LIQUID PHASE HYDROGENATION OF OLEFINS ON SUPPORTED PALLADIUM—ALUMINA CATALYST

A THESIS

submitted in fulfilment of the requirements
for the award of the degree
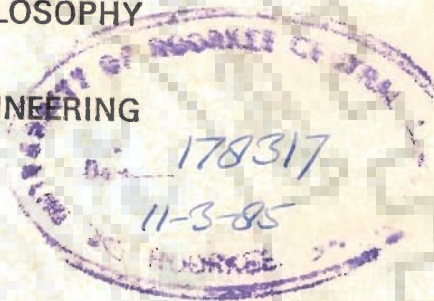*of*
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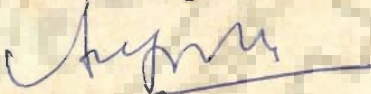*in*
CHEMICAL ENGINEERING

By

ASHOK KUMAR GUPTA

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF ROORKEE
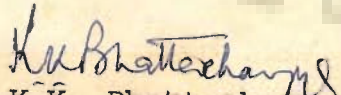ROORKEE-247667 (INDIA)

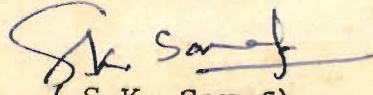September, 1983

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled, 'LIQUID PHASE HYDROGENATION OF OLEFINS ON SUPPORTED PALLADIUM - ALUMINA CATALYST' in fulfilment of the requirement for the award of the Degree of Doctor of Philosophy, submitted in the Department of CHEMICAL ENGINEERING of the University is an authentic record of my own work carried out during a period from September 1978 to ~~sept.~~ July, 1983 under the supervision of Dr.K.K.Bhattacharyya, Deputy Director & Head Petrochemistry Division, Indian Institute of Petroleum, Dehradun and Dr. S.K. Saraf, Professor, Department of Chemical Engineering, University of Roorkee, Roorkee.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

(ASHOK KUMAR GUPTA)
Candidate's Signature

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

(K.K. Bhattacharyya)
Deputy Director &
Head Petrochemistry Division
Indian Institute of Petroleum,
DEHRADUN-248 005

(S.K. Saraf)
Professor
Dept.of Chemical Engg.,
University of Roorkee,
ROORKEE-247 667

Signature(s) of Supervisor(s)

2.9.1983

ABSTRACT

These investigations are concerned with the hydro-genation of some specific long chain olefins in liquid phase over a supported $Pd-Al_2O_3$ catalyst at moderate temperature and pressure conditions.

As olefin feeds, a straight chain olefin, n-octene and a branched chain olefin isooctene (codimer of isobutene) were chosen for detailed investigations. Later, the hydrogenation of isododecene – a trimer of isobutene was also studied to know the effect of increasing chain-length on the reaction rate. The hydrogenation experiments were carried out in a $1.0 \times 10^{-3} m^3$ stainless steel stirred autoclave with external heating and internal cooling arrangements. A commercial catalyst containing 0.5 % palladium on alumina support was used in the powdered form (-170 + 250 mesh) which was suspended in the liquid medium containing the olefin dissolved in n-heptane. Hydro-genation was then carried out, with adequate stirring, under pressure varying the operating conditions in the following ranges to study their effects on the reaction rate:

Reaction temperature: 303 – 333 K

Reaction pressure: 0.5 – 2.0 MPa

Olefin concentration: 0.19 – 1.50 $kmol.m^{-3}$

Catalyst loading: 5.56 - 19.50 kg.m^{-3}

Stirring speed: 200 - 1200 r.p.m.

In the beginning the effect of the stirrer speed was determined and then series of experiments were conducted at the stirring rate ensuring kinetic regime beyond the mass transfer limitation range. The conversion with time was followed by analysing olefin concentrations by bromine number. Complete analysis of the product was done by GLC.

Using the experimental reaction rates and theoretical correlations the Thiele parameter for the powdered catalyst was computed and found to be about 10^{-1}. This indicated that pore diffusion limitations with this catalyst were negligible.

The influences of above mentioned operating conditions on the hydrogenation rate were studied for the three olefins separately. The reaction rate was observed to rise initially with increasing speed of the agitator and then levelled off at about 600 r.p.m. and above. The effects of other variables were, therefore, studied at the stirrer speed of 800 r.p.m.

For the three olefinic feed stocks used in these studies the reaction rate was found to increase linearly with catalyst concentration. The rate of hydrogenation also increased with increasing hydrogen pressure,though

non-linearly. Solubility of hydrogen in the reaction medium, which increases with pressure, was, therefore, considered for evaluating the rate dependence on hydrogen availability in the bulk liquid.

Alongwith hydrogenation on this palladium catalyst some isomerisation of the double bond was also found to occur. By the time about 5 - 10 % conversion was attained, the distribution of olefins with terminal and internal double bonds almost reached the equilibrium composition.

In general, the hydrogen concentration influenced the reaction rate more pronouncedly than olefin. In respect of olefin structures, the rate was found to decrease with branching in the molecule as well as with increase of the chain length. With the three olefins studied, the relative reaction rates were in the order:

n-octene > isooctene > isododecene

The results were then evaluated for the development of kinetic models for the hydrogenation of these olefins.

From the effect of total pressure, initial olefin concentration and temperature on the initial reaction rate, it was found that surface reaction may be the controlling step. Hence several models

were postulated for this controlling step and rate expressions formulated accordingly. In the development of these rate equations, the reverse reaction of olefin dehydrogenation was neglected since the thermodynamic calculations showed high equilibrium constant values.

A non-linear least square analysis was then performed to compare the data obtained in experimental runs upto 90 minutes with the rate equations formulated. This covered the range of conversion upto about 94 %. Two independent techniques namely the Grid-Search and the Marquardt method were used for this analysis; computer programs were developed for use on an IBM 370/145 computer which minimized the sum of squares of residuals of experimental and predicted reaction rates.

The rate equation which yielded no zero or negative constants and fitted the experimental data best was selected finally on the basis of an approximate statistical criteria and analysis of residuals.

The results of the non-linear analysis led to the selection of the following model as the most satisfactory one to represent the experimental data for all the three olefins over the entire ranges of temperature and concentration studied.

$$r = \frac{k \, K_A \, K_B \, C_A \, C_B}{(1 + \sqrt{K_A C_A})^2 \, (1 + K_B C_B)}$$

where k is the specific reaction rate constant; K_A and K_B the equilibrium adsorption constants for hydrogen and olefin respectively; and C_A and C_B are the hydrogen and olefin concentrations in the liquid phase.

The average error between the rates calculated from this model and those from the experimental data were $\pm$ 1.32, $\pm$ 1.69 and 3.01 % for isooctenes, n-octenes and isododecenes respectively.
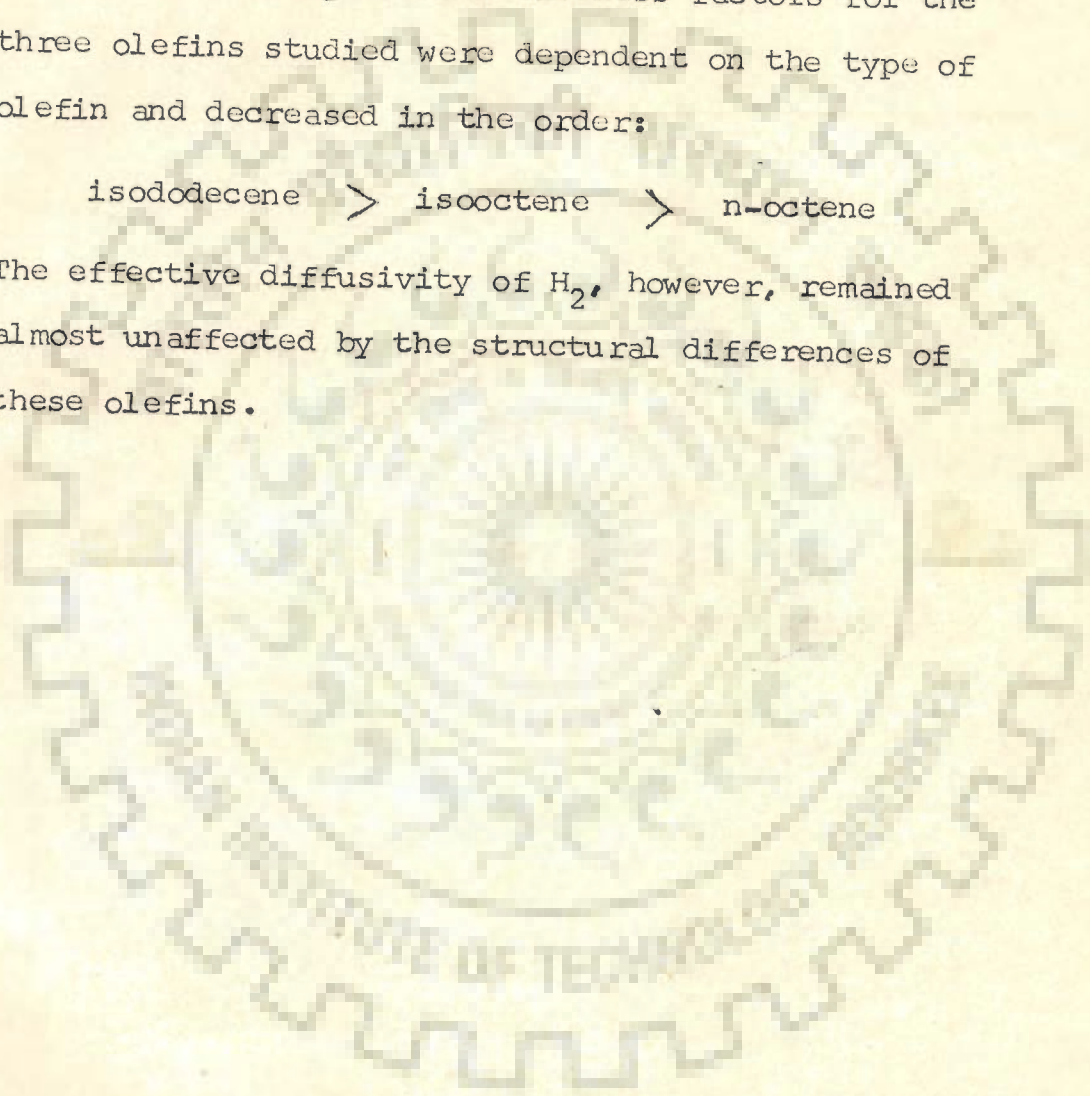
This model suggests that hydrogen in dissociated form and the olefin molecules are non-competitively adsorbed on the active sites of the catalyst. The constants in this rate equation are related to temperature in a similar way as Arrhenius relationship. The energies of activation were found to be 67.94, 69.65 and 64.42 kJ/mol for n-octene, isooctene and isododecene respectively. An attempt was made to correlate the rate of hydrogenation of these olefins with the molecular configuration of olefins & energetic factors.

The effects of diffusion in liquid filled pores on the rates of hydrogenation were also investigated by using catalyst pellets instead of powder, in a $1.0 \times 10^{-3} m^3$ stirred basket reactor. The same palladium catalyst originally obtained as cylindrical pellets of 4 mm x 4 mm size was used in these experiments. With these pellets the reaction rates were found to be lower down to about 20 to 30 % of the rates

observed with powdered catalyst; thus the effect of pore diffusion was quite significant. The effectiveness factor for these catalyst pellets and effective diffusivity of H_2 were computed from the catalyst characterisation data using a simplified theoretical model. The catalytic effectiveness factors for the three olefins studied were dependent on the type of olefin and decreased in the order:

isododecene $>$ isooctene $>$ n-octene

The effective diffusivity of H_2, however, remained almost unaffected by the structural differences of these olefins.

ACKNOWLEDGEMENT

T A B L E   O F   C O N T E N T S

L I S T   O F   T A B L E S

.....

L I S T   O F   F I G U R E S

LIST OF SYMBOLS

A	=	hydrogen
AS, BS, CS	=	chemically adsorbed A, B, C
a_1, a_2, a_3	=	constants in Eq. 3.1
a_{gl}	=	gas-liquid interfacial area
B	=	olefin
BR	=	bromine number
C_A	=	concentration of hydrogen in liquid phase
C_B	=	concentration of olefin in liquid phase
$C_{A,g}^*, C_{H,g}^*$	=	equilibrium concentration of hydrogen at gas-liquid interface
C_C	=	concentration of products in liquid phase
C_{AS}	=	moles of A adsorbed/unit mass of catalyst
C_{BS}	=	moles of B adsorbed/unit mass of catalyst
C_{CS}	=	moles of C adsorbed/unit mass of catalyst
C_S, C_{S1}, C_{S2}	=	concentration of vacant active sites $S, S1, S2$
C_T	=	total concentration of active sites, total moles of sites/unit mass of catalyst
C_{T1}, C_{T2}	=	total concentration of active sites $S1, S2$
D	=	diffusivity
D_A	=	diffusivity of H_2
$D_{eff,A}$	=	effective diffusivity of H_2 inside the catalyst pores
$D_{eff,B}$	=	effective diffusivity of olefin inside the catalyst pores
$D_{eff,C}$	=	effective diffusivity of products inside the catalyst pores

D_B $=$ $D_{eff,B} / D_{eff,A}$

D_P $=$ $D_{eff,P} / D_{eff,A}$

d_p $=$ diameter of catalyst particle

E_B $=$ ratio of surface concentration of olefin and H_2, C_{BS}/C_{AS}

E_P $=$ ratio of surface concentration of Product and H_2, C_{PS}/C_{AS}

e $=$ average absolute error %,

$$\frac{1}{N} \sum_{i=1}^{N} \left[(r_i - \hat{r}_i)/r_i \right] \times 100$$

F $=$ ratio between the square mean due to regression and square mean due to error calculated with the model (Eq. 4.41)

FE $=$ ratio between the square mean due to error calculated with the model and the experimental error variance (Eq. 4.42)

FT, FET $=$ Corresponding values of F-test tables

f $=$ ratio of bulk to surface concentration of H_2, C_A / C_{AS}

g $=$ acceleration due to gravity

$(\Delta G_f^o)_{298 K}$ $=$ standard free energy of formation

$(\Delta H_f^o)_{298 K}$ $=$ standard heat of formation

$(\Delta H^o)_{298 K}$ $=$ standard heat of reaction

J_A, J_B, J_P $=$ molal mass flux of H_2, olefin and products inside the catalyst pores

K $=$ equilibrium constant

$\vec{K}$ $=$ vector of parameters to be estimated

K_A, K_B, K_C	=	adsorption equilibrium constants for H_2, olefin, products
K_{gl}	=	gas-liquid mass transfer coefficient
K_{ls}	=	liquid-solid mass transfer coefficient
k, k_v	=	kinetic rate constants
k_s	=	surface reaction rate constant
k'	=	composite constant, $(1/K_{ls} + 1/k_s)$
$k_1, k_2, k_3, k_4,$ $K_{-1}, K_{-2},$ k_{-3}, k'_1, k'_{-1}	=	rate constants of elementary reactions involved in the mechanisms
L	=	thickness of catalyst layer
M	=	molecular weight in Eq. 4.1 and otherwise
M_O	=	ratio of TMP-1/TMP-2
m	=	catalyst loading
N	=	number of points
N_p	=	number of parameters
P	=	products
p, q	=	parameters in power law rate equation, Eq. 4.7
R	=	gas constant
R^2	=	determination index, Eq. 4.40
r	=	reaction rate
r_o, r_{vo}	=	initial rates
r_i	=	observed reaction rate
$\hat{r}_i$	=	calculated reaction rate
s, s_1, s_2	=	active sites in the catalyst

$S^o_{298\ K}$ = standard entropy of formation

S^2_1 = sum of squares of residuals, Eq.4.39

s = standard deviation

T = temperature

t = time

V_b = molal volume at normal boiling point (N.B.P.)

X = dimensionless distance, x/L; also association parameter in Eq. 4.1

X_i = olefin concentration at 90 minutes

x = distance inside the catalyst pore

Y_i = bromine number

$\overline{Y}$ = average bromine number

Greek letters

θ = porosity of catalyst pellet

μ = viscosity

ρ_a = apparent density of liquid-filled catalyst particle

ρ_l = density of liquid

ρ_p = density of catalyst particle

ϕ = Thiele parameter, $L\sqrt{kK_A K_B C_{AS}/D_{eff,A}}$

ϕ_p = Thiele parameter, Eq. 4.63

ψ = parameter defined by $\sqrt{K_A C_{AS}}$

η = catalytic effectiveness factor

η_{expt} = experimental value of effectiveness factor

η_P = effectiveness factor computed from Figure 4.40

τ = tortuosity factor

σ^2 = experimental error variance

Subscripts

A = hydrogen

B = olefin

C = paraffinic products

g = gas phase

j = component, j

l = liquid phase

o = initial

s = surface

v = volume
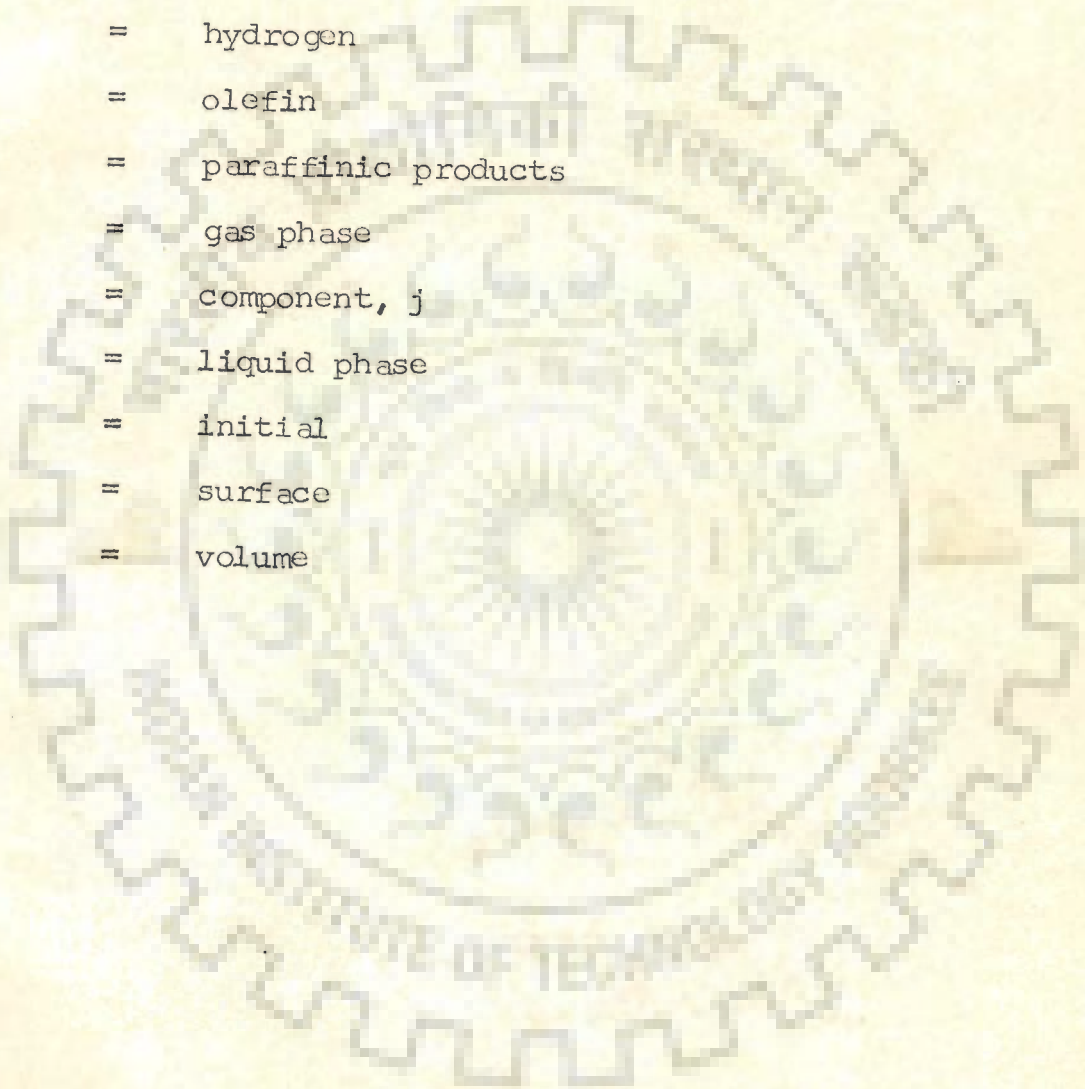
C H A P T E R - I

INTRODUCTION

For the proper design of a chemical reactor, it is desirable to study and understand the kinetics and mechanisms of the chemical reactions involved, the mass transfer and related phenomena and their combined effect on the overall rate process. A knowledge of the kinetics of reaction enable effective utilization of present day design and computing techniques for achieving the optimal design and operation of a chemical reactor. The intrinsic reaction rate and other informations derived from such studies constitute the basic components for the development of process correlations and reliable design parameters. Further, for precise and efficient operation of chemical plants, sophisticated control systems, like closed-loop computer control, are increasingly being used in the present day chemical industry. To adopt such control systems, it is necessary to develop an appropriate mathematical model of the process; this in turn, requires precise kinetic data.

Catalytic hydrogenation of olefinic bonds is applied in many commercial processes in the petroleum refining and petro-chemical industries. A few important examples are - hydrogenation of coker kerosine and gas oil, cracked

liquid streams like pyrolysis gasoline, single compounds like benzene, isooctene and crotonaldehyde, and selective hydrogenation of acetylene and butadiene in C_3 and C_4 olefinic streams[1-3]. Such hydrogenation of unsaturated compounds, in several cases, is carried out in vapour phase in fixed bed reactors. But in some cases, hydrogenation is preferred to be carried out in liquid phase.

Hydrogenation of olefins is a highly exothermic reaction, liberating about 115-125 MJ/k mol for hydrogenation of each double bond in an olefin molecule. In vapour-phase reaction the temperature used is relatively high and due to that the olefins and the di-olefins, which are very reactive, tend to form polymeric compounds which may remain deposited on the catalyst surface and thus impair catalyst activity and life.

Liquid-phase hydrogenation offers several advantages in respect of high equilibrium potential and better selectivity at low reaction temperatures, better uniformity and control of temperature in the reactor and low energy requirements. For these reasons hydrogenation of some specific olefinic compounds, selective hydrogenation of some mixed olefinic feed stocks and liquid streams containing heavier olefinic compounds in particular, is preferably carried out in the liquid phase.

On industrial scale, liquid-phase hydrogenation is generally carried out under pressure in trickle-bed, expanded bed or slurry reactors. When feed quantities are not very large or the olefin content is not very high, hydrogenation in slurry reactors seems to be attractive. Such liquid phase processes are applied commercially for the hydrogenation of vegetable oils, hydrogenation of benzene to produce cyclo-hexane and many other streams. Cracked petroleum products containing olefins create problems in storage and handling due to their tendencies of polymerization and oxidation. In many cases these olefins are removed by acid clay or other physical treatments; otherwise they are blended with fuel oil. Hydrogenation of these cracked petroleum products is being increasingly practised now for producing higher value liquid fuels or petrochemical feed stocks.

In catalytic hydrogenation of unsaturated compounds in the liquid phase, however, there are some additional complexities than in the analogous gas-phase processes, which have still remained unamenable to precise analysis for correlating the kinetics. These complexities relate to the following:

1. Presence of three phases (gas, liquid and solid), which necessitates adequate consideration of dispersion of phases, hydrodynamics and the

material transport in the three phase system.

2. The catalyst is generally used as fine powder and the system has to be operated under such turbulence that the catalyst granules are uniformly dispersed.

3. The pores of the catalyst particles are generally filled with liquid, which may create some limitations in the diffusion of reactants and products. The exact nature of the inward diffusion of reactants and outward diffusion of products with different sizes of the molecules is still not definable in terms of measurable parameters.

4. Diversities in composition and molecular structure of the unsaturated liquid reactants may lead to solvation effects in the reaction medium, hydrogen bonding and cage effects in the system.

5. For hydrogenation of olefins, catalysts containing different metals, particularly, Ni, Pt and Pd are being generally used. There can be some differences in the reaction paths alongwith the reaction rates, when catalysts of different types are used.

The reaction between gaseous olefins and hydrogen have been extensively studied to explain the various aspects of catalysis. Investigations with long chain olefins have been indeed very few and still fewer

investigations are known which paid adequate attention to the following important aspects:

- hydrogenation of long-chain olefins, particularly with branching in liquid phase in slurry reactor,

- the reaction under moderate pressure of H_2 and in proper kinetic regime,

- accurate determination of intrinsic reaction rates over a wide range of conversion,

- the effects of branching and chain lengths of olefinic molecules having more than six carbon atoms on the reaction rate.

Most of the investigations, reported in the literature, were carried out at atmospheric pressure to throw light on the mechanism or to determine the initial reaction rates or the overall reaction rates without taking proper care to evaluate the mass transfer effects under the reaction conditions actually applied. The equilibrium constants for hydrogenation of olefins have high values; however, for liquid phase reaction, the diffusion coefficient of H_2 in liquid hydrocarbons is low. The rate of hydrogen diffusion is enhanced under pressure. Therefore, for reasonable and acceptable rates of reaction, this hydrogenation in the liquid

phase should necessarily be carried out under moderate to high pressures.

In view of the importance of hydrogenation of higher olefins for more efficient utilization of cracked products or unsaturated byproducts from refineries and petrochemical plants, accurate informations about the reaction kinetics, and mass transfer effects in slurry reactors, on which gaps exist as mentioned above, a fundamental study of the hydrogenation of C_8 and C_{12} olefinic compounds in slurry reactor was taken up for investigations.

1.1 OBJECT AND SCOPE

The primary purpose of this work was to study the liquid-phase hydrogenation of long chain olefins on a supported noble metal catalyst at moderate pressures. As olefin feed, a straight chain olefin, n-octene and a branched chain olefin, iso-octene, - a codimer of iso-butene were chosen for detailed investigations. The hydrogenation of isododecene, a trimer of isobutene, was also studied. Because of their structural differences and possible variations in adsorption due to the orientation of molecules on the active sites of the catalyst, it could be assumed that these three olefinic compounds would show variations in their reactivities.

The study with these olefins would indicate the effects of branching in the olefin molecule as well as that of increasing chain length on the hydrogenation rates. The experimental results could then be evaluated for establishing the appropriate rate expression as well as the mechanism and see if a uniform rate expression can be applicable for all these olefins. Such a rate expression would be useful for the design of reactors for hydrogenation of pure or mixed olefins of this range. This investigation of reaction kinetics in such a reaction system is necessarily preceded by an examination of the effects of mass transfer and related aspects.

1.2 OUTLINE OF THE INVESTIGATION PROGRAMME

To accomplish the objectives setforth in this work, the following programme was followed:-

1. A literature survey on catalytic hydrogenation of olefins with special reference to liquid phase operation was carried out. The reaction mechanisms and the types of rate equations proposed by various authors were emphasised in this study.

2. The intrinsic kinetic studies were carried out using powdered catalyst in a stirred autoclave. The catalyst comprised of 0.5 % palladium supported on alumina commercially available in

the form of cylindrical pellets. A stirred
reactor was used, because, unlike other equipment
often used to study hydrogenation reactions such
as for example, the type which measures quantity
of hydrogen adsorbed, aliquots of the reacting
mixture can be withdrawn and analysed for olefin
content without upsetting the experiment. The use
of stirred slurry reactor also allows one to
analyse the chemical kinetics readily because the
gas bubbles can be regarded as being well mixed[4]
as well as the slurries and likewise to examine
the mass transfer characteristics between gas and
the liquid and the catalyst particle. Several
investigators have used the stirred reactors for
studying the hydrogenation of unsaturated
compounds[5-7]. The hydrogenation with catalyst
pellets was conducted in a rotating basket
reactor, similar to that described by Carberry[8].

3. The analytical procedures for the determination of
unreacted olefins were based on standard well
established methods.

4. The experimental data thus obtained was used to
analyse the controlling regimes and to develop
appropriate rate equation, based on Langmuir-

Hinshelwood-Hougen-Watson (L - H - H - W) models,
for each olefin feed. The catalyst effectiveness
factor and effective diffusivities of hydrogen in
the liquid-filled catalyst pores were also
estimated.

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CHAPTER - 2

LITERATURE REVIEW

2.1 INTRODUCTION

For an appraisal of the problems of hydrogenation of olefins over supported metal catalysts, the available published informations are reviewed here. In this review, attention is mainly focus..ed on the hydrogenation of olefins (a) over catalysts containing metals of Group VIII together with Cu, Au and W , (b) the effects of reaction parameters, (c) the effects of molecular structure of reacting olefins on adsorption and reaction rates on different types of catalysts; and also the influence of solvents, if used; and (d) the kinetics and mechanism of hydrogenation. For relevance to the objective of this study, pertinent informations about olefins hydrogenation in the liquid phase have been summarised.

2.2 GENERAL FEATURES OF HYDROGENATION REACTIONS

Catalytic hydrogenation is by definition a bi-molecular reaction and is highly exothermic in nature. The extent of heat liberation depends upon the type of bond to be hydrogenated; saturated hydrocarbons-paraffins and naphthenes- consume hydrogen with cracking or ring opening and yield 29-42 k J/mol of H_2; saturation of aromatics liberates 58-67 kJ/mol of H_2; and the saturation of an olefinic bond yields 113-115 kJ/mol of H_2[10].

Hydrogenation reactions are thermodynamically more favourable at low temperatures and the values of equilibrium constants are fairly high which indicate that the reactions can be carried out essentially to completion.

2.2.1 Reaction Systems

Catalytic hydrogenation of unsaturated compounds may be carried out either in vapour phase in continuous fixed-bed reactors wherein the reactants and the products are completely in vapour phase or in liquid phase in which the reactants and products remain partially or completely in liquid phase[11]. In vapour-phase operation, generally high H_2- to -oil ratio and moderate to high temperatures are used for maintaining the reactants and products in the vapour phase. The use of very high H_2-to-oil ratio requires large reactor volumes and recirculation of large volumes of hydrogen which makes it relatively costlier; use of high temperatures, on the other hand, tend to promote undesirable side reactions, such as cracking, polymerisation etc. which accelerate catalyst deactivation.

Generally speaking, for hydrogenation reactions, vapour-phase operations are adopted for continuous throughputs in large plants, particularly when high

operating temperatures are required for acceptable
rates of conversions; liquid phase operation, on the
other hand, although more complex and considerably
less understood than the former, is advantageous when
the reaction rates are fairly high at relatively low
temperatures and for selective hydrogenations of
specific unsaturated components, such as, acetylenes,
propadiene and butadiene for production of high purity
C_2, C_3 and C_4 olefins[2,3]. In between these two
systems is the trickle bed system used for hydroprocess-
ing of heavy feedstocks wherein the reactants and
products pass through fixed catalyst beds partially in
vapour phase and partially in liquid phase, for example,
in hydrodesulphurisation and hydrocracking processes.

Liquid-phase hydrogenation has long been used for
small scale hydrogenations in the industry. These
reactions are generally carried out in slurry reactors,
the most common being the stirred autoclave[11]. A few
specific examples of liquid phase hydrogenation employed
industrially are:

(i)   Selective hydrogenation of methyl and vinyl
       acetylene in C_3 and C_4 olefins production[2,3]
       in cooled tubular reactor.

(ii)   Hydrogenation of double bonds in crotonaldehyde
       to produce butyraldehyde in stirred reactors[12].

(iii) Hydrogenation of unsaturated fats, using finely divided nickel catalysts[13] in large cylindrical reactors.

(iv) Hydrogenation of coal as coal-oil slurry by the Bergius process; high pressure autoclaves are used (H-Coal Process).

(v) Fischer-Tropsch process in which CO reacts with H_2 in the presence of a catalyst suspended in a liquid medium to form a mixture of hydrocarbons[15] (slurry reactor).

Recently, interest has also been shown in other forms of slurry reactors employing mixing by gas lift, circulation of the liquid phase through an external heat exchanger etc., for wider applications in accomplishing hydrogenations on industrial scale [11,16-20]. For large scale operations, such as, hydrodesulphurization of petroleum fractions and hydrocracking, trickle-bed reactors are widely employed; technologies are also being developed to use bubble column slurry reactors and gas-liquid up-flow fluidized bed reactors[11,20].

2.2.2 Catalysts

Hydrogenation reactions are most efficiently catalysed by metals[21]. Those which have been found to possess good hydrogenation activities are the Group VIII metals; of these, Ni, Pd and Pt have

been most extensively studied. Investigations have also been reported using Re, Cu, Au and W metals. These metal catalysts have been employed in a variety of forms as wires, foils, granules, powders, colloidal suspensions, blacks, evaporated-metal films and by far most extensively as supported catalysts in which different concentrations of metal are dispersed on a carrier such as alumina, silica or carbon[22]. On industrial scale, due to ease of handling and for maximum utilization of the catalytically active metal, supported metal catalysts are often preferred and have been used[23]. These catalysts are generally prepared by depositing the metal as oxide, carbonate, oxalate etc. and reduced by hydrogen to the metallic form before use. Metal oxides have also been used as hydrogenation catalysts[24] although less commonly than in metallic form.

Minachev et al[25] have reported the use of unexchanged X and Y zeolites and various metal exchanged Y zeolites for the hydrogenation of olefins. They found that the unexchanged zeolites have low activity for hydrogenation, while the reduced cation zeolites namely, Pt/NaY, Pd/NaY and Ni/NaY are highly active catalysts for olefin hydrogenation.

Petroleum or coal derived feedstocks contain various sulphur compounds which adsorb on the surface

of the metal catalysts and render it catalytically
inactive. Complete removal of these sulphur compounds
before hydrogenation of the materials involve costly
operation; so it was suggested that metal sulphides,
provided as such or formed by the reaction of sulphur
compounds in the feed stocks, be used as catalysts[26].
Starting from coal hydrogenation, metal sulphides are
now widely used as catalysts for hydrogenation of a
variety of materials, such as those containing acetylinic
and olefinic bonds, aromatic and heterocyclic ring
systems, hydrogenolysis of C-S bonds (hydrodesulphurisa-
tion), also for hydrogenation of carboxylic acids to
alcohols and nitro-compounds to amines[27]. The hydro-
genation catalysts are often also good dehydrogenation
catalysts, though at higher temperatures; the noble
metal and sulphide catalysts are also used to
catalyse the dehydrogenation and isomerisation of
hydrocarbons and the dealkylation of alkylaromatics.

The sulphides with catalytic properties are those
of the first-row transition metals as well as the
sulphides of Mo, W, Rh, Pd, Pt, Ag, Zn and Cd. The
most common sulphide catalysts are MoS_2 and WS_2.

Apart from sulphides and mono-metallic catalysts,
in selective hydrogenation, the use of various
combinations of transition metals have also been

found to give enhanced selectivity of hydrogenation of specific unsaturated compounds[28,29].

In recent years some interest has also been shown in soluble metal complexes as hydrogenation catalysts in liquid-phase operations[30], but they have so far attained little industrial significance.

The literature review indicates that for the hydrogenation of olefins, the preferred and widely used catalysts are those containing Ni, Pd or Pt. The selection of a suitable metal catalyst for a particular hydrogenation reaction is, however, dependent upon a number of factors, such as the type of the unsaturated compounds in the feed, desired end products, the impurities in the feed, operating conditions to be employed, type of the reactor system to be used, thermal effects, catalyst stability and life and the overall economics of the process.

2.2.3 Supported Catalysts

A supported catalyst generally consists of two parts, (i) active metal and (ii) carrier or support; in special cases promotors or inhibitors may also be included[31]. The preparation of supported catalysts usually involves two steps, the dispersion of the metal on the support and the formation of catalyst into usable forms. For the dispersion of metal on the support, processes such as impregnation,

co-precipitation or gel formation are used. Other methods of preparation like wet mixing, thermal fusion, chemical reaction and leaching have also been used in special cases. The forming step consists of converting the catalyst into suitable usable forms such as pellets, extrudates, granules, powder etc. [31]

A variety of supports, including such diverse substances as carbon, alumina, silica, alkaline earth carbonates and sulphates etc., have been used to disperse metals [22,31]. Supported metal catalysts used for hydrogenation reactions usually contain low amounts of metals; in case of noble metals, the content is less than 1 %; special purpose catalysts containing as much as 30 - 40 % by wt. of metal are also used commercially [32].

According to Innes [33] the support imparts several desirable properties to the catalyst; the important ones are:

(a)   provide larger exposed surface of the active
      metal,

(b)   increase the catalyst stability,

(c)   modifies the catalytic activity, selectivity
      and poison resistance,

(d)   improve the accessibility of reactants to the
      active sites,

(e)   helps to dissipate heat and thus prevent local
       over heating.

The relationship between the catalyst performance
and the support is quite complex. The carrier or
support affects the nature of the catalyst in a number
of ways[34,35]. Carrier may have a role through its
own contribution of surface area and pore structure by
preserving or altering the crystal size of the active
metal (Geometrical factors); through its contribution
to surface properties, e.g., acidic or basic sites
(surface factors) or through an electronic interaction
with the metal (Electronic factors).

Dependence of activity and selectivity of a
catalyst on pore structure has been demonstrated by
several workers using different supports and reactions[36,40].
For example, Taylor and Staffin[39] observed activity
differences for the hydrogenation of cyclohexene and
ethyl crotonate with various Pt-supported catalysts
(Table 2.1). The difference in activity decreased with
the increase of mean pore radius of the support.

Alongwith the geometry, the magnitude of the
available surface in a carrier also determines the
activity and selectivity by setting a certain crystallite
size. For such catalysts as Ni on silica and Ni on
silica-alumina, the contribution of a carrier in
influencing the crystallite size and the activity for

TABLE 2.1

EFFECT OF PARTICLE SIZE ON RATE OF HYDROGENATION OVER

Pt CATALYSTS *

Support	Mean pore radius nm	Activity difference for cyclohexene and ethyl crotonate at peak ratio, $m^3/min \times 10^5$
Al_2O_3, I	2.1	26.0
Cr_2O_3	13.6	20.0
Al_2O_3, II	22.4	13.8
ZrO_2	28.2	11.8

* Reference - 30.

reactions like ethane hydrogenolysis and benzene hydrogenation has been amply demonstrated by Taylor et al.[36-39]. These authors observed from the results that depending upon the choice of carrier and the metal concentration the crystallite sizes differ and which in turn decrease or increase the activity.

The acidity of the carrier was also found to affect the activity of catalysts and product distribution in a variety of hydrocarbon conversion reactions[41]. Besides these, the carrier also affects the mode and rate of

transport of reactant and product molecules through the porous structure of the carrier[31].

Many of the above mentioned studies which examined the effect of carrier on the performance of supported catalysts were carried out in vapour phase. On the other hand, relatively little effort has been made in liquid phase catalysis to disentangle these multiple contrib-utions, both physical and chemical, of a support to catalyst performance, but in special cases, particular characteristics have been singled out. For instance, the activity differences found in $Pt-Al_2O_3$, $Pt-zirconia$ and $Pt-Cr_2O_3$ when used for hydrogenation of cyclohexene and ethyl crotonate have been related to the mean pore radius of these supports[39] (see Table 2.1). Correla-tions between activity and metal surface areas of Pt and Pd catalysts were, however, not evident[42].

2.3 KINETICS OF HYDROGENATION OF OLEFINS IN VAPOUR PHASE

Extensive informations are available on the catalytic hydrogenation of lower olefins over metal catalysts. Many of the investigations were conducted to evaluate the activity of catalysts, reaction rates and mechanism, and the effect of operating parameters such as temperatures and partial pressures on the selecti-vity and yield. The studies were, however, mostly concerned with 2-4 carbon-atoms olefins.

For a general appreciation of the kinetics of the hydrogenation of olefins in vapour phase a brief review of the pertinent experimental investigations is presented here. In this context, mention is also being made of the studies which reported the effects of molecular structure of the olefins on the activity parameters in hydrogenation.

