
	50	25	0.710	0.118	0.828

Table 3. (continued)

3A2 The Orders of Reaction

Temp. °C	Order w.r.t. Deuterium			Order w.r.t. Methane		
	a	c	m	b	d	n
149.0	-0.56		-0.57	0.78		0.78
160.0	-0.56	-0.8	-0.60	0.76	0.7	0.75
171.0	-0.57	-0.8	-0.59	0.75	0.7	0.76
182.0	-0.55	-0.8	-0.58	0.73	0.7	0.61
avg. order.	-0.56	-0.8	-0.58	0.75	0.7	0.76

Table 3. (continued)

3B Hydrocarbon Compositions after 20 and 70 hrs., $P_D = P_M = 50$ torr.

Temp. °C	After 20 hrs. Percent of Total Methane					After 70 hrs. Percent of Total Methane				
	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
130.0						7.58	22.80	43.61	22.19	3.82
149.0	7.11	21.95	43.60	22.34	5.00	4.99	13.13	40.36	31.31	10.20
160.0	4.85	16.62	39.44	30.47	8.61	3.69	14.52	37.00	33.12	11.67
171.0	5.84	15.11	36.51	32.04	10.50	4.70	14.35	36.23	33.13	11.60
182.0	4.64	14.03	37.11	33.02	11.19	3.18	13.31	39.46	32.88	11.16

At 182.0°C, after 70 hrs., $X_\infty = 3.18$, $\phi_\infty = 235.52$.

Table 3. (continued)

3C1 The Rate Constants, ($P_D = P_M = 50$ torr.).

Temp. °C	k_ϕ	k_o %/min.	R_s %/min.	R_m %/min.	$M = k_\phi/k_o$
130.0	0.177	0.178	0.15	0.01	1.00
149.0	0.608	0.586	0.46	0.04	1.04
160.0	1.164	1.129	0.91	0.07	1.03
171.0	2.430	2.326	1.54	0.23	1.05
182.0	4.236	3.734	2.55	0.48	1.14

k_ϕ in D atoms entering 100 methane molecules/min.

3C2 Activation Energy, Frequency Factor, and Specific Activity.

Exchange Process	E kcal/mole	Log A	Specific Activity at 160.0°C
Appearance of Deuterium in hydrocarbon	22.4	11.63	2.08
Disappearance of Methane	21.7	11.23	1.98
Stepwise Exchange	20.0	10.26	1.47
Multiple Exchange	27.2	12.94	0.16

A in same units as that of specific activity.

Table 4

Results Over 60% Cu-40% Ni on Silica Catalyst

Weight of catalyst = 1.013 gm. metal-nitrate silica.

Weight of reduced catalyst = 0.6129 gm. metal silica

Equivalent amount of metal = 0.1226 gm. metal

4A1 Dependence of initial rates on initial pressures of the reactants.

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
170.0	50	50	0.385	0.040	0.425
	75	50	0.340	0.030	0.370
	50	130	0.832	0.065	0.897
	50	100	0.650	0.050	0.700
	50	75	0.503	0.045	0.548
	50	25	0.198	0.022	0.220
	25	50	0.475	0.055	0.530
	130	50	0.275	0.015	0.290
	100	50	0.305	0.020	0.325
180.0	50	50	0.585	0.060	0.645
	50	75	0.788	0.090	0.878
	75	50	0.485	0.055	0.540
	25	50	0.785	0.095	0.880
	50	25	0.300	0.030	0.330
	50	100	0.930	0.100	1.030

Table 4. (continued)

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
180.0	50	130	1.170	0.104	1.274
	130	50	0.345	0.030	0.375
	100	50	0.430	0.035	0.465
193.0	130	50	0.675	0.060	0.735
	100	50	0.720	0.090	0.810
	75	50	0.790	0.105	0.895
	50	130	1.560	0.208	1.768
	50	100	1.260	0.160	1.420
	50	75	1.125	0.135	1.260
	50	25	0.470	0.083	0.553
	25	50	1.060	0.180	1.240
	50	50	0.850	0.105	0.955

4A2 The Orders of Reaction

Temp. °C	Order w.r.t. Deuterium			Order w.r.t. Methane		
	a	c	m	b	d	n
170.0	-0.32	-0.7	-0.34	0.85	0.7	0.83
180.0	-0.35	-0.7	-0.40	0.85	0.7	0.81
193.0	-0.32	-0.7	-0.31	0.84	0.7	0.80
avg. order	-0.33	-0.7	-0.35	0.85	0.7	0.81

Table 4. (continued)

4B Hydrocarbon Compositions after 20 and 70 hrs., $P_D = P_M = 50$ torr.