2.3.1 Hydrogenation of ethylene

The hydrogenation of ethylene in vapour phase has been extensively studied over a wide variety of metal catalysts. Table 2.2 summarizes the reported data of the overall kinetics and effects of temperature and pressure. In most of these studies only initial reaction rates were evaluated. These data indicate that although there is considerable variation in the values of the reaction orders with respect to H_2 and C_2H_4, in general, the order with respect to hydrogen is approximately unity and that for C_2H_4 is either zero or slightly negative. This shows that the adsorption of ethylene would be much stronger relative to hydrogen. Further, the variation of the activation energy found with different catalysts is rather small; this is especially true for silica-supported metal catalysts, where E was found to be 35.2 kJmol^{-1}. Such observations led Beck[58] and Schmit and VanReijen[43] to suggest that the variation in specific activity for

TABLE 2.2

KINETICS AND ACTIVATION ENERGIES FOR ETHYLENE HYDROGENATION

$$\text{Rate} = k \, P_{H_2}^{x} \, P_{C_2H_2}^{y}$$

Catalyst	x	y	Temp. K	E_a (kJ.mol^{-1})	Ref.
Fe/SiO$_2$	0.91	-0.04	303	32.2(? temp.) [a]	43
Fe Film	0.87	-0.6	305	30.5(305-353)	44
Co/SiO$_2$	0.55	-0.19	213	35.2(? temp.)	43
Ni Film	1	0	417	42.7(293-423)	45
Ni wire	1	0	429	58.6(333-373)	46
Ni Powder	1	L	372-438	?	47
Ni/SiO$_2$	0.67	-0.08	233	35.2(? temp.)	43
Ni/Al$_2$O$_3$	1	L	343	48.6(303-353)	48
Ni/Silica-Alumina	1.09	0.21	401	50.2(363-408)	49
Cu/SiO$_2$	0.69	0.06	353	35.2(? temp.)	43
Cu Powder	1	0	373	45.2(423-473)	50
Ru/Al$_2$O$_3$	1	-0.02	319	36.4(305-353)	51
Ru/SiO$_2$	0.95	-0.59	197	35.2(? temp.)	43
Rh/Al$_2$O$_3$	1	0	352	50.2(343-373)	52
Rh/SiO$_2$	0.85	-0.74	197	35.2(? temp.)	43
Pd/SiO$_2$	0.66	-0.03	243	35.2(? temp.)	43
Pd/Al$_2$O$_3$	1	0	255	47.7(323-350)	52
Re/SiO$_2$	0.9	-0.6	377	33.5(298-423)	53
Os/Al$_2$O$_3$	1	0	323	35.6(290-320)	51

Ir/SiO$_2$	-	-	-	35.2(? temp.)	52
Ir/Al$_2$O$_3$	1.6	-0.4	333	57.8(353-393)	54
Pt Foil	1.3	-0.8	?	41.8(273-423)	55
Pt/Al$_2$O$_3$	1.2	-0.5	273-291	41.4(273-323)	56
Pt/Al$_2$O$_3$	1.0	-0.3	273	62.8(273-313)	57
Pt/SiO$_2$	0.77	0.25	233	35.2(? temp.)	43
Pt/SiO$_2$	1.0	-0.2	333	87.9(333-393)	58
Ni Film	1	0	?	44.8(193-423)	58
Ni Film	1	0	?	33.5(273-369)	59
Ni Film	0.5	0	≈173	29.3(173-393)	60
Pt/Carbon	-	L	278-308	35.6(278-308)	61

Notes: a- these figures represent the temperature, K.

....

different metals must be attributed to the differences in the temperature independent term A (pre-exponential factor), in the Arrhenius equation. According to Van Reijen, the general rate equation,

$$ -\frac{d(P_{C_2H_4})}{dt} = A(P_{C_2H_4})^y (P_{H_2})^x \exp(-E/RT) \quad ....(2.1) $$

may be simplified by assuming x = 1, and y = 0 and the values of A may thus be computed.

2.3.2 Hydrogenation of propylene

Compared with the extensive studies of the kinetics of ethylene hydrogenation, the kinetics of the hydrogena-

tion of propylene have received much less attention.
Table 2.3 summarizes the kinetics and activation energies
for vapour phase hydrogenation of C_3H_6 obtained by various
authors.

Bond and Turkevich[62] hydrogenated propylene over
platinum-pumice catalysts in vapour phase and near
atmospheric pressure at 291 K, the rate was observed to
be given by

$$rate = k (P_{C_3H_6})^{-0.5} (P_{H_2})^{0.5} \qquad \ldots\ldots (2.2)$$

while the energy of activation was found to be $\simeq 26.3$ kJ.
mol^{-1}. In another study of hydrogenation of propylene
over Pd-Al$_2$O$_3$ catalyst under similar conditions,
Kayser et al.[63] found the activation energy as 48.9 kJ.
mol^{-1}. More recently Mann and Lien[39] reported that
the hydrogenation of propylene on pumice-supported Ni,
Fe, Co, Pt, Pd, Rh, Ir, Ru and Os catalysts at
298-523 K and initial C_3H_8 and H_2 pressures of 4 k Pa
and 4-26.6 k Pa the kinetic rate law was,

$$rate = k P_{H_2}^{x} P_{C_3H_6}^{y} \qquad \ldots\ldots (2.3)$$

where the value of x was unity or slightly less and that
of y was zero or slightly negative; the values of the
activation energies for the above catalysts were found
to be 54.4, 41.9, 33.9, 67.0, 46.0, 54.4, 62.8, 27.2
and 31.0 kJ.mol^{-1} respectively. Based upon the initial

TABLE 2.3

KINETICS AND ACTIVATION ENERGIES FOR PROPYLENE HYDROGENATION

$$\text{Rate} = k \, P_{H_2}^{x} \, P_{C_3H_8}^{y}$$

Catalyst	x	y	Temp. (K)	E_a (kJ.mol^{-1})	Ref.
Ni Wire	-	-	-	25.1 (333-383) [a]	65
Pt/Pumice	0.5	0.5	291	26.3 (255-403)	62
Pd/Al$_2$O$_3$	-	-	-	48.9 (? temp.)	63
Pt/Carbon	-	L	278-308	-	61
Ni/Pumice	1.0	0	313-373	54.4 (353)	64
Fe/Pumice	0.65	0	323-383	41.9 (353)	64
Co/Pumice	0.95	0	325-398	33.9 (353)	64
Pt/Pumice	0.80	0	362-402	67.0 (353)	64
Pd/Pumice	0.80	0	393-434	46.0 (353)	64
Rh/Pumice	0.75	-0.05	313-373	54.4 (353)	64
Ir/Pumice	1.0	-0.05	333-388	62.8 (353)	64
Ru/Pumice	0.75	-0.05	323-403	27.2 (353)	64
Os/Pumice	1.6	0	383-461	31.0 (353)	64

Notes:

   a - These figures represent the temperature in K.

rate of hydrogenation per unit weight of catalyst the activities were found to be in the sequence of

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

However, no attempt was made to allow for possible variations in the metal loadings and surface areas and hence the validity of the above sequence may be doubtful.

The reaction of C_3H_6 with D_2 over several catalysts and the reaction of C_2H_4 with D_2 [52,62] showed close similarities suggesting that the general features of the mechanism are the same for both the reactions. However, there were some important differences in the detail of the two reactions, particularly over Pd and Ir. On Pd, olefin exchange occurs more readily with C_3H_6 than with C_2H_4. This may be due to easier desorption of C_3H_6 or possibly due to a different type of mechanism contributing to olefin exchange.

2.3.3 Hydrogenation of n-butenes

Relatively few reports on the catalysed reactions of n-butenes with H_2 were available upto the early 1960s. Those studies which had been performed were mainly over Ni catalyst. The major problem was the difficulty of chemical analysis of the reaction products. However, with the advent of gas chromatography as a general analytical technique, the analysis of the reaction

products has become a relatively simple task and accordingly over the last 15 years the hydrogenation of C_4-olefins has received considerable attention. The results of some important investigations on the kinetics of hydrogenation of butenes in vapour phase are summarized in Table 2.4.

One of the earliest studies of n-butene hydrogenation was reported by Twigg[66] who observed that for the reaction of 1-butene with H_2 over a nickel wire at temperatures in the range of 249-399 K, both hydrogenation and double-bond migration occured. Hydrogenation and double-bond migration followed the same kinetic rate law, namely,

$$Rate = k \; P_{H_2}^{0.5} \; P_{1-B}^{0.5} \quad \ldots\ldots\ldots (2.4)$$

The activation energies were 10.5 kJ.mol^{-1} for hydrogenation and 24.7 kJ.mol^{-1} for double-bond migration. Subsequently, Taylor and Diebler[67] studied the reactions of all three n-butenes with H_2 and D_2 over a nickel wire catalyst. Rates of hydrogenation were in the order, butene-1 > cis-butene-2 $\approx$ trans-butene-2; at 248 K cis-trans isomerisation was about 4-5 times faster than hydrogenation. The kinetics of hydrogenation and double-bond migration were similar and dependent upon both the total pressure and the H_2/but-1-ene ratio; when P_{H_2} and P_{1-B} was less than 0.133 k Pa,

the rate expression was of the form,

$$Rate = k \ P_{H_2}^{0.5} \ P_{1-B}^{0.5} \quad \ldots\ldots (2.5)$$

But with large excess of H_2, the rate was independent of H_2 pressure and proportional to the but-1-ene partial pressure.

The reactions of n-butenes with H_2 and with D_2 catalysed by supported noble metals of Group VIII have been extensively studied[52,68-71]. From the variation of product compositions with the extent of hydrogenation for typical reactions in vapour phase over Pd-Al$_2$O$_3$[69], at 310 K, 13.33 k Pa total pressure and initial butene to H_2 ratio of 1.0, over Ru-Al$_2$O$_3$[68] at 306 K and 16 k Pa total pressure and over Rh-Al$_2$O$_3$[70] at 298 K and 6-20 k Pa pressure with butene to H_2 ratio of 4-2, it was observed that as the reaction proceeded, the butenes attained their thermodynamic equilibrium proportions; although in the early stages of reaction the cis/trans ratio was in excess of that expected from the thermodynamic equilibrium. In contrast to Ru and Rh catalysts, results obtained with Pt[52] and Ir[71] catalysts showed only little isomerisation. Osmium[68] exhibited a behaviour intermediate between ruthenium and platinum. Furthermore, Bond and Winterbottom[69] observed broad similarities in the reactions of n-butenes with H_2 and with D_2 over noble metal catalysts with the reactions of C_2H_4 and C_3H_6 with H_2 and with D_2.

These broad similarities between the reactions of C_2H_4, C_3H_6 and n-butenes over noble metals may be taken as an indication that the primary features of the mechanisms of hydrogenation of the three olefins may be similar.

2.3.4 Hydrogenation of higher aliphatic olefins

Compared with the extensive studies of the kinetics of hydrogenation of C_2-C_4 olefins, the reaction between higher aliphatic olefins and H_2 in vapour phase has received little attention. A kinetic study of hydrogenation of isooctene was first reported by Beckmann, Pufahl and Hougen [72] in the year 1943. They conducted the investigation in vapour phase over supported nickel catalyst in a fixed-bed reactor at temperatures between 448-548 K and 0.5 M Pa pressure. The hydrogen to isooctene ratio in the feed was varied from 0.5 to 2.0 and the space velocity was varied from 0.0076 - 0.143 k mol.s^{-1}(m^{-3} cat.). They examined a number of kinetic expressions to fit the data; from this analysis they observed that the surface reaction between molecularly adsorbed hydrogen and adsorbed isooctene was rate controlling and that equilibrium was maintained between the gas phase and the adsorbed components. Tschernitz, Bornstein, Beckmann and Hougen [73] extended this work of hydrogenation of mixed isooctenes on supported nickel catalyst in the temperature range of

TABLE 2.4

KINETICS AND ACTIVATION ENERGIES FOR BUTENES HYDROGENATION

$$\text{Rate} = k\, P_{H_2}^{x}\, P_{B}^{y}$$

Catalyst	Olefin	x	y	Temp. (K)	E_a (KJ.mol^{-1})	Ref.
Ni wire	1-butene	0.5	0.5	?	10.5(349-419)[c]	66
Ni wire	1-butene	0.5	0.5	?	8.4(333-408)	66
Ni wire	2-butene	-	-	-	13.8(333-408)	65
Ni wire	Cis-1-butene				14.6(348-403)	66
Ni wire	Trans-1-butene	-			14.6(348-403)	66
Ni wire	Isobutene	-	-		13.8(333-383)	65
Pt/Pumice	1-butene	~0	0.4	373	12.1(286-419)	21
Pt/Pumice	Isobutene	0.4	0.5	373	7.9(357-403)	21
Ru/Al$_2$O$_3$	1-butene	1.0	0.0	273	60.7(285-318)	68
	Cis-2-butene	1.0	0.0	333	60.7(302-339)	68
Os/Al$_2$O$_3$	1-butene	1.0	-0.0	351.5	35.6(335-395)	68
Rh/Al$_2$O$_3$	1-butene	1.0	-0.05	339	20.9(329-378)	70
Rh/SiO$_2$	1-butene	1.0	-0.1	327	38.5(255-291)	70
Ir/Al$_2$O$_3$	1-butene	1.0	0.0	273	-	54
	Cis-2-butene	1.0	0.0	273	-	
Ir/Al$_2$O$_3$	1-butene	0.6	?	353	39.8(355-423)	71
	1-butene	1.0	?	393	52.3 (Temp ?)	
Pd/Al$_2$O$_3$	1-butene	0.3	0.0	273	52.3[a](Temp ?)	69
	Cis-2-butene	0.5	0.0	273	55.4[b](Temp ?)	
	t-2-butene	0.3	0.0	273	69.0[a](Temp ?)	
					53.1[b](Temp ?)	
Pt/Al$_2$O$_3$	1-butene	1.0	0.0	336	-	54
	Cis-2-butene	1.0	0.0	333	21.3(340-358)	

Note: a - Olefin/hydrogen ratio = 1.0;   b - Olefin/hydrogen = 0.33;
c - These figures represent temperature in K.

473-598 K at pressures of 0.1-0.35 M Pa. As in the previous work[71] they evaluated the results for the best rate equation, based on Langmuir-Hinshelwood mechanism by linear-least square method and suggested that the surface reaction between adsorbed hydrogen and isooctene was the rate controlling step. The deviations of experimental values of reaction rate from those computed using the best fitting rate model was, however, high about ± 8.5 %.

2.3.5 Effect of olefin structure on hydrogenation reaction

In a number of investigations, attempt was made to measure the relative rates of hydrogenation of different olefins and their temperature dependence[65,74]. It has generally been established that over nickel and platinum catalysts the rates decrease with increasing substitution of alkyl groups around the double bond of the olefins; studies on this using other metal catalysts are only few. Thus for example, the following comparable times of half-reaction have been quoted[75] for the hydrogenation of olefins over a Ni-charcoal catalyst: C_2H_4, 480 s; C_3H_6, 6240 s; 1-butene, 13500 s and isobutene, 66000 s. The relative reactivities of olefins were estimated by reacting model mixtures of two olefins with insufficient H_2 and estimating the hydrogenation products; Table 2.5 shows some of these results[75].

TABLE 2.5

THE RELATIVE REACTIVITIES OF OLEFINS IN HYDROGENATION
OVER Pt-CATALYST *

Reacting mixture		% A reacted	% B reacted
A	B		
Propylene	butene-2	90	20
Butene-1	butene-2	79	21
Isobutene	trimethyl-ethylene	99	44

* reference - 75.

The results obtained for lower olefins containing
upto 4 carbon atoms (Tables 2.2-2.5) show that the
differences between the increase in the rates of hydrogena-
tion with increasing temperature and hence the apparent
activation energies decrease with increasing alkyl
substitution[65,76]. Although, widely varying activation
energies were reported for ethylene hydrogenation,
consistently low values have been observed for hydrogena-
tion of n-butenes. A normal compensation effect is
apparently operative over nickel wire[49] at 333 K, where
the hydrogenation rates for C_2H_4, C_3H_6 and $2-C_4H_8$ were
nearly the same; in these systems the change in activa-
tion energy was nearly the same as the change in the heat

of hydrogenation. Similar results were also observed with supported Pt catalysts[49], although strictly comparable values are not available.

This decrease in the activation energy with increasing substitution of methyl groups in an olefin molecule is not easily explained. Bond[23] indicated that the following two effects may be operating simultaneously:

(i) the heat of adsorption of the olefin decreases with increasing substitution, and

(ii) with increasing substitution there may be a progressively greater number of sites on which H_2 may adsorb without competing with olefin. For these reasons the true activation energy may be changing, but the steric and thermochemical factors are not readily determinable.

2.4 LIQUID-PHASE HYDROGENATION OF OLEFINS OVER SUPPORTED METAL CATALYSTS

The liquid phase hydrogenation system with a microporous catalyst is much more complex in comparison with that of the vapour-phase reaction and requires additional consideration of mass transfer between the three phases (gas, liquid and solid) involved in the system[77]. Diffusion limitations may exist in the gas, liquid and solid phases and at their interfaces; in addition, there is a kinetic resistance and an

intraparticle diffusion resistance inside the catalyst pores. In the hydrogenation reactions, particularly of large and complex unsaturated molecules, both mass transfer and catalyst structure have considerable influence upon the reaction rate and the selectivity[78-81]. The chemical nature of the liquid and the structure of unsaturated compound also have considerable influence on the diffusion limitations, the reaction velocity and the mechanism of catalytic hydrogenation in solutions[80,82].

Liquid phase hydrogenation over a solid catalyst may be considered to occur through the sequence of several steps[81]:

(i)   absorption of hydrogen into the surface film of the liquid, which is in contact with gas phase.

(ii)   transfer of hydrogen through the bulk liquid to the film at the catalyst surface.

(iii)   molecular diffusion of hydrogen through the laminar liquid film at the catalyst surface.

(iv)   internal diffusion of hydrogen and reactant through the catalyst pores filled with liquid,

(v)   adsorption of reacting components on the catalyst surface,

(vi)   reaction between adsorbed components or adsorbed component and component in the bulk phase,

(vii)   desorption of the product from the catalyst surface,

(viii) diffusion of the product through the catalyst
pores filled with liquid to the catalytic
surface,

(ix) diffusion of the products through the laminar
liquid film at the catalyst surface into the
bulk liquid phase.

Depending upon the hydrodynamics inside the
reactor and state of the catalyst, one or more of the
above steps may control the overall reaction. For a
quantitative investigation of the effect of the composi-
tion of the reaction mixture on the rate of hydrogenation
of unsaturated compounds in the liquid phase on solid
catalysts, it is necessary to define the experimental
conditions adequately so that the collected data enable
determination of this effect. Kinetic studies of
catalytic reactions have, therefore, to be carried out
under conditions in which the restrictions due to mass
transfer on the chemical rate processes are eliminated.
Hence, each study of this type must be preceded by
finding the so-called kinetic regime, which is a state
in which the reaction rate is determined solely by the
surface adsorption, desorption and surface reaction
(steps v, vi and vii). In the studies reported earlier
on the olefin hydrogenation, these requirements were
not always met, but in recent works considerable
attention has been given to these aspects[83-87].

The criteria indicating that a state has been reached in which the effect of external mass transport, on the reaction rate is ruled out consists in the independence of the reaction rate of the intensity of mixing[88]. By a suitable choice of the amount of catalyst, it is possible in vigorously shaken[81,89] or stirred[90] reactors to reach this region even for rapidly reacting substances. Several investigators followed this approach of establishing the intensity of agitation to ensure the attainment of kinetic regime in liquid phase catalytic hydrogenation and then studied the effects of kinetic parameters. Under such conditions, the reaction rate was found to increase linearly with catalyst concentration in many cases.

Freildin and Polkovnikov[91,92] investigated the hydrogenation of cyclopentadiene on platinum black and Raney nickel in alcohol and cyclohexane solvents respectively. They first established that the intensity of agitation was such that the reaction was in kinetic regime; under this condition, the hydrogenation rate was found to be proportional to the amount of platinum (24.4 to 99.8 mg) and Raney nickel (0.12 - 1.26 g).

Muskat and Knapp[93] also found that the hydrogenation rate of phenyl butadiene stereo isomers under intense agitation was proportional to the amount of Adams platinum.

Heck and Smith[94] studied the hydrogenation of acetylene over Raney nickel in a 75 mm i.d., 3.6 m long jacketed glass bubble column slurry reactor operated at 310-330 K and atmospheric pressure. Water was used as solvent and the H_2/C_2H_2 ratio was varied between 1:1 and 4:1. Only two reaction products ethane and ethylene were detected. The concentration of ethylene and ethane in the product stream increased with increasing temperature, while the selectivity remained essentially constant over the temperature range studied. Acetylene conversion increased with increasing catalyst loading upto 1.0 kg/m³; the mole fraction of both ethylene and ethane in the product increased with increasing catalyst concentration. The conversion of ethylene increased markedly with increasing H_2/C_2H_2 ratio in the feed.

Gormonov et al.[95] in their investigations of the liquid phase hydrogenation of vinyl acetylene on $Pd-SiO_2$ catalyst found that the intensity of agitation had no effect on the selectivity of hydrogenation of vinyl acetylene in the range of 200 to 500 vibrations/min.

Davis, Thompson and Grandall[96] carried out the first systematic study of the effect of the amount of catalyst on the rate of heterogeneous processes whose rate is influenced by diffusion of the reactants. In studying the effect of the amount of platinum oxide on

the hydrogenation rate of trimethyl ethylene, 2-pentene
and isopropyl ethylene in a mixture of 95% ethanol and
5% methanol, the hydrogenation rates of these compounds
were found to be different when a small amount of
catalyst was used. As the amount of catalyst was
increased, the relative differences in the rate
diminished and the rate of hydrogenation of all these
compounds approached a limiting value. They explained
their results by the assumption that the hydrogen in
passing from the gaseous phase to the catalyst surface
must overcome the resistance of two stationary films at
the phase interfaces of gas-liquid and liquid-solid.
The rate of hydrogenation was expressed as follows:

$$r = k \, (C^{*}_{liq} - C_{cat}) \; / \; (R_1 + R_2 /_m) \quad \ldots\ldots \; (2.6)$$

where C^{*}_{liq} and C_{cat} are the hydrogen concentrations at
gas-liquid interface and catalyst surface respectively,
R_1 and R_2 are the resistances at the gas-liquid & liquid-
solid interfaces and m is the amount of catalyst. At
low and constant rate of agitation, when $C_{cat} \ll C^{*}_{liq}$,
Equation 2.6 can be written in the form,

$$\frac{1}{r} = A + B/m \qquad \ldots\ldots\ldots (2.7)$$

Thus for $m \longrightarrow \infty$, the rate of reaction $r \longrightarrow \frac{1}{A}$; the
value of $1/_A$, obtained by extrapolation, corresponds
to the maximum hydrogenation rate at a specified rate
of agitation. This maximum hydrogenation rate was found

to be approximately equal to the initial rate of hydrogen dissolution, the latter, in turn, being proportional to the surface of the gas-liquid interface as determined by the intensity of agitation. Thus when sufficient amount of catalyst is present, the rate of hydrogenation is determined by the rate of dissolution of hydrogen in the liquid phase.

Köelbel and Maening[97] reported a laboratory investigation on liquid phase hydrogenation of ethylene using Raney nickel catalyst of about 0.0005 cm size, suspended in paraffin oil in a 3.8 cm i.d. bubble column. The runs were conducted at atmospheric pressure at superficial gas velocity in the range of 0.01-0.06 m/s, temperatures of 303-333 K and catalyst loadings of 2.5 - 10 kg/m^3. The feed gas composition was also varied; the H_2/C_2H_4 molar ratios were 0.765, 1.0 and 1.35. They did not analyse the results for mass transfer effects; from the data of conversions and rate, they, however, postulated that the adsorption of ethylene was rate controlling and that hydrogen adsorbed strongly on the active sites. It is possible that under the experimental conditions, there were restrictions for the transport of C_2H_4 to the catalyst surface.

Sherwood and Farkas[98] reanalysed the experimental data of liquid-phase hydrogenation of ethylene obtained

by Koelbel and Maening[97] and confirmed that mass transfer
did not affect the reaction. In the kinetic regime, the
adsorption of ethylene on the catalyst sites was rate
controlling and that hydrogen adsorbed more strongly.
The surface reaction occurred rapidly and the equilibrium
strongly favoured the formation of ethane.

Kawakami, Ohgi and Kusunoki[84] reported the
investigations of hydrogenation of ethylene and
propylene in the presence of a 5 % Pt/carbon catalyst
(particle diameter, 0.0006 cm; particle density 1 g/cm^3;
porosity, 0.5) suspended in water catalyst loadings
0.1 to 0.5 kg/m^3 at 278-308 K and atm. pressure. They
used a mechanically stirred glass reactor, 75 mm in I.D.
180 mm high, with four baffle plates. The rates of
hydrogenation of the individual olefins in the region of
excess hydrogen were found to be controlled by the gas-
liquid and liquid-particle mass transfer of olefin. In
the region of excess olefin the external mass transfer
and the pore diffusion resistances of hydrogen could not
be ignored. An intrinsic kinetic expression was derived
assuming the adsorption of molecular hydrogen as the
rate determining step. For fitting the collected data
the following Langmuir-Hinchelwood type rate equations
were selected:

For the hydrogenation of ethylene:

$$r = \frac{k \, a_c \, \eta \, C_{SH_2}}{1 + KC_{SC_2H_4}} \qquad \ldots\ldots (2.8)$$

For the hydrogenation of propylene:

$$r = \frac{k' \; a_c \; \eta \; C_{SH_2}}{1 + K' \; C_{SC_3H_6}} \qquad \ldots\ldots\ldots\ldots (2.9)$$

where, a_c = specific external area of catalyst; k, k' = reaction rate constants for ethylene and propylene; K, K' = adsorption constants for ethylene and propylene; C_{SH_2}, $C_{SC_2H_4}$ and $C_{SC_3H_6}$ = concentration of hydrogen, ethylene and propylene on catalyst surface. With a mixture of C_2H_4 and C_3H_6, for competitive hydrogenations of ethylene and propylene, the selectivity in the region of excess hydrogen was determined solely by the ratio of the mass transfer rate of propylene to that of ethylene. For the expression of the intrinsic reaction rate in the region of excess olefin, a model was proposed assuming two kinds of sites, consisting of the active sites available for the adsorption of ethylene alone and those available for the competitive adsorption of both olefins.

Bond and Rank[99] studied the liquid phase hydrogenation of pentene-1 over supported Pd, Rh, Ru, Pt and Ir catalysts at around 293 K using MeOH, i-PrOH, glacial acetic acid, benzene and n-octane as solvents; the metal concentration on catalyst was 5 % w/w in each case and charcoal, Al_2O_3, $CaCO_3$ and $MgCO_3$ were used as supports. The hydrogenation was carried out in 10 ml glass ampules kept at constant temperature in a

shaking machine. The results showed that Pd and Ru catalysts, in addition to hydrogenation, also catalysed the isomerisation of pentene-1, while Pt and Ir showed very little isomerisation activity. The isomerisation activity was in the sequence:

$$Pd \gg Ru > Rh > Pt \gg Ir.$$

The relative rate of pentene isomerisation was insensitive to agitation conditions over a wide range of vibrating speeds (2-7 vibrations/sec) and is not greatly influenced by the nature of the solvent nor the catalyst support used. From the independence of isomerisation reaction of the agitation conditions, it appears that mass transfer effects were insignificant.

Kawakami and Kusunoki[100] reported the results of a study of liquid-phase consecutive hydrogenation of phenyl-acetylene to ethyl benzene in the presence of a 0.5 % Pt-Al$_2$O$_3$ catalyst (3.17 mm x 3.17 mm cylindrical pellets) at 293 K and atm. pressure. The initial concentration of phenyl-acetylene in ethanol solvent was varied in the range of 0.0164 - 0.0758 k mol/m^3 and the H$_2$ partial pressure, using N$_2$ as inert, in range of 15.2 - 101 k Pa. Experiments were performed in a stirred reactor fitted with basket impellers in which the catalyst pellets were held as well as in a stirred slurry reactor in which the finely powdered pellets (average diameter 0.003 cm) were suspended. The

intrinsic equations were derived empirically from the rate measurements with the powdered catalyst. The following equations were selected to represent the data:

For hydrogenation of phenylacetylene to styrene:

$$r_1 = \frac{k_1 C_P^n C_H}{(1 + \alpha C_{Po})(1 + K_1 C_P^n + K_2 C_S^n C_H^m)}$$

For hydrogenation of styrene to ethyl benzene:

$$r_2 = \frac{k_2 C_S^n C_H}{(1 + \alpha C_{Po})(1 + K_1 C_P^n + K_2 C_S^n C_H^n)}$$

where r_1 and r_2 are the rates of hydrogenation of phenyl acetylene and styrene respectively; C_P = concentration of phenyl acetylene; C_{Po} = initial concentration of phenylacetylene; C_H = concentration of hydrogen; C_S = concentration of styrene. The numerical values of the parameters were evaluated using non-linear least square technique and found to be $k_1 = 7.94 (1^{1.4}/mol^{0.4}, cm^3$- cat.sec), $k_2 = 1.19 (1^{1.4}/mol^{0.4}, cm^3$-cat.sec), $K_1 = 1126.0 (1/mol)^{0.4}$, $K_2 = 1487.0 (1/mol)^{0.4}$, $\alpha = 17.7$ (1/mol), $m = n = 0.4$. Under the intrinsic kinetic limitation, the yield of styrene was independent of both the initial concentration of phenylacetylene and the hydrogen concentration. With the catalyst pellets the hydrogenation rates and the yields were significantly influenced by the intraparticle diffusion.

Kawakami, Ura and Kusunoki[83] studied the liquid phase hydrogenation of styrene on 0.5 % Pt-Al$_2$O$_3$ catalyst (cylindrical pellets of 3.17 mm x 3.17 mm and powdered pellets of mean diameter 0.003 cm at 268 to 293 K and atmospheric pressure in a stirred slurry and basket reactors. Hydrogen partial pressure was varied between 10 - 101 K Pa. Absence of gas-liquid, liquid-particle mass transfer resistances and the pore diffusion resistance was first established using available correlations. They observed a zero order dependence of hydrogenation with respect to styrene and proposed the following kinetic model based on Langmuir-Hinshelwood mechanisms

$$r = k K_H C_H^* / (1 + \sqrt{K_H C_H^*})^2 \quad \ldots\ldots (2.9)$$

where r = rate of reaction, C_H^* = hydrogen concentration in liquid phase. The constants k and K_H followed Arrhenius behaviour, the energy of activation was found to be 96.83 kJ.mol^{-1}. They also suggested that the dissociated hydrogen and styrene molecules are non-competitively adsorbed on the active sites of the catalyst. With pellets, the rate of hydrogenation was found to be influenced by pore diffusion of hydrogen.

An early investigation of liquid phase hydrogenation was that of Babcok, Majdell and Hougen[101] who studied hydrogenation of α-methyl styrene in a stainless steel, 1.25 m long and 38.1 mm I.D.

differential flow trickle-bed reactor. They used several catalysts-palladium, platinum, rhodium, ruthnium and nickel supported on alumina in the form of cylindrical pellets of 3.17 mm x 3.17 mm size. The experiments were done at temperatures 297.3 - 330.2 K and 0.1 - 1.2 M Pa pressures. From the kinetic data, they concluded that with palladium catalyst at pressures above 0.3 MPa the apparent rate controlling step was surface reaction between dissociated hydrogen and α-methyl styrene adsorbed in different types of active sites. Using the least square technique, the following rate equation was proposed which gave an average deviation of 3 %.

$$r = k_s K_H K_o Px \ / \ (1 + \sqrt{K_H P})^2 (1 + K_o x) \ldots (2.10)$$

where, r = rate of reaction; K_H, K_o = adsorption constants for hydrogen and α-methyl styrene; P = hydrogen pressure; k_s = reaction rate constant; x = mole fraction of α-methyl styrene in liquid phase. At low pressures below 0.3 MPa the kinetics were found to be somewhat different - the reactants competed for the similar active sites. With platinum catalyst, the rate controlling step was surface reaction between dissociated hydrogen and α-methyl styrene on similar active sites; the reaction rate could be best represented by Equation 2.11.

$$r = \frac{k_s K_H K_o \ P x}{(1 + \sqrt{K_H P} + K_o x)^3} \quad \ldots \ldots (2.11)$$

Rhodium and nickel catalysed the polymerization of

α-methyl styrene together with slow hydrogenation.

Ruthenium had negligible activity for catalysing the

hydrogenation under moderate conditions employed in

these studies.

Later, Satterfield, Ma and Sherwood[86] reported

another study on the hydrogenation of α-methyl styrene

in liquid phase over a 0.5 % Pd-Al$_2$O$_3$ catalyst

(cylindrical pellets of 3.17 mm x 3.17 mm, and powdered

pellets of average diameter of 0.005 cm) in a stirred

batch reactor at temperatures in the range of 343-388 K

and atmospheric pressure. By suitable calculations and

experimental observations they showed that for the

catalyst powder, mass transfer resistances to the out-

side of the catalyst particle and the pore diffusion

resistance inside the catalyst pores were negligible.

In contrast to other authors, they found that the reaction

was first order with respect to both hydrogen and

α-methyl styrene. The activation energy of the

reaction was found to be 31.8 kJ/ mol at temperatures

of 343-373 K. For the hydrogenation with pellets the

tortuosity factor of the palladium catalyst was found

to be 3.9 and the catalytic effectiveness factor

varied in the range of 0.07 - 0.13.

Recently, Clarke, Lloydlangston and Thomas[85]

reported a detailed study of the hydrogenation of

α-methyl styrene on supported copper magnesia-

silica catalyst (size 10^{-3} cm) in a stirred slurry reactor operated at 373-423 K and 0.1 - 0.3 MPa pressure. Under efficient agitation (Impeller Reynolds number of about 2.5×10^4 at 383 K and 4.0×10^4 at 403 K) and catalyst loadings of less than 2 kg.m^{-3}, the conversion was found to be chemically controlled. From the data of experiments at 423 K, they observed that the agitation was insufficient to sustain a chemically controlled reaction. At higher catalyst loadings or with less efficient agitation, the reaction rate was limited by the transfer of hydrogen through the liquid. They, however, did not study the kinetics of the reaction in detail.

Cyclohexene and substituted cyclohexenes were taken by many workers as the suitable liquid olefins for hydrogenation in liquid phase.

Smith and Meriwether[102] hydrogenated cyclohexene and cyclohexadiene 1,3 and 1,4 on Adams catalyst in glacial acetic acid at around ambient temperature and an initial pressure of 0.4 MPa. Within the narrow limits of variables studied, it was established that the hydrogenation was kinetically controlled. The reaction rate increased in direct proportion to the amount of catalyst. The rate was found to be of first order with respect to H_2 pressure and zero order with respect to unsaturated compound. The reaction rate

increased with increase of temperature; energies of
activation were found to be 10.04 kJ.mol^{-1} for cyclo-
hexene, 18.83 kJ.mol^{-1} for cyclohexadiene-1,4. During
the reaction, the control of temperature was unsatisfactory
and some temperature rise was observed in each run; the
accuracy of the results was, therefore, unsatisfactory.

Price and Schiewetz[103] obtained similar results
in the hydrogenation of cyclohexene at 279 - 298 K and
hydrogen pressures of 0.53 -0.84 kPa in presence of 5%
Pt on Al_2O_3 catalyst of 300 mesh size. The experiments
were conducted semi-batch-wise in a stirred glass reactor
in which hydrogen was continuously bubbled through the
solution of cyclohexene in cyclohexane; the catalyst was
kept suspended in the liquid. When the rate of stirring
was 1000 rpm, the reaction was independent of cyclohexene
concentration and was proportional to the hydrogen
pressure. With small amounts of catalyst (upto 1 g) the
reaction rate was proportional to the amount of catalyst.
When larger quantities of catalyst were used the reaction
rate reached a limiting value and then remained constant.
It is known that in the presence of large amounts of
catalyst the reaction may be limited by the transport
of hydrogen through the gas-liquid interface, but
these authors offered another explanation for their
results; they said that at high catalyst concentrations,
a part of the catalyst settles down and does not play
any appreciable role in the overall process.

Farcas and Sherwood[98] studied the hydrogenation of cyclohexene at 312.6 to 330.1 K and atm. pressure in an aqueous suspension of 0.003 cm particles of palladium black catalyst; they also investigated the hydrogenation of α-methyl styrene to cumene at 107 -111 kPa total pressure and 301 -339 K temperature using 0.0055 cm particles of palladium black. In both of these studies glass bubble column of 2.5 cm i.d. was used and they found that the mass transfer to the catalyst particles was rate controlling.

Liquid-phase hydrogenation of cyclohexene on a supported platinum catalyst at ambient conditions was studied by Dmitrienko et al.[104]. They used a stirred slurry reactor. The reaction rate followed a zero order dependence on cyclohexene concentration only upto 50 % conversion and then gradually shifted towards first order at higher conversions.

Sokolskii et al.[105] studied the hydrogenation of cyclohexene, acetone and their mixtures in mixed n-hexane and methyl alcohol as solvents on Pd and Pt blacks at 293, 303 and 313 K and atmospheric pressure. In the hydrogenation of a mixture of cyclohexene and acetone on Pt in mixed solvent, cyclohexene was found to hydrogenate first followed by the hydrogenation of acetone. The rates of reaction were affected by solvent composition (i.e. hexane, methyl-alcohol ratio); a solvent containing 73 vol % hexane in MeOH gave

minimum rate of cyclohexene hydrogenation. On the other hand, the hydrogenation rate of cyclohexene on Pd did not depend upon the composition of solvent used. There was practically no hydrogenation of acetone on the Pd catalyst.

Hussey et al.[106] reported the results of a study on the liquid-phase hydrogenation of 18 cycloalkenes in admixture with cyclohexane as solvent using 0.52-0.97 % Pt on alumina at near atmospheric pressure and 298 K. The reactions were found to be of 1st order in hydrogen partial pressure and also with respect to catalyst concentration and zero order in cycloalkene. No isomerisation was observed to accompany the hydrogenation reaction; the rate of hydrogenation increased linearly with increasing Pt content of the catalyst. The kinetic data were explained by a modified Horiuity-Polanyi mechanism:

$$H_2 + 2^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2H^* \qquad \qquad \ldots\ldots (2.13\ a)$$

$$E + 2^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E \qquad \qquad \ldots\ldots (2.13\ b)$$

$$E^{**} + H \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} 2^* + HE^* \quad \text{(associative reaction)} \quad \ldots (2.13\ c)$$

$$HE^* + H^* \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} H_2E + 2^* \quad \text{(associative adsorption)} \quad \ldots (2.13\ d)$$

where E denotes the alkene and * denotes the active sites.

In another study Hussey and Nowack[107] reported
the hydrogenation of cyclopentene, cyclohexene, cyclo-
heptene and cyclooctene in solutions of cyclohexene on
0.57 - 0.74 % Pd-Al_2O_3 (150-200 mesh) at 298 K in
agitated glass reactor. In this also they observed the
rate to be proportional to the amount of catalyst.
They correlated the initial rates of hydrogenation using
a power law equation; the reaction rate was found to be
fractional order with respect to both olefin and hydrogen.
This fractional order dependence of the rates upon the
cycloalkene concentration was explained by them in terms
of reversible chemisorption of cycloalkene while the
fractional order dependence upon hydrogen pressure was
viewed to reflect an intrinsic zero order dependence
upon which is superimposed a first order pore diffusional
process involving hydrogen. The modified Horiuti-
Polanyi mechanism in which hydrogen and alkene were non-
competitively adsorbed on active sites, as proposed by
them earlier, was further supported by these results.

For cyclohexene hydrogenation in the liquid phase,
various bi-metallic as well as sulphided catalysts
have also been studied by several authors. These
investigations appear to have been mainly concerned
with catalyst activities and the general kinetics-
such as reaction rates and reaction order, without
specifying whether the mass transfer was satisfactory
or not. These informations are, therefore, of limited value.

Bond and Webstar[28] in a series of publications reported the activities of many bi-metallic catalyst such as, Ru-Pt, Ru-Pd, Ir-Pt, Rh-Pd, Ni-Pt, Ni-Pd, Co-Pt, Fe-Pt, Ru-Rh and Pt-Pd, for the hydrogenation, though mainly of nitrobenzene in methyl butanol, but also of cyclohexene and pentene-1. The results are shown in Table 2.6. These bi-metallic catalysts showed a 3-5 times enhancement of the rate of hydrogenation obtained with mono-metallic catalysts. Higher catalytic activity of bi-metallic catalysts in hydrogenation of unsaturated compounds have been reported also by several other authors[108-109].

TABLE 2.6

ACTIVITY ENHANCEMENT IN LIQUID-PHASE HYDROGENATION

Catalyst A B	Temperature (K)	Reactant	Enhancement (Relative to A)	Optimum composition (atom% B)	Reference
Pt - Ru	303	Cyclohexene	3	40	28
Pt - Ru	303	Benzene	5+	65	28
Pt - Ir	303	Cyclohexene	3-4	10-25	28
Pt - Pd	303	Pentene-1	2-3	Ca. 70	28
Ru - Pd	433	Benzene	2	10	108
Rh - Pd	293	Heptene-1	1.5	10-20	109

Recently Sokolova, Popova and Sokolskii [109] investigated different compositions of Pd-Rh bi-metallic catalysts for the hydrogenation of cyclohexene and heptene-1 at 293 K in water and in aqueous solutions of ethyl alcohol in a thermostated shaking reactor. The most active catalyst formulation consisted of 5 % loading of 10.5 atom.% of Rh in Pd-Rh on alumina. The cyclohexene hydrogenation rate was observed to be a linear function of the concentration of weakly adsorbed hydrogen. The general level of activity was, however, modest (Table 2.6).

Voorhoeve and Stuiver [110] studied hydrogenation of cyclohexene over non-supported and alumina supported Ni- W-S catalysts at 473-673 K and 4.85 MPa pressure using a H_2 / cyclohexene ratio of 35; CS_2, 1-10 %, was added to the feed to maintain sulphur concentration in the catalyst. They found that the hydrogenation was first order in cyclohexene, showing that the reaction rate was strongly dependent on the adsorption of cyclohexene. The Arrhenius plot was non-linear; hence the activation energies changed with temperature (e.g.,553 K, 117 kJ.mol^{-1}; 593 K, 79 kJ.mol^{-1}). The activation energies were the same for supported and unsupported catalysts although reaction rate was much higher (by a factor of 180) on the supported catalysts.

Gonzo and Boudart [111] studied the liquid phase hydrogenation of cyclohexene on six different palladium

catalysts at 264 to 308 K and H_2 pressures of 4 to 89 kPa;
cyclohexene concentrations were varied from 0.15 to 3.0 M.
The catalysts supported on silica and alumina had the
following composition:

2.84% Pd- SiO_2; 4.88% Pd-Al_2O_3; 3.75 Pd-SiO_2; 0.57% Pd-
SiO_2; 1.39% Pd-SiO_2; 1.45% Pd-SiO_2. The average palladium
particle size of the catalyst was varied from 1 to 8 nm.
Under the above operating conditions, the turnover
frequency was found to be independent of the particle
size, the nature of the support and the nature of the
solvent (methanol, n-heptane, ethyl acetate and cyclo-
hexane) used for catalyst suspension. The order of
reaction was 0.5 with respect to hydrogen and zero with
respect to cyclohexene concentration.

Recently, Madon, O'connell and Boudart[87]
investigated the liquid-phase hydrogenation of cyclo-
hexene on supported platinum catalysts at constant
hydrogen pressure, normally atmospheric, between 275 and
316 K. The reaction was studied in a pyrex gradientless
slurry reactor of 170 cm^3 total capacity. They
confirmed their earlier finding that the overall rate
of hydrogenation was neither dependent on the nature
of the support nor on the particle size of the metal
and was also independent of the nature of the solvent
if the concentration of hydrogen was expressed in
terms of its solubility. It was concluded that

hydrogen was adsorbed on the catalyst in dissociated form and the hydrocarbon species almost completely covered the metal surface. Apparent first order kinetics with respect to hydrogen and zero order with respect to cyclohexene was observed.

Earlier Dmitrienko et al.[104] obtained lower rate of cyclohexene hydrogenation under similar operating conditions. This may be either due to the presence of poisons in the liquid reagents or their data may have been influenced by diffusion; they, however, have not mentioned of any tests made to check for mass transfer effects.

More recently the kinetics of cyclohexene hydrogenation in liquid phase on 0.5 % Pt-Al$_2$O$_3$ catalyst (of 0.002 cm size) at 293 K and atm. pressure was studied by Kawakami, Yamamoto and Kusunoki[112]. From the results of semibatch hydrogenation in a slurry reactor they concluded that the surface reaction between the dissociated hydrogen and cyclohexene molecule adsorbed non-competitively on the catalytic sites was rate controlling. Fitting the experimental data by non-linear least squares method, the following rate expression was selected as optimal:

$$r = \frac{k \, K_H K_C C_H C_C}{(1 + \sqrt{K_H C_H})^2 (1 + K_C C_C)} \qquad \ldots\ldots\ldots (2.14)$$

where r = reaction rate; k = reaction rate constant; K_H, K_C = adsorption constants for hydrogen and cyclohexene; C_H, C_C = concentration of hydrogen and cyclohexene in liquid phase. On conducting the hydrogenation in stirred basket reactor using cylindrical catalyst pellets of 3.56 mm x 3.27 mm size, the rate of reaction was found to be influenced by internal diffusion. The effective diffusions of hydrogen and cyclohexene were also computed; from the effective diffusivities the tortuosity factors were calculated and found to be 3.1 and 2.5 respectively.

Cornubert and Thomas[113] investigated the effect of the amount, Raney nickel catalyst on the hydrogenation rate of 3,5 dimethyl cyclohexene-2 at low intensity of agitation (240 swings per minute). They found that at low range of catalyst loadings the hydrogenation rate increased at a higher rate than proportional increase of nickel concentration. For instance, an increase in the amount of catalyst from 1.0 to 20 g caused the average reaction rate to jump from 3 to 167 ml/min, i.e. by a factor of 56. As the amount of catalyst was further increased, such increase of the reaction rate was retarded.

Earlier Pall and Schwarz[114] also observed similar phenomena in the liquid phase hydrogenation of acetylene and other unsaturated compounds.

Sokolskii and Fasman[115] studied the hydrogenation of hexene-1 in the liquid phase at near ambient conditions using Raney nickel catalyst. The results indicated that when small amount of catalyst was used, the reaction is controlled by pore diffusion or chemical reaction; with large quantities of catalyst and intense agitation, the transport of hydrogen through the gas-liquid interface was the rate determining step.

Watt and Walling[116] investigated the hydrogenation of hexene-1 in a magnetically stirred reactor at low temperatures of 275-303 K using Adams platinum, Raney nickel, rhodium and palladium catalysts. In experiments with small amounts of Adams platinum, the rate first increased to a sharp maxima and then decreased continually. For larger amounts of Adams platinum the maximum broadened so that, in the limit, the kinetic curve followed a zero-order rate equation. In contrast, for all other catalysts used the rate varied linearly with catalyst amount in the region of low catalyst concentration and attained a limiting value for large amounts of catalyst; the reaction was of zero order with respect to olefin and first order w.r.t. hydrogen. Their findings of low activation energies (4-9 kJ/mol) and dependence of the reaction rate on the intensity of agitation indicates that in these studies the diffusion of hydrogen to the catalyst surface was the restricting factor.

Smith and Burwell[117] reported a study of hydroge-
nation of hexene-1 over PtO_2 catalyst suspended in
glacial acetic acid at room temperature. They used
glass bubble column reactor of 1.1 sq. cm. cross section.
Very little isomerisation was observed to accompany the
hydrogenation. The mechanism of reaction closely
resembled the vapour-phase reaction. They, however,
did not evaluate the mass transfer effects on the
reaction rate.

Červeny' et al.[118] reported the hydrogenation of
mixed 1- and 2-hexenes over noble metal catalysts at
temperatures in the range of 286 to 313 K and hydrogen
pressures of 101.3 - 202 kPa using ethanol as solvent.
For hydrogenation at near atmospheric pressure they
used a 125 ml glass reactor in which mixing was done
by shaking at a frequency of 1000 vibrations per
minute. The hydrogenation at elevated pressures were
carried out in a 100 ml autoclave placed in a shaker
operating at 100 -780 vibrations/min. The following
supported catalysts were used:

5 % $Pd-SiO_2$, surface area 294 m^2/g; 4 % Pd-C,
surface area 1234 m^2/g; 4% $Rh-SiO_2$, surface area
222 m^2/g and 14% $Pt-SiO_2$, surface area 221 m^2/g.

The selectivity of hydrogenation was found to
depend mainly on the nature of the active metal
component; it decreased in the order Pt > Rh > Pd and

did not change with temperature or catalyst poison.
Isomerisation accompanied the hydrogenation reaction
and both the reactions probably took place on similar
active sites; their extents were probably determined by
the strength of bonds between the olefin and the active
centers of the catalyst. The experimental results were
explained in terms of a semi-hydrogenated adsorbed
intermediate product.

In an early study of hydrogenation of heptene-1
on Raney nickel catalyst without a solvent, Heilmann
and Gaudemaries[119] observed a linear dependence of
reaction rate on the catalyst loading. They, however,
did not study the kinetics in detail.

Gartsman et al.[120] reported a study of liquid
phase hydrogenation of heptene-1 over Raney nickel
catalyst in fixed bed and fluidized-bed reactors
operated at 296 K and hydrogen pressures of 0.21 to
0.23 MPa. For fixed-bed operation, catalyst particles
of 1.6 - 3.4 mm diameter were used; the liquid and gas
velocities were varied in the range of 0.0012 -0.02 m/s
and 0.022 - 0.121 m/s respectively. They found that
the observed reaction rate was dependent on the hydro-
dynamic conditions within the reactor. The results
showed that at low liquid velocities (0.0012-0.0045 m/s)
the transfer of reactants to the catalyst surface
controlled the reaction. For higher liquid velocities

(0.008 - 0.02 m/s), the rates of external and internal mass transfer processes became commensurate.

For the hydrogenation in fluidized-bed reactor they used catalyst particles of 0.10 -0.19 mm diameter; the liquid and gas velocities were varied in the ranges of 0.0061 - 0.022m/s and 0.017 - 0.08 m/s respectively. The observed reaction rate was found to depend upon the linear gas and liquid velocities, the size of the catalyst particle and fluidization conditions.

An interesting patent by Mertzweiller and Tenney[121] describes the hydrogenation of octene-1 over alumina supported metal-sulphide catalysts activated by treatment with triethylaluminium in n-heptane. They claimed that the activated catalysts so prepared are more stable, more active and less susceptible to poisoning than conventional sulphide catalysts. The authors suggested that Et_3Al reacts with the metal sulphide and the alumina support and after heat treatment very small metal-hydride-sulphide crystallites, e.g. (Al_2O_3) -O-Al Et-S-Ni-H, are formed which are catalytically very active.

Koppova et al.[112] investigated the hydrogenation of isomeric octynes (acetylinic bond) dissolved in n-heptane on supported nickel kieselguhr catalyst at 303 K. The catalysts were poisoned by sulphur

compounds adsorbed from solutions in n-heptane; hydro-
genation rates decreased as the amounts of adsorbed
sulphur increased, but the selectivity was not affected.
Independent of sulphiding, the rates of hydrogenation
decreased in the order 1- $>$ 3- $\geqslant$ 4- $>$ 2-
octyne.

Consecutive liquid-phase hydrogenation of 1-octyne
to octane on palladium oxide catalyst suspended in C_1 -
nC_4 alcohols and nC_6 - nC_8 alkanes as solvent at one
atm. pressure and 303 K, was reported by Caga et al[123].
They used a 80 ml round-bottom flask fitted with a
variable shaker at 1600 vibrations per minute and 5 %
vol. solvent. They studied the effects of catalyst
concentration and type of solvent on the hydrogenation
activity of the catalyst. Reduction of the palladium
oxide in situ showed better activity in alcoholic
solvents than in the n-alkanes and a non-linear varia-
tion of rate with catalyst weight was observed. When
the catalyst was pre-reduced in the solvent before
alkene addition, the rate varied linearly with
catalyst weight and the catalyst gave a better activity
in n-hexane. They, however, did not investigate the
kinetics and mechanism of the reaction.

2.5

SUMMARY OF LITERATURE SURVEY

The published informations relevant to the
kinetics of catalytic hydrogenation of olefins in vapour
and liquid phases have been presented in the foregoing
pages. From these informations, the following observa-
tions can be made:

(i)   Catalytic hydrogenation is a well studied branch
       of heterogeneous catalysis, though mostly with
       simple systems. Many of the investigations were
       concerned with the mechanism of activation of the
       reactants, specially of hydrogen, and the overall
       reaction rates, mainly in vapour-phase. Studies
       in the liquid-phase, particularly on intrinsic
       kinetics of hydrogenation of olefins and di-
       olefins, have been rather few and these have
       been generally concerned with the effects of
       reaction parameters like catalyst concentration,
       type of solvent, temperature and pressure at/or
       slightly higher than atmospheric pressure.

(ii)   These hydrogenation reactions can be considered
       to occur through a series of physical and
       chemical steps involving diffusion of reactants
       from the bulk to the catalyst surface and inside
       the catalyst pores, the reaction at the active
       sites and then diffusion of reaction products

back into the bulk liquid or gas phase. The
slowest of these steps is rate controlling. By
varying the temperature, pressure, intensity and
method of mixing, the reactor type and also the
quantity, dispersity and activity of the catalyst,
it is possible to shift the reaction from the
diffusional controlled into the kinetic controlled
and vice-versa. The kinetic behaviour of a
particular reaction is different in the two types
of controlling regimes.

In liquid phase hydrogenation reactions
on solid catalysts, the situation becomes more
complicated due to the presence of three phases
(gas, liquid and solid) and liquid diluents. In
addition to these the diffusion coefficients of
H_2 in the liquid phase are about 3-5 orders of
magnitude lower than those in the gas phase.
Very little quantitative information is available
about diffusion coefficients of H_2 in higher
olefins having 6 and more carbon atoms. In most
of the kinetic studies, the physical effects
were either omitted or not properly taken care
of. Further, the pores of the catalyst remain
filled with the liquid. Now this liquid inside
the pores influences the diffusion of reactants
and products and thus the overall reaction rates,
have been the subject of many studies. In many

cases, however, the phenomenon has been treated only empirically.

(iii) In majority of these studies, the reaction was carried out at atmospheric pressure and in many of them only initial reaction rates have been reported. Practically, very little data on kinetics and mass transfer are available in the high pressure region, where the solubility of H_2 is enhanced.

(iv) It has been well established that mechanistically, the hydrogenation reactions are complex in nature and involve multisteps. In the earlier studies, the kinetics of these reactions was elucidated in terms of simple power law equations, which do not reflect on the mechanism of these reactions. In later studies, however, rate equations based on Langmuir-Hinshelwood and Rideal mechanisms were often proposed and in a few cases the reaction sequence was explained in terms of a semi-hydrogenated state, first proposed by Houriti and Polanyi.

(v) The hydrogenation of olefins has mostly been studied over transition metals of Group VIII. These can be broadly considered into two groups. Metals in the first group, Fe, Ni, Pd in addition to hydrogenation, are also active in isomerization and olefin exchange, while the metals in

the second, Pt and Ir, are active mainly for hydrogenation. Ru, Rh and Os occupy an inter-mediate position.

(vi) The activation mechanism for the reactants, the unsaturated compound and especially H_2, has been studied in sufficient detail for many cases of hydrogenation of lower acetylenes and olefins such as C_2H_2, C_2H_4, etc. For higher olefins very little information is available in this area.

(vii) For lower olefins containing upto 4 carbon atoms, the rate of hydrogenation was found to depend upon the catalyst characteristics, operating conditions and the olefin substrate. In general, with Ni and Pt catalysts, the rates decrease with increasing substitution of alkyl groups in the vicinity of the double bond and also with increasing chain length, but for other catalysts the results are not extensive. With transition metal catalysts the activation energy for the hydrogenation of n-butenes are reported to be lower than those for ethylene.

(viii) The hydrogenation of a number of unsaturated compounds, for example, acetylene, ethylene, propylene, n-butenes, hexene , heptene, styrene, α-methyl styrene and cycloalkenes in liquid

phase have been reported in the literature. These
investigations led to different kinetic rate
expressions depending upon the type of olefinic
compound being hydrogenated, type of catalyst
and operating conditions; the type of rate equation
obtained in a few of these cases are given in
Table 2.7. The type of solvent used also affected
the reaction rates in some cases. The effect of
substituents and chain length on the hydrogenation
of higher olefins having 6 or more carbon atoms,
however, have not been studied in detail.

A study of the kinetics of liquid phase
hydrogenation of olefins having more than 6 carbon
atoms at high pressures may be important to
understand the effects of branching and chain
length in olefin molecule, mechanism and mass
transfer effects in these reactions.

TABLE 2.7

RATE EQUATIONS FOR HYDROGENATION REACTIONS IN LIQUID PHASE

Substance	Catalyst	Temp. K	Pressure	Rate equation	Reference
α-methyl styrene	$Pd-Al_2O_3$	297–230	> 3 atm.	$r = \dfrac{k_s K_H K_O P x_O}{(1 + \sqrt{K_H P})^2}$	101
α-methyl styrene	$Pd-Al_2O_3$	"	< 3 atm.	$r = \dfrac{k_s K_H K_O P x_O}{(1 + \sqrt{K_H P} + K_O x_O)^2}$	101
α-methyl styrene	$Pt-Al_2O_3$	"	1–12 atm.	$r = \dfrac{k_s K_H K_O P x_O}{(1 + \sqrt{K_H P} + K_O x_O)^3}$	101
Styrene	$Pt-Al_2O_3$	268–293	Atmospheric	$r = \dfrac{k K_H C_H}{(1 + \sqrt{K_H C_H})^2}$	83
Ethylene	Pt–Carbon	278–308	Atmospheric	$r = \dfrac{k C_H}{(1 + K_O C_O)}$	84
Propylene	Pt–Carbon	278–308	Atmospheric	$r = \dfrac{k C_H}{(1 + K_O C_O)}$	84
Phenyl acetylene	$Pt-Al_2O_3$	293	Atmospheric	$r = \dfrac{k C_p^n C_H (1 + C_{p_O})}{(1 + K_1 C_p^n + K_2 C_S^n C_H^n)}$	100
Cyclo-hexene	$Pt-Al_2O_3$	293	Atmospheric	$r = \dfrac{k K_H C_H C_C}{(1 + \sqrt{K_H C_H})^2 (1 + K_C C_C)}$	112

C H A P T E R - 3

EXPERIMENTAL

3.1 APPARATUS

The experimental apparatus used in this study of C_8 and C_{12} olefins hydrogenation is shown schematically in Figure 3.1. The key consisted of a well stirred cylindrical stainless steel reactor of one litre-capacity fitted with a gas inlet nozzle, a thermowell (a pressure gauge) and a sampling tube for withdrawal of liquid samples. It is heated from outside by close fitting electrical oven and also contain a stainless steel cooling coil inside. A safety valve is provided on the top flange. In the experiments with powdered catalyst, the agitation of the reactor contents was done by a 6-bladed pitched turbine type stainless steel impeller attached to the shaft entering vertically through the stuffing box assembly on the top flange. For hydrogenation with pellets a stainless steel impeller was used which contained four baskets equally-spaced around the shaft, in which the catalyst pellets were placed; the design was similar to that used by Carberry[9]. The stuffing-box was provided with teflon packings and an outside jacket for circulation of cooling water; this water circulation prevented over-heating of stuffing box packings. The agitator shaft rotated smoothly due to the lubricating qualities of teflon packings; it was driven by a 1/10 hp A.C. motor
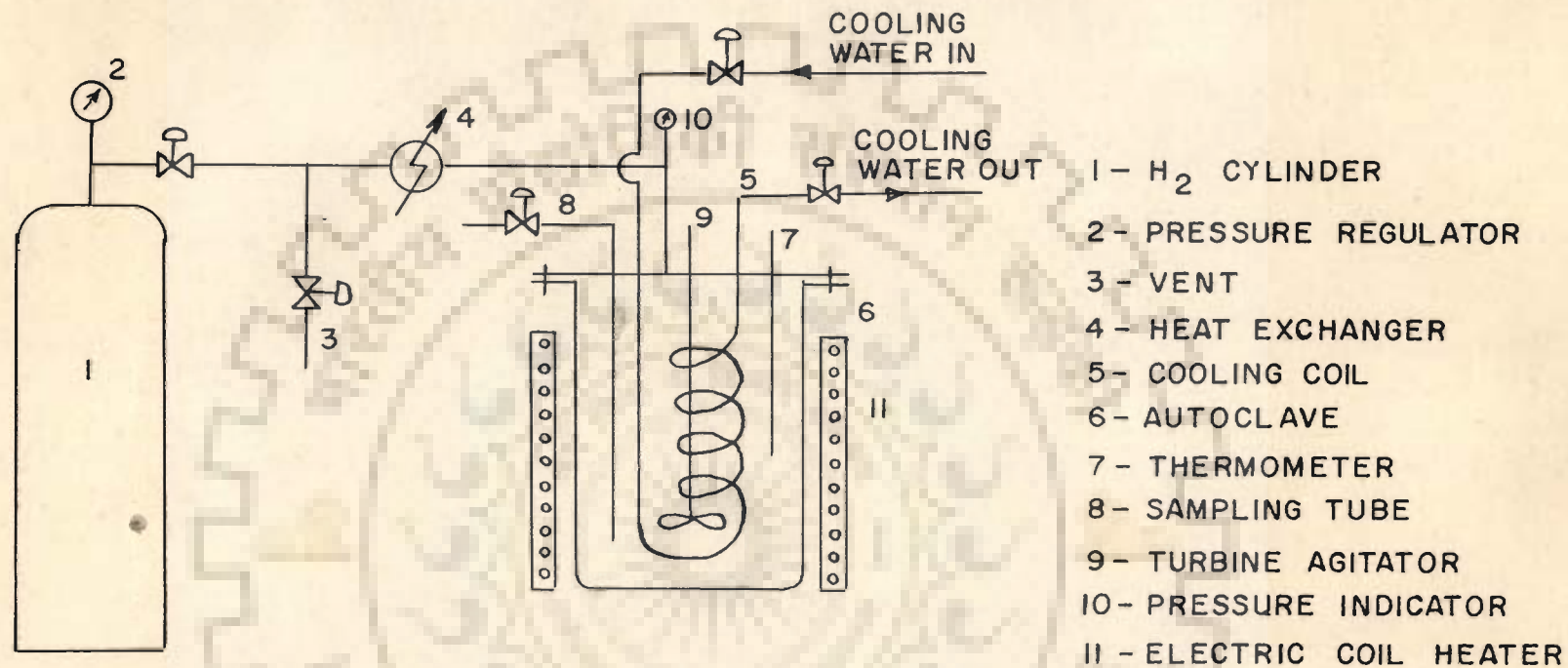
FIG. 3·1 — DIAGRAM OF THE APPARATUS.

1 — H₂ CYLINDER
2 — PRESSURE REGULATOR
3 — VENT
4 — HEAT EXCHANGER
5 — COOLING COIL
6 — AUTOCLAVE
7 — THERMOMETER
8 — SAMPLING TUBE
9 — TURBINE AGITATOR
10 — PRESSURE INDICATOR
11 — ELECTRIC COIL HEATER

COOLING WATER IN

COOLING WATER OUT

through a V-belt and pulley arrangement. The rotational speed of the agitator could be varied by changing the diameter of the pulley. Hydrogen was fed into the reactor from a cylinder and the reactor pressure was maintained by two-stage pressure regulator fitted in the line.

3.2 PROCEDURE

For the kinetic studies, measured amounts of n-heptane and olefin feed were taken in the reactor and weighed amount of reduced powdered catalyst (-170 mesh + 270 mesh) was dipped into the liquid avoiding contact with air. H_2 was then passed through the reactor to flush out air; the inlet valve was then closed and heating commenced. The stirrer was switched on to keep the catalyst powder in suspension. When the required temperature was reached, hydrogen was introduced rapidly into the reactor to a predetermined pressure which was maintained throughout the reaction period by feeding hydrogen. The temperature of the reaction mixture was maintained by controlled heating outside and / or by passing cold water through the cooling coils. The reaction was conducted under near isothermal conditions ($\pm$ 1 °C). Although hydrogenation of olefins is a highly exothermic reaction, the rate of heat transfer through the metal wall of the reactor and through the circulating water inside cooling coil was high enough to maintain the temperature under near isothermal conditions. The pressure in each run

was kept constant (± 0.2 atm) by continuously feeding the hydrogen. Each run lasted for 1.5 to 2 hours; during this time six to seven liquid samples (4 - 5 ml) were withdrawn at regular intervals and analysed for bromine number to monitor the olefin concentrations. Some of the liquid samples were also analysed to determine the presence of olefin isomers by gas chromatography.

In the experiments using catalyst pellets the baskets fitted to the stirrer were completely packed with the catalyst pellets, amounting to about 4 - 5 gms. The rest of the procedure was the same as described above. The activity of the catalyst was found to be maintained satisfactorily over periods of 3-4 weeks; this was checked periodically by a standard run. The range of the operating variables covered in this investigation is shown in Table 3.1.

3.3 PREPARATION OF OLEFIN FEEDS AND THEIR COMPOSITION

The olefins used in these studies were isooctenes, branched dodecenes (dimers and trimers of isobutene) and n-octenes. The isooctene was prepared by the dimerisation reaction of isobutene using 65 % sulphuric acid as catalyst[10]. The olefin mixture thus produced

TABLE 3.1

RANGE OF OPERATING VARIABLES

Temperature, K	303 - 333
Hydrogen pressure	0.5 - 2.0 MPa
Solvent	n-heptane
Liquid volume, m^3	0.45×10^{-3}
Initial concentration of olefin, $k \, mol/m^3$:	
- Isooctenes	0.192 - 1.4232
- Isododecenes	0.255 - 1.3251
- n-octenes	0.1863 - 1.520
Catalyst loading, kg/m^3:	
- Powder	5.56 - 19.50
- Pellets	8.90 - 11.0
Stirring speed, rpm:	
- for runs with pellet catalyst	200 - 1200
- for runs with powder catalyst	460 - 800

was purified first by treating with dilute alkali solution and subsequently washing with distilled water for making it completely free from traces of acid and alkali. The washed olefins were then steam distilled and the first distillate fraction comprising nearly 50 % of the charge, was then fractionated in a 20-plate glass distillation column operated at high reflux (1:15) to obtain a product containing only the iso-octenes. A fraction rich in 2,4,4-trimethyl pentene-1 was also prepared by distilling these iso-octenes in a 150-plate spinning-band distillation column.

Trimers of isobutene were recovered by further distillation of the oligomer residue left after removal of the isooctenes. n-octenes were prepared by vapour-phase dehydration of n-octanol over Al_2O_3 catalyst in a fixed bed glass reactor 26 mm I.D. operated at 650-675 K and atmospheric pressure; the liquid hourly space velocity of alcohol feed was in the range of 1.5 - 2.0 hr^{-1}. The dehydration products, on standing, separated into two layers- the upper organic and the lower aqueous layer. The organic layer was separated in a separating funnel and distilled in a packed glass column at a reflux ratio of 1:15. The compositions of these three olefin feedstocks were determined by gas chromatography; they are given in Table 3.2.

TABLE 3.2

COMPOSITION AND PHYSICAL CHARACTERISTICS OF OLEFIN FEEDS

I.   MIXED ISOOCTENES (FEED 1):

Boiling range, K	374 - 388
Bromine number	139.8

Composition, wt.%

Lower boiling fraction	0.1
2,4,4-trimethyl pentene-1	47.2 X
2,4,4-trimethyl pentene-2	19.3 X X 66.5
2,3,3-trimethyl pentene-1 X	9.7
2,3,4-trimethyl pentene-1 X	
2,3,4-trimethyl pentene-2 X	
3,4,4-trimethyl pentene-2 X	23.4
Others:dimethyl hexenes,alcohol etc.	0.3
Total:	100.00

II.   MIXED ISOOCTENES (FEED 2):

Boiling range, K	374 - 377.5
Bromine number	141.4

Composition, wt.%

Lower boiling	0.1
2,4,4 trimethyl pentene-1	83.2
2,4,4 trimethyl pentene-2	16.4
3,4,4 trimethyl pentene-2	traces
2,3,4 trimethyl pentene-2	traces

2,3,4 trimethyl pentene-1 X
                         X   0.3
2,3,3 trimethyl pentene-1 X

                    Total :   100.00

III.   MIXED ISOOCTENES (FEED 3):

Boiling range, K	374 - 380
Bromine number	142.8

Composition, wt.%

Lower boiling	0.9
2,4,4-trimethyl pentene-1	74.9
2,4,4-trimethyl pentene-2	18.3
2,4,4-trimethyl pentene-1	0.4
2,3,3-trimethyl pentene-1 X	
X	3.4
2,3,4-trimethyl pentene-1 X	
2,3,4-trimethyl pentene-2 X	
X	1.5
3,4,4-trimethyl pentene-2 X	
Others dimethyl hexenes, alcohols etc.	0.6

                    Total :   100.00

IV.   MIXED n-OCTENES

Boiling range, K	394 - 398
Bromine number	140.5

Composition, wt.%

Lower boiling	0.5
octene-1	31.7

Trans-octene-4	6.9
Cis-octene-4	2.8
Cis-octene-3)(	
)(	
Trans-octene-3)(	17.9
Cis-octene-2	23.7
Trans-octene-2	16.5
Total:	100.00

V.   MIXED ISODODECENES

Boiling range, K	450 - 453
Bromine number	93.24

Composition, wt.%

4-methylene 2,2,6,6 tetra-methyl heptane	58.3
2,2,4,6,6-pentamethyl heptene-3	29.8
2,4,4,6,6-pentamethyl heptene-1)(	
)(	11.9
2,4,4,6,6-pentamethyl heptene-2)(	
Higher boiling	traces
Total:	100.00

3.4 ACTIVATION OF CATALYST

The catalyst used in this study was a commercial
catalyst containing 0.5 % palladium supported on
alumina; it was in the form of cylindrical pellets of

0.44 x 0.44 cm size. The physical characteristics of catalyst pellets are shown in Table 3.3. The major part of the experimental work was carried out with powdered catalyst; for this the pellets were finely ground and the particles of -170 + 270 mesh size were sieved for use. Before use in the hydrogenation reaction, the catalyst was dried and reduced by hydrogen. For reduction, the catalyst powder was kept in a glass tube of 2.5 cm diameter, fitted with a sintered glass plate and placed vertically in an electrically heated furnace. The glass tube was flushed by passing a nitrogen stream; the catalyst was then dried by heating at 423 K for 4 hours, the flow of nitrogen still continued. The catalyst was then reduced with H_2 flowing at high velocity ($1.5 \times 10^3 m^3/hr/m^3$-cat.)) for 8 hours at 620-625 K. After cooling in hydrogen atmosphere, the reduced catalyst was kept immersed in dried n-heptane completely avoiding contact with air.

3.5 CHEMICALS

n-heptane free from unsaturates (Br_2 No. < 0.1) was used as solvent. The hydrogen was of 99.9 % purity obtained from commercial sources. All the chemicals were dried before use over freshly regenerated 3A type molecular sieves.

TABLE - 3.3

PHYSICAL CHARACTERISTICS OF THE CATALYST PELLETS

Average pellet size:

diameter, cm	0.44
height, cm	0.44
Surface area, m^2/g	188
Pore volume, cm^3/g	0.38
Average pore radius, A^o	40
Bulk density, g/cm^3	1.633
Porosity	0.60
Depth of Palladium layer, cm	0.04 (approx.)

3.6 ANALYTICAL PROCEDURES:

The bromine number of the olefines was determined by the standard UOP-304-59 method; the details are described elsewhere[11].

For identification of the isomers of various olefins, samples were analysed by gas chromatography using flame ionization detector. For this, a stainless steel capillary column of 20 meter length packed with squalane '30' was used; the temperature of the column was raised during the analysis from room temperature

to 263 K at a programmed rate of 1 K/min; the flow of the H_2 was kept constant at 105 c.c./min.

3.7 REPRODUCIBILITY ON HYDROGENATION RUNS:

Reproducibility of the experimental results was checked by conducting three experiments at a fixed set of conditions indicated in Table 3.4.

The results shown in Table 3.5 indicate good reproducibility for kinetic studies.

The maximum value of $(Y_i - \bar{Y})/s$ in these runs was in the case of A3 and this was 1.0932.

For testing of the reproducibility of experimental runs t-test was applied. If the condition $(Y_i - \bar{Y})/s \geq t$ (tabulated value), i.e. t-expt. $<$ t-table, at a given confidence level is satisfied, the results are reproducible. t-test tables[89], for degree of freedom N-1 (= 2) at 95 % confidence level, gives t = 4.303. This shows that the experimental values of 't' is smaller than the tabulated values of 't' table; thus the results may be considered reproducible and satisfactory.

3.8 CALCULATION OF REACTION RATES:

To obtain the rates of reaction precisely the data was fitted by least square technique, for each set of conditions to an equation of the form -

TABLE - 3.4

TEST FOR REPRODUCIBILITY OF EXPERIMENTAL RUNS: OPERATING CONDITIONS FOR RUNS

Temperature, K	313
Initial volume of reactants, m^3	0.45×10^{-3}
Bromine number of feed	12.97
Initial concentration of isooctenes, $k \, mol/m^3$	0.5572
Pressure, MPa	-
Catalyst concentration, kg	7×10^{-3}
Duration of run, minutes	90

TABLE - 3.5

TEST FOR REPRODUCIBILITY OF EXPERIMENTS : STATISTICAL EVALUATION OF RESULTS

Run No.	Br_2 No. of reaction mixture at 90 minutes, (Y_i)	Olefin concentration (at 90 min), $k \, mol/m^3$, (X_i)
A1	9.0594	0.3892
A2	9.1641	0.3937
A3	8.8609	0.3808

Table 3.5 contd........

Average value of Br_2 No., $\overline{Y}$ = 9.291

Maximum deviation-absolute = 0.165

-percentage = 1.83

Standard deviation, s $= \sqrt{\dfrac{(\overline{Y} - Y_i)^2}{N-1}}$ 0.154

Maximum experimental value
of 't' $= \left[(Y_i - \overline{Y})/s\right]$ = 1.0932

At 95 % confidence level, for two degrees of freedom,
t (tabulated) = 4.303.

$$C_B = a + bt + ct^2 + dt^3 \qquad\qquad (3.1)$$

Analytical differentiation of this equation gave
directly the rate of reaction at a given time. The
values of the initial reaction rates, r_o, were also
obtained from the above equation by calculating the
rate at initial olefin concentration (i.e. at t = 0).
The experimental data for each run along with the
reaction rates, calculated using Equation 3.1 are
given in Appendix 1.

C H A P T E R - 4

RESULTS AND DISCUSSION

4.1 PHYSICO-CHEMICAL DATA

The liquid-phase hydrogenation reactions of
olefins in the three-phase system can be considered to
occur through the following sequence of steps:

Hydrogen is transferred from the gas phase to
the bulk liquid phase; both hydrogen and olefin are
transferred from the liquid to the surface of catalyst
particles and then the hydrogenation reaction occurs
after adsorption of reactant. Finally, the products
are desorbed and transferred to the bulk liquid phase.
The rate of transfer of hydrogen from the gas phase to
the catalyst surface, through the liquid is dependent
upon the diffusivity and the solubility of hydrogen in
the liquid medium and the hydrodynamics inside the
reactor. For analysis of the experimental data in such
a system, the diffusivity and solubility of hydrogen in
the reacting liquid phase under the experimental
conditions employed is necessary to be determined.

In this experimental study, n-heptane
constituted the bulk of the liquid medium, the olefin
content was less than 30 % by weight. Hence, the
diffusivity of hydrogen in the liquid phase can be
approximated to be the same as the diffusivity of

hydrogen in pure n-heptane. Since the viscosity of the solution in the range of temperature (303-333 K) employed was low (about 0.27 - 0.34 cp), the diffusion coefficients of hydrogen and the olefins, used as reactants, in n-heptane were estimated using the following correlation suggested by Wilke and Chang[124].

$$(D\mu /T) = 7.4 \times 10^{-8} (XM)^{0.5} /v_b^{0.6} \quad \ldots\ldots (4.1)$$

The values of diffusivities, obtained are summarized in Table 4.1. The molar volume of the olefins, v_b, used in these calculations was estimated by the method of Le Bas as described by Reid and Sherwood[125]; the values of viscosity of n-heptane were taken from the literature[126].

The data on solubility of hydrogen in n-heptane is reported by Lachowiez et al[127]; these authors have experimentally determined the solubility of hydrogen in n-heptane and n-octane at 298-423 K under high pressure upto 30.3 MPa. They also compared their results at atmospheric pressure with those obtained by Cook et al.[128] and found that the values of the Henry's law constant were in excellent agreement and this can be applied in this range of pressure. The solubility of hydrogen in n-heptane, under the experimental conditions used in this study, are given in Table 4.2. Other physical and concerned

TABLE 4.1

DIFFUSION COEFFICIENTS OF H_2 AND OLEFINS IN n-HEPTANE

Temperature solute	303 K	313 K	333 K
	Diffusion Coefficient $cm^2/sec \times 10^5$		
Hydrogen	12.46	14.37	18.25
Octene-1	2.77	3.18	4.06
2,4,4-trimethyl-pentene-1	2.77	3.18	4.06
Isododecene	2.15	2.47	3.15

TABLE 4.2

SOLUBILITY OF HYDROGEN IN n-HEPTANE

Pressure, atm	5	10	15	20
Temperature,K	Solubility of hydrogen, $kmol.m^{-3} \times 10^2$			
303	2.892	5.302	7.712	10.122
313	3.020	5.543	8.060	10.579
333	3.270	6.020	8.736	11.466

properties of n-heptane, olefins and paraffins were taken from the literature[125,126,129].

4.2 THERMODYNAMICS OF THE REACTION

Hydrogenation of olefin is a highly exothermic reaction liberating large amounts of heat; the hydrogenation of n-octene, isooctene and isododecene can be represented by the following equations:

$$n\text{-}C_8H_{16} + H_2 \rightleftharpoons n\text{-}C_8H_{18} \qquad \ldots\ldots \text{(4.2)}$$

$$\triangle H^O_{298K} \simeq 125.6 \quad kJ/gmol$$

$$i\text{-}C_8H_{16} + H_2 \rightleftharpoons i\text{-}C_8H_{18}$$

$$\triangle H^O_{298K} \simeq 118.2 \; kJ/gmol \qquad \ldots\ldots \text{(4.3)}$$

$$i\text{-}C_{12}H_{24} + H_2 \rightleftharpoons i\text{-}C_{12}H_{26}$$
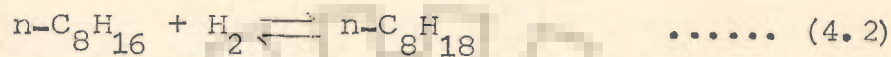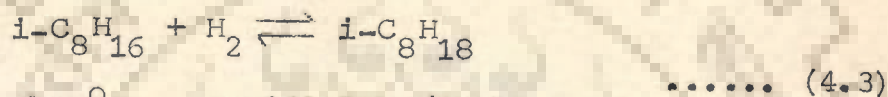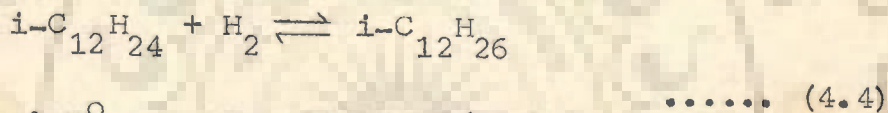
$$\triangle H^O_{298K} \simeq 133.5 \; kJ/gmol \qquad \ldots\ldots \text{(4.4)}$$

The standard heats of reactions $\triangle H^O_{298K}$ were estimated from the heat of formation data given in Table 4.3. The equilibrium constants for these reactions were also estimated using free energy data and are summarized in Table 4.4; the values of the equilibrium constants of hydrogenation of the three olefins are of the order of 10^{12} to 10^{15} in the temperature range of 298-400 K; such high values indicate that these reactions are essentially irreversible and the reverse reaction of dehydrogenation of alkanes can be neglected. In an earlier study of the vapour phase hydrogenation of isooctene

TABLE 4.3

THERMODYNAMIC PROPERTIES OF PARAFFINS AND OLEFINS

Compound	Heat of formation $(H_f^o)_{298K}$ Kcal/mol	Free energy of formation $(G_f^o)_{298K}$ Kcal/mol	Entropy $S,$ cal/mol K
2,2,4-trimethyl pentane	−53.57	3.27	101.15
2,2,3-trimethyl pentane	−52.61	4.09	101.62
2,3,3-trimethyl pentane	−51.73	4.52	103.14
2,3,4-trimethyl pentane	−51.97	4.52	102.31
n-octane	−49.82	3.92	111.55
Isododecane	−79.37*	11.98	148.79 *
2,3,3-trimethyl pentene-1	−23.50	23.49	103.03
2,3,4-trimethyl pentene-1	−23.74	23.50	102.02
2,4,4-trimethyl pentene-1	−25.34	22.20	101.04
2,3,4-trimethyl pentene-2	−26.27	21.14	101.47
2,4,4-trimethyl pentene-2	−26.85	20.74	100.87
3,4,4-trimethyl pentene-2	−25.89	21.56	101.34
octene-1	−19.82 *	24.91	110.55
cis-octene-2	−21.49 *	23.27	110.36 *
trans-octene-2	−22.42 *	22.63	109.39 *
cis-octene-3	−21.43 *	23.33	110.37 *
trans-octene-3	−22.42 *	22.63	109.40 *
cis-octene-4	−21.43 *	23.33	110.37 *
trans-octene-4	−21.49 *	23.56	109.40 *
isododecene	−50.26 *	32.95	147.00 *

* Notes: Calculated using group contribution method.

TABLE 4.4

EQUILIBRIUM CONSTANTS FOR HYDROGENATION OF OLEFINS

Temperature, K		298	400
Reaction	Olefin	Equilibrium constant, K	
4.2	2,4,4-trimethyl pentene-1	3.70×10^{13}	3.62×10^{8}
4.3	Octene-1	2.44×10^{15}	5.63×10^{9}
4.4	isododecene	4.00×10^{12}	_

Hougen et al.[130] also showed that upto a temperature of about 573 K the reverse reaction is negligible.

4.3 HYDROGENATION WITH POWDERED CATALYST

4.3.1 Mass transfer effects:

As mentioned earlier, this reaction system for hydrogenation of olefins comprises of three phases- gas, liquid and solid. Compared with the description of a two phase reaction system using a microporous catalyst, the description of a three-phase reaction system needs the added consideration of mass transfer between the gas and liquid phases and through their interface. The rate of transfer of a reactant (hydrogen in this case) from the gas phase to the bulk liquid is governed by the

product of gas absorption coefficient and gas-liquid interfacial area, $K_{gl}a_{gl}$. To reach the exterior surface of a catalyst particle, the reactants dissolved in the liquid phase must overcome the fluid-particle mass transfer resistance arising from the liquid boundary layer surrounding the catalyst particle. The use of well stirred system implies that convective mixing of bulk liquid phase is quite vigorous and no concentration gradient exists in that phase. Finally, within a porous catalyst particle there is a kinetic resistance and intraparticle diffusional resistance and the two external diffusion steps act in series with the diffusion and reaction within the catalyst; the rates of the three steps must be equal under steady-state conditions. These external and intraparticle diffusional resistances cannot be ignored, and a knowledge of intrinsic kinetic rate expression, free of any mass transport inhibition, is required for the reactor design. In the development of a rate expression from laboratory experimental data, it is important to quantitatively determine the rate controlling step (s) and to find the reaction conditions necessary to eliminate the physical transport constraints (both external and intraparticle) on the rate of reaction and thus provide a measure of the uninhibited rate for the chemical reaction. Determination of these conditions

ensuring absence of mass transfer resistances usually
involve a combination of experimental tests and calcula-
tions using proper correlations. Satterfield[131] and
Smith[132] have proposed the following model (Eqn.4.5)
for stirred-slurry reactors based on the concept of
first-order resistances in series i.e. those associated
with, (1) mass transfer from the gas-liquid interface
to the bulk liquid phase, (2) mass transfer from the
bulk liquid to the external surface of the catalyst
particle, and (3) surface reaction on the porous
catalyst particles.

$$\frac{1}{r_o} = \frac{1}{K_{gl}\, a_{gl}\, C^*_{H,g}} + \frac{\rho_p d_p}{6\, C^*_{H,g}} \left[\frac{1}{K_{ls}} + \frac{1}{k_s}\right]\frac{1}{m} \quad ..(4.5)$$

In the absence of prior knowledge of the reaction order,
it would not be possible to use this equation for
estimating the three coefficients K_{gl}, K_{ls} and k_s,
although the equation is still conceptually useful.
Even for first-order kinetics, it is only possible to
determine the mass transfer coefficient, K_{gl}, for the
gas-liquid interface, but not the coefficient, K_{ls},
for the mass transfer from the bulk liquid to the
catalyst surface and the surface reaction rate
constant, k_s, separately as they are combined together
in the slope of a plot of $1/r_o$ Vs $1/m$. An additional
problem is to estimate the effectiveness factor η to
obtain the true surface reaction rate constant k_s. Thus,

to establish the regimes of control in the hydrogenation of olefins, more general considerations were required to be invoked. For this, as earlier stated, two types of approaches (a) experimental approach and, (b) calculative approach were followed. In the analysis described in this section, a pseudo-steady state has been assumed; the initial reaction rates have been used since mass transport limitations are expected to be maximum under the initial condition.