Temp. °C	After 20 hrs. Percent of Total Methane					After 70 hrs. Percent of Total Methane				
	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
138.0						6.84	27.29	42.97	19.55	3.35
157.0	8.66	29.02	40.38	19.11	2.82	4.79	17.94	43.73	26.94	6.61
170.0	4.79	14.33	42.32	29.97	8.59	3.19	11.78	37.79	34.78	12.46
180.0	9.87	9.72	28.23	38.32	13.86	3.07	11.93	35.47	35.60	13.93
193.0	5.97	10.98	40.41	32.30	10.34	4.67	11.83	37.75	34.08	11.68

At 180.0°C, after 70 hrs., $X_\infty = 3.07$, $\phi_\infty = 245.4$.

Table 4. (continued)

4C1 The Rate Constants, ($P_D = P_M = 50$ torr).

Temp. °C	k_ϕ	k_o %/min.	R_s %/min.	R_m %/min.	$M = k_\phi/k_o$
138.0	0.156	0.153	0.14	0.01	1.02
157.0	0.555	0.545	0.41	0.03	1.02
170.0	1.060	1.052	0.77	0.08	1.01
180.0	1.647	1.545	1.17	0.16	1.07
193.0	2.806	2.498	1.70	0.21	1.12

k_ϕ in D atoms entering 100 methane molecules/min.

4C2 Activation Energy, Frequency Factor, and Specific Activity.

Exchange Process	E kcal/mole	Log A	Specific Activity at 160.0 C
Appearance of Deuterium in hydrocarbon	19.9	10.04	0.96
Disappearance of Methane	19.3	9.72	0.93
Stepwise Exchange	17.5	8.71	0.73
Multiple Exchange	22.3	10.08	0.066

A in same units as that of specific activity.

Table 5

Results Over 80% Cu-20% Ni on Silica Catalyst

Weight of catalyst = 1.9818 gm. metal-nitrate silica.

Weight of reduced catalyst = 1.2335 gm. metal silica.

Equivalent amount of metal = 0.2468 gm. metal silica.

5A1 Dependence of initial rates on initial pressures of the reactants.

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
187.0	50	50	0.290	0.035	0.325
	35	50	0.300	0.055	0.350
	75	50	0.225	0.023	0.248
	21	50	0.365	0.060	0.425
	130	50	0.165	0.015	0.180
	100	50	0.190	0.020	0.210
	50	35	0.186	0.024	0.210
	50	65	0.293	0.039	0.332
	50	121	0.484	0.048	0.532
	50	80	0.344	0.040	0.384
	50	20	0.108	0.014	0.122
200.0	50	50	0.510	0.090	0.600
	130	50	0.310	0.045	0.355
	100	50	0.360	0.050	0.410
	35	50	0.520	0.115	0.635
	20	50	0.575	0.195	0.770

Table 5. (continued)

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
200.0	75	50	0.440	0.055	0.495
	50	100	0.750	0.150	0.900
	50	80	0.720	0.080	0.800
	50	65	0.572	0.091	0.663
	50	35	0.340	0.070	0.410
	50	20	0.22	0.050	0.270
212.0	50	50	0.775	0.200	0.975
	100	100	1.050	0.210	1.260
	130	50	0.535	0.105	0.640
	130	100	1.030	0.140	1.170
	130	25	0.285	0.060	0.345
	100	50	0.605	0.110	0.715
	100	25	0.363	0.080	0.443
	100	130	1.443	0.273	1.716
	100	75	0.923	0.157	1.080
	75	50	0.740	0.160	0.900
	75	100	1.200	0.260	1.460
	75	25	0.413	0.100	0.513
	50	25	0.543	0.132	0.675
	50	75	1.058	0.255	1.313
	50	100	1.240	0.310	1.550
	50	130	1.456	0.390	1.846

Table 5. (continued)

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
212.0	25	130	1.365	0.481	1.846
	25	100	1.280	0.430	1.710
	25	75	1.088	0.352	1.440
	25	25	0.588	0.217	0.805
	25	50	1.010	0.365	1.375

5A2 The Orders of Reaction

Temp. °C	Order w.r.t. Deuterium			Order w.r.t. Methane		
	a	c	m	b	d	n
187.0	-0.40	-0.8	-0.45	0.83	0.7	0.80
200.0	-0.39	-0.8	-0.45	0.79	0.7	0.75
212.0	-0.38	-0.8	-0.45	0.63	0.6	0.71
avg. order.	-0.39	-0.8	-0.45	0.75	0.7	0.75

Table 5. (continued)

5B Hydrocarbon Compositions after 20 and 70 hrs., $P_D = P_M = 50$ torr.

Temp. °C	After 20 hrs. Percent of Total Methane					After 70 hrs. Percent of Total Methane				
	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
150.0	25.06	42.57	26.09	5.59	0.70	5.35	24.27	42.54	23.29	4.55
171.0	4.19	19.25	43.11	26.76	6.68	2.36	10.40	36.29	36.02	14.94
187.0	2.91	8.43	35.28	37.00	16.38	1.66	1.50	25.38	41.10	30.36
200.0	2.65	3.45	26.55	41.14	26.20	1.51	3.39	23.27	41.17	30.65
212.0	3.94	2.97	34.48	39.47	19.14	6.03	1.84	29.31	40.39	22.43

At 200.0°C, after 70 hrs., $X_\infty = 1.51$, $\phi_\infty = 296.06$.

Table 5. (continued)

5C1 The Rate Constants, ($P_D = P_M = 50$ torr).

Temp. °C	k_ϕ	k_o %/min.	R_s %/min.	R_m %/min.	$M = k_\phi/k_o$
150.0	0.156	0.159	0.13	0.01	0.98
171.0	0.535	0.510	0.38	0.04	1.05
187.0	0.795	0.715	0.58	0.07	1.11
200.0	1.507	1.307	1.02	0.18	1.15
212.0	2.883	2.272	1.55	0.40	1.27

k_ϕ in D atoms entering 100 methane molecules/min.

5C2 Activation Energy, Frequency Factor, and Specific Activity.

Exchange Process	E kcal/mole	Log A	Specific Activity at 160.0°C
Appearance of Deuterium in hydrocarbon	18.3	8.58	0.22
Disappearance of Methane	16.7	7.78	0.21
Stepwise Exchange	16.0	7.29	0.17
Multiple Exchange	23.5	10.04	0.015

A in same units as that of specific activity.

Table 6

Results Over Silica Supported Copper Catalyst

Weight of catalyst = 2.001 gm. Cu-nitrate silica.

Weight of reduced catalyst = 1.2813 gm. Cu silica.

Equivalent amount of metal = 0.2569 gm. Cu.

6A1 Dependence of initial rates on initial pressures of the reactants.

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
402.0	50	100	0.270	0.030	0.300
	100	50	0.145	0.020	0.165
	130	50	0.140	0.015	0.155
	75	50	0.145	0.025	0.170
	50	130	0.338	0.039	0.377
	50	75	0.214	0.034	0.248
	50	25	0.076	0.014	0.090
	25	50	0.156	0.018	0.174
	50	50	0.147	0.022	0.169
420.0	130	50	0.230	0.030	0.266
	100	50	0.230	0.033	0.263
	75	50	0.250	0.040	0.290
	50	130	0.533	0.072	0.605
	50	100	0.455	0.065	0.520

Table 6. (continued)

Temp. °C	P_D torr	P_M torr	R_s torr/min.	R_m torr/min.	R_o torr/min.
420.0	50	75	0.368	0.052	0.420
	50	25	0.121	0.020	0.141
	25	50	0.238	0.040	0.278
	50	50	0.250	0.038	0.288
440.0	100	50	0.408	0.070	0.478
	75	50	0.410	0.080	0.490
	50	75	0.593	0.113	0.706
	50	100	0.655	0.130	0.785
	50	130	0.819	0.143	0.962
	50	25	0.215	0.045	0.260
	25	50	0.390	0.085	0.475
	130	50	0.405	0.070	0.475
	50	50	0.408	0.078	0.486