4.3.1.1 Experimental evaluation of mass transfer constraints Effect of agitation

A very direct test of the importance of gas-liquid transport can be made by running several experiments at different agitation rates with all other variables held constant. If the observed reaction rate varies with the agitation, this constitutes a strong evidence that gas-liquid mass transfer controls, or atleast influences, the reaction rate. If no effect is observed, the resistance to gas liquid mass transfer is probably insignificant in comparison with other possible resistances.

Figures 4.1, 4.2 and 4.3 show such a series of experiments for hydrogenation of isooctene, n-octene and isododecene respectively; these experiments were conducted with powdered catalyst at 313 K and 5 atm ($\simeq$ 0.5 MPa) pressure; the agitator speed was varied

OLEFIN- ISO OCTANE, TEMP. =313K   PRESSURE =0.5 MPa
INITIAL OLEFIN CONC. =0.5572 - 0.576 kmol/m^3 CATALYST LOADING=7X10^{-3}
Kg., POINTS 1-3 - REF. 135
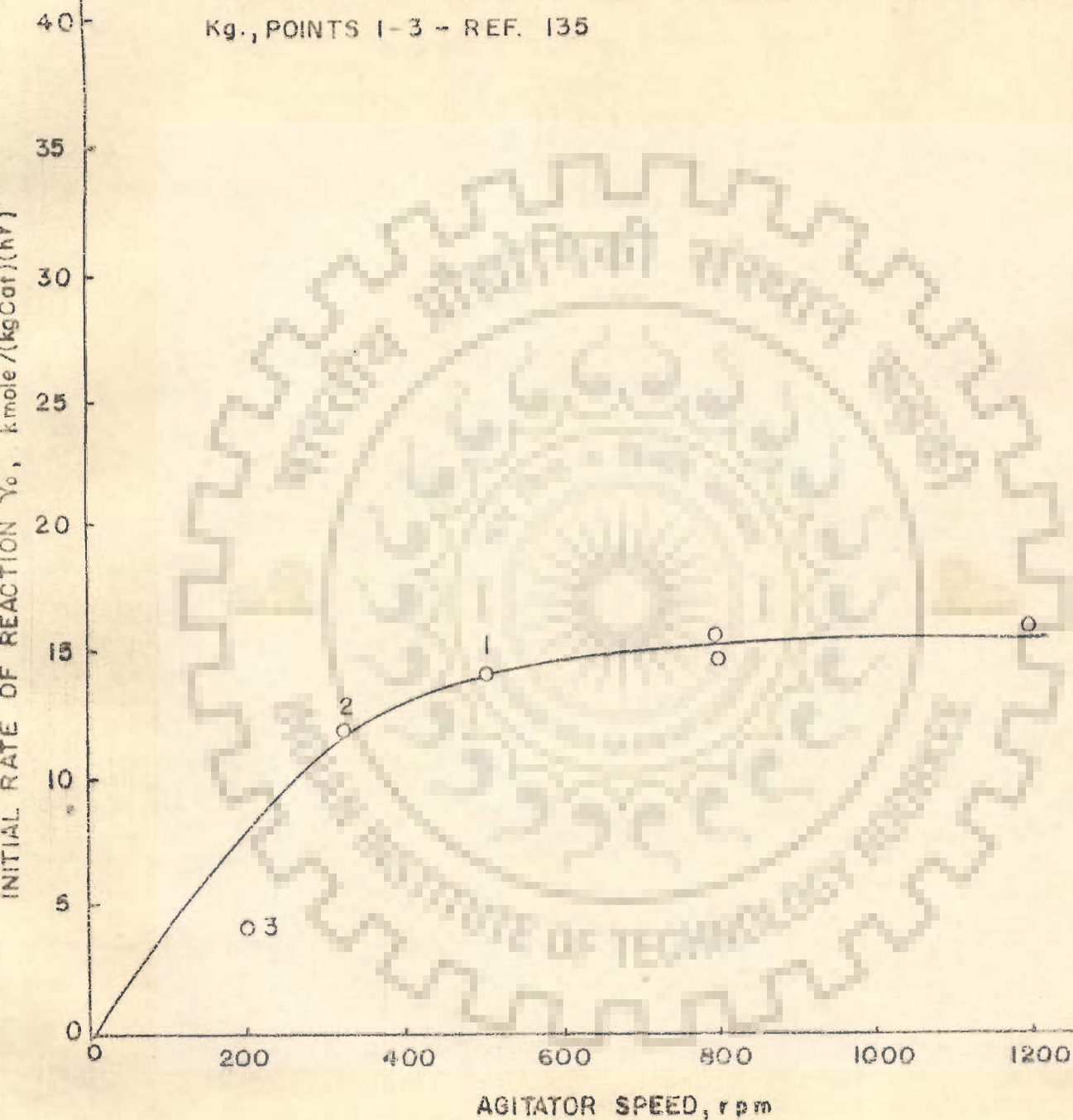
FIG41- EFFECT OF AGITATION ON REACTION RATE .
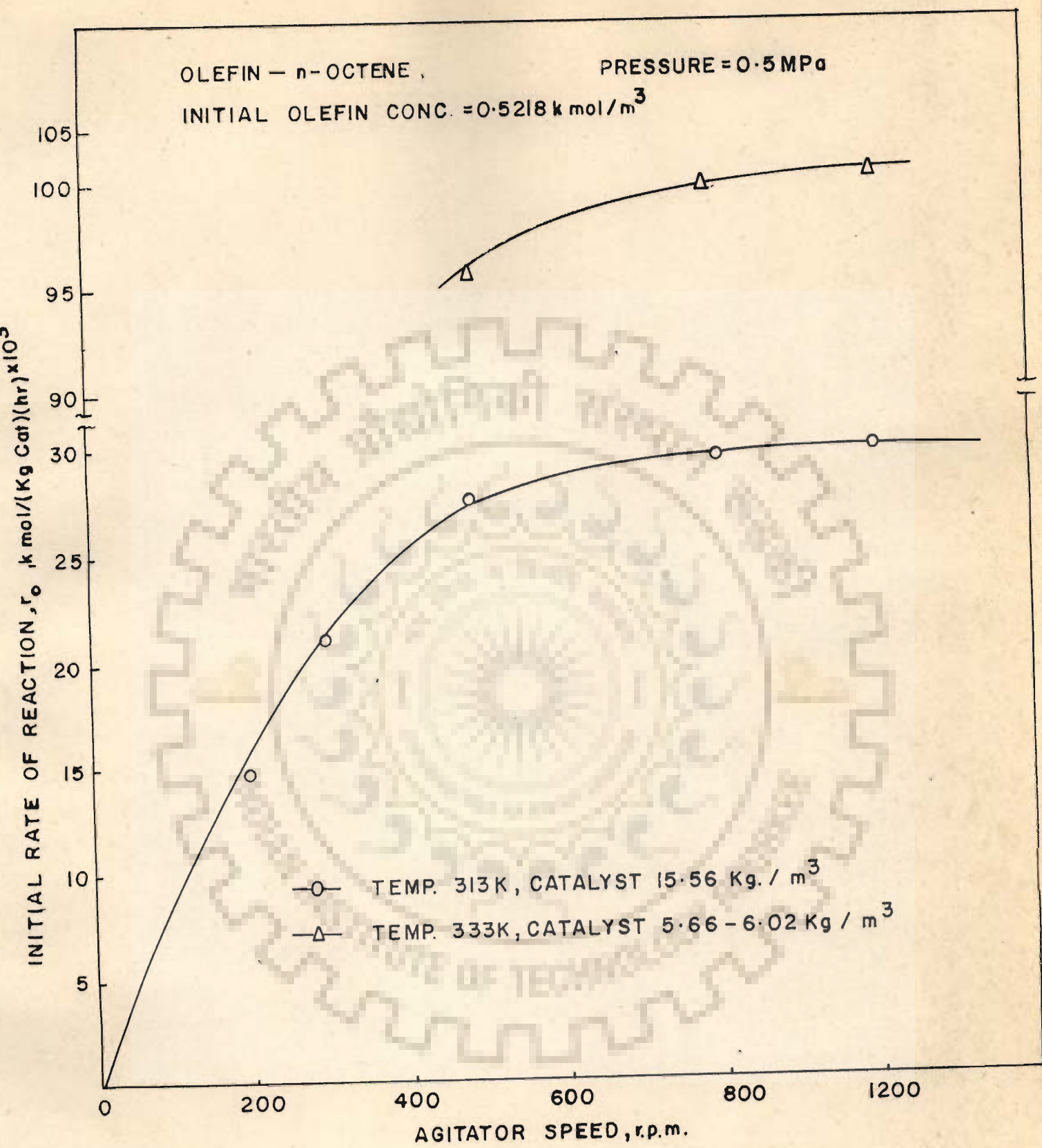
FIG. 4·2 — EFFECT OF AGITATION ON REACTION RATE.

OLEFIN – ISODODECENE , TEMP. = 313 K , PRESSURE = 0·5 MPa
INITIAL OLEFIN CONC. = 0·3730 kmol/m^3, CATALYST LOADING $\approx 8 \times 10^{-3}$ Kg

INITIAL RATE OF REACTION r_0 , kmol/(Kg CAT.)(hr) $\times 10^3$

AGITATOR SPEED, rpm
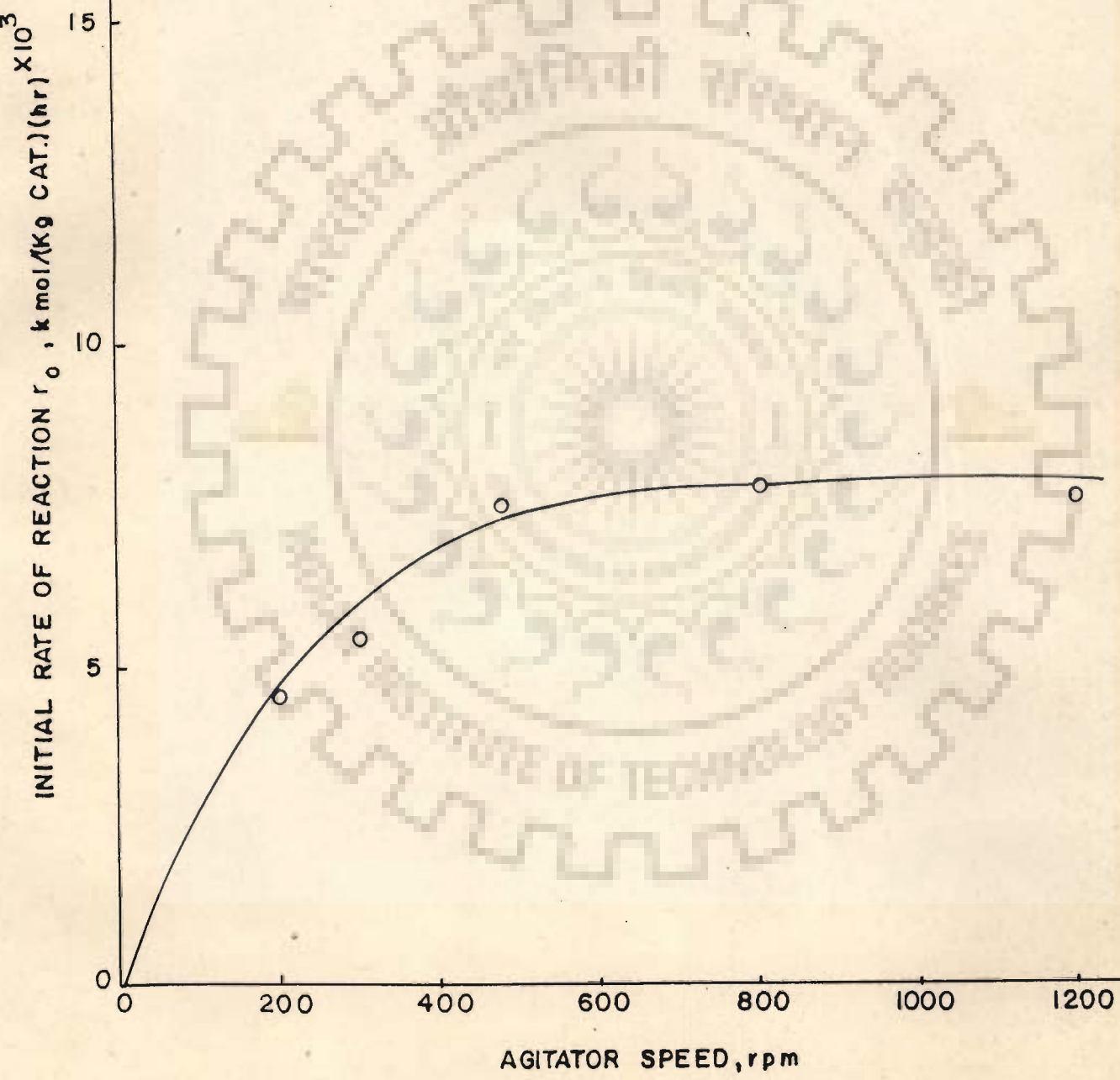
FIG. 4·3 – EFFECT OF AGITATION ON REACTION RATE .

in the range of 200 -1200 rpm. At similar rates of agitations, n-octenes showed higher rate of hydrogenation than isooctenes and isododecenes. Hence, a few runs for the hydrogenation of n-octenes were also conducted at 333 K varying the agitator speed to check the mass transfer effects at higher temperatures. At low agitation speeds, the stirring speed had a pronounced effect on the observed rates of hydrogenation. Clearly, the rate of hydrogenation of isooctenes at 200 rpm was significantly less than at, say 600 rpm (Fig. 4.1); this was probably due to the increase in the value of gas-liquid mass transfer coefficient, K_{gl}, with increasing agitation. In other words, low speed of agitation was insufficient to produce the proper chemical rate, either because the catalyst was not uniformly suspended or because of a large resistance across the gas - liquid interface due to incomplete development of interfacial area at low agitation speeds. At stirring speeds of about 600 rpm and above, the observed reaction rate was no longer sensitive to agitation.

With n-octenes, the influence of agitation on the rate of reaction was more pronounced than with isooctenes; the trend, however, remained similar. At stirring speeds of above 700 rpm (Fig. 4.2) the rate of disappearance of n-octene remained almost

constant. At 333 K, the effect of agitator speed on the rate of hydrogenation of n-octene was more pronounced; on increasing the stirring rate from 460 rpm to 800 rpm, the rate increased by about 10%. When the agitation was further increased from 800 to 1200 rpm, the increase of reaction rate was only about 1-2 % showing a negligible effect of gas-liquid mass transfer in this mixing range.

In case of isododecenes, the influence of agitation on the reaction rate was very small; the reaction rate increased from 4.52×10^{-3} at 200 rpm to 7.59×10^{-3} kmol.(kg-Cat^{-1}).hr^{-1} at 480 rpm and then leveled off. From the above experimental observations, it was concluded that to avoid a strong influence of gas-liquid mass transfer in this system, experiments should be conducted at stirring speeds in excess of about 700 rpm.

Effect of catalyst concentration

There is no direct way of ensuring the absence of influence of liquid/solid mass transfer resistance, but an approximate indication of the effect can be had by (1) examining the variations in reaction rate as a function of catalyst loading, and (2) by assuming first-order kinetics, plotting $1/r_0$ Vs $1/m$, in accordance with Equation 4.5, and determining the slope of the resulting straight line.

The results obtained by observing the rates of hydrogenation of isooctenes, n-octenes and isobutene trimers (isododecenes) as a function of catalyst mass in the slurry are presented in figures 4.4, 4.5 and 4.6 respectively. These experiments were carried out at a temperature of 313 K, 0.5 MPa pressure and 800 rpm; the amount of catalyst was varied in the range of 2.5×10^{-3} kg to 8.66×10^{-3} kg. The total volume of liquid was 0.45×10^{-3} m^3 in each case. With iso-octene, the rate of hydrogenation increased from 0.1275 kmol.m^{-3}.hr^{-1} at 3.88×10^{-3} kg catalyst to 0.28 kmol.m^{-3}.hr^{-1} at 7.81×10^{-3} kg catalyst, while in case of isododecenes (Fig. 4.6) the reaction rate increased from 0.07 kmol.m^{-3}.hr^{-1} to 0.149 kmol.m^{-3}.hr^{-1} with corresponding increase in the amount of catalyst from 3.97×10^{-3} to 8.66×10^{-3} kg. For n-octenes the rate of hydrogenation showed a similar trend and increased from 0.163 kmol.m^{-3}.hr^{-1} to 0.456 kmol.m^{-3}.hr^{-1} at catalyst loadings of 2.52×10^{-3} kg and 7.18×10^{-3} kg respectively (Figure 4.5).

For the three olefinic feed stocks used in the present studies, the rates of hydrogenation increased almost linearly as the catalyst loading was increased. A similar behaviour of proportional change in hydrogenation rate with the amount of catalyst was also observed by many workers while

OLEFIN — ISOOCTENE, INITIAL CONC. = 0.5572 kmol/m^3, TEMP. = 313 K, PRESSURE = 0.5 MPa, rpm = 800, VOLUME OF LIQUID REACTANTS = 0.45 × 10^{-3} m^3.
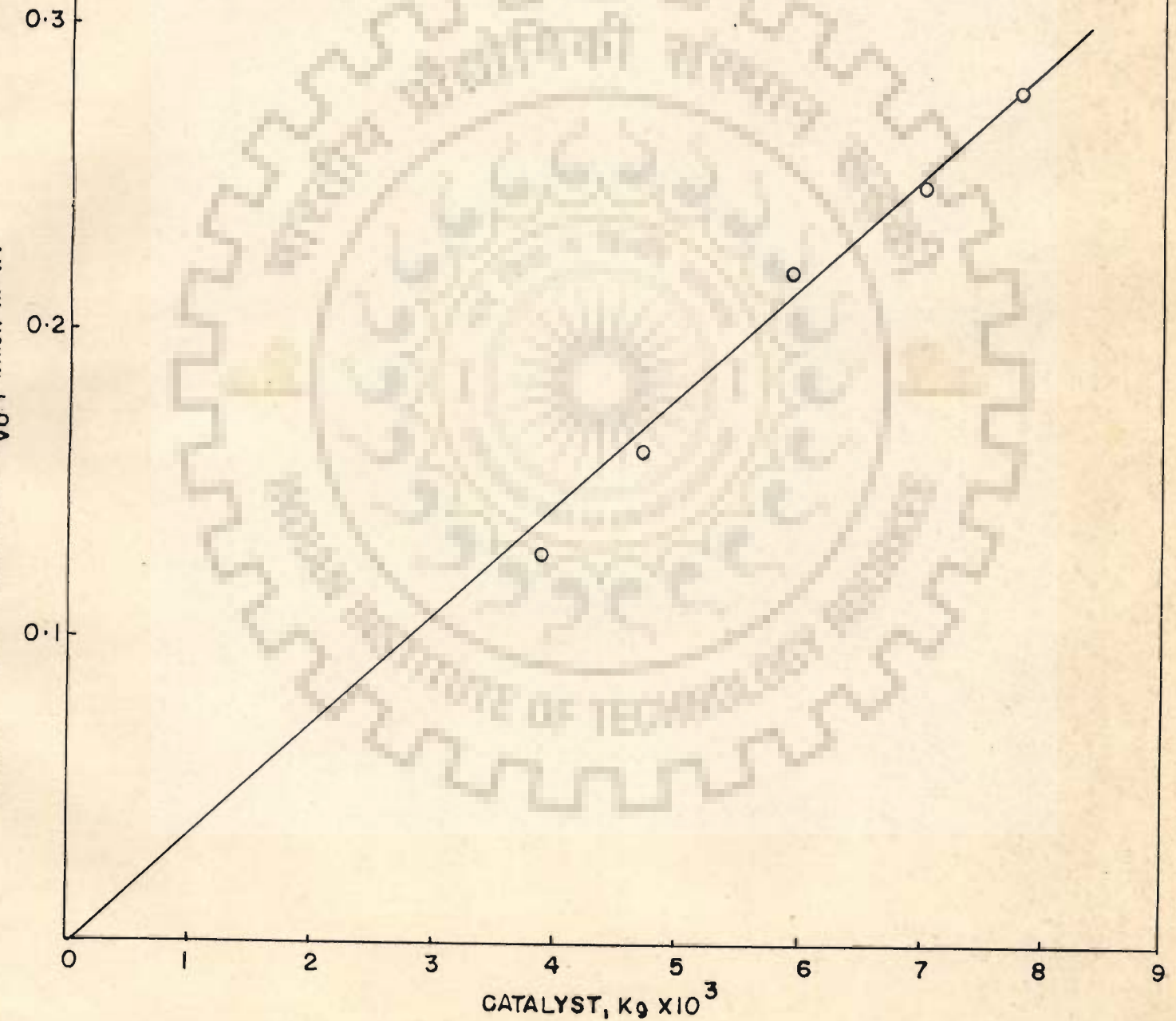
FIG. 4.4 — EFFECT OF CATALYST LOADING ON RATE OF HYDROGENATION.

OLEFIN − n −OCTENE (INITIAL CONC. = 0.5218 k mol / m^3)

TEMP. = 313 K , PRESSURE = 0.5 MP_a , r p m = 800 , REACTANTS   VOLUME = 0.45 x10^{-3} m^3
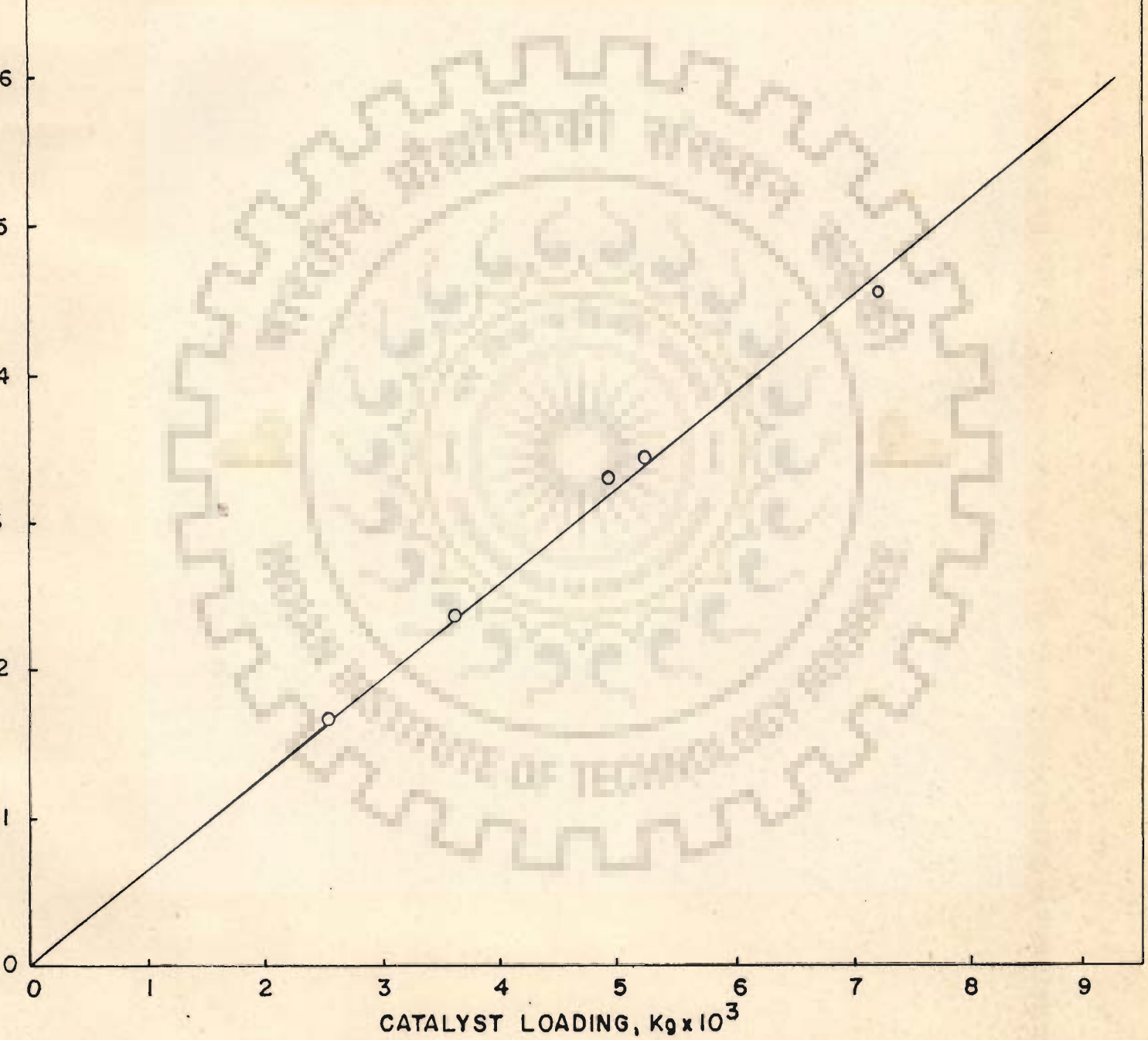
FIG. 4·5 − EFFECT OF CATALYST LOADING ON RATES OF HYDROGENATION.

OLEFIN — ISODODECENE, INITIAL CONC. = 0·3730 kmol/m^3, TEMP. = 313 K, PRESSURE = 0·5 MPa, rpm = 800, REACTANTS VOLUME = 0·45×10^{-3} m^3

CATALYST, Kg ×10^3
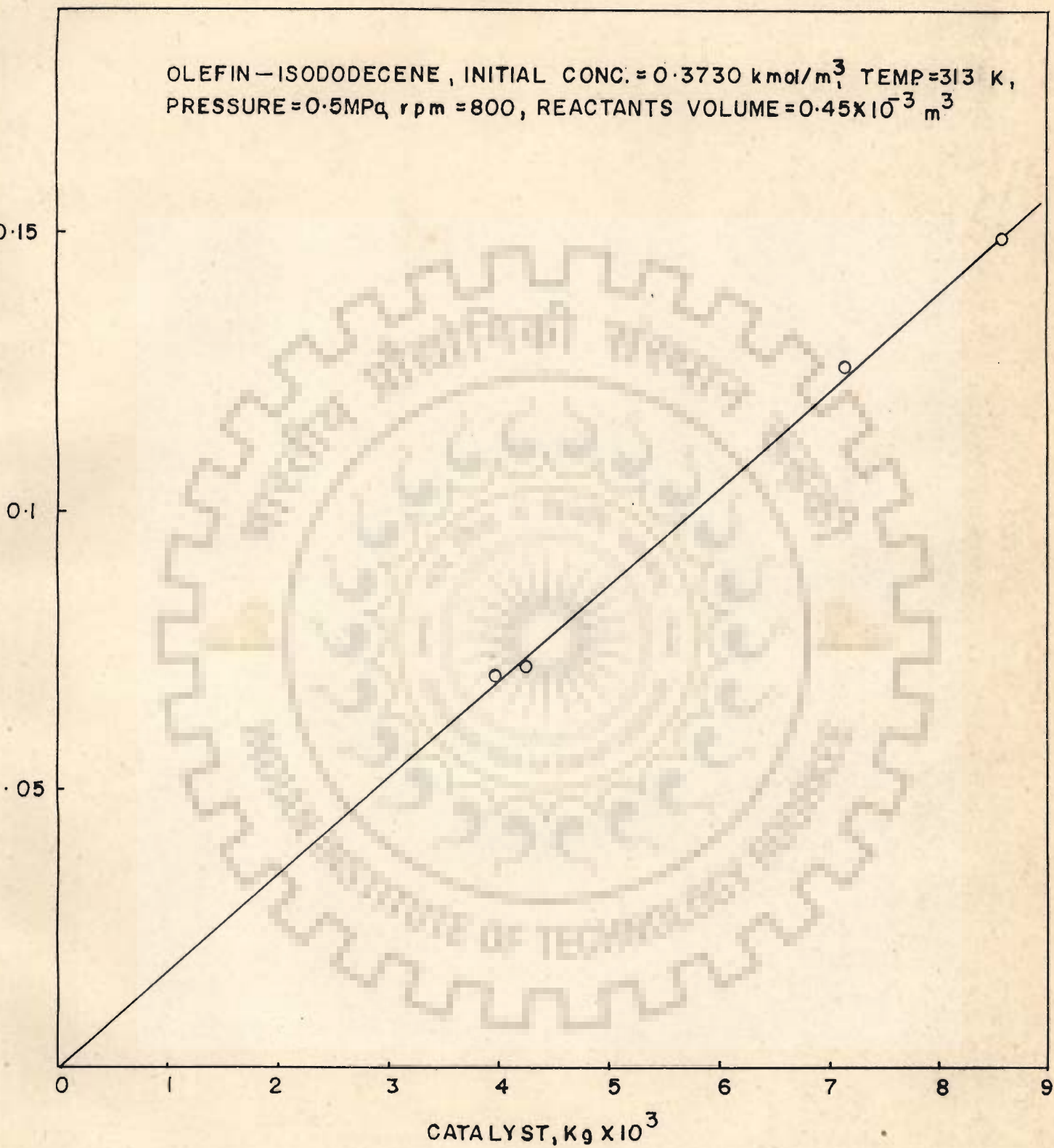
FIG. 4·6 — EFFECT OF CATALYST LOADING ON RATE OF HYDROGENATION.

hydrogenating unsaturated compounds under conditions in the kinetic region[91-93, 102,113,119]. Such linear relationship is expected when the rate of the reaction is chemically controlled.

To further test the influence of external mass transfer on the rates of hydrogenation, these data on the variation of reaction rates with the amounts of catalyst were analysed by replotting as $1/r_o$ Vs $1/m$. Such plots are shown in Figures 4.7, 4.8 and 4.9. These plots were based on Equation 4.5. As expected, the curves are straight lines with intercepts = $1/K_{gl} a_{gl} C^*_{H,g}$ and,

$$\text{slope} = \frac{\rho_P d_P}{6 C^*_{H,g}} \left[1/K_{ls} + 1/k_s \right]$$

It can be seen from Equation 4.5 that the intercept is exactly equal to the rate that would exist if the reaction were controlled by gas-liquid mass transfer. To be certain that gas-liquid mass transfer is not controlling, the actual experimental value of $1/r_o$ should be much larger than the intercept. Then from a knowledge of ρ_P, d_P, $C_{H,g}$ and slope, the combined effect of surface reaction and liquid-solid mass transfer was obtained by estimating a composite constant $k' = (1/K_{ls} + 1/k_s)$; this value was compared with the liquid-solid mass transfer coefficient, K_{ls}, estimated by the correlation of

OLEFIN – ISOOCTENE , TEMP. =313 K , PRESSURE = 0·5 MPa
r.p.m. = 800 , REACTANTS VOLUME = 0·45×10⁻³ m³
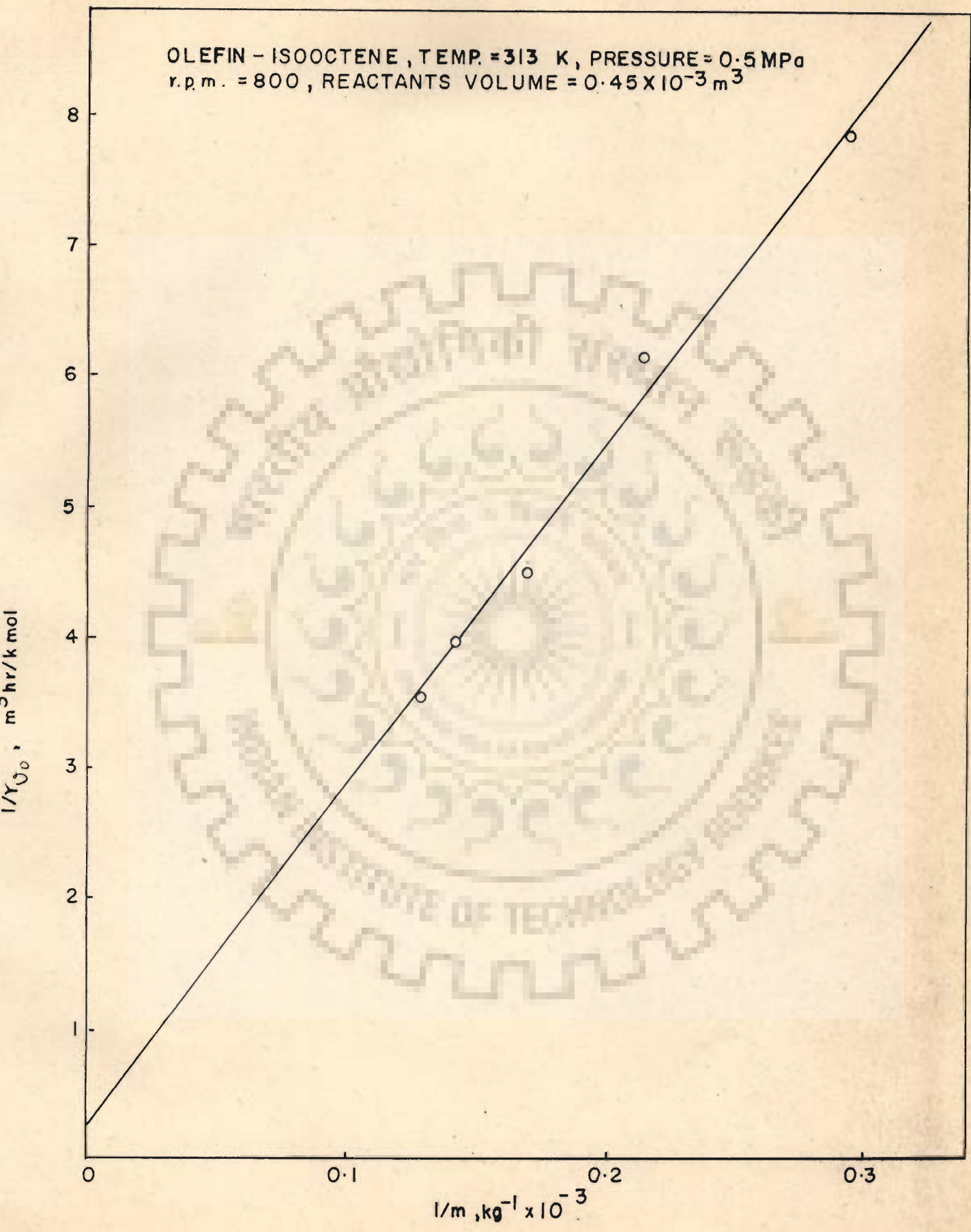
FIG. 4·7 — PLOT OF $1/m$ Vs $1/r_{v_0}$ ACCORDING TO EQUATION 4·5

OLEFIN – n-OCTENES, TEMP. = 313 K, PRESSURE = 0·5MPa, r.p.m. = 800
REACTANTS VOLUME = 0·45 X 10^{-3} m^3

1/m, Kg^{-1} X 10^{-3}
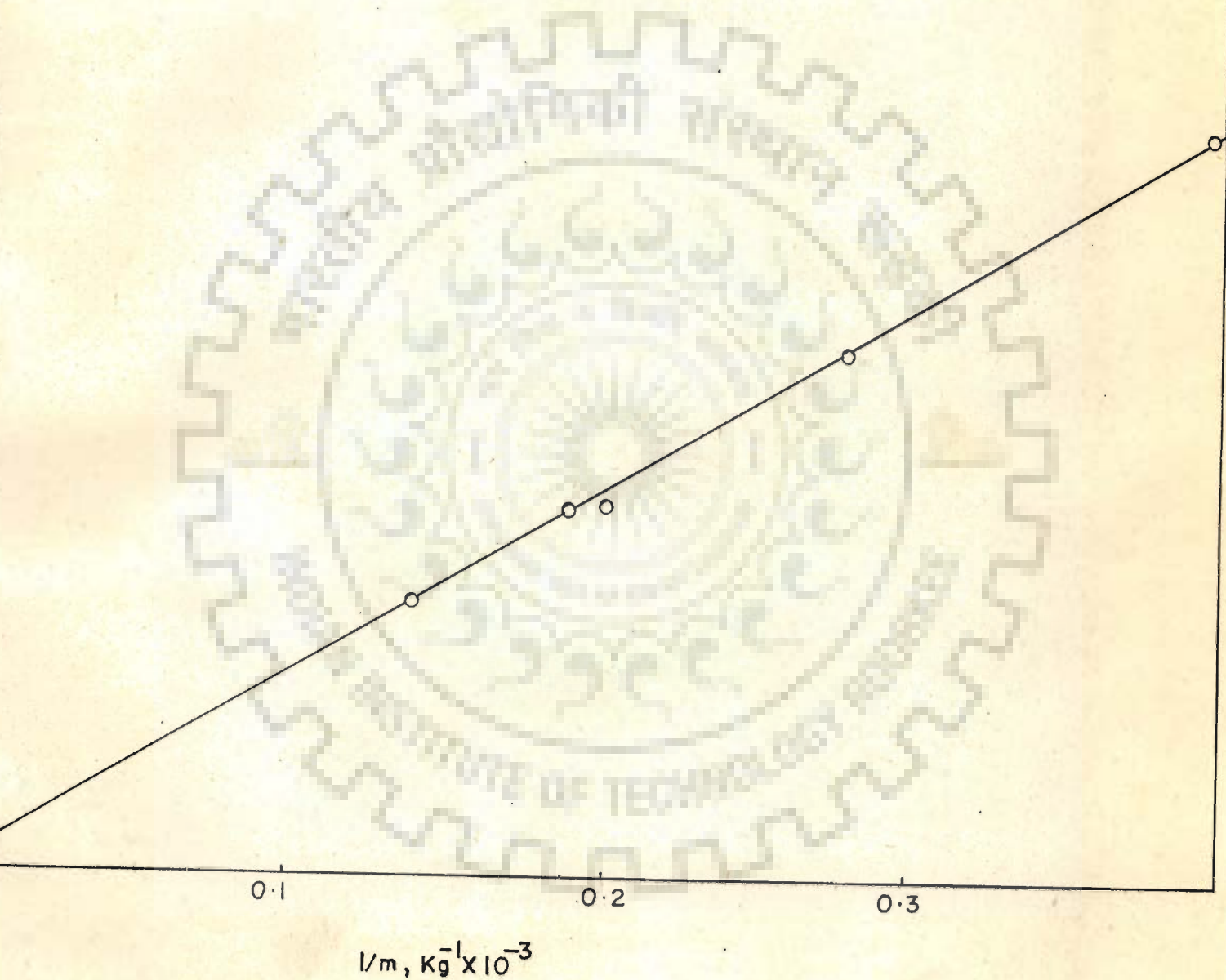
FIG. 4·8 — PLOT OF 1/m Vs 1/r_{v_0}, ACCORDING TO EQUATION 4·5

OLEFIN – ISO DODECENE , TEMP. = 313 K , PRESSURE = 0·5 MPa
r.p.m. = 800 , REACTANTS VOLUME = 0·45 × 10^{-3} m^3
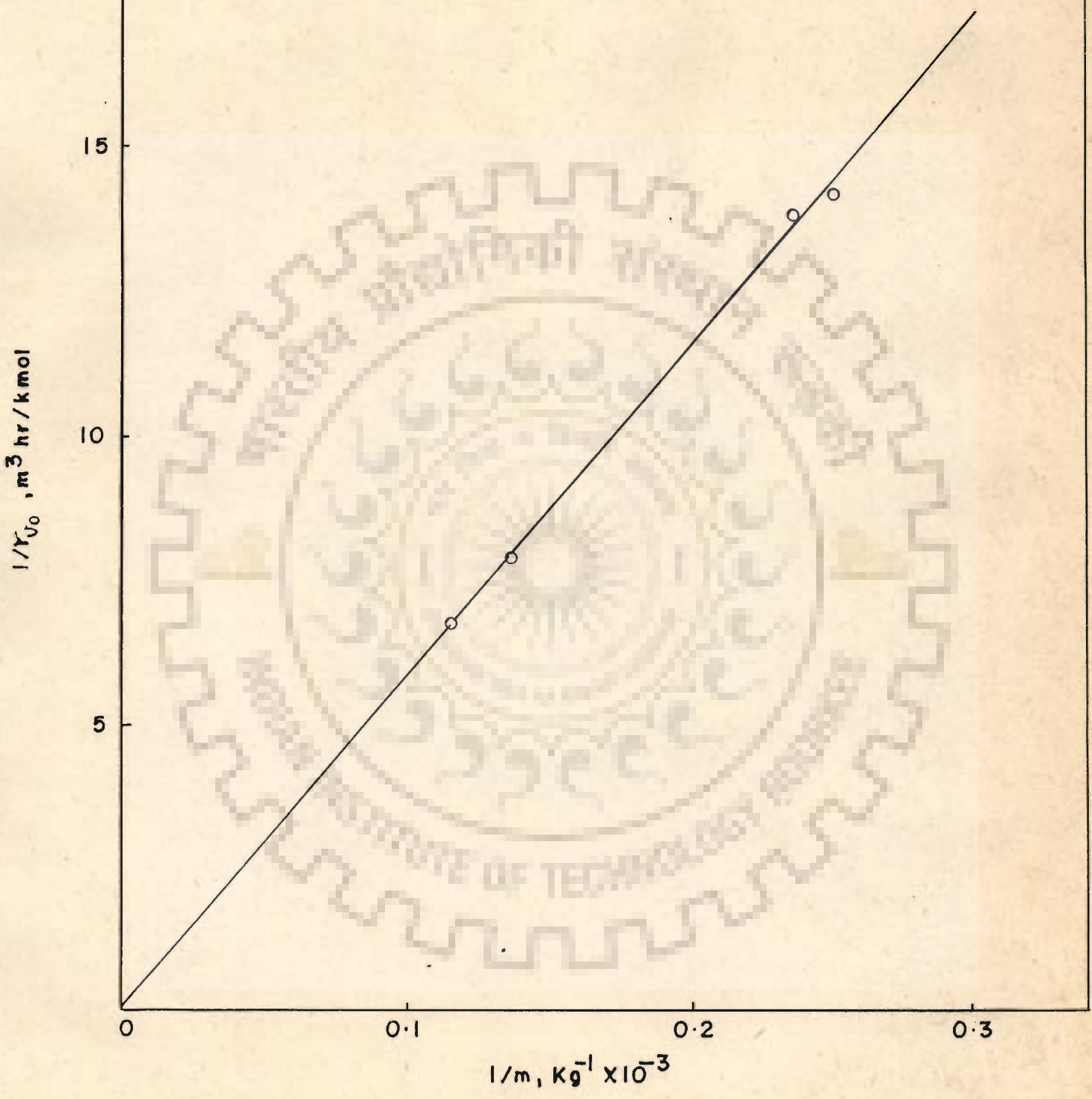
FIG. 4·9 — PLOT OF 1/m Vs 1/r_{v_0} ACCORDING TO EQUATION 4·5

Brain and Hales[133]. In the analysis described below the intercept and slope of $1/r_0$ Vs $1/m$ plots were estimated by linear least square method.

Figure 4.7 is a plot based on Equation 4.5 for isooctene hydrogenation. It is clear that the intercept of the straight line in this plot is small compared to the value of $1/r_0$ for the run with the lowest catalyst loading; the actual values are 0.26672 $m^3.hr.kmol^{-1}$ for the intercept and 7.844 $m^3.hr.kmol^{-1}$ for the experiment. This figure shows that the gas-liquid resistance for this run was only about 3.4 % of the total resistance; evidently the transfer of hydrogen from the gas to the bulk liquid did not control the reaction rate. For the run with the highest catalyst loading (the data point farthest on the left side in Fig. 4.7), the intercept is about 7.48 % of the actual value of the ordinate; 3.56252 $m^3.hr.kmol^{-1}$ versus 0.26672 $m^3.hr.kmol^{-1}$. Therefore, for isooctenes, at agitation of 800 rpm, with catalyst loadings in the range of 2.88 x 10^{-3} - 7.81 x 10^{-3} kg (6.4-17.35 kg/m^3) used in these experiments, the gas-liquid mass transfer was negligible.

Figure 4.8, which is a similar plot for the hydrogenation of isododecenes at 800 rpm and 313 K, shows even a lesser effect of gas-liquid mass transfer on the overall reaction rate; the value of

the intercept is 0.105667 which is about 0.73 % of
the ordinate (1.4285 m^3.hr.kmol^{-1}) for the experiment
at lowest catalyst loading (catalyst 3.97 x 10^{-3} kg)
and about 1.5 % of the run with highest catalyst
loading (catalyst, 8.66 x 10^{-3} kg; ordinate,
6.70465 m^3.hr.kmol^{-1}).

A similar plot for the hydrogenation of
n-octene (Fig. 4.9) at 800 rpm, 313 K and 0.5 MPa
pressure gave an intercept of 0.20 m^3.hr.kmol^{-1},
showing negligible effect of gas-liquid mass transfer
on the overall reaction rate. This was only about
3.0 % and 8.20 % for the runs at lowest (2.52 x 10^{-3} kg)
and highest catalyst loadings (7.18 x 10^{-3} kg)
respectively.

4.3.1.2 Theoretical Evaluation of Inter and Intra Particle
Mass Transfer Resistances

In order to determine if liquid-solid mass
transport, and the pore diffusion are significantly
affecting the reaction, it is often useful to
perform simple calculations as discussed by
Satterfield[131].

Solid-liquid mass transport:

As indicated earlier, the values of liquid-
solid mass transfer coefficients, K_{ls}, were
estimated using the following correlation suggested
by Brain and Hales[133]:

$$\left(\frac{K_{ls} d_P}{D_A} \right)^2 = 4.0 + 1.21 \left[\frac{g \, d_P^3 \, (\rho_a - \rho_l)}{18 \mu D_A} \right]^{2/3} \quad \text{..(4.6)}$$

The values of the composite constant, k' (defined earlier) were obtained from the slopes of $1/r_o$ versus $1/m$ plots at 313 K and a stirrer speed of 800 rpm. The values of K_{ls} and k' thus obtained are summarized in Table 4.5. The relative order of magnitudes of K_{ls} and k' indicate that, k' was sufficiently lower than K_{ls}. This provides acceptable indication that liquid-solid mass transfer did not affect the reaction.

Pore diffusion:

Recent studies by Furusawa and Smith[134] have shown that pore diffusional effects in slurry reactors can be serious when particle sizes greater than about 0.02 cm are used but it is negligible for smaller particle sizes. In the present case, the average particle size was of the order of 0.0075 cm. The Thiele modulus, ϕ for the maximum observed reaction rate at 333 K was calculated for this size, using the method described by Satterfield et al.[7] and are summarized in Table 4.6. The values of ϕ at 313 K and 0.5 MPa pressure are also shown in Table 4.6. The corresponding values of effectiveness factors, η were estimated using the published ϕ vs η charts[132] and found to be

TABLE 4.5

COMPUTED VALUES OF K_{1s} AND k' AT 313 K AND 800 r.p.m.

Olefin	K_{1s} cm/hr	$k' = (1/K_{1s} + 1/k_s)$
isooctene	327.9	15.47
n-octene	330.0	26.85
isododecene	326.0	7.02

TABLE 4.6

VALUES OF THIELE MODULUS FOR POWDERED CATALYST

Olefin	Thiele Modulus, $\emptyset \times 10^2$	
	313 K	333 K
isooctene	0.16	0.17
n-octene	0.28	0.30
isododecene	0.07	0.10

approximately unity. Values of $\emptyset$ indicate that the pore diffusion with this powdered catalyst can be assumed to be negligible. A sample calculation for Thiele modulus from these data is shown in Appendix A.

4.3.1.3. Check of controlling regimes based on Arrhenius plots

The most conclusive criteria for discriminating the controlling regime is perhaps the magnitude of the activation energy. The Arrhenius plots of r_o at a given catalyst loading are shown in Figures 4.10 to 4.12; these linear plots show that in the range of temperature studied, there was no shift in the controlling mechanism from kinetic to mass transfer control. The activation energies were estimated from these plots and found to be in the range of 55 -60 kJ.mol^{-1}. Since the pore diffusion effects were eliminated, the value of activation energy of about 55 kJ.mol^{-1} represents the activation energy for the intrinsic reaction.

Based on the observations presented in the foregoing pages (at 700 rpm and above), kinetic control can safely be assumed to prevail in the system for the hydrogenation of isooctene, iso-dodecene and n-octene. In an earlier study[13] on the liquid phase hydrogenation of isooctene using the same palladium catalyst and apparatus, the author had observed that both external and pore diffusional resistances were negligible even at agitator speeds of 480 rpm.
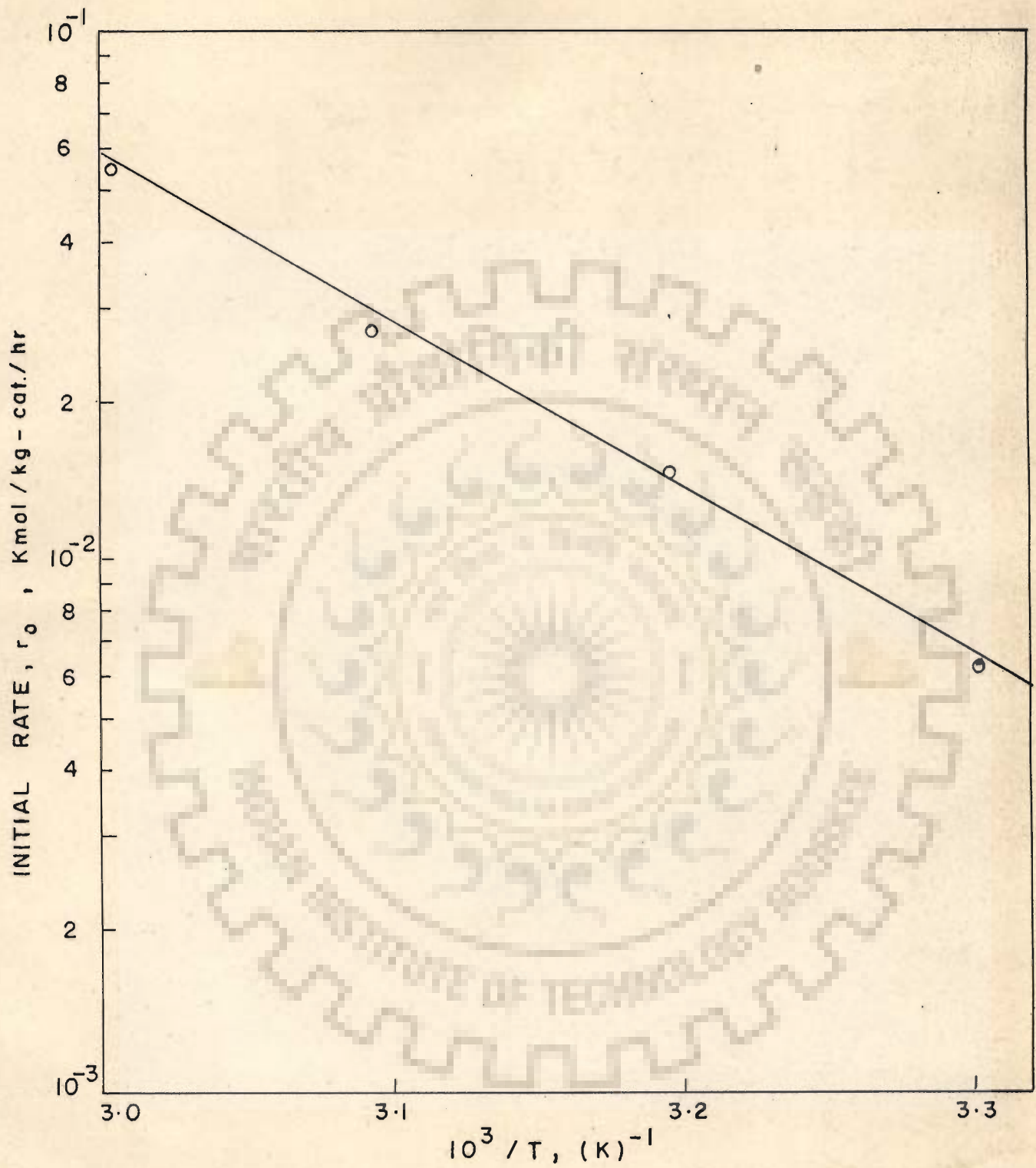
FIG. 4·10 ARRHENIUS PLOT OF INITIAL RATE OF HYDROGENATION
OF ISOOCTENE
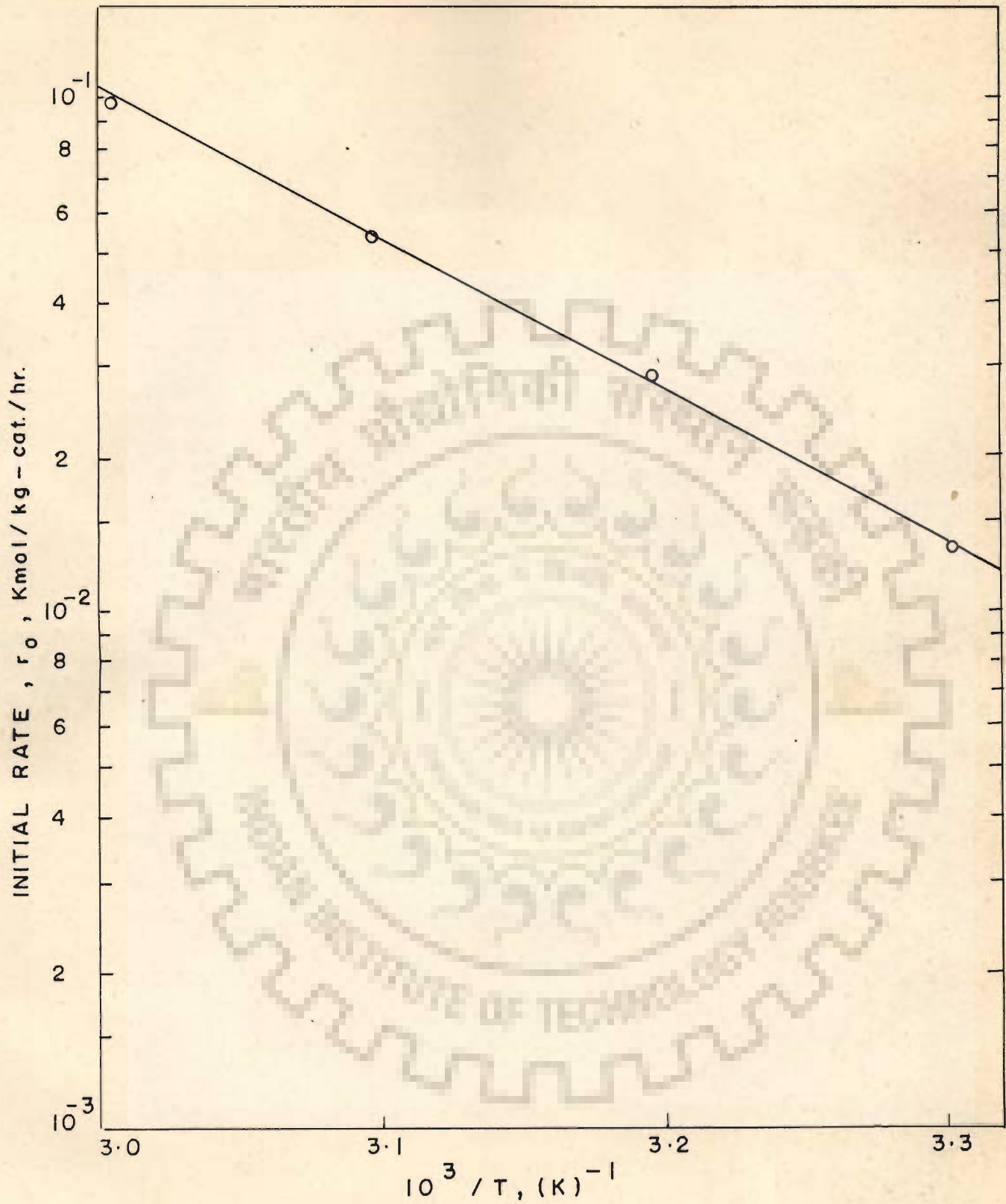
FIG. 4·11 – ARRHENIUS PLOT OF INITIAL RATE OF
HYDROGENATION OF n – OCTENE.
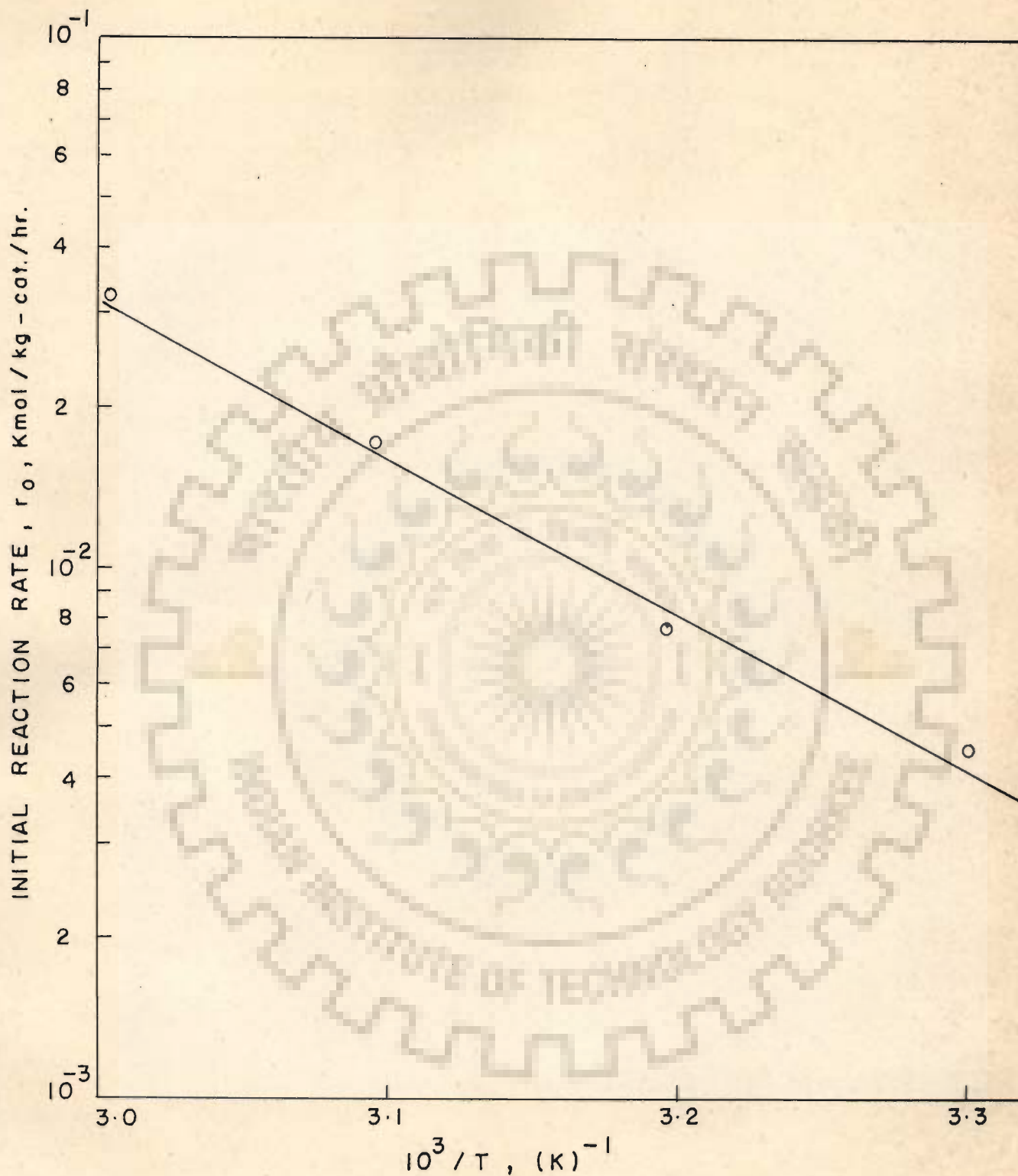
FIG. 4·12 - ARRHENIUS PLOT OF INITIAL REACTION RATE OF HYDROGENATION OF ISODODECENE

4.4 KINETIC STUDIES

4.4.1 Effect of process variables

After establishing that, with the powdered catalyst, at impeller speeds of 700 rpm and above, the resistance to mass transfer was negligible, series of hydrogenation using the three olefins as feeds, experiments were carried out at 800 rpm. In these experiments, (a) the initial concentration of olefin in the liquid phase, (b) reaction temperature, and (c) the hydrogen pressure were varied. The results obtained were evaluated in terms of reaction rates; the observations and results of these experiments are described below for each olefin separately.

4.4.1.1 Hydrogenation of isooctenes
Effect of initial isooctenes concentration:

The effect of initial isooctenes concentration on the rate of reaction was studied over the temperature range 303-333 K and hydrogen pressure of 0.5 MPa and an agitator speed of 800 rpm. Figure 4.13 shows typical results obtained and represents the effect of initial isooctene concentrations on the initial reaction rate at temperatures of 303, 313 and 333 K. The initial rate of hydrogenation was found to level off at isooctene concentration of 0.5 kmol/m^3 and above. The increase of rate thereafter was negligible; this showed an almost zero order behaviour with respect to isooctene concentration.
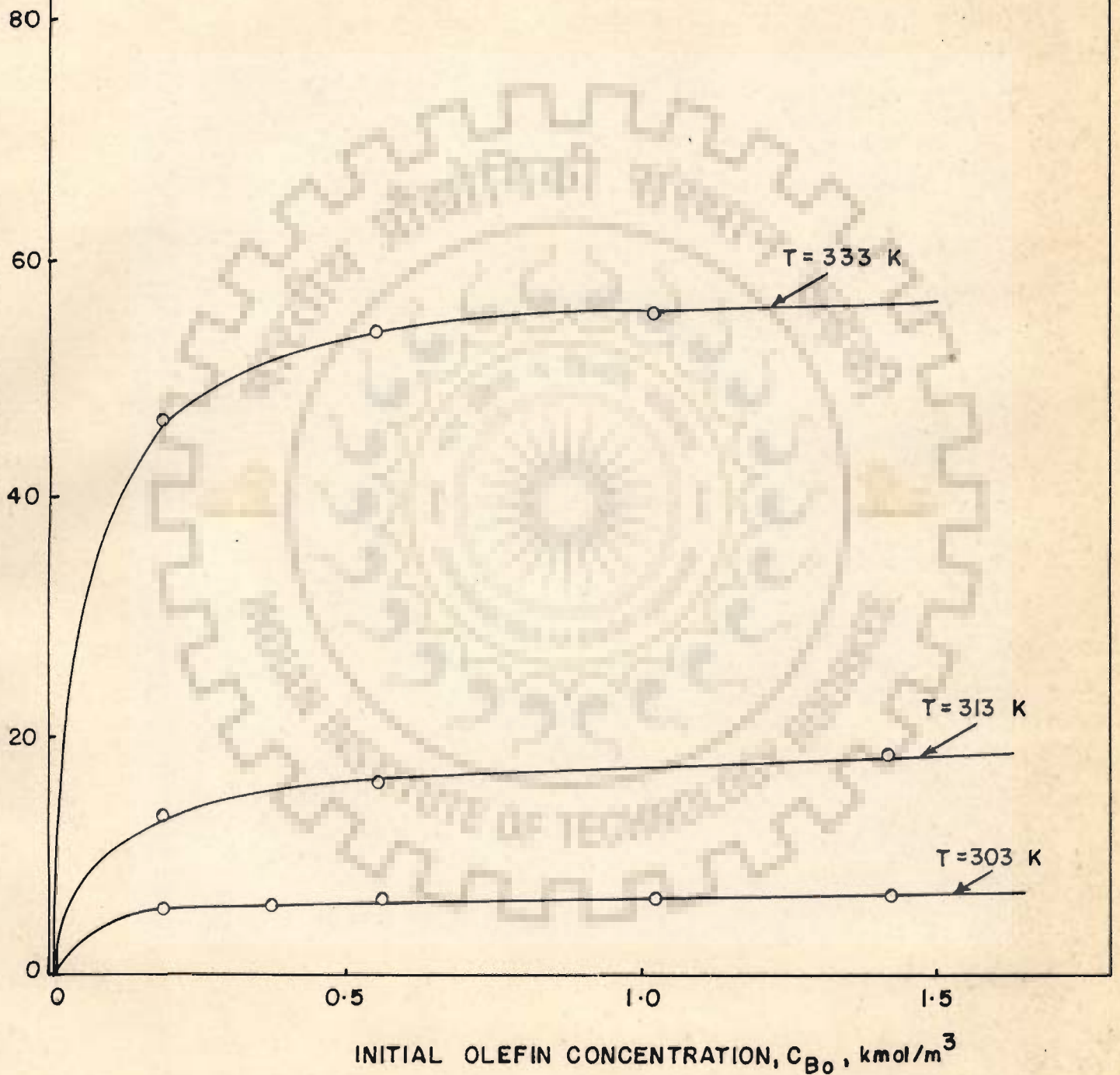
FIG. 4·13 – VARIATION OF INITIAL REACTION RATE WITH INITIAL OLEFIN CONCENTRATION AND TEMPERATURE.

At very low isooctene concentrations ($<$ 0.5 kmol.m^{-3}), however, the trend was towards first order. With increase of temperature the reaction rate rose substantially, showing a temperature dependence; for example, at the initial isooctene concentration of 0.5572 kmol.m^{-3}, the rate increased from 0.6293 x 10^{-2} kmol.(kg-cat)$^{-1}$.hr^{-1} at 303 K to about 1.6 x 10^{-2} kmol.(kg-cat)$^{-1}$hr^{-1} at 313 K.

Effect of hydrogen pressure

The influence of hydrogen pressure on the initial rate of hydrogenation of isooctenes at 303, 313 and 333 K is shown in Figure 4.14. It was found that the rate of hydrogenation increased rapidly with increase of hydrogen pressure upto 0.5 MPa and then very slowly; the rate of increase was more pronounced at higher temperatures. At 303 K, for example, the initial rate increased from 0.542 x 10^{-1} kmol.(kg-cat)$^{-1}$hr^{-1} at a pressure of 0.5 MPa to about 0.76 x 10^{-1}kmol.(kg-cat)$^{-1}$ hr^{-1} at 2.0 MPa.

Since the hydrogen concentration in the liquid phase is almost proportional to the total hydrogen pressure in the system (Table 4.2), the influence of hydrogen concentration in the liquid phase on the rate of hydrogenation followed a similar trend as with total pressure (Figure 4.15). For eavluating
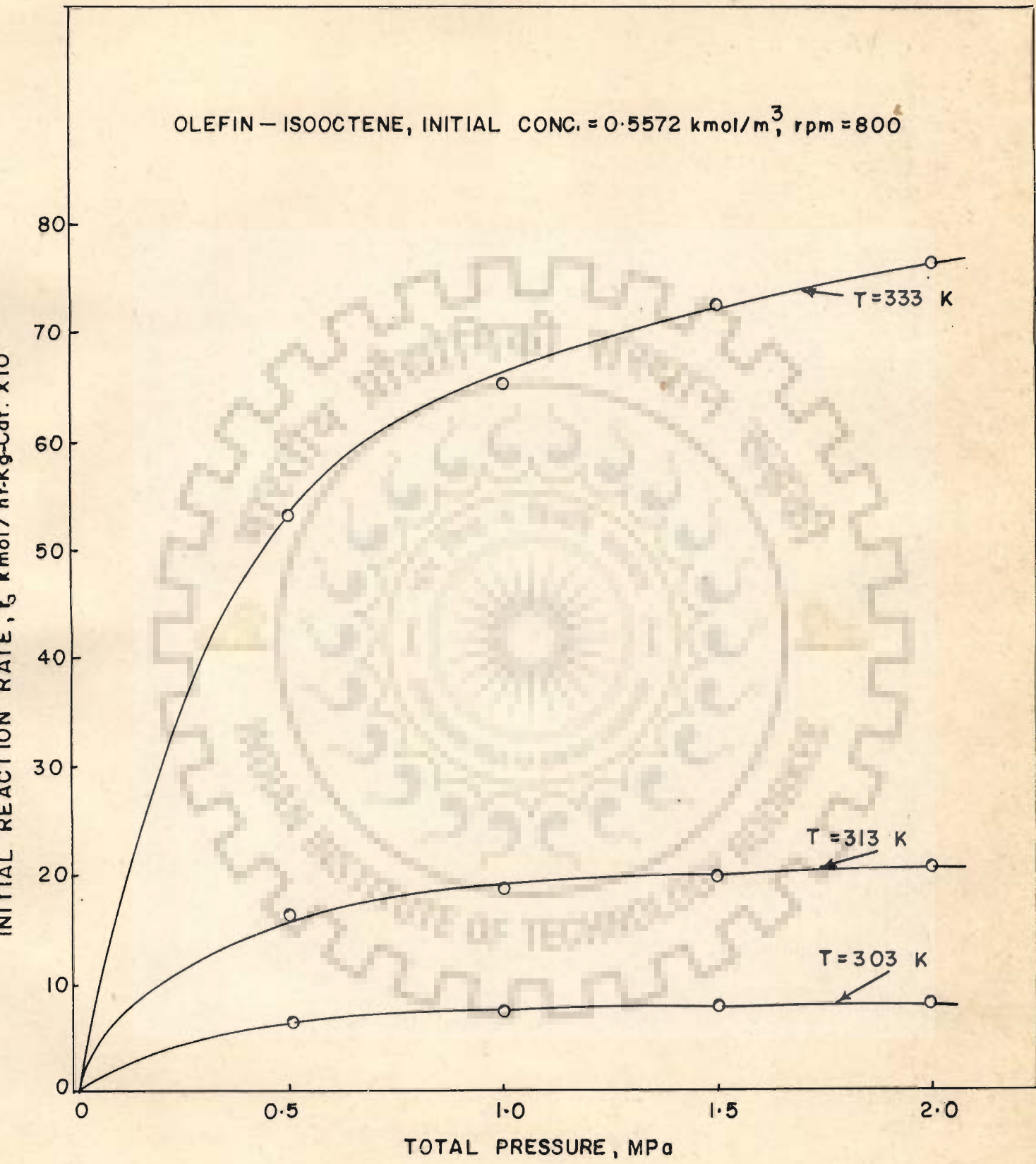
FIG. 4·14 – EFFECT OF TOTAL PRESSURE ON THE INITIAL RATE OF REACTION.
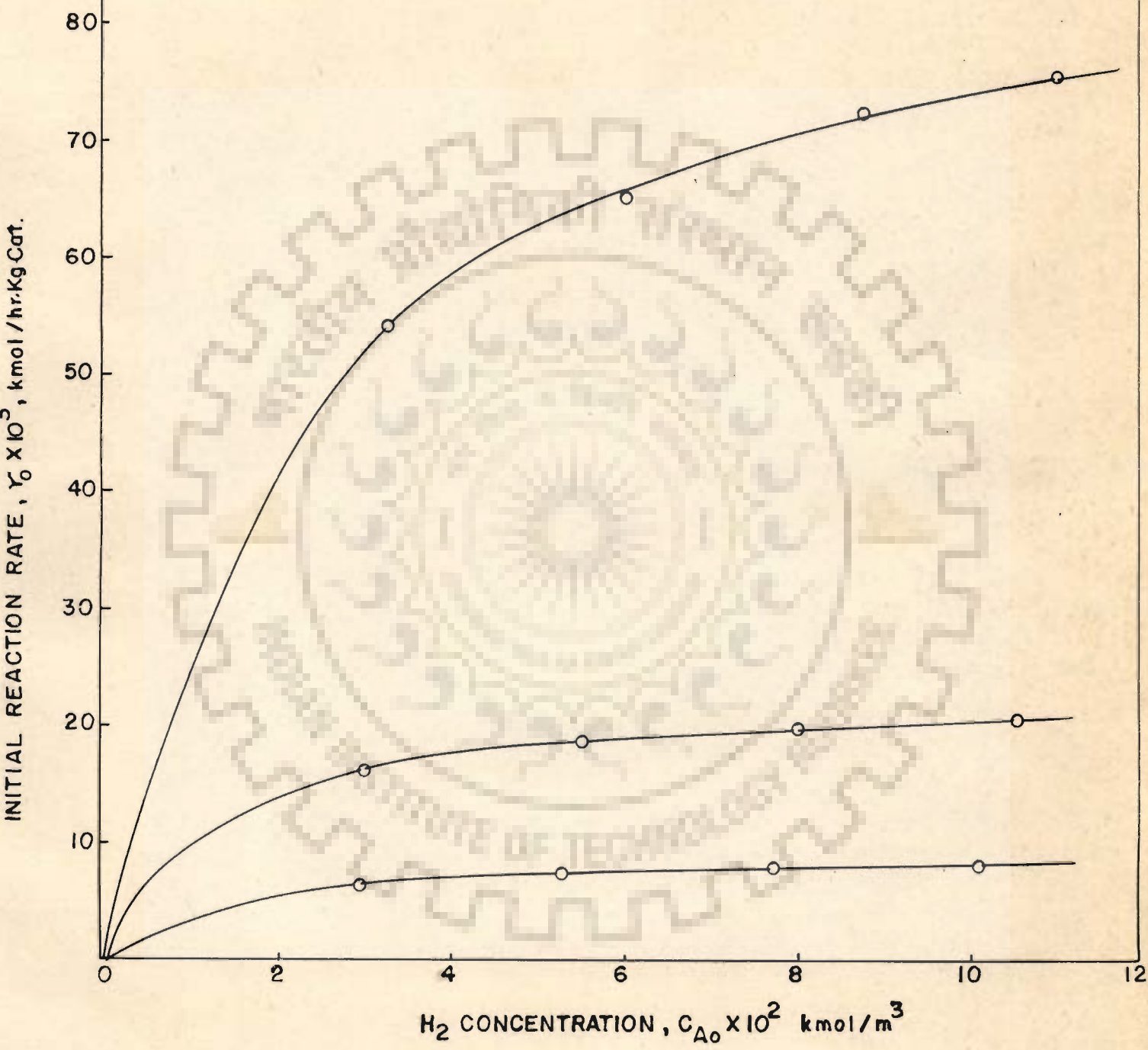
FIG. 4·15 —EFFECT OF HYDROGEN CONCENTRATION IN LIQUID PHASE ON INITIAL RATES OF REACTION.

and correlating the rates, this hydrogen concentration in the liquid phase was considered.

The apparent order of reaction with respect to hydrogen and isooctene were computed by fitting the initial reaction rates and corresponding olefin and hydrogen concentrations into a power law rate equation graphically and are given in Table 4.7. The data show that the rate was more influenced by hydrogen concentration than olefin concentration. The apparent order, with respect to both hydrogen and olefin, slightly increased with increase in temperature.

During hydrogenation of olefins, isomerisation through shifting of the double bond has also been reported to occur by some investigators[136-139]. This, of course, depends upon the type and properties of the catalyst used. The possibility of occurrence of isomerisation was also examined in this case. In some experiments, carried out at 333 K, the liquid samples withdrawn at intervals were analysed by glc for the ratio of trimethyl pentene-1 to other isomers of isooctene, M. Figure 4.16 shows the variation of this ratio with reaction time at 333 K and 0.5 MPa pressure for feeds containing two different concentrations of 2,4,4-TMP-1. It can be seen that when the ratio M of 2,4,4-TMP-1 to 2-TMP's was slightly higher, it decreased rapidly to a value which remained constant

TABLE 4.7

APPARENT ORDER OF REACTION COMPUTED FROM INITIAL RATES

| Olefin feed | Order of reaction | | | | | |
| | w.r.t. H_2 | | | w.r.t. olefin | | |
Temp:	303 K	313 K	333 K	303 K	313 K	333 K
Isooctene	0.203	0.205	0.276	0.060	0.059	0.100
n-octene	0.162	0.215	0.334	0.036	0.091	0.076
Isododecene	0.121	0.223	0.326	0.054	0.055	0.062

upto about complete conversion ($\simeq 90\%$). This ratio M appeared to be the equilibrium ratio at this temperature.

These observations are based on the analysis data. The differences in the initial isomer compositions were small and one may consider these to be within experimental errors. If the glc analyses data are taken to be highly accurate, then it can be inferred that the olefins get isomerised rapidly in the beginning to their equilibrium ratio. This could occur on the feeble acidic sites of the alumina support.
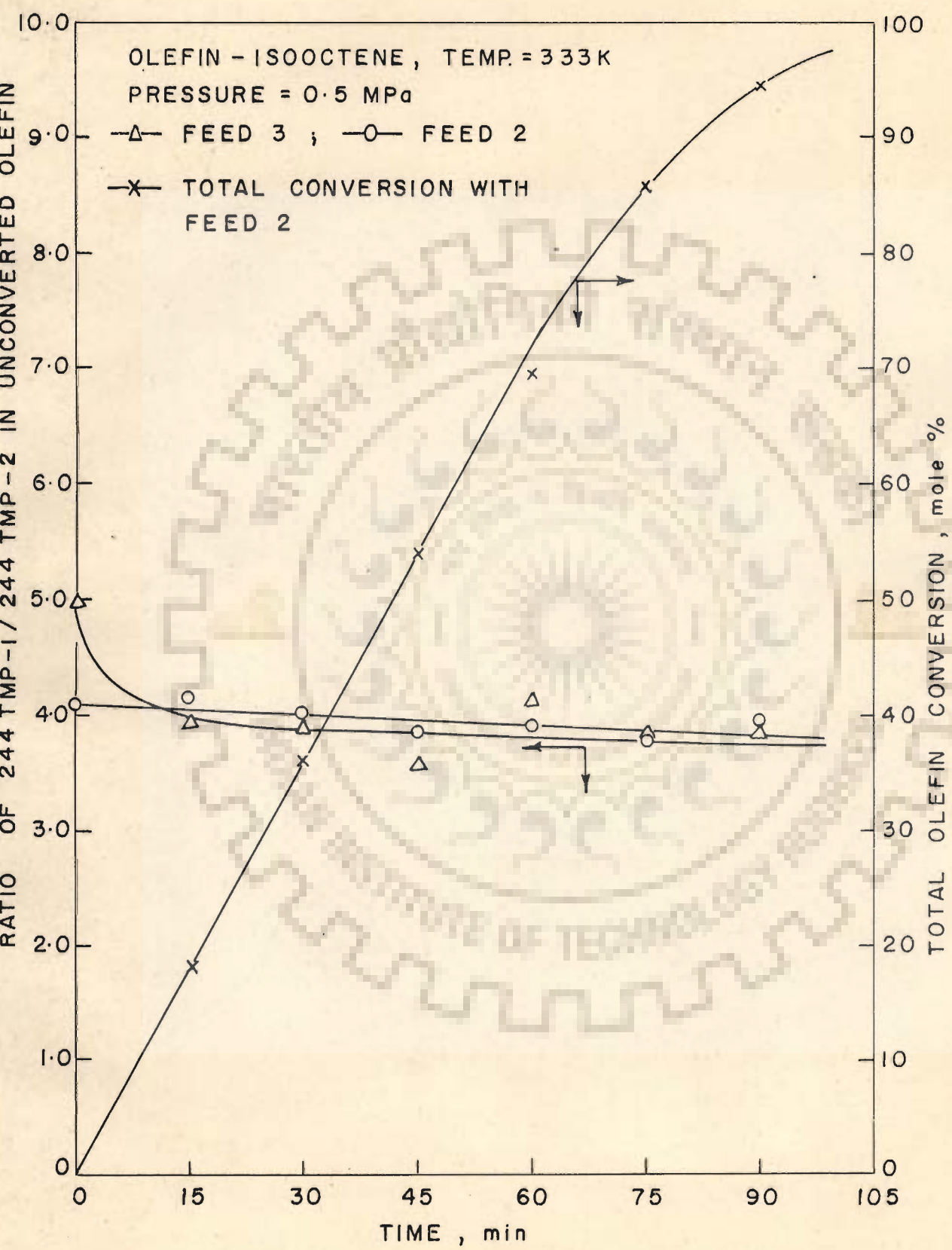
FIG. 4·16 — VARIATION OF TERMINAL TO INTERNAL OLEFIN WITH RESIDENCE TIME

4.4.1.2 Hydrogenation of n-octenes

Effect of initial n-octenes concentration

The dependence of the initial hydrogenation rates on initial concentration of n-octenes at 313 K and 0.5 MPa pressure is shown in Figure 4.17. It could be seen that the variation of the initial reaction rate with olefin concentrations and temperature showed a similar trend as in the case of isooctene; the absolute rates were, however, substantially higher. The apparent order of reaction with respect to n-octenes concentration at 303, 313 and 333 K was determined from the initial reaction rates and found to be 0.036, 0.091 and 0.076 respectively (Table 4.7).

Effect of hydrogen pressure

Figures 4.18 and 4.19 show the effect of hydrogen pressure and the hydrogen concentration in the liquid phase on the initial rate of hydrogenation of n-octenes at 313 K and 0.5 MPa pressure. The data indicated that the effect of hydrogen concentration was more pronounced at higher temperature (333 K). It was further observed (Figures 4.17 and 4.19) that the reaction rate was more dependent on the hydrogen concentration than on the olefin concentration. The apparent order of reaction with respect to hydrogen also supports this observation (Table 4.7).