Table 6. (continued)

6A2 The Orders of Reaction

Temp.	Order w.r.t. Deuterium			Order w.r.t. Methane		
C	a	c	m	b	d	n
402.0	-0.04		-0.04	0.90	0.7	0.86
420.0	-0.04	-0.1	-0.05	0.86	0.7	0.82
440.0	0.00	-0.1	0.00	0.83	0.7	0.78
avg. order	-0.03	-0.1	-0.03	0.86	0.7	0.82

Table 6. (continued)

6B Hydrocarbon Compositions after 20 and 70 hrs., $P_D = P_M = 50$ torr.

Temp. °C	After 20 hrs. Percent of Total Methane					After 70 hrs. Percent of Total Methane				
	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
360.0	47.59	28.89	18.13	3.49	1.91	6.78	23.90	39.13	23.47	6.71
379.0	14.31	33.98	36.56	11.20	3.95	1.73	6.28	34.79	40.32	16.88
402.0	4.52	20.26	40.26	25.82	9.14	2.20	2.71	26.24	41.07	27.79
420.0	4.09	7.90	32.38	36.87	18.76	2.82	2.35	23.03	41.28	30.52
440.0	3.17	7.38	30.77	39.85	18.82					

At 420.0°C, after 70 hrs., $X_\infty = 2.82$, $\phi_\infty = 294.34$.

Table 6. (continued)

6C1 The Rate Constants, ($P_D = P_M = 50$ torr).

Temp. °C	k_ϕ	k_o %/min.	R_s %/min.	R_m %/min.	$M = k_\phi/k_o$
360.0	0.102	0.085	0.067	0.01	1.20
379.0	0.196	0.177	0.13	0.02	1.11
402.0	0.428	0.366	0.293	0.043	1.17
420.0	0.771	0.653	0.50	0.075	1.81
440.0	1.375	1.143	0.815	0.155	1.20

k_ϕ in D atoms entering /100 methane molecules/min.

6C2 Activation Energy, Frequency Factor, and Specific Activity.

Exchange Process	E kcal/mole	Log A	Specific Activity at 160.0°C
Appearance of Deuterium in hydrocarbon	29.3	9.01	0.0
Disappearance of Methane	29.0	8.85	0.0
Stepwise Exchange	28.4	8.52	0.0
Multiple Exchange	30.3	8.34	0.0

A in same units as that of specific activity.

Table 7

Summary of Results

7A Specific Activity at 160.0°C.

Catalyst % Cu of Metal Loading	$\overline{k}_{\phi}$	k'_{ϕ}	$\overline{k}_{o}$ %/min./ gm. cat.	k'_{o} %/min./ gm.metal	$\overline{R}_{s}$ %/min./ gm. cat.	R'_{s} %/min./ gm.metal	$\overline{R}_{m}$ %/min./ gm. cat.	R'_{m} %/min./ gm.metal
0	1.54	7.71	1.37	6.86	1.15	5.77	0.138	0.689
20	3.65	18.24	3.47	17.34	2.49	12.45	0.37	1.87
40	2.08	10.39	1.98	9.88	1.47	7.35	0.16	0.81
60	0.96	4.81	0.93	4.65	0.73	3.66	0.066	0.33
80	0.22	1.08	0.21	1.07	0.17	0.86	0.015	0.074
100	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.000

$\overline{k}_{\phi}$, in D atoms entering 100 methane molecules per min. per gm. catalyst.

k'_{o} , in D atoms entering 100 methane molecules per gm. metal.

Table 7. (continued)

7B Activation Energy.

Catalyst % Cu of Metal Loading	Activation Energy, kcal/mole			
	E_{ϕ}	E_o	E_s	E_m
0	17.4	16.3	14.5	21.4
20	22.0	21.6	19.2	27.3
40	22.4	21.7	20.0	27.2
60	19.9	19.3	17.5	22.3
80	18.3	16.7	16.0	23.5
100	29.3	29.0	28.4	30.3

7C Frequency Factors.