OLEFIN – n – OCTENE , PRESSURE = 0·5 MPa, rpm = 800
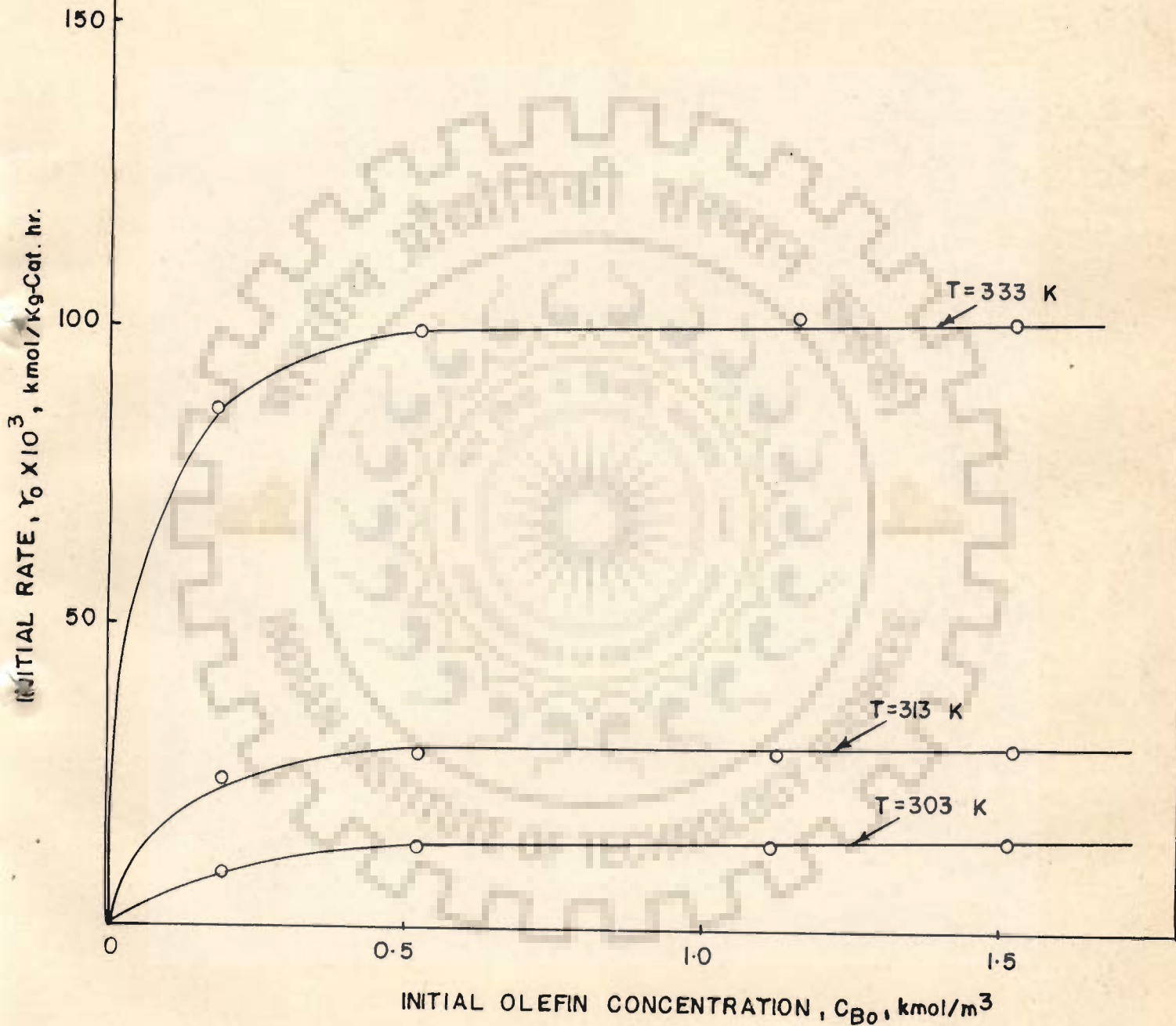
FIG. 4:17 — VARIATION OF INITIAL REACTION RATES WITH INITIAL OLEFIN CONCENTRATION AND TEMPERATURE.

FIG. 4·18 — EFFECT OF TOTAL PRESSURE ON INITIAL REACTION RATE.

OLEFIN–n–OCTENE, INITIAL OLEFIN CONC. = 0.5218 k mol/m³, r.p.m. = 800

T = 333 K

T = 313 K

T = 303 K

H₂ CONCENTRATION, C_A × 10², k mol/m³
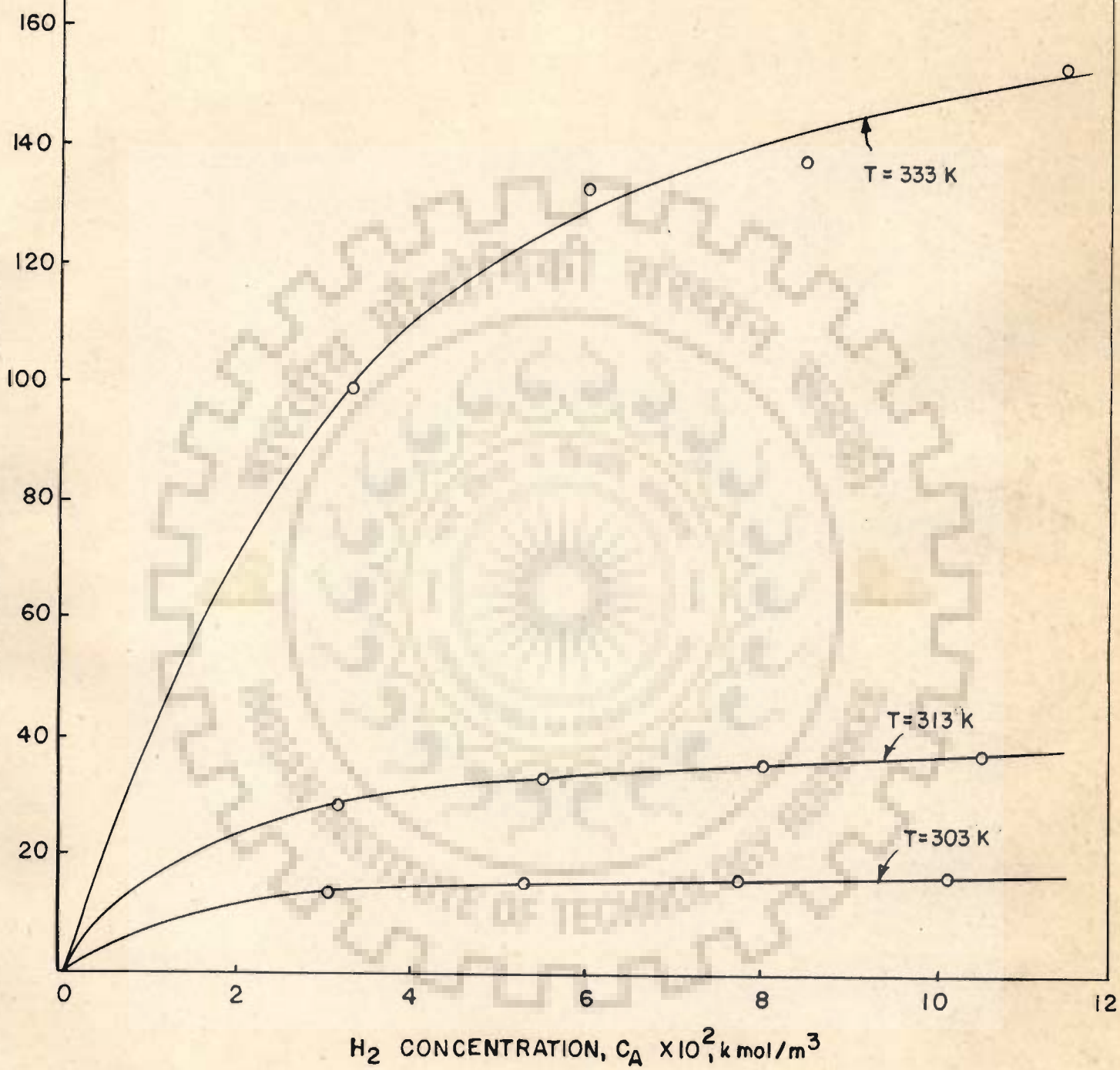
FIG. 4·19 — EFFECT OF HYDROGEN CONC. IN LIQUID PHASE ON INITIAL
REACTION RATE .

The variation of unreacted n-octenes composition with residence time at 303 K and 0.5 MPa pressure is shown in Figure 4.20; the corresponding total conversion of n-octenes versus residence time is also shown on this plot. It can be seen that the distribution of isomers of n-octene attained almost equilibrium distribution after about 10 % conversion level. At 333 K this equilibrium was established more rapidly (Figure 4.21).

4.4.1.3 Hydrogenation of isododecenes

Effect of initial isododecene concentration:

The variation of initial rate of hydrogenation with initial isododecene concentration at 303, 313 and 333 K and 0.5 MPa pressure is shown in Figure 4.22. The initial rate increased rapidly when the isododecene concentration was increased about 0.3 $kmol.m^{-3}$ and then remained almost constant while the initial isododecene concentration was increased 5-fold to about 1.5 $kmol/m^3$. This showed a zero order dependence of the rate on olefin concentration above 0.3 $kmol.m^{-3}$. The overall reaction rates at the three temperatures and the pressure range applied in this study were lower than that obtained for isooctenes and n-octenes under similar operating conditions.
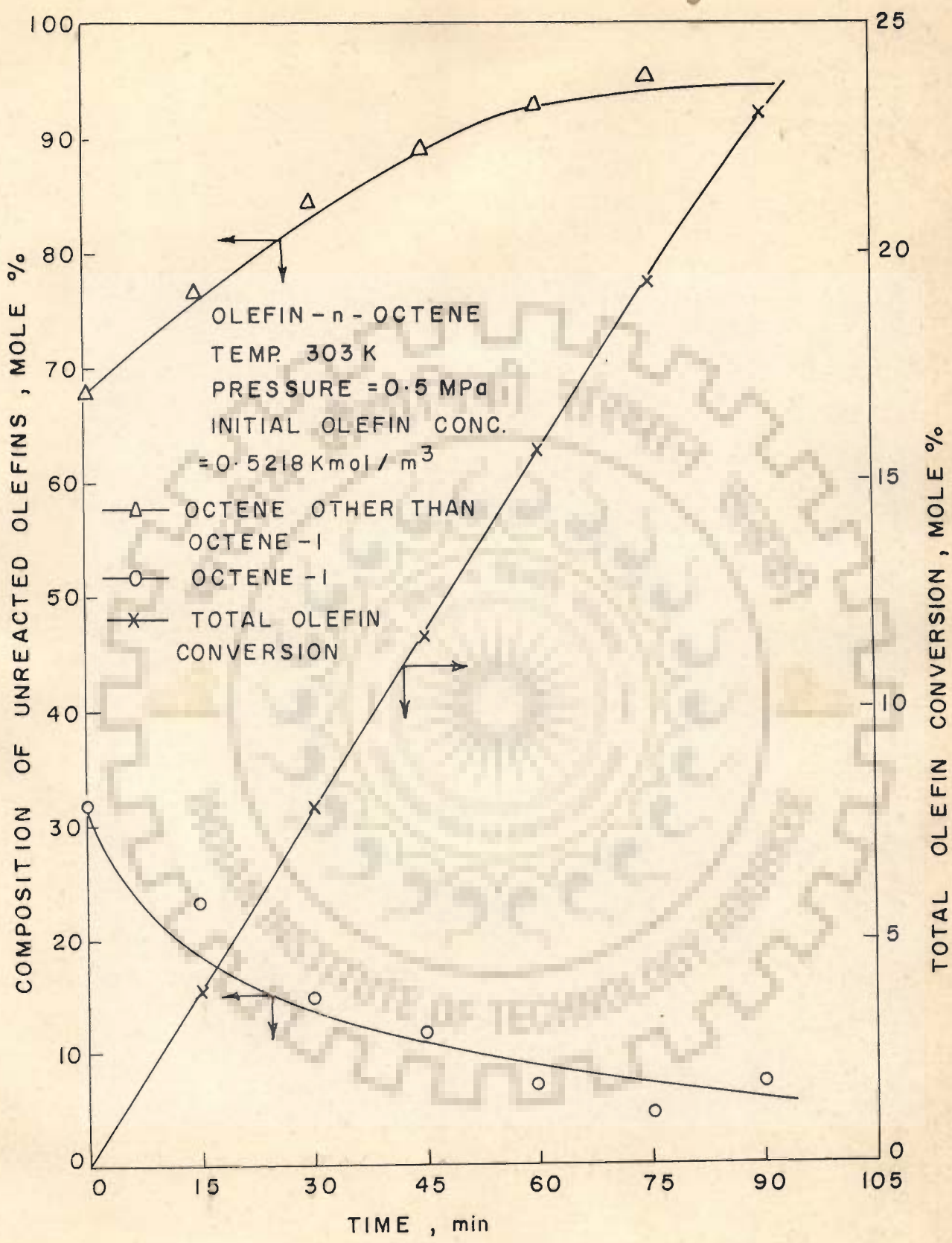
FIG. 4·20 - VARIATION OF COMPOSITION OF OLEFIN WITH RESIDENCE TIME
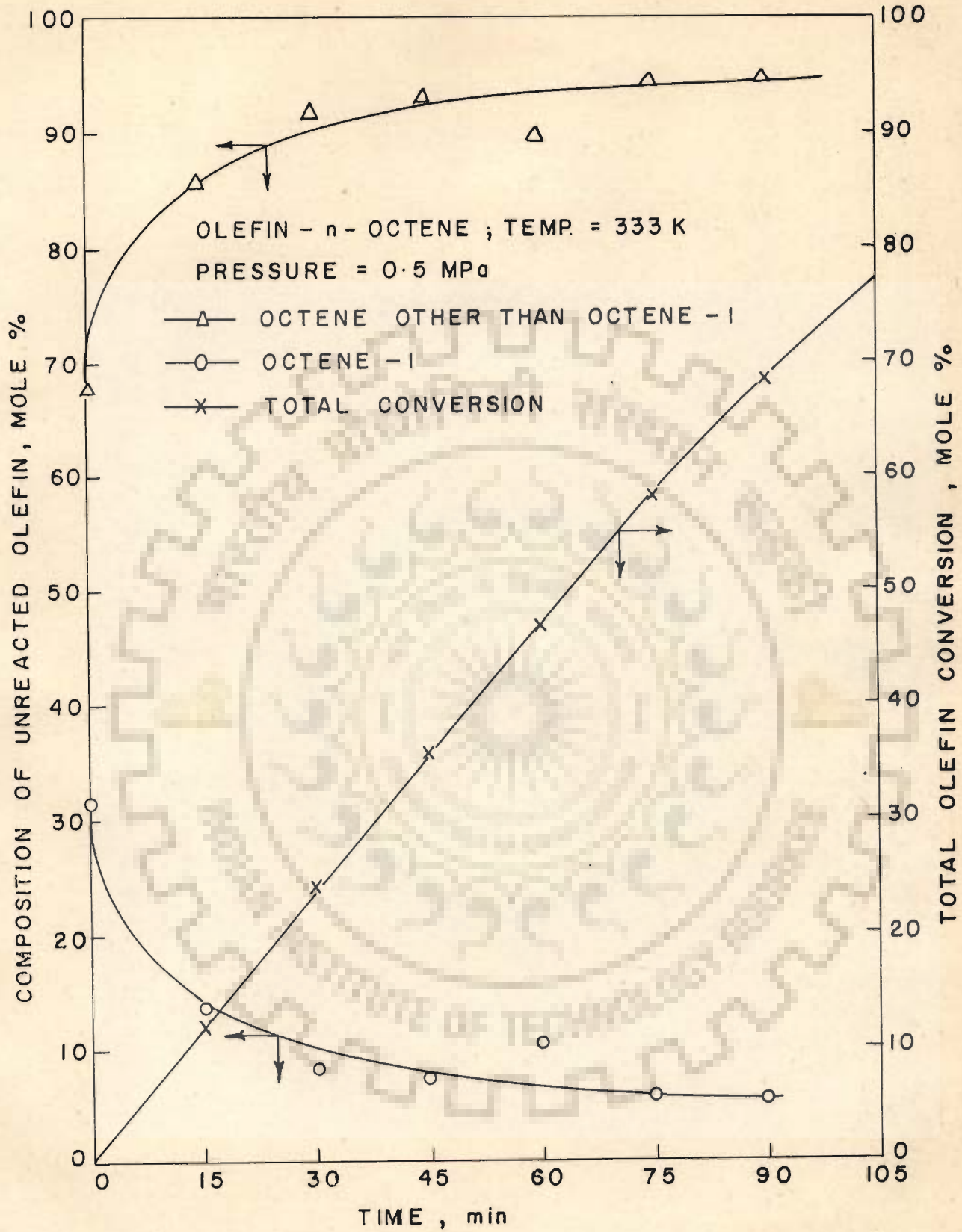
FIG. 4·21 – VARIATION OF COMPOSITION OF OLEFIN WITH RESIDENCE TIME
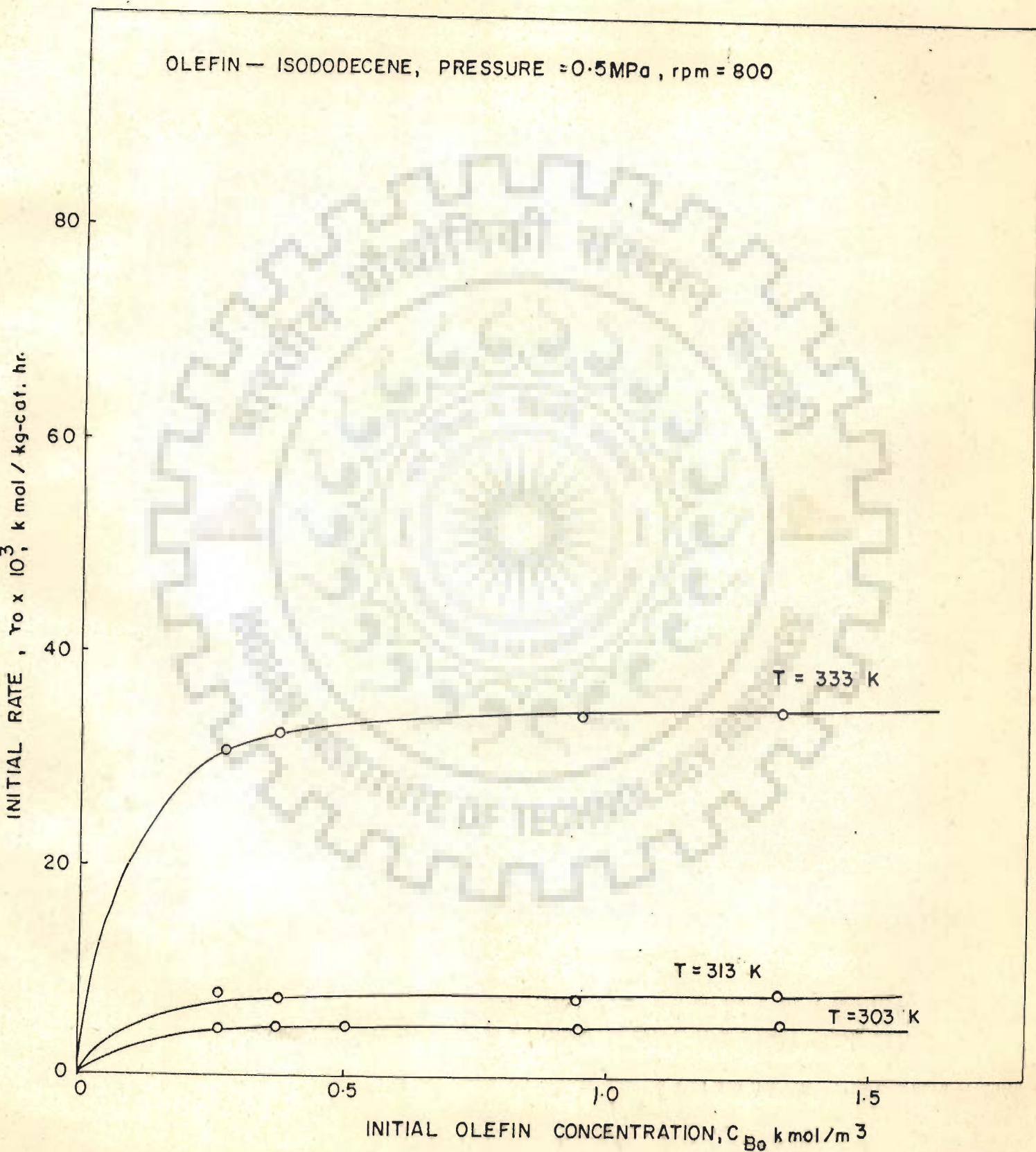
FIG. 4·22— VARIATION OF INITIAL REACTION RATES WITH INITIAL OLEFIN
CONCENTRATION & TEMPERATURE.

Effect of hydrogen pressure:

Figure 4.23 shows the effect of variation of total hydrogenation pressure on the initial rate of reaction at the olefin concentration (0.373 $kmol.m^{-3}$) in the feed. Hydrogen pressure seemed to affect the reaction rate of this longer chain olefin relatively more than in the cases of the C_8-olefins, though the overall rates were lower. At 303 and 313 K, the rate first increased with increase of pressure and then almost levelled off at hydrogen pressures of above 1.0 MPa; on the other hand, at 333 K, the rate increased rapidly upto about 1.0 MPa, but beyond that also showed an ever increasing trend determined upto 2.0 MPa.

The variation of the initial rates of hydrogenation with the corresponding hydrogen concentrations in the liquid phase are shown in Figure 4.24.

4.4.2 ANALYSIS OF KINETIC DATA

4.4.2.1 Power law model

At first the variation of the hydrogenation rates with concentrations of olefin and dissolved hydrogen over the entire range of conversion was evaluated in terms of the power law model:

$$r = k \ c_A^p \ c_B^q \qquad \dots\dots (4.7)$$

OLEFIN – ISODODECENE, INITIAL OLEFIN CONC. = 0.373 kmol/m^3, rpm = 800

T = 333 K

T = 313 K

T = 303 K
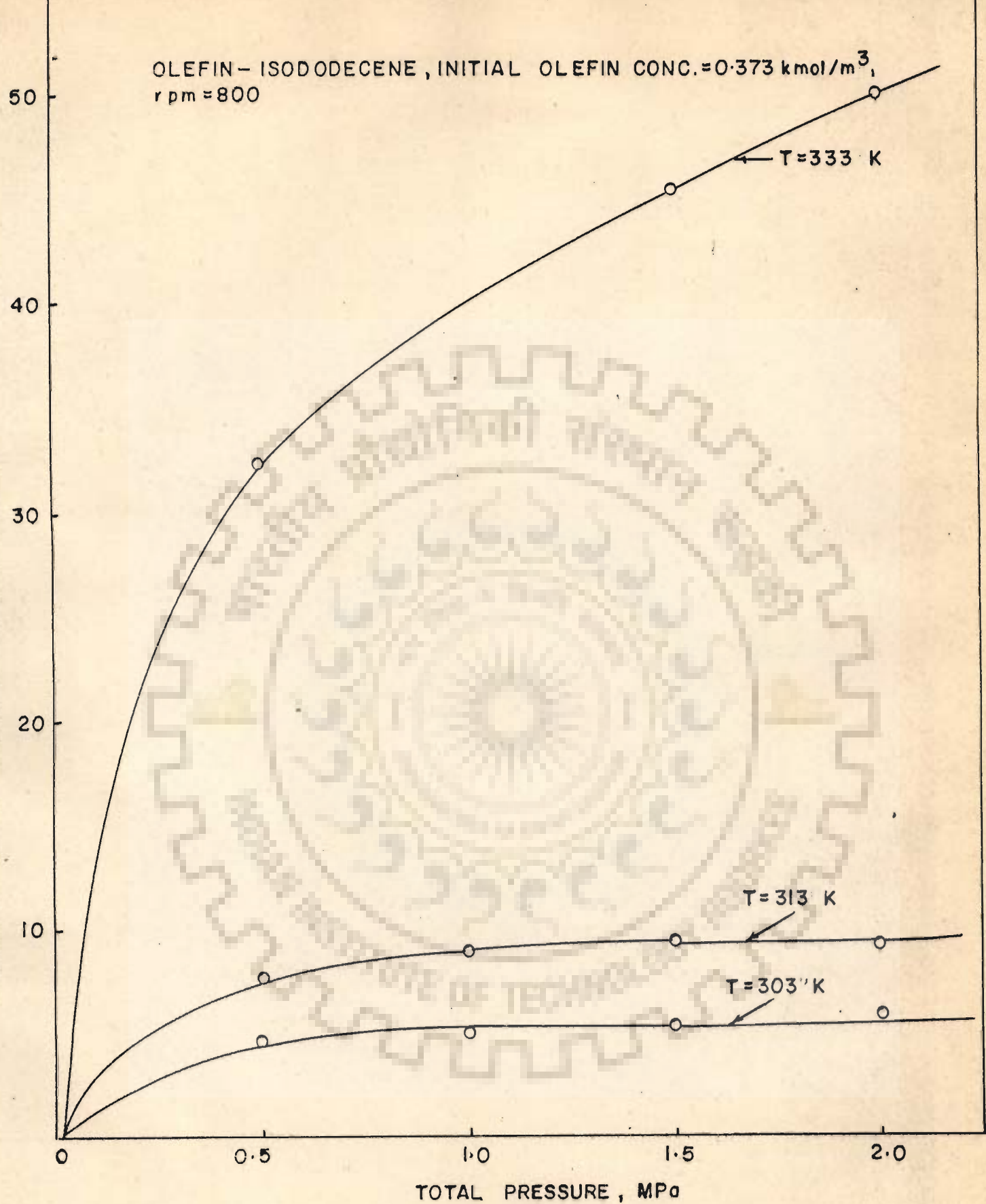
TOTAL PRESSURE, MPa

FIG. 4.23 – EFFECT OF TOTAL PRESSURE ON THE INITIAL RATES OF REACTION.
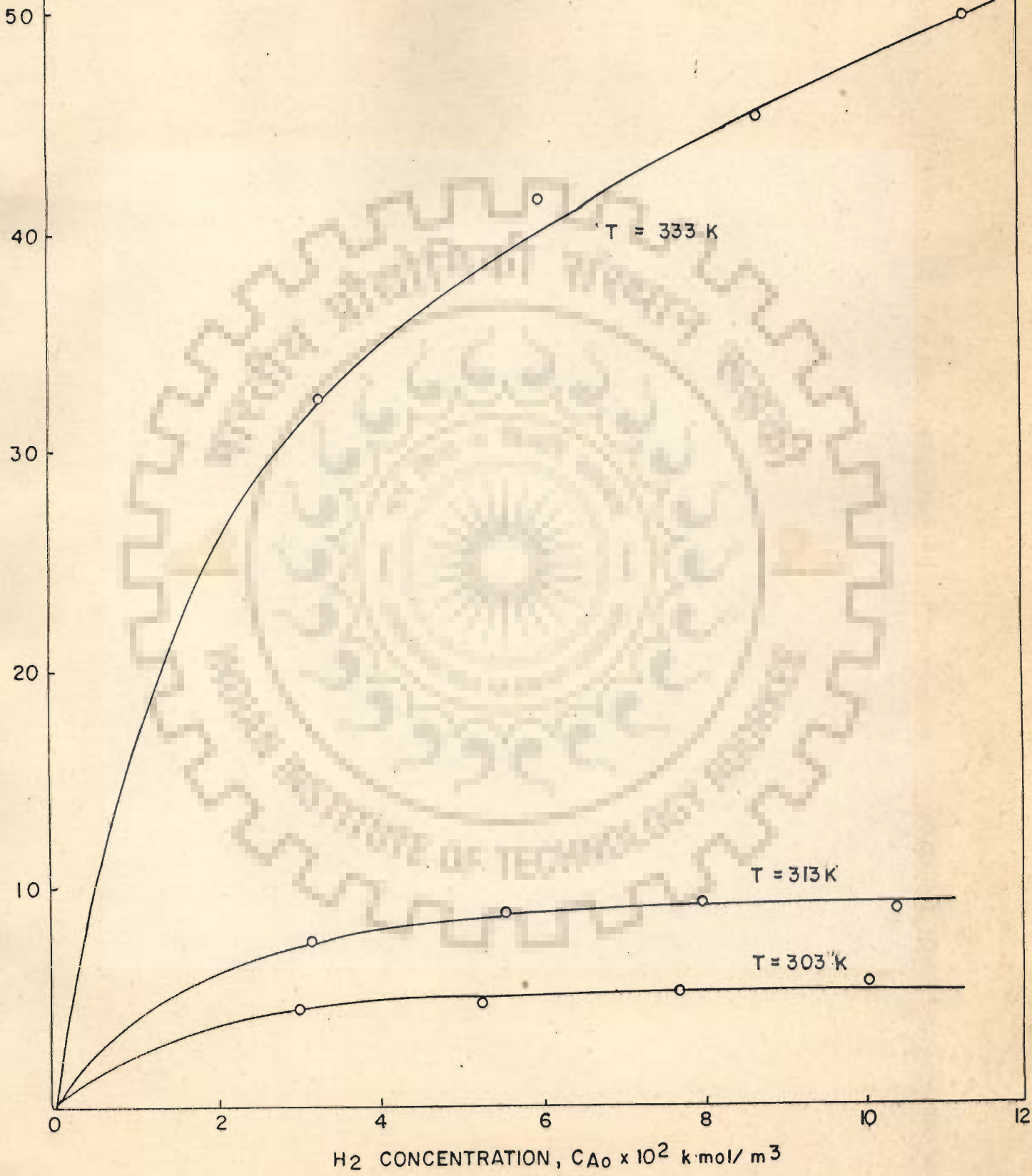
FIG. 4·24 - EFFECT OF H_2 CONC. ON INITIAL REACTION RATES.

Equation 4.7 was processed after fitting the rate data using non-linear least square technique. The estimated values of the parameters k, p and q alongwith the average absolute error and sum of squares of residuals, S_1^2 are given in Table 4.8. It can be seen that the values of p and q are not constant over the entire temperature range. A close look at the values of S_1^2 and the average absolute error in Table 4.8 shows that the kinetic data fits the power law model in the low temperature range. For isooctenes and isododecenes a large deviation is observed at 333 K, while for n-octenes large deviations are observed even at 313 K. This power law equation, therefore, did not appear to be very satisfactory over the entire range of temperature and for all the three olefins.

4.4.2.2 Mechanistic Models

Although the power law rate equation fitted most of the kinetic data, it can be used only for generalised relationship. It, however, does not give much information about the mechanism of the reaction. Several rate equations were, therefore, derived based on Langmuir-Hinshelwood and Rideal mechanisms and examined for precise matching with the kinetic data.

As already mentioned, the diffusional steps were not rate controlling under the operating conditions employed. Hence the adsorption of reactants,

TABLE 4.8

PARAMETERS FOR POWER-LAW MODEL (k,p,q) WITH r IN
$kmol.kg-cat^{-1}.hr^{-1}$

olefin	T K	p	q	$k \times 10^2$	Avg.% abs. error e	S_1^2
isooctenes	303	0.2125	0.0625	1.390	1.03	0.3793×10^{-6}
	313	0.2312	0.1000	3.810	3.88	0.2994×10^{-4}
	333	0.3125	0.1188	16.530	5.18	0.6738×10^{-3}
isododecenes	303	0.1812	0.0438	0.896	1.24	0.8840×10^{-6}
	313	0.2000	0.0687	1.988	0.93	0.1361×10^{-5}
	333	0.2687	0.1312	9.078	5.27	0.8136×10^{-3}
n-octenes	303	0.2375	0.1125	3.176	2.63	0.1206×10^{-4}
	313	0.2312	0.1063	6.700	6.09	0.2265×10^{-3}
	333	0.3125	0.1750	31.180	30.82	0.1596×10^{-1}

the surface reaction and the adsorption of products were considered for the development of kinetic relationship.

A preliminary screening of these rate controlling steps was done using the effects of temperature, total pressure and initial olefin concentration on the initial rates of hydrogenation; these were discussed earlier in section 4.4.1 and shown in Figs. 4.13-14, 4.17-19, and 4.22-24. These plots were compared with the standard plots given by Yang and Hougen[140]. From this comparative study the following conclusions were drawn:-

a. The reaction rate was not proportional to hydrogen pressure, hence, the adsorption of hydrogen was not rate controlling.

b. The initial rate of hydrogenation was not proportional to the first or higher power of initial olefin concentration; this indicated that the adsorption of olefin was probably not the rate controlling step.

c. The possibility of desorption of product being rate controlling can be ruled out because the reaction was not independent of olefin concentration and of hydrogen pressure at various temperatures.

Therefore, it appeared that the surface reaction may be rate controlling[140].

On the basis of surface reaction as the controlling step several models were postulated and the kinetic rate expressions were developed for them. The method developing the rate equations as described by Yang and Hougen[140] was followed for this study. For developing the rate expressions, following assumptions were made:

(i) The organic substance, i.e. olefin, is adsorbed without dissociation and that hydrogen can be adsorbed with or without dissociation, or that it may react directly from the gaseous phase.

(ii) The reverse reaction of dehydrogenation of paraffinic product was neglected, since from thermodynamic calculations, described earlier, it did not appear to be significant at all in the operating range covered. The success of the final correlation also substantiated this.

Further, in addition to these equations based on assumption of competitive adsorption of the reaction components on the catalyst surface, equations based on the concept of non-competitive adsorption of the reactants were also derived and examined.

Derivation of kinetic models

The overall reaction of hydrogenation of the olefins can be expressed by the following Equation:

$$A + B \rightleftharpoons C \qquad \dots \dots (4.8)$$
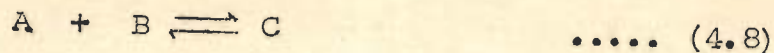
Hydrogen   Olefin   Products

The deductions of various rate equations for this reaction based on the surface reaction as controlling step are described below:

MODEL -1

A and B are associatively adsorbed on adjacent sites and react to form a molecule of product paraffin which is adsorbed on the same sites originally occupied by hydrogen and olefin. Equation 4.7 can be divided into following elementary steps:

First step: adsorption of hydrogen on the catalyst surface,
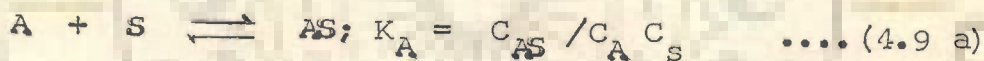
$$A + S \rightleftharpoons AS; \quad K_A = C_{AS}/C_A C_S \qquad \dots (4.9\ a)$$

Second step: adsorption of olefin on the catalyst surface,

$$B + S \rightleftharpoons BS; \quad K_B = C_{BS}/C_B C_S \qquad \dots (4.9\ b)$$

Third step: surface reaction between adsorbed A and B

$$AS + BS \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CS + S \qquad \dots \dots (4.9\ c)$$

Fourth step: desorption of products,

$$CS \rightleftharpoons C + S; \quad K_C = C_C C_S / C_{CS} \qquad \dots (4.9\ d)$$
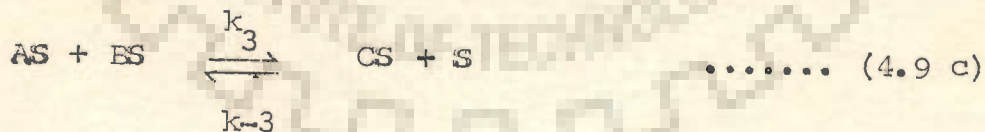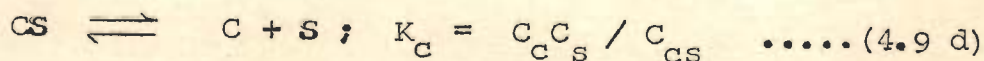
When the surface reaction (third step) is rate controlling then the rate of reaction is given by

$$r = k_3 \ C_{AS} \ C_{BS} \qquad \dots \dots (4.10)$$

The reverse reaction of dehydrogenation of saturates has been neglected.

The concentration of total number of active sites, C_T, is given by

$$C_T = C_{AS} + C_{BS} + C_S + C_{CS} \qquad \dots \dots (4.11)$$

Substituting the values of C_{AS}, C_{BS} and C_{CS} in terms of the equilibrium constants, K_A, K_B and K_C in Equation 4.11, and eliminating C_{AS} and C_{BS} from Equation 4.10, we get

$$r = \frac{k_3 \ K_A \ K_B \ C_T^2 \ C_A \ C_B}{(1 + K_A C_A + K_B C_B + K_C C_C)^2} \qquad \dots \dots (4.12)$$

Substituting k for $k_3 C_T^2$, and neglecting the adsorption of products, C, we get model Equation 1.

$$r = \frac{k \ K_A \ K_B \ C_A \ C_B}{(1 + K_A C_A + K_B C_B)^2} \qquad \dots \dots (4.13 \ )$$

MODEL -2

In this model A is dissociatively adsorbed; B is adsorbed associatively and surface reaction between adsorbed A and adsorbed B is rate controlling. The sequence of the elementary steps then becomes:

First step: adsorption of hydrogen
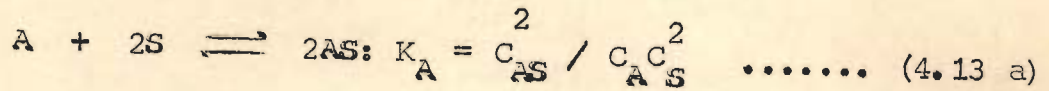
$$A + 2S \rightleftharpoons 2AS : K_A = C_{AS}^2 / C_A C_S^2 \quad \ldots\ldots\ldots (4.13 \text{ a})$$

Second step: adsorption of olefins

$$B + S \rightleftharpoons BS ; K_B \quad C_{BS} / C_B C_S \quad \ldots\ldots\ldots (4.13 \text{ b})$$

Third step: surface reaction

$$BS + 2AS \underset{K_{-3}}{\overset{k_3}{\rightleftharpoons}} C_S + 2S \quad \ldots\ldots\ldots (4.13 \text{ c})$$

Fourth step:

$$C_S \rightleftharpoons C + S : K_C = C_C C_S / C_{CS} \quad \ldots\ldots\ldots (4.13 \text{ d})$$
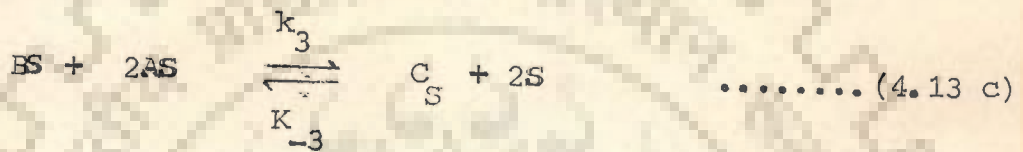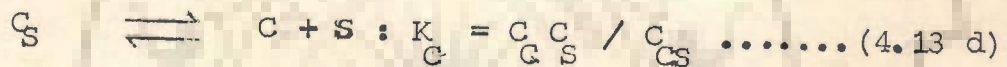
Total concentration of active sites is given by

$$C_T = C_{AS} + C_{BS} + C_S + C_{CS} \quad \ldots\ldots\ldots (4.14)$$

When the surface reaction, step 3, is rate controlling, the rate of reaction is given by

$$r = k_3 \ C_{BS} \ C_{AS}^2 \quad \ldots\ldots\ldots (4.15)$$

Eliminating, C_{AS} and C_{BS} from Equations 4.14 and 4.15 and substituting the value of C_s in terms of adsorption equilibrium constants, K_A, K_B and neglecting the adsorption of products, we get,

$$r = \frac{k \ K_A \ K_B \ C_A \ C_B}{(1 + \sqrt{K_A C_A} + K_B C_B)^3} \quad \ldots\ldots\ldots (4.16)$$

where $k = k_3 C_T^3$

MODEL -3

A is adsorbed associatively; B not adsorbed but reacts from solution; surface reaction is rate controlling. If in the elementary steps of model-1, the second step namely, the adsorption of olefin, is neglected keeping all other steps the same, then following the similar procedure, the resultant Equation is,

$$r = \frac{k \, K_A \, C_A \, C_B}{(1 + K_A \, C_A)} \qquad \cdots\cdots\cdots (4.17)$$

MODELS -4

In this A is adsorbed dissociatively; B is not adsorbed and surface reaction is rate controlling. In mechanism-2, if the adsorption of olefin is neglected, then following a similar procedure, the model Equation 4.18 is obtained,

$$r = \frac{k \, K_A \, C_A \, C_B}{(1 + \sqrt{K_A \, C_A})^2} \qquad \cdots\cdots\cdots\cdots (4.18)$$

MODEL -5 & 6

A is adsorbed on sites S_1; B is adsorbed associatively on sites S_2 non-competitively. The sequence of elementary steps then is,

First step: adsorption of hydrogen on sites S_1
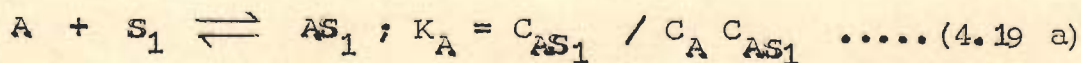
$$A + S_1 \rightleftharpoons AS_1 \, ; \, K_A = C_{AS_1} / C_A \, C_{AS_1} \quad \cdots\cdots (4.19 \text{ a})$$

Second step: adsorption of olefin on sites S_2

$$B + S_2 \rightleftharpoons BS_2 \; ; \; K_B = C_{BS_2} / C_B C_{S_2} \quad \ldots\ldots\ldots (4.19 \; b)$$

Third step: surface reaction between adsorbed A and adsorbed B,

$$AS_1 + BS_2 \; \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \; CS_2 + S_1 \quad \ldots\ldots\ldots (4.19 \; c)$$

Fourth step: desorption of products

$$CS_2 \rightleftharpoons C + S_2 \; ; \; K_C = C_C C_{S_2} / C_{CS_2} \quad \ldots\ldots\ldots (4.19 \; d)$$
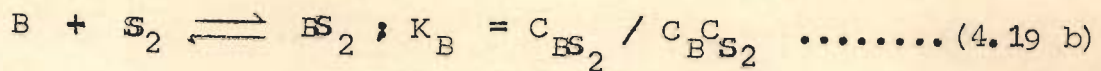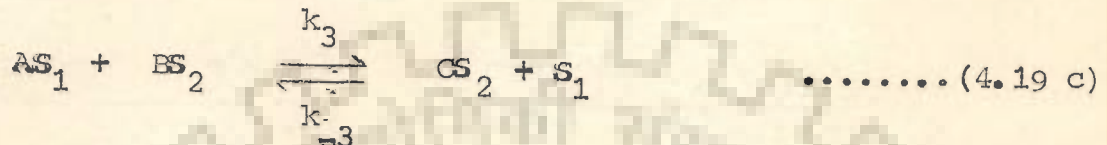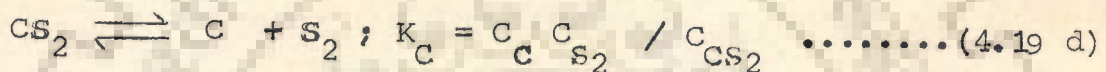
The total concentration of sites S_1 and S_2 is given by

$$C_{T_1} = C_{AS_1} + C_{S_1} \quad \ldots\ldots\ldots (4.20)$$

$$C_{T_2} = C_{BS_2} + C_{CS_2} + C_{S_2} \quad \ldots\ldots\ldots (4.21)$$

When surface reaction, i.e. step 3, is rate controlling the rate of reaction is given by

$$r = k_3 \, C_{AS_1} \, C_{AS_2} \quad \ldots\ldots\ldots (4.22)$$

Eliminating C_{AS_1} and C_{AS_2} from equations 4.19 – 4.22, we get,

$$r = \frac{k_3 \, C_{T_1} \, C_{T_2} \, K_A \, K_B \, C_A \, C_B}{(1 + K_A C_A)(1 + K_B C_B + K_C C_C)} \quad \ldots\ldots (4.23)$$

Substituting k for $k_3 \, C_{T_1} \, C_{T_2}$ and neglecting the adsorption of saturates, the resultant equation becomes model–5, i.e.

$$r = \frac{k \, K_A \, K_B \, C_A \, C_B}{(1 + K_A \, C_A)(1 + K_B \, C_B)} \qquad \cdots\cdots\cdots\cdots (4.24)$$

In model -6, A is assumed to be adsorbed dissociatively on sites S_1; B is adsorbed associatively on sites S_2 and the surface reaction between adsorbed A and adsorbed B is rate controlling. Under these assumptions, the sequence of elementary steps are:

First step: adsorption of hydrogen on sites S_1
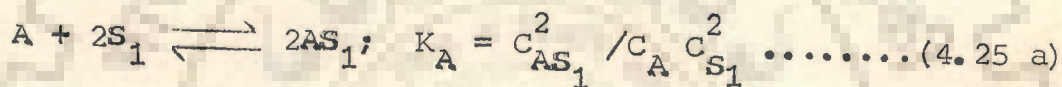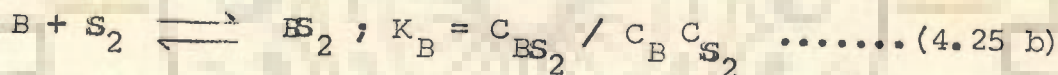
$$A + 2S_1 \rightleftharpoons 2AS_1 ; \quad K_A = c_{AS_1}^2 \, / c_A \, c_{S_1}^2 \quad \cdots\cdots\cdots (4.25 \text{ a})$$

Second step: adsorption of olefin on sites S_2

$$B + S_2 \rightleftharpoons BS_2 ; \quad K_B = C_{BS_2} \, / \, C_B \, C_{S_2} \quad \cdots\cdots\cdots (4.25 \text{ b})$$

Third step: surface reaction between adsorbed A and adsorbed B

$$BS_2 + 2AS_1 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CS_2 + 2S_1 \qquad \cdots\cdots\cdots (4.25 \text{ c})$$

Fourth setp: desorption of products

$$CS_2 \rightleftharpoons C + S_2 ; \quad K_C = c_C \, c_{S_2} \, / \, c_{CS_2} \quad \cdots\cdots\cdots (4.25 \text{ d})$$
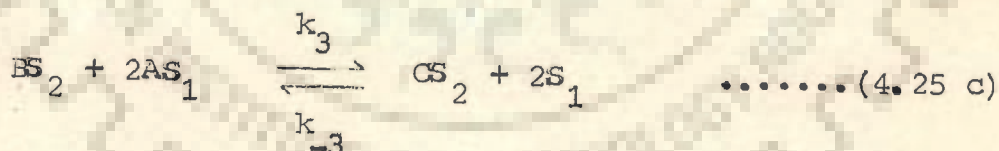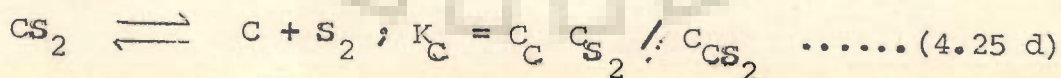
Following the similar procedure as described for model-5, the resultant rate equation becomes,

$$r = \frac{k_3 \, c_{T_1}^2 \, c_{T_2} \quad K_A \, K_B \, C_A \, C_B}{(1 + \sqrt{K_A \, C_A})^2 (1 + K_B C_B + K_C \, C_C)} \qquad \ldots\ldots (4.26)$$

Substituting k for $k_3 \, c_{T_1} \, c_{T_2}$ and taking the term $K_C \, C_C$ (adsorption of saturates to be negligible as compared to $1 + K_B C_B$, Equation 4.26 reduces to

$$r = \frac{k \, K_A \, K_B \, C_A \, C_B}{(1 + \sqrt{K_A C_A})^2 (1 + K_B C_B)} \qquad \ldots\ldots\ldots\ldots (4.27)$$

MODELS -7 & 8

In these models, olefin is assumed to be adsorbed competitively as well as non-competitively with hydrogen. Following the similar procedure as described above for the deduction of models 5 and 6, the following resultant rate equations are obtained for models 7 and 8 respectively.

$$r = \frac{k \, K_A \, K_B \, C_A \, C_B}{(1 + \sqrt{K_A C_A + K_B C_B})^2 (1 + K_B C_B)} \qquad \ldots\ldots (4.28)$$

$$r = \frac{k \, K_A \, K_B \, C_A \, C_B}{(1 + K_A C_A + K_B C_B)(1 + K_B \, C_B)} \qquad \ldots\ldots (4.29)$$

Model Equations 5 and 7 can also be derived on the basis of a mechanism in which addition of hydrogen takes place in two steps via a half-hydrogenated

state as suggested by Horuity and Polanyi.[161] The

modified mechanism steps for this are given below:

<u>Step 1</u> - equilibrium of hydrogen in liquid phase and
catalyst,

$$A^{(1)} \rightleftharpoons A^{(p)} \qquad \ldots\ldots\ldots (4.31)$$
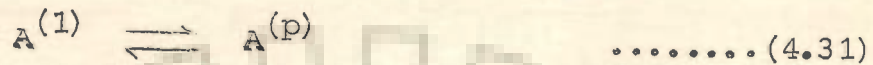
<u>Step 2</u>- dissociative adsorption of hydrogen on surface
on sites S_1

$$A + 2S_1 \rightleftharpoons 2AS_1 \; ; \; K_A = c_{AS_1}^2 / c_A \, c_{S_1}^2 \quad \ldots\ldots (4.32a)$$
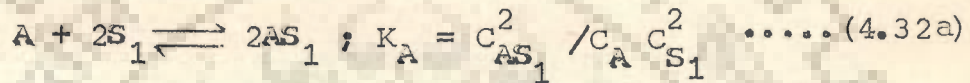
<u>Step 3</u>- associative adsorption of olefin on the
catalyst surface through π-complex on
sites S_2

$$B + S_2 \rightleftharpoons BS_2 ; \; K_B = c_{BS_2} / c_B \, c_{S_2} \quad \ldots\ldots (4.32\,b)$$
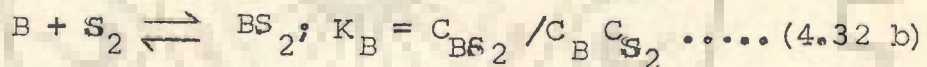
<u>Step 4</u>- addition of first hydrogen atom to the
adsorbed olefin in form of a semi-hydrogenated
state, which is adsorbed on sites S_2

$$BS_2 + AS_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} BAS_2 + S_1 \quad \ldots\ldots\ldots (4.32\,c)$$
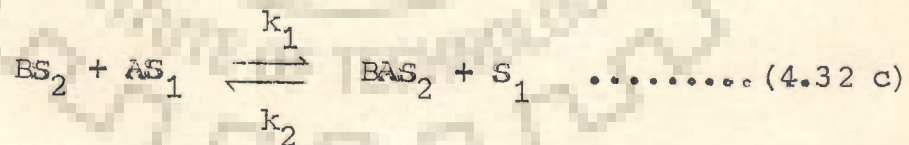
<u>Step 5</u>- addition of second hydrogen atom, leading to
the formation of products

$$BAS_2 + AS_1 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} CS_2 + S_1 \quad \ldots\ldots (4.32\,d)$$

Step 6- desorption of products

$$CS_2 \rightleftharpoons C + S_2 \; ; \; K_C = C_C \, C_{S_2} / C_{CS_2} \quad \ldots\ldots(4.32 \text{ e})$$
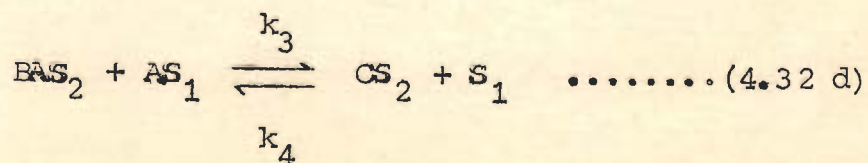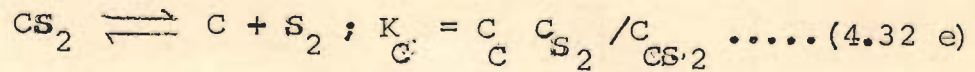
The total concentration of sites S_1 and S_2 are given by

$$C_{T_1} = C_{AS_1} + C_{S_1} \quad \ldots\ldots\ldots \quad (4.33)$$

$$C_{T_2} = C_{BS_2} + C_{CS_2} + C_{S_2} \quad \ldots\ldots\ldots (4.34)$$

The concentration of sites occupied by the semi-hydrogenated species and the paraffin products are assumed to be negligible.

Now, the stationary state as applied to steps 4 and 5 may be expressed in the following form:

$$k_1 C_{BS_2} \, C_{AS_1} - k_2 \, C_{BAS_2} \, C_{S_1} - k_3 \, C_{BAS_2} \, C_{AS_1} + k_4 \, C_{CS_2} C_{S_1} = 0$$

therefore,

$$C_{BAS_2} = \frac{k_1 C_{BAS_2} \, C_{AS_1} + k_4 \, C_{CS_2} + C_{S_1}}{k_2 + k_3 \, C_{AS_1}}$$

neglecting $k_3 C_{AS_1}$ in comparison to k_2, this reduces to,

$$C_{BAS_2} \simeq \frac{k_1}{k_2} C_{BS_2} C_{HS_1} + \frac{k_4}{k_2} C_{CS_2} \, C_{S_1}^2 \quad \ldots\ldots (4.35)$$

At lower temperatures, the dehydrogenation of saturated hydrocarbon is almost absent, i.e. $k_4 \ll k_1$, so that only the first term remains on the RHS of Equation (4.35).

Hence, the rate of hydrogenation, i.e. the rate of formation of paraffin product, C, is given by

$$r = k_3 C_{BAS_2} C_{AS_1}$$

or
$$r = k_3 \frac{k_1}{k_2} C_{BS_2} C_{AS_1}^2 \quad \dots\dots\dots\dots (4.36)$$

Now, elimination of C_{BS_2} and C_{AS_1} from equations 4.33, 4.34 and 4.36 and substituting the values of C_{S_1} and C_{S_2} in terms of equilibrium constants, K_A and K_B and neglecting the adsorption of paraffin, the following rate Equation is obtained:

$$r = \frac{k_3 k_1 C_{T_1}^2 C_{T_2} K_A K_B C_A C_B}{k_2 (1 + \sqrt{K_A C_A})^2 (1 + K_B C_B)} \quad \dots\dots\dots (4.37)$$

assuming $\dfrac{k_3 k_1}{k_2} C_{T_1}^2 C_{T_2} = k$, this reduces to the following resultant equation, which is the same as that of model-5.

$$r = \frac{k K_A K_3 C_A C_B}{(1 + \sqrt{K_A C_A})^2 (1 + K_B C_B)} \quad \dots\dots\dots (4.38)$$

When both competitive and non-competitive adsorption of olefin are considered, a similar procedure as discussed above leads to model Equation 7.

All the models, assumptions and the corresponding rate equations are summarised in Table 4.9.

TABLE 4.9

RATE MODELS TESTED

Model	Assumptions	Rate equation[a]
1.	Langmuir-Hinshelwood model-equilibrium concentration of C_8H_{16} and H_2 on same sites-reaction occuring between adsorbed reactants	$r = k\, K_A K_B C_A C_B\, /\, (1+K_A C_A+K_B C_B)^2$
2.	Langmuir-Hinshelwood model-equilibrium concentration of C_8H_{16} and dissociated H_2 on same sites-reaction occuring between adsorbed reactants.	$r = k\, K_A K_B C_A C_B\, /\, (1+ \sqrt{K_A C_A}+K_B C_B)^3$
3.	Rideal model-C_8H_{16} not adsorbed, reaction occuring between adsorbed H_2 and liquid phase C_8H_{16}	$r = k\, K_A C_A C_B\, /\, (1 + K_A C_A)$
4.	Rideal model-C_8H_{16} not adsorbed, H_2 dissociatively adsorbed, reaction between dissociated H_2 and C_8H_{16} rate controlling.	$r = k\, K_A C_A C_B\, /\, (1 + \sqrt{K_A C_A})^2$
5.	Langmuir-Hinshelwood model-equilibrium concentration of C_8H_{16} and dissociated H_2 on different sites-reaction occuring between adsorbed reactants.	$r = k\, K_A K_B C_A C_B\, /\, (1+ \sqrt{K_A C_A})^2 /(1+K_B C_B)$
6.	Langmuir-Hinshelwood model-equilibrium concentration of C_8H_{16} and H_2 on different sites reaction occuring between adsorbed reactants.	$r = k\, K_A K_B C_A C_B\, /\, (1+ K_A C_A) /(1+K_B C_B)$
7.	Langmuir-Hinshelwood model-equilibrium concentration of C_8H_{16} and dissociated H_2 on different sites, olefin complete for the same sites also-reaction occuring between adsorbed reactants.	$r = k\, K_A K_B C_A C_B\, /\, (1 + \sqrt{K_A C_A}+K_B C_B)^2 /\, (1+ K_B C_B)$
8.	Langmuir-Hinshelwood model-equilibrium concentration of C_8H_{16} and H_2 on different sites; olefin complete for the same sites also-reaction occuring between adsorbed reactants.	$r = k\, K_A K_B C_A C_B\, /\, (1 +K_A C_A+K_B C_B) /\, (1 + K_B C_B)$

(a) where k = kinetic rate constant, $kmol.kg\text{-}cat.^{-1}hr$; K_A and K_B are adsorption equilibrium constants for H_2 and olefin respectively, $m^3.kmol^{-1}$.

PARAMETER ESTIMATION AND MODEL DISCRIMINATION:

The experimental rate data were fitted into the above mentioned rate equations, separately for each olefin, for finding the best fitting equation.

The procedure usually adopted in the treatment of kinetic data to find the best fitting rate equation is that the assumed rate equation (which for hetero- geneous catalytic reactions is usually non-linear with respect to parameters) is transformed to a linear form[130]. By the method of linear regression, estimates of the constants of the linearised equation are then obtained and the suitability of different kinetic models for representing the experimental data, expressed as variables of the linearized rate equation, is then assessed. Finally, the parameters of the original rate equation are calculated from the estimates of the constants of the linearized equation. This procedure has lately been criticized by several authors in the literature[141-147] from the stand point of statistical methods. The main argument against the procedure outlined above is that by transforming the experimental data into variables by the linearized equation, the normal distribution of the error of dependent variable is distorted and this invalidates the basic assumption of the regression analysis applied. When this assumption is not

fulfilled, the application of linear least square method may yield incorrect estimates of the kinetic constants and can lead to the establishment of an inappropriate order of suitability of the different kinetic models, with the possible result that a particular model may erroneously be rejected[148, 149].

As suggested in the cited papers, these inadequacies can be obviated by using non-linear regression analysis in which the optimum values of the parameters of the model assumed are determined, for example, by applying the criterion of minimum sum of squares of deviation between the experimentally determined and calculated values of the kinetic variables (reaction rate, conversion etc), without prior transformation (linearization) of the experimental results.

The authors of the above mentioned papers have used non-linear regression[142-146, 150-152] for re-evaluating some older data on heterogeneous catalytic reactions. The procedure has not been described by them in detail; usually it consisted of a combination of the Gauss-Newton[153-155] and the steepest descent[156] methods as developed by Marquardt[157]. Like other iterative procedures, it requires at the start an approximate estimate of the parameters to be determined. Kittrell et al.[121] mentioned some methods of obtaining such first

estimates; among these they mention grid search method. In this work, we used the grid search technique with sparse grid points to estimate the initial estimates of the parameters. Some approximate estimates were obtained from the earlier investigations on hydrogenation[135] in which the linear least square analysis was used to estimate the model parameters. From these initial estimates, precise estimates of the parameters were made using the grid search technique by continuously reducing the grid size till no change in the sum of squares of residuals between the experimental and calculated reaction rates was obtained. Later, Marquardt method[158] was also used to estimate the parameters of some of the good fitting models. Computer programs were developed for both of these methods of parameter estimation for use in IBM 370/145 computer. These programs estimated the parameters, K, by minimizing the residual sum of squares:

$$S_1^2 = \frac{\min}{\vec{K}} \sum_{i=1}^{N} (r_i - \hat{r}_i)^2 \qquad \ldots\ldots\ldots (4.39)$$

The results of such non-linear analysis is summarised in Tables 4.10(a), (b) and (c); both Grid search as well as Marquardt method gave closely agreeing results; however, the computer time required for the grid search method was considerably large. The parameter

TABLE 4.10(a)

NON-LINEAR PARAMETER ESTIMATION RESULTS :
HYDROGENATION OF ISOOCTENES (GRID SEARCH METHOD)

Model No.	Temp. K	k kmol.hr^{-1} kg-cat^{-1}	K_A m^3.kmol^{-1}	K_B m^3.kmol^{-1}	Avg. Abs.% error e	Residual sum of squares S_1^2 (kmol.hr^{-1} kg-cat^{-1})^2
1	303	0.920	0.375	7.50	40.46	0.6646×10^{-3}
	313	1.807	0.375	6.875	29.26	0.29380×10^{-2}
	333	3.866	0.375	2.250	32.66	0.25160×10^{-1}
2	303	0.0797	394.375	3.500	8.77	0.2429×10^{-4}
	313	0.1791	1102.50	6.875	10.87	0.2416×10^{-3}
	333	0.9949	88.750	3.125	10.86	0.3248×10^{-2}
3	303	0.04173	7.875	—	38.76	0.4625×10^{-3}
	313	0.05321	28.75	—	50.34	0.5558×10^{-2}
	333	0.1294	1150.0	—	51.76	0.8407×10^{-1}
4	303	0.1257	3.5	—	38.92	0.4665×10^{-3}
	313	0.0833	48.75	—	50.70	0.5635×10^{-2}
	333	0.1277	5890	—	51.97	0.8410×10^{-1}
5	303	0.01149	331.88	34.38	0.27	0.6535×10^{-7}
	313	0.03154	258.13	26.87	1.22	0.4396×10^{-5}
	333	0.1408	92.50	24.38	2.48	0.9570×10^{-4}
6	303	0.00927	83.12	34.37	0.70	0.20818×10^{-6}
	313	0.0250	70.00	26.88	1.3	0.41890×10^{-5}
	333	0.1001	39.38	24.37	1.6	0.90197×10^{-4}
7	303	0.0107	57845.0	7.25	5.08	0.7679×10^{-5}
	313	0.0286	54390.0	7.87	4.82	0.5756×10^{-4}
	333	0.1522	3305.0	4.75	8.15	0.1923×10^{-2}
8	303	0.0092	6211.25	4.50	4.38	0.3082×10^{-3}
	313	0.0260	821.00	9.38	4.80	0.3502×10^{-4}
	333	0.1136	251.25	7.50	7.06	0.1024×10^{-2}

TABLE 4.10(b)

NON-LINEAR PARAMETER ESTIMATION RESULTS :

HYDROGENATION OF n-OCTENES (GRID SEARCH METHOD)

Model No.	Temp. K	k kmol.hr^{-1} kg-cat^{-1}	K_A m^3.kmol^{-1}	K_B m^3.kmol^{-1}	Avg. Abs.% error e	Residual sum of squares S_1^2 (kmol.hr^{-1} kg-cat^{-1})^2
1	303	1.204	0.375	0.375	25.39	0.1185 x 10^{-2}
	313	2.168	0.38	1.63	38.22	0.8563 x 10^{-2}
	333	0.1124	62.50	1.62	56.58	0.11060 x 10^{-1}
2	303	0.1726	506.88	5.00	18.41	0.5557 x 10^{-3}
	313	0.4424	216.25	3.75	16.35	0.1599 x 10^{-2}
	333	1.8960	112.50	3.13	30.82	0.3172 x 10^{-1}
3	303	0.5304	0.375	--	32.10	0.1573 x 10^{-2}
	313	0.0716	65.0	--	66.70	0.3402 x 10^{-1}
	333	0.3031	40.0	--	71.08	0.4258 x 10^{0}
4	303	0.7699	0.375	--	32.99	0.1673 x 10^{-2}
	313	0.08891	253.75	--	67.01	0.3425 x 10^{-1}
	333	0.4176	100.625	--	71.13	0.4293 x 10^{0}
5	303	0.02343	346.88	40.62	0.98	0.5116 x 10^{-5}
	313	0.05598	258.13	28.13	1.21	0.2325 x 10^{-4}
	333	0.2637	96.87	19.37	2.38	0.1236 x 10^{-2}
6	303	0.0190	83.75	41.88	1.6	0.5625 x 10^{-5}
	313	0.0446	70.00	27.5	1.3	0.2477 x 10^{-4}
	333	0.1892	40.63	18.75	2.16	0.1221 x 10^{-2}
7	303	0.1151	104.37	1.00	13.29	0.4401 x 10^{-3}
	313	0.04689	50028.0	11.00	7.457	0.4023 x 10^{-3}
	333	0.2478	9315.0	5.38	26.78	0.2100 x 10^{-1}
8	303	0.01674	766.87	46.25	4.80	0.4173 x 10^{-4}
	313	0.04540	1090.00	11.87	6.27	0.26514 x 10^{-3}
	333	0.2041	359.38	7.50	25.49	0.1748 x 10^{-1}

TABLE 4.10(c)

NON-LINEAR PARAMETER ESTIMATION RESULTS : HYDROGENATION OF ISODODECENES (GRID SEARCH METHOD)

Model No.	Temp. K	k $kmol.hr^{-1}$ $kg\text{-}cat^{-1}$	K_A $m^3.kmol^{-1}$	K_E $m^3.kmol^{-1}$	Avg. Abs.% error e	Residual sum of squares S_i^2 $(kmol.hr^{-1} kg\text{-}cat^{-1})^2$
1	303	0.5161	0.375	0.375	30.14	0.1737×10^{-3}
	313	0.6879	0.375	1.625	36.66	0.9413×10^{-3}
	333	0.0344	70.0	2.25	38.08	0.1445×10^{-1}
2	303	0.07937	110.62	2.25	6.04	0.7154×10^{-5}
	313	0.1374	231.63	3.50	7.55	0.4852×10^{-4}
	333	0.6916	85.60	3.12	18.02	0.4243×10^{-2}
3	303	0.1087	1.625	-	38.79	0.2420×10^{-3}
	313	0.0225	58.75	-	56.24	0.2493×10^{-2}
	333	0.1014	48.125	-	56.18	0.4156×10^{-1}
4	303	0.3250	0.375	-	38.60	0.2449×10^{-3}
	313	0.0286	205.62	-	56.66	0.2513×10^{-2}
	333	0.1322	148.75	-	65.55	0.4183×10^{-1}
5	303	0.007749	424.38	43.75	0.81	0.8978×10^{-6}
	313	0.01834	274.37	31.88	0.23	0.8384×10^{-6}
	333	0.07798	124.30	23.75	7.99	0.1021×10^{-2}
6	303	0.0064	93.75	42.5	1.2	0.9259×10^{-6}
	313	0.0148	71.25	20.62	0.77	0.1085×10^{-5}
	333	0.0576	46.25	33.12	6.8	0.1034×10^{-2}
7	303	0.04053	108.13	1.00	9.74	0.1992×10^{-4}
	313	0.02569	347.0	3.50	3.80	0.1155×10^{-4}
	333	0.04932	587.90	22.87	13.45	0.2395×10^{-2}
8	303	0.00845	518.75	5.00	-	0.1952×10^{-5}
	313	0.01552	249.38	7.50	-	0.2409×10^{-4}
	333	0.05799	910.63	16.87	-	0.1211×10^{-2}

estimates for models 1, 5 and 8 obtained by Marquardt method are given in Tables 4.11 a, 4.11 b and 4.11 c.

Criteria for discrimination among models

For the discrimination among various models, the following four criteria were used;

1. The values of rate and adsorption constants should be positive.

2. The variation of rate parameters with temperature should be amenable to correlation using Arrhenius plot; the equilibrium adsorption constants should follow Vant Hoff's criteria.

3. A judgement of the behaviour of models may be achieved through the analysis of values of the statistical parameters R^2, F and FE. The parameters F and FE were compared with the corresponding values of the F test tables multiplied by the safety coefficients. If at the same time, FE $<$ 3 FET and F $>$ 10 FT the model may be considered good[159], 3 and 10 are safety coefficients. Tables 4.12 a, 4.12 b and 4.12 c show the results of such statistical analysis for the hydrogenation of isooctenes, isododecenes and n-octenes respectively. In Tables 4.12 a, 4.12 b and 4.12 c, R^2 is the determination index:

TABLE 4.11(a)

RESULTS OF NON-LINEAR PARAMETER ESTIMATION
(BY MARQUARDT METHOD) FOR HYDROGENATION OF ISOOCTENES

Model No.	Temp. K	k kmol.kg-cat^{-1} hr^{-1}	K_A m^3.kmol^{-1}	K_B m^3.kmol^{-1}	S_1^2 (kmol.kg-cat^{-1}.hr^{-1})^2
2	303	0.07990	390.00	10.00	0.2911×10^{-4}
	313	0.17790	1098.11	6.83	0.2340×10^{-3}
	333	0.95690	100.38	3.29	0.3130×10^{-2}
5	303	0.01150	332.63	34.10	0.6632×10^{-7}
	313	0.03160	260.21	26.58	0.4388×10^{-5}
	333	0.14140	93.03	24.19	0.9558×10^{-4}
8	303	0.00996	862.46	8.11	0.5095×10^{-5}
	313	0.02600	852.01	9.60	0.3486×10^{-4}
	333	0.01163	234.64	7.18	0.1017×10^{-2}

TABLE 4.11(b)

RESULTS OF NON-LINEAR PARAMETER ESTIMATION
(BY MARQUARDT METHOD) FOR HYDROGENATION OF n-OCTENES

Model No.	Temp. K	k kmol. kg-cat^{-1} hr^{-1}	K_A m^3.kmol^{-1}	K_B m^3.kmol^{-1}	S_1^2 (kmol.kg-cat^{-1}.hr^{-1})^2
2	303	0.33580	423.20	1.45	0.4364×10^{-3}
	313	0.45020	183.73	3.49	0.1509×10^{-2}
	333	2.07310	74.69	2.63	0.2943×10^{-1}
5	303	0.02344	347.56	40.70	0.5101×10^{-5}
	313	0.05617	258.18	27.19	0.2323×10^{-4}
	333	0.26590	96.29	19.01	0.1235×10^{-2}
8	303	0.01673	7597.80	45.99	0.4172×10^{-4}
	313	0.04532	1118.16	12.05	0.2646×10^{-3}
	333	0.20510	348.48	7.38	0.1735×10^{-1}

TABLE 4.11(c)

RESULTS OF NON-LINEAR PARAMETER ESTIMATION

(BY MARQUARDT METHOD) FOR HYDROGENATION OF ISODODECENES

Model No.	Temp. K	k kmol. kg-cat^{-1} hr^{-1}	K_A m^3.kmol^{-1}	K_B m^3.kmol^{-1}	S_1^2 (kmol.kg-cat^{-1}.hr^{-1})^2
2	303	0.09470	86.07	1.99	0.6896×10^{-5}
	313	0.15550	141.53	2.80	0.4465×10^{-4}
	333	0.68810	75.02	2.96	0.3954×10^{-2}
5	303	0.00775	424.82	43.73	0.8977×10^{-6}
	313	0.01842	273.17	21.61	0.8368×10^{-6}
	333	0.07814	123.08	23.53	0.1020×10^{-2}
8	303	0.00895	346.89	5.34	0.3054×10^{-5}
	313	0.01740	443.86	6.55	0.1091×10^{-4}
	333	0.05420	1038.94	15 74	0.1989×10^{-2}

TABLE 4.12(a)

STATISTICAL ANALYSIS OF KINETIC MODELS :
HYDROGENATION OF ISOOCTENE

Model No.	Temp. $^\circ K$	R^2	F	$10 \times FT$	FE	$3 \times FET$
1	303	0.7360	7.9774×10^4	27.8631	169.450	58.444
	313	0.8301	1.8039×10^4	27.8631	749.100	58.444
	333	0.8898	2.106×10^3	27.8631	6415.000	58.444
2	303	0.9903	2.182×10^6	27.8631	6.190	58.444
	313	0.9860	2.193×10^5	27.8631	61.600	58.444
	333	0.9857	1.631×10^4	27.8631	828.140	58.444
3	303	0.8162	1.145×10^5	31.7479	117.920	58.444
	313	0.6786	9.535×10^3	31.7479	1417.130	58.444
	333	0.6319	6.304×10^2	31.7479	21435.490	58.444
4	303	0.8147	1.136×10^5	31.7479	118.940	58.444
	313	0.6742	9.405×10^3	31.7479	1436.760	58.444
	333	0.6317	6.302×10^2	31.7479	21443.140	58.444
5	303	0.9999	8.110×10^8	27.8631	0.017	58.444
	313	0.9997	1.205×10^7	27.8631	1.121	58.444
	333	0.9995	5.538×10^5	27.8631	24.401	58.444
6	303	0.9999	2.545×10^8	27.8631	0.053	58.444
	313	0.9997	1.265×10^7	27.8631	1.060	58.444
	333	0.9996	5.876×10^5	27.8631	22.998	58.444
7	303	0.9969	6.901×10^6	27.8631	1.958	58.444
	313	0.9966	9.207×10^5	27.8631	14.676	58.444
	333	0.9915	2.756×10^4	27.8631	490.311	58.444
8	303	0.8775	1.719×10^5	27.8631	78.582	58.444
	313	0.9979	1.513×10^6	27.8631	8.929	58.444
	333	0.9955	5.175×10^4	27.8631	281.091	58.444

TABLE 4.12 (b)

STATISTICAL ANALYSIS OF KINETIC MODELS :
HYDROGENATION OF ISODODECENE

Model No.	Temp. K	R^2	F	$10 \times FT$	FE	$3 \times FET$
1	303	0.8616	3.051×10^5	27.8631	44.288	58.444
	313	0.8524	5.630×10^4	27.8631	240.005	58.444
	333	0.8194	3.667×10^3	27.8631	3684.300	58.444
2	303	0.9943	7.408×10^6	27.8631	1.824	58.444
	313	0.9924	1.092×10^6	27.8631	12.371	58.444
	333	0.9469	1.249×10^4	27.8631	1081.000	58.444
3	303	0.8072	2.190×10^5	31.7479	61.703	58.444
	313	0.6092	2.125×10^5	31.7479	635.645	58.444
	333	0.4806	1.275×10^3	31.7479	10596.600	58.444
4	303	0.8049	2.164×10^5	31.7479	62.442	58.444
	313	0.6061	2.109×10^4	31.7479	640.744	58.444
	333	0.4773	1.267×10^3	31.7479	10665.400	58.444
5	303	0.9993	5.903×10^7	27.8631	0.229	58.444
	313	0.9998	6.321×10^7	27.8631	0.214	58.444
	333	0.9872	5.190×10^4	27.8631	260.326	58.444
6	303	0.9992	5.724×10^7	27.8631	0.236	58.444
	313	0.9998	4.884×10^7	27.8631	0.276	58.444
	333	0.9870	5.125×10^4	27.8631	263.641	58.444
7	303	0.9841	2.660×10^6	27.8631	5.079	58.444
	313	0.9982	4.588×10^6	27.8631	2.945	58.444
	333	0.9700	2.212×10^4	27.8631	610.657	58.444
8	303	0.9984	2.715×10^6	27.8631	0.498	58.444
	313	0.9962	2.200×10^6	27.8631	6.142	58.444
	333	0.9842	4.376×10^4	27.8631	308.771	58.444

TABLE 4.12 (c)

STATISTICAL ANALYSIS OF KINETIC MODELS :
HYDROGENATION OF n-OCTENES

Model No.	Temp. K	R^2	F	10 x FT	FE	3 x FET
1	303	0.8991	4.472×10^4	27.8631	302.140	58.444
	313	0.8508	6.1894×10^3	27.8631	2183.320	58.444
	333	0.9628	4.7920×10^2	27.8631	28199.000	58.444
2	303	0.9527	9.537×10^4	27.8631	141.680	58.444
	313	0.9721	0.3314×10^4	27.8631	407.700	58.444
	333	0.9893	1.6708×10^3	27.8631	8087.710	58.444
3	303	0.8661	3.3693×10^4	31.7479	401.070	58.444
	313	0.4076	1.5579×10^3	31.7479	8674.140	58.444
	333	0.8566	1.2444×10^2	31.7479	108592.000	58.444
4	303	0.8576	3.1679×10^4	31.7479	401.070	58.444
	313	0.4076	1.5579×10^3	31.7479	87327.800	58.444
	333	0.8554	1.2345×10^2	31.7479	109459.000	58.444
5	303	0.9995	1.0359×10^7	27.8631	1.304	58.444
	313	0.9996	2.2795×10^6	27.8631	5.928	58.444
	333	0.9996	4.2880×10^4	27.8631	315.140	58.444
6	303	0.9995	9.4222×10^6	27.8631	1.434	58.444
	313	0.9996	2.1396×10^6	27.8631	6.315	58.444
	333	0.9996	4.3407×10^5	27.8631	311.320	58.444
7	303	0.9625	1.2042×10^5	27.8631	112.210	58.444
	313	0.9929	1.3174×10^5	27.8631	102.570	58.444
	333	0.9930	2.5238×10^3	27.8631	5354.400	58.444
8	303	0.9965	1.2700×10^6	27.8631	10.630	58.444
	313	0.9954	1.9989×10^5	27.8631	67.600	58.444
	333	0.9941	3.0320×10^3	27.8631	4456.900	58.444

$$R^2 = 1 - \sum_{i=1}^{N} (r_i - \hat{r}_i)^2 \Big/ \sum_{i=1}^{N} r_i^2 \quad \ldots (4.40)$$

F is the ratio between the square mean due to regression and the square mean due to error calculated with the model:

$$F = \frac{\left[\sum_{i=1}^{N} r_i^2 - \sum_{i=1}^{N} (r_i - \hat{r}_i)^2 \right] / N_p}{\sum_{i=1}^{N} (r_i - \hat{r}_i)^2 / (N - N_p)} \quad \ldots (4.41)$$

FE is the ratio between the square mean due to error calculated with the model and experimental error variance (σ^{-2}):

$$FE = \frac{\sum_{i=1}^{N} (r_i - \hat{r}_i)^2 / (N - N_p)}{\sigma^{-2}} \quad \ldots (4.42)$$

4.   Problems of discriminating between two or more models which satisfy the above three criteria are solved by considering the degree of correlation of the data and analysis of residuals for each model.

Selection of best kinetic model

From Tables 4.10 a, b and c, it can be seen that all the models have positive rate and adsorption constants for isooctenes, n-octenes and iso-dodecenes and satisfy criterion 1. Models 5 and 6 showed the lowest values of s_1^2 and average absolute

error and, therefore, can be considered to be suitable to describe the kinetic data. The constants of both models 5 and 6 also showed a regular trend with temperature in cases of isooctenes and n-octenes; k increased with increase of temperature, while both K_A and K_B decreased with increasing temperature. For isododecenes, however, K_B for model 6 first decreased from 42.5 $m^3.kmol^{-1}$ at 303 K to 20.62 $m^3.kmol^{-1}$ at 333 K and then increased to a value of 33.12 $m^3.kmol^{-1}$ at 333 K. This indicates that atleast for isododecenes, model 6 is unsuitable conforming to the criteria.

The results of statistical analysis (Table 4.12 a, b & c) also show that models 5 and 6 appear to be adequate to describe the kinetic data.

It may be noted that the degree of correlation of the kinetic data differ slightly from one temperature to another. These differences can be due to the imprecisions of the results at the higher temperature. At 333 K, for isododecenes and n-octenes the values of FE were slightly higher than 3 FET for both models 5 and 6. This, however, does not invalidate these models. From the relative magnitudes of e, S_1^2, F and FE, it appears that model 5 is superior to model 6 to represent the hydrogenation data for all the three olefins.

The above conclusion that model 5 fits the data better than model 6 is also supported by the

plots of calculated rates versus the observed rates
for the two models. These plots are shown in Figures
4.25 - 4.33. From these plots it can be seen that for
model 5, the overall trend does not exhibit any
heteroscedatic pattern while for model 6, the points
are not randomly distributed along the line of unity
slope. Although model 5 was thus selected as the most
favourable one for reasons discussed above, a further
test was performed to see whether the model truely
represents the data. Plots of the residual $r_i - \hat{r}_i$,
versus the predicted value, $\hat{r}_i$, based on the two models
are shown in Figures 4.34-4.36. From these plots it
can be seen that the points for model 5 are well
distributed on both sides of zero deviation line, while
for model 6 the points show a trend. In other words,
the residuals for model 5 are randomly distributed,
which indicate that model 5 is superior to model 6.