Catalyst % Cu of Metal Loading	Log (A)			
	Log (A_{ϕ})	Log (A_o)	Log (A_s)	Log (A_m)
0	8.96	8.38	7.39	9.93
20	11.66	11.46	10.07	13.36
40	11.63	11.23	10.26	12.94
60	10.04	9.72	8.71	10.08
80	8.58	7.78	7.29	10.04
100	9.01	8.85	8.52	8.34

A_{ϕ}, A_o, A_s, and A_m in same units as $\overline{k}_{\phi}$, $\overline{k}_o$, $\overline{R}_s$, and $\overline{R}_m$ respectively.

APPENDIX III

SAMPLE CALCULATIONS

(A) Preparation of 20% Cu-80% Ni on silica catalyst

4.953 gm. Ni-nitrate = 1 gm. Ni

3.802 gm. Cu-nitrate = 1 gm. Cu

Weight of Cab-O-Sil = 4.00227 gm.

Weight of Ni-nitrate = 3.96542 gm.

Weight of Cu-nitrate = 0.76272 gm.

Weight of Cab-O-Sil + weight of nitrates = 8.73041 gm.

Weight of Ni = (3.96542) / (4.953) = 0.80061 gm.

Weight of Cu = (0.76272) / (3.802) = 0.20061 gm.

Weight of total metal = 0.80061 + 0.20061 = 1.00122 gm.

Weight of Cab-O-Sil + Weight of total metal = 4.00227+1.00122
= 5.00349 gm.

Metal compositions: % Ni = (0.80061) / (1.00122)x100 = 80%

% Cu = (0.20061) / (1.00122)x100 = 20%

Metal-silica compositions:

wt % silica = (4.00227) / (5.00349) x 100 = 80%

wt % metal = (1.00122) / (5.00349) x 100 = 20%

1 gm. metal nitrate silica = 0.57311 gm. metal silica
= 0.11468 gm. metal

(B). Specific activity at 160.0°C and frequency factor

Sample calculation of $\overline{k}_o$, k'_o for silica supported nickel catalyst.

Weight of reduced catalyst = 0.5482 gm. metal silica

Equivalent amount of metal = 0.1096 gm. Ni.

From computer program CP3, log k_o at 160.0°C = KD16

log k_o = -0.124 = $\bar{1}$.876 log A_o = 8.114

k_o = 0.75162 %/min.

$\bar{k}_o$ = (0.75162) / (0.5482) = 1.37 % per min. per gm. catalyst

k'_o = (0.75162) / (0.1096) = 6.86 % per min. per gm. metal

log A_o = 8.114

A_o = 1.3002 x 10^8 %/min.

A_o = (1.3002 x 10^8) / (0.5482) = 2.372 x 10^8 % per min. per gm. catalyst

log A_o = 8.38

(C) Chances of finding a bare site on catalyst

Sample calculation for silica supported nickel catalyst. These calculations are based on the method described elsewhere (9,47).

Stepwise exchange - mechanism I, $\theta_F \propto P_D^x P_M^y$

$R_s \propto P_M P_D^{0.5} \theta_F^2 \propto P_D^a P_M^b$

$P_M P_D^{0.5} \theta_F^2 \propto (\bar{P}_D^{0.45}) (P_M^{-0.72})$

$\theta_F^2 \propto (P_D^{-0.95}) (P_M^{-0.28})$

$\theta_F \propto (P_D^{-0.475}) (P_M^{-0.14})$

Multiple exchange - Mechanism II, $\theta_{F'} \propto P_D^{x'} P_M^{y'}$

$R_m \propto P_M \theta_{F'}^2 \propto P_D^c P_M^d$

$$P_M\,\theta_F^2 \propto (P_D^{-0.6})\,(P_M^{0.7})$$

$$\theta_F \propto (P_D^{-0.3})\,(P_M^{-0.15})$$

Disappearance of methane - Mechanism III, $\theta_G \propto P_D^{x''}\ P_M^{y''}$

$$R_0 \propto P_M\,\theta_G^2 \propto P_D^m\ P_M^n$$

$$P_M\,\theta_G^2 \propto (P_D^{-0.46})\,(P_M^{0.72})$$

$$\theta_G \propto (P_D^{-0.23})\,(P_M^{-0.14})$$

a, b, c, d, m, and n, are experimentally determined orders of reaction.