Thus, examining models 5 and 6 from different
angles as discussed above, model 5 can be accepted to
be the most plausible one which represents the data
well over the whole range of variables studied. The
constants k, K_A and K_B in the rate equation for
model 5, which obeyed Arrhenius behaviour, can be
expressed as a function of temperature in the cases
of the 3 olefins used as feed are given below:
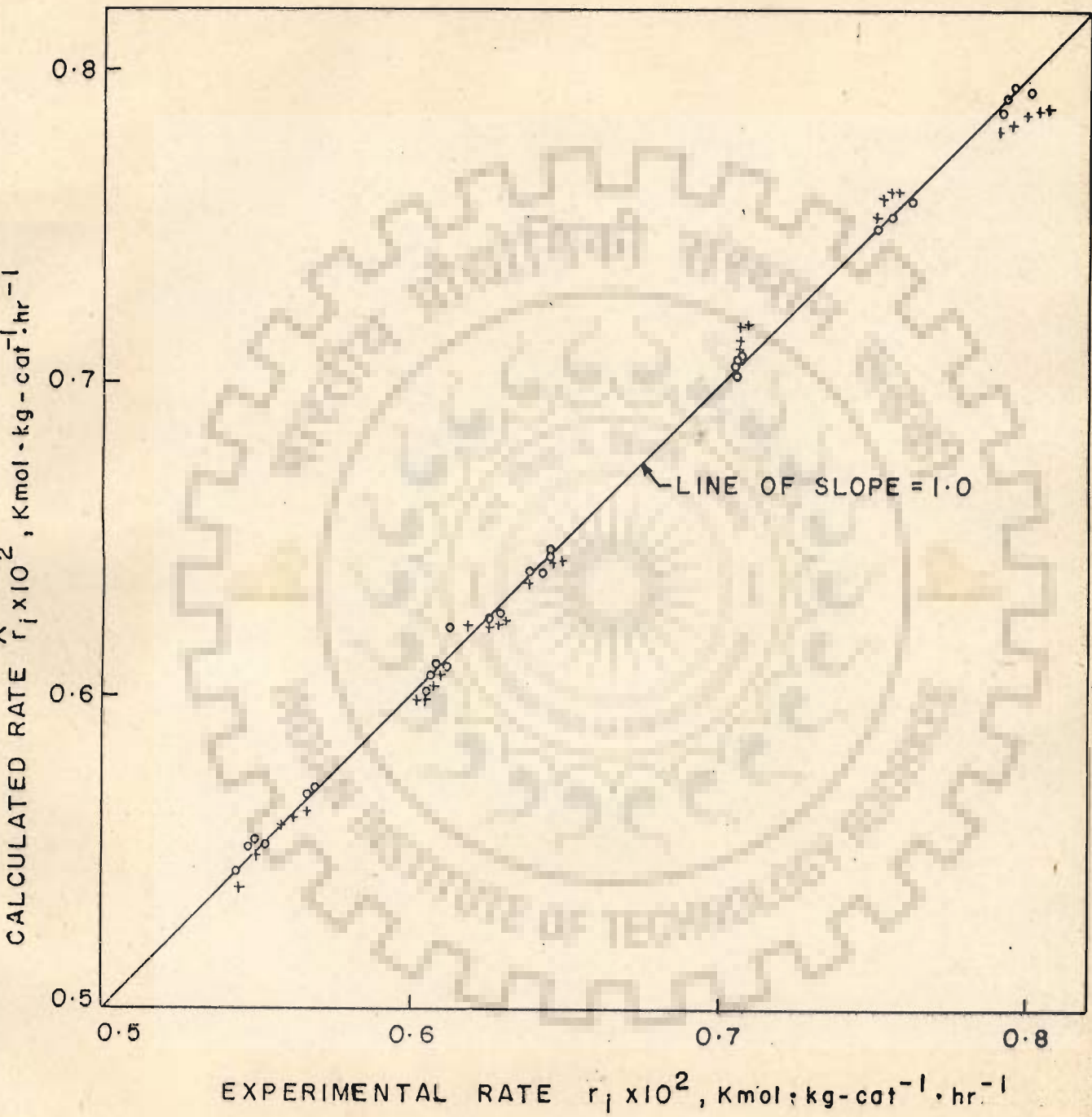
FIG. 4·25 - CALCULATED VERSUS OBSERVED REACTION RATES:
(o) MODEL 5, AT 303K; (+) MODEL 6 AT 303 K;
OLEFIN - ISOOCTENE.
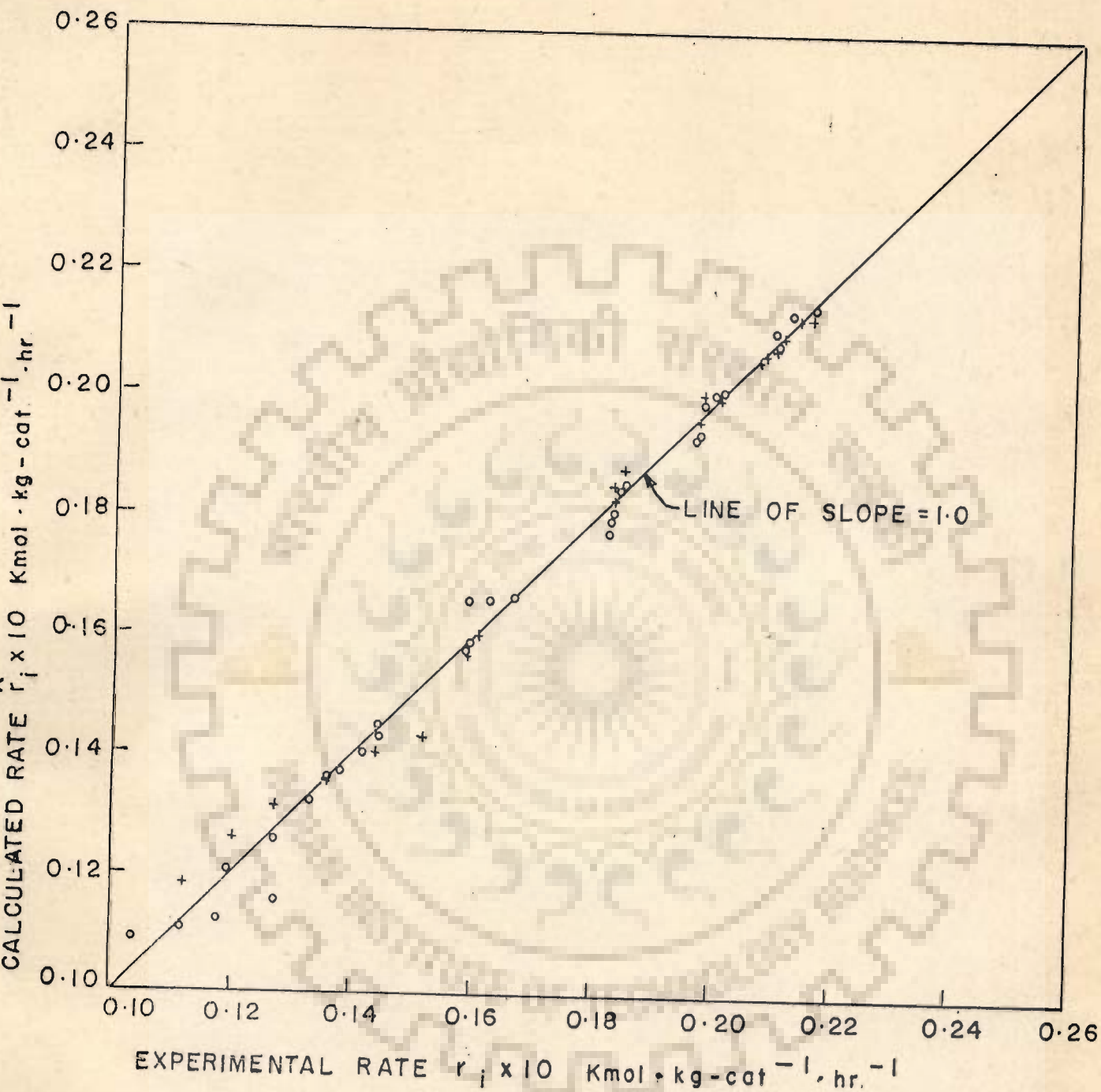
FIG. 4·26 — CALCULATED VERSUS OBSERVED RATES : (o) MODEL 5 AT 313 K ; (+) MODEL 6 AT 313 K ; OLEFIN – ISOOCTENE.
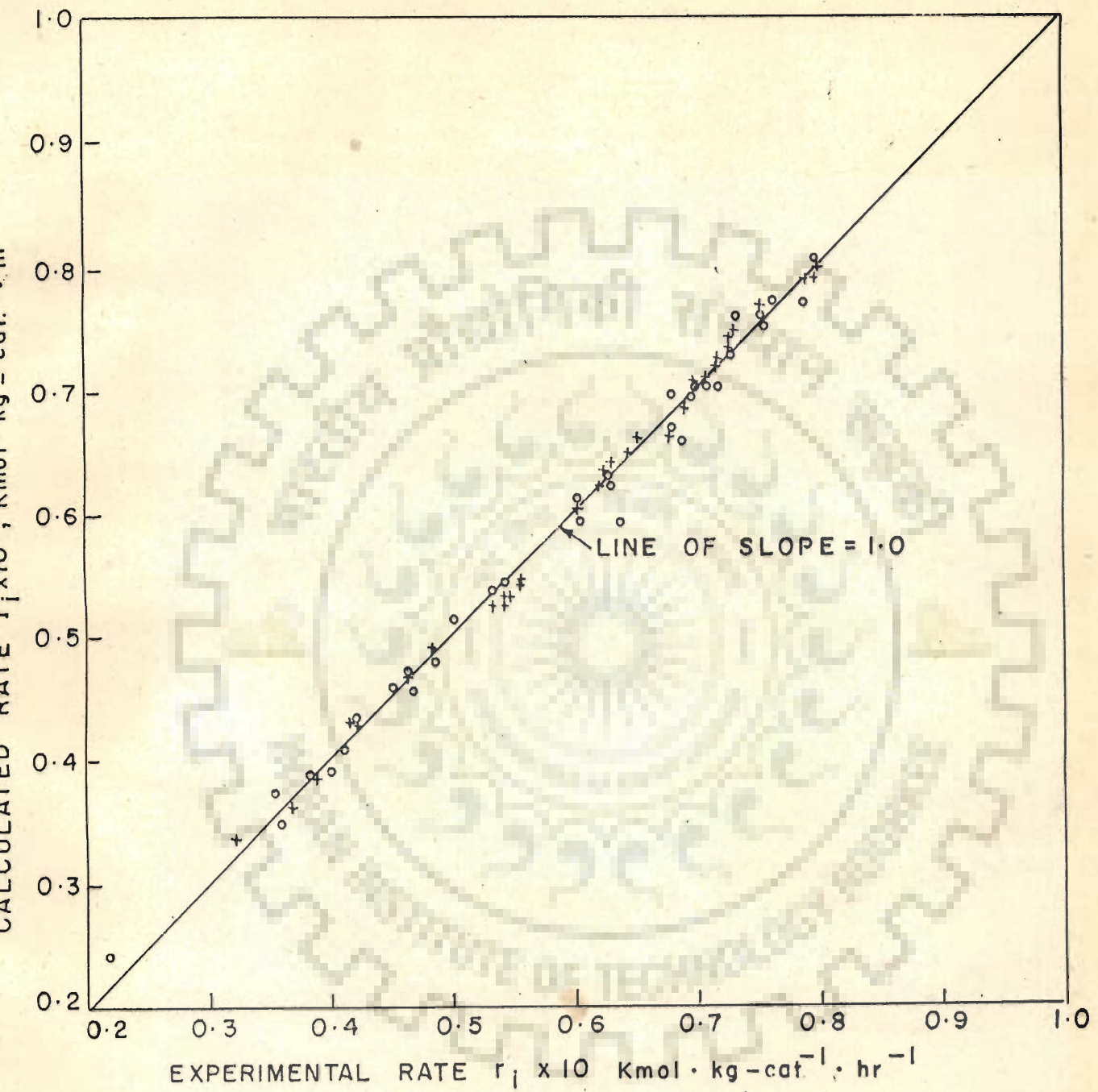
FIG. 4·27 - CALCULATED VERSUS OBSERVED REACTION RATES:
(o) MODEL 5 AT 333 K ; (+) MODEL 6 AT 333 K ;
OLEFIN - ISOOCTENE.
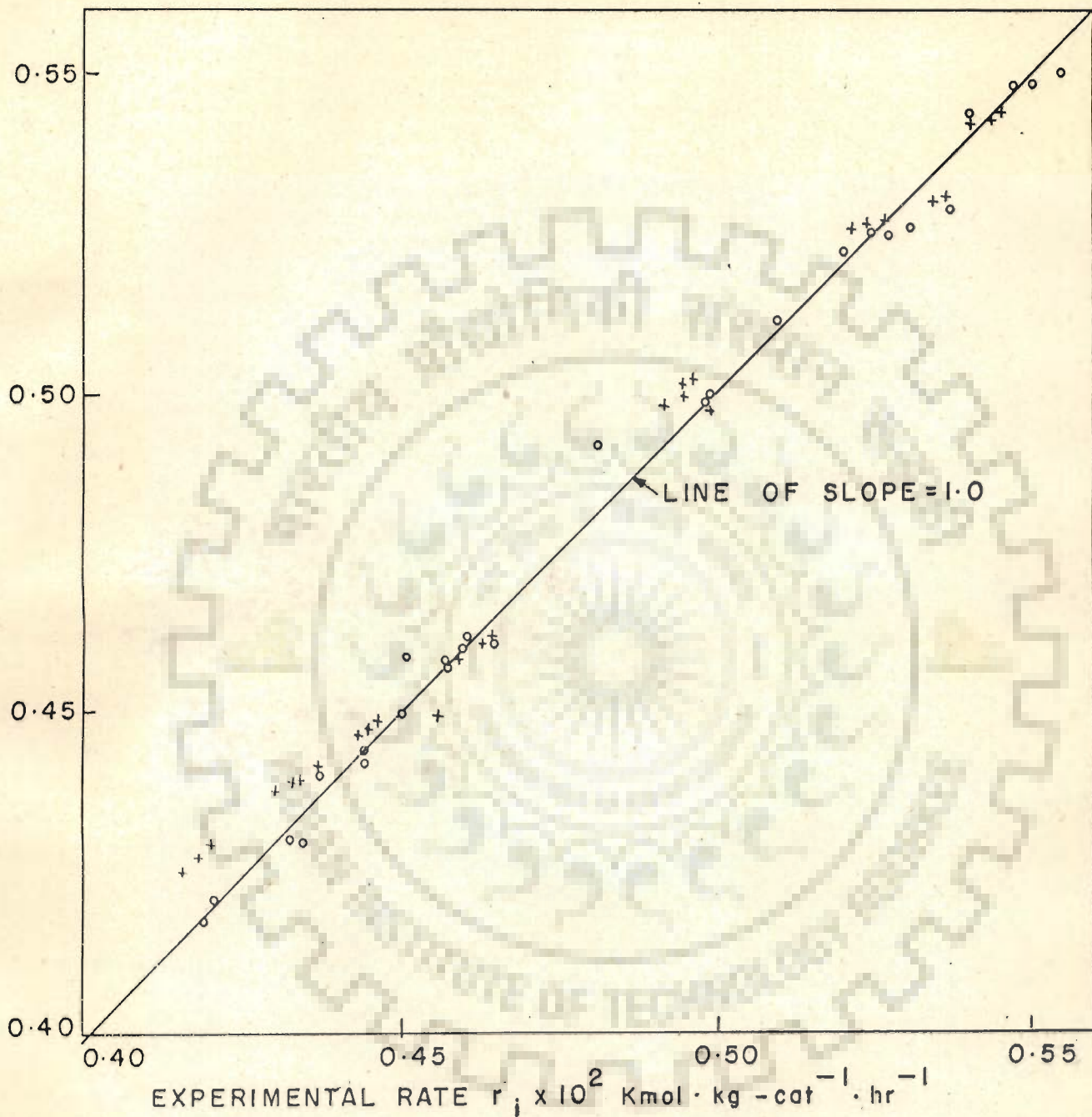
FIG. 4·28 - CALCULATED VERSUS OBSERVED REACTION RATES:
(o) MODEL 5 AT 303 K ; (+) MODEL 6 AT 303 K ;
OLEFIN - ISODODECENE.
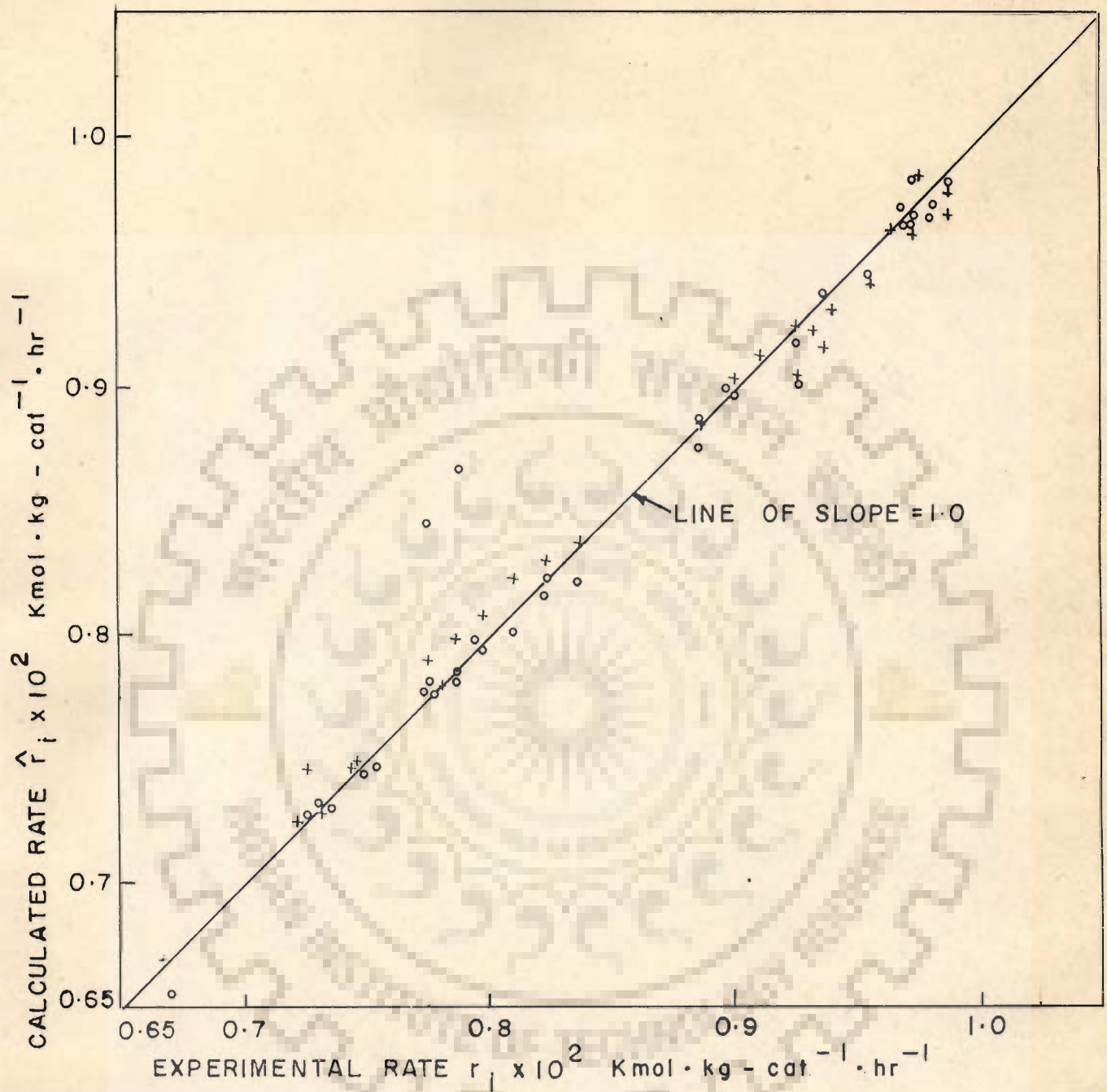
FIG. 4·29 - CALCULATED VERSUS OBSERVED REACTION RATES:
(o) MODEL 5 AT 313K ; (+) MODEL 6 AT 313 K ;
OLEFIN – ISODODECENE.
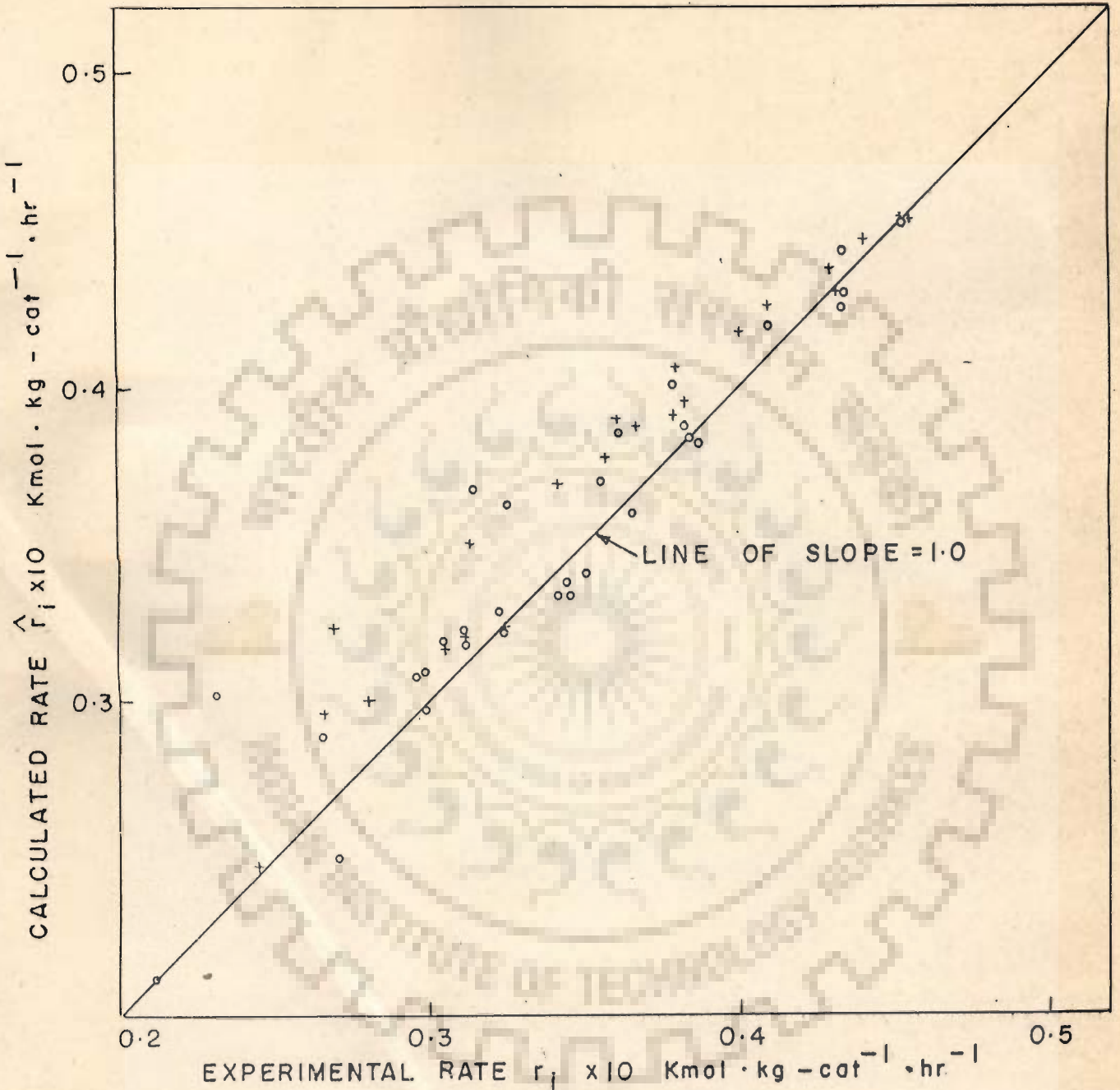
FIG. 4·30 – CALCULATED VERSUS OBSERVED REACTION
RATES AT 333 K : (o) MODEL 5 ; (+) MODEL 6 ;
OLEFIN – ISODODECENE.
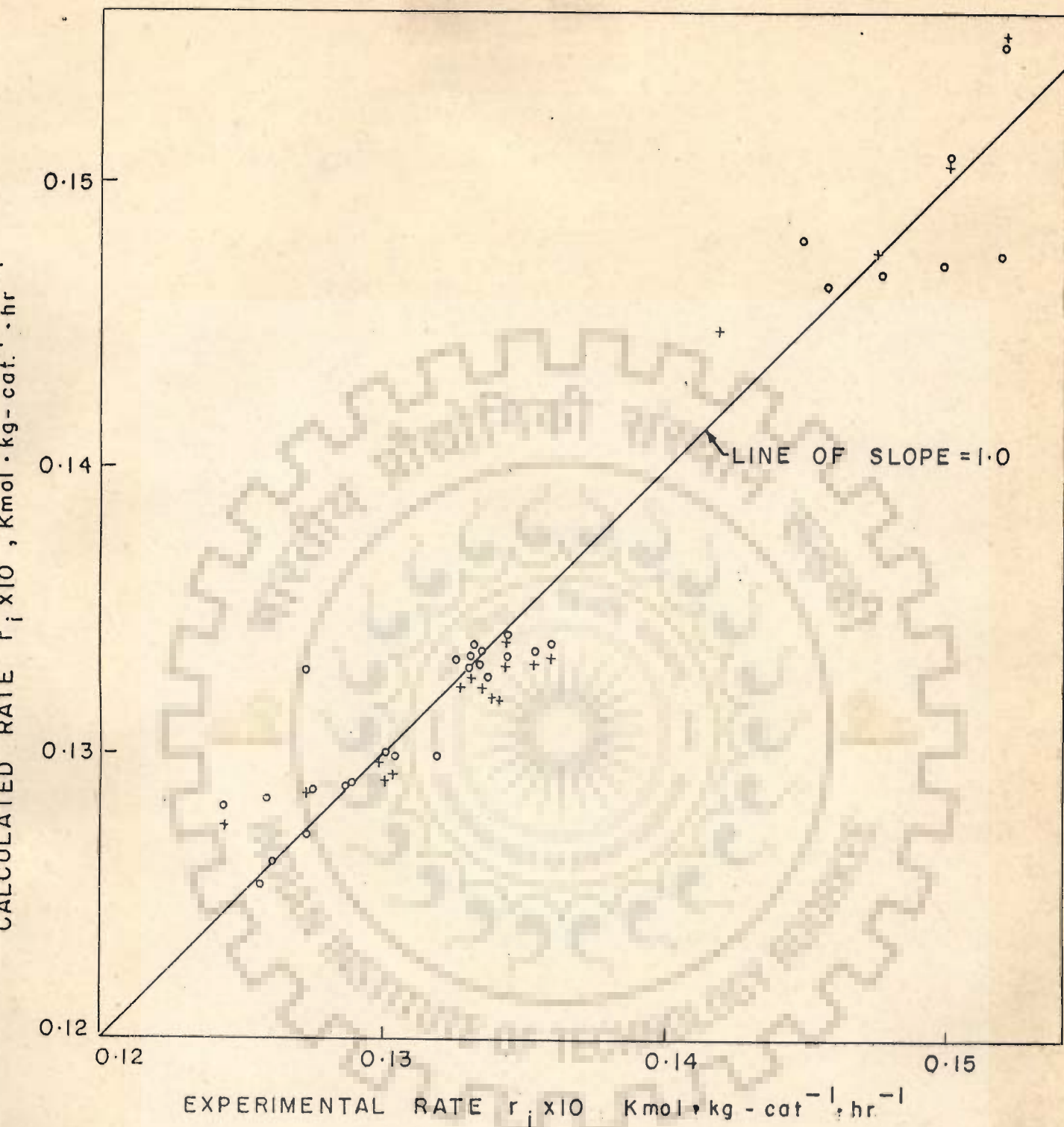
FIG. 4·31 – CALCULATED VERSUS OBSERVED REACTION RATES :
(o) MODEL 5 AT T = 303 K;(+) MODEL 6 AT T = 303 K
OLEFIN – n – OCTENE.
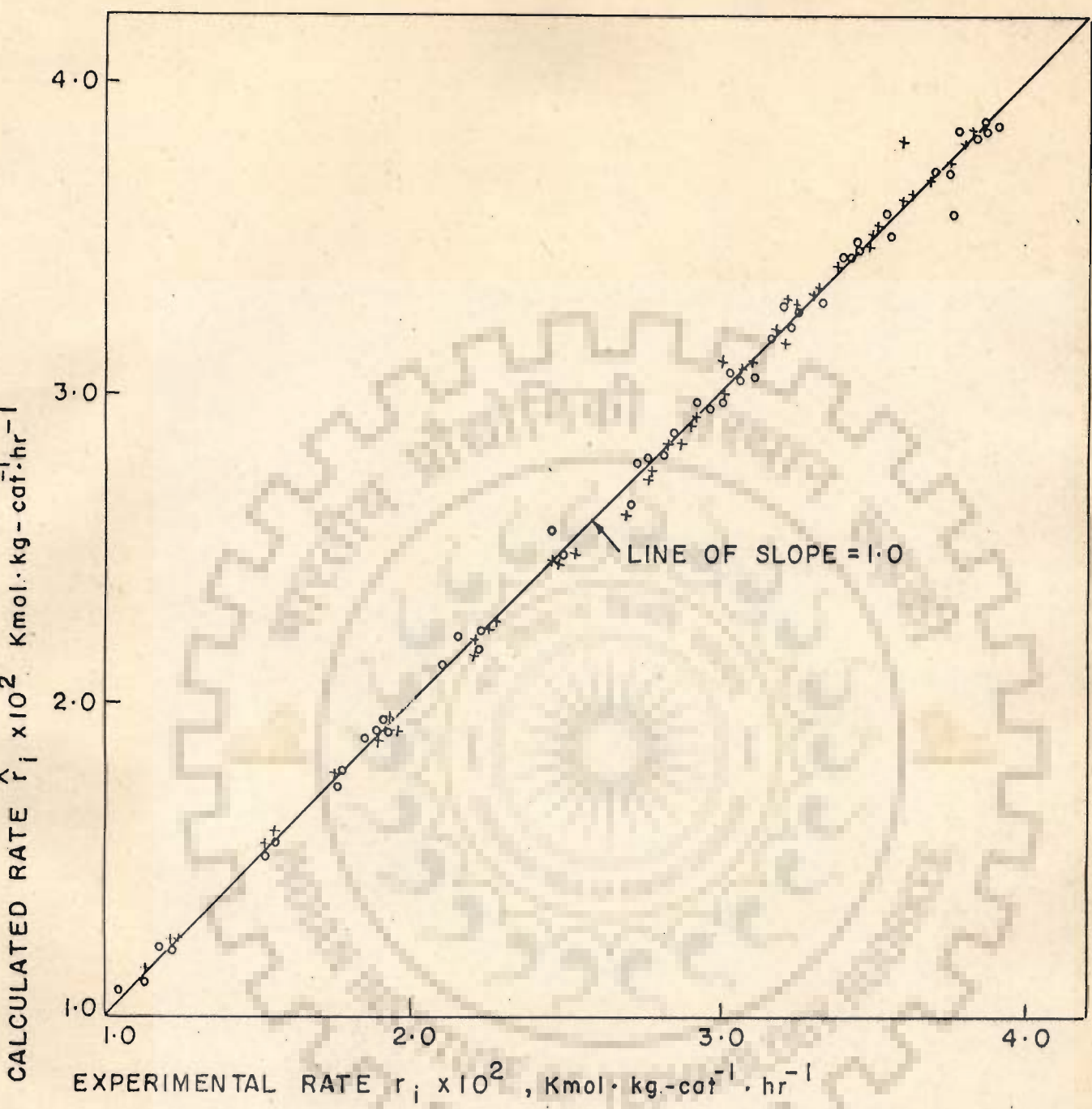
FIG. 4·32 – CALCULATED VERSUS OBSERVED REACTION RATES:
(o) MODEL 5 ; T = 313 K ; (+) MODEL 6 ; T = 313 K ;
OLEFIN – n – OCTENE.
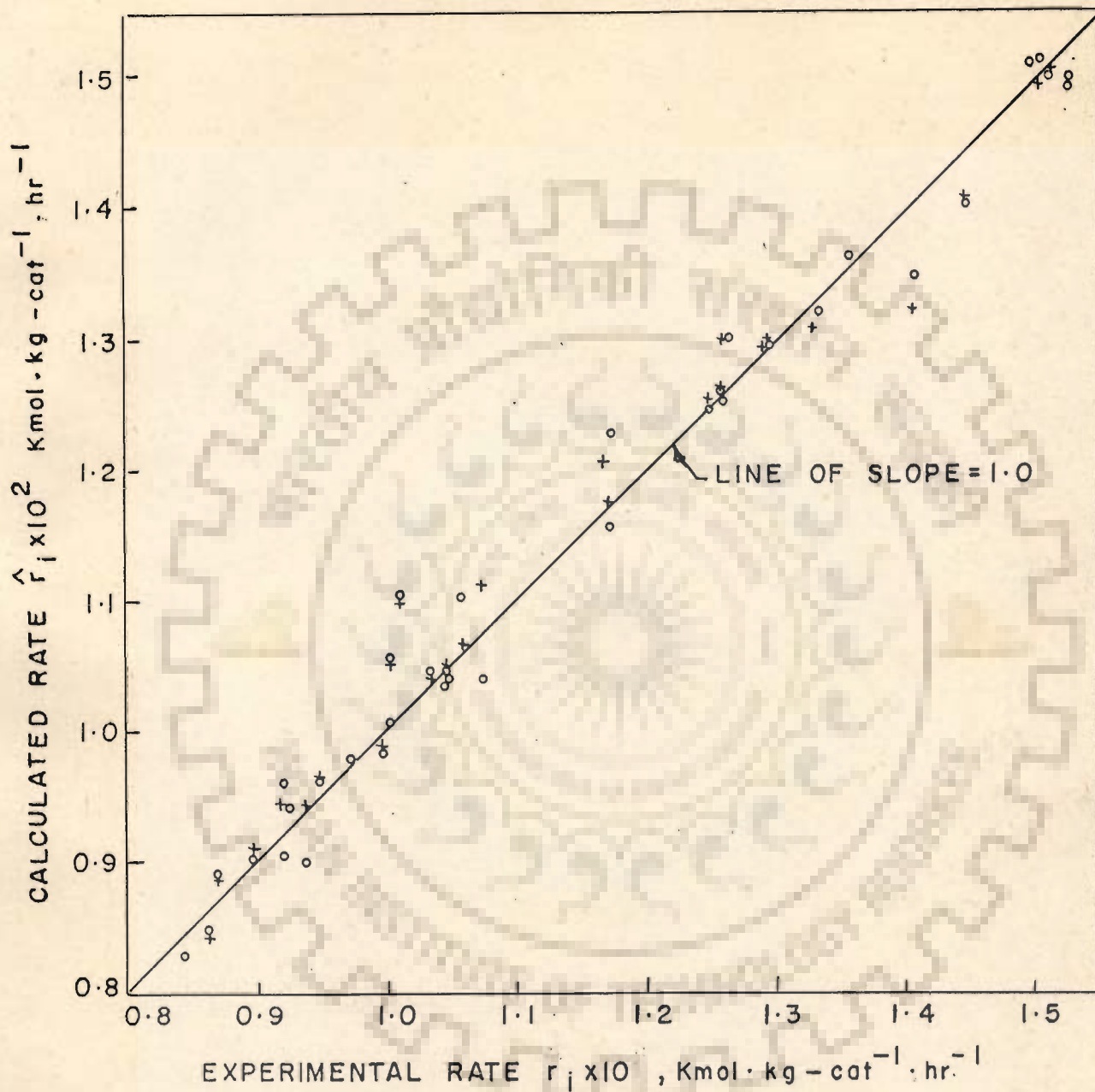
FIG. 4·33 – CALCULATED VERSUS OBSERVED REACTION
RATES: (o) MODEL 5 AT T = 333 K; (+) MODEL 6
AT T = 333 K;
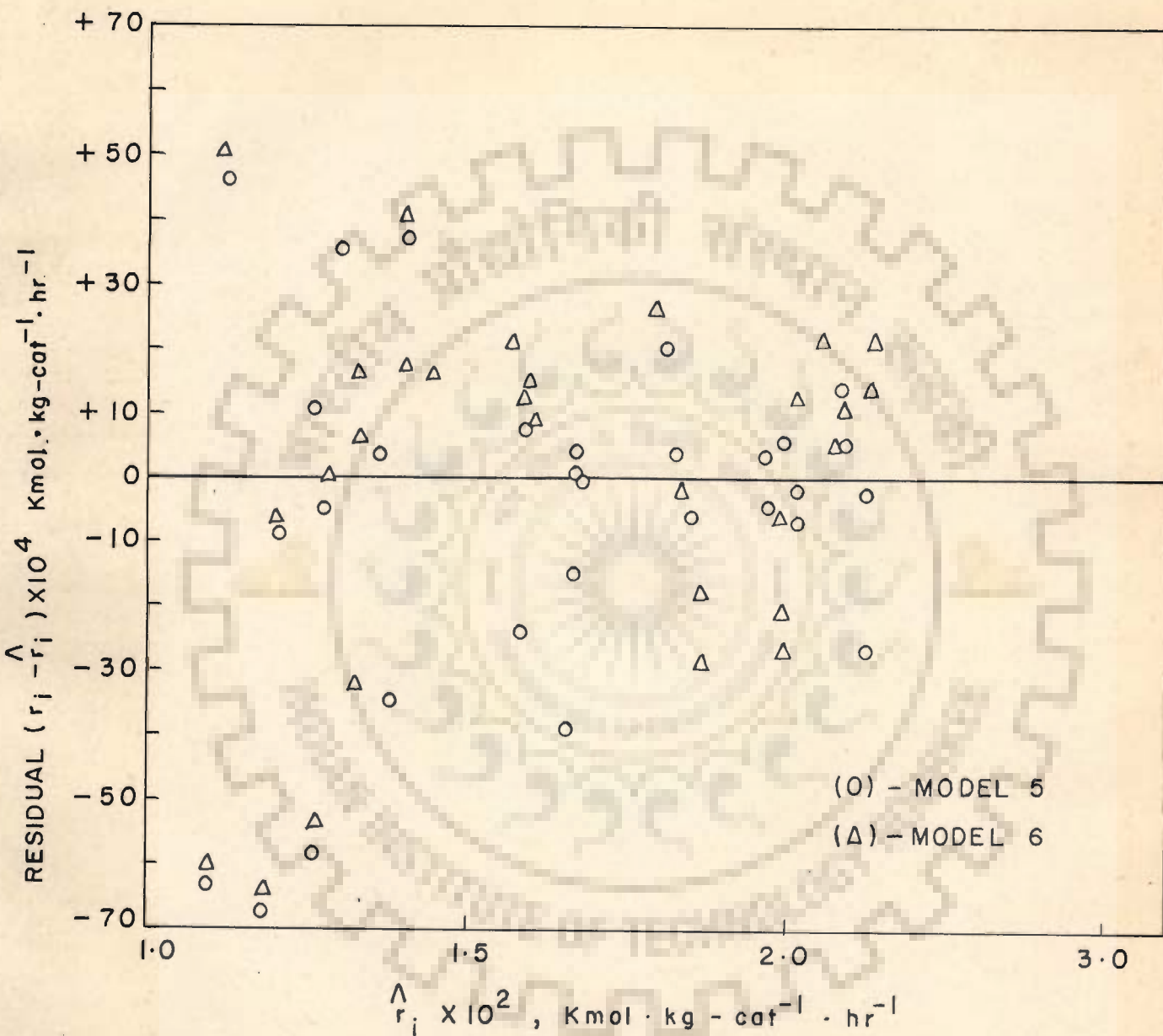
FIG. 4·34 — PLOT OF CALCULATED REACTION RATE Vs RESIDUALS FOR HYDROGENATION OF ISOOCTENE AT 313 K.
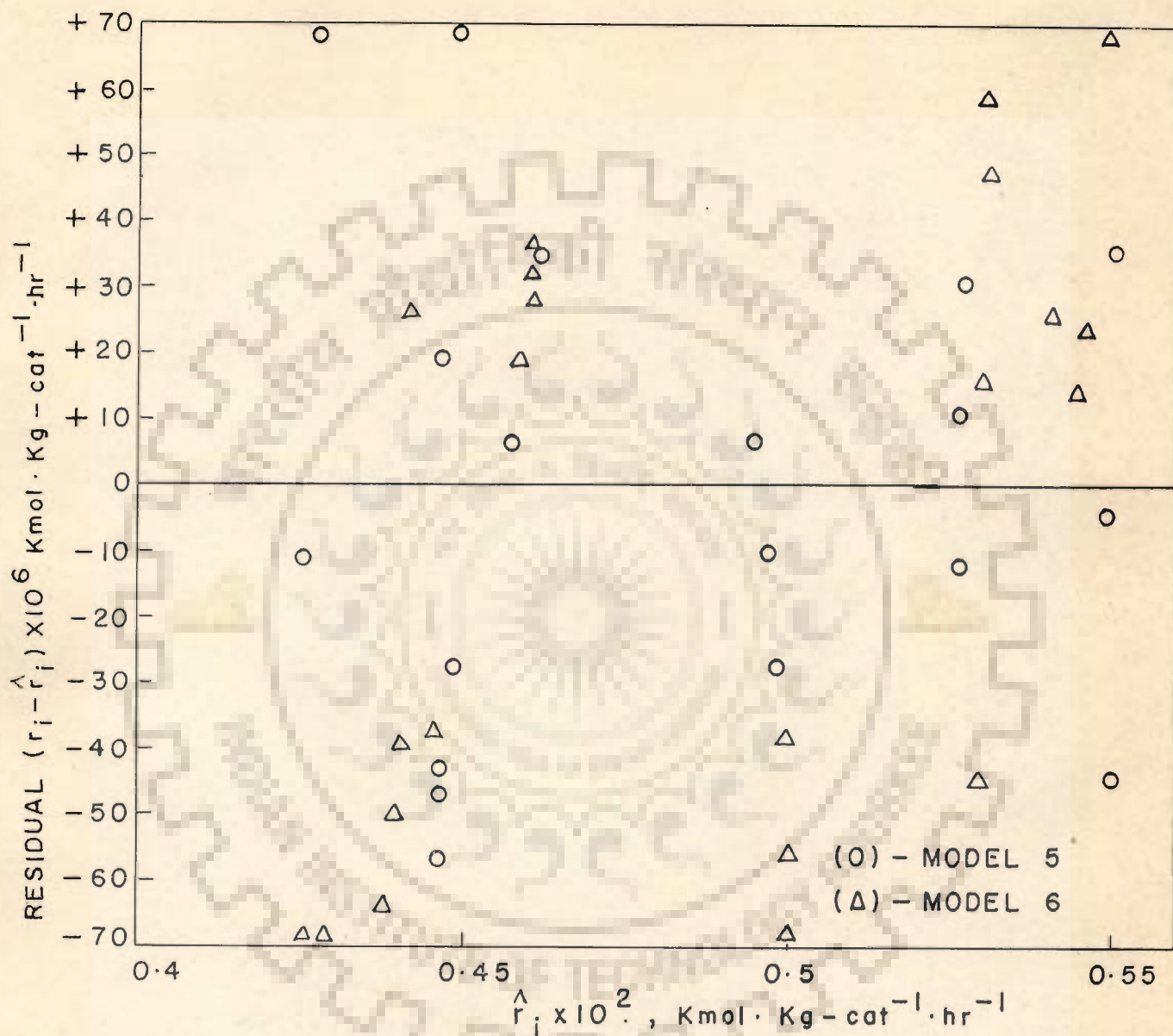
FIG. 4·35 — PLOT OF CALCULATED REACTION RATES Vs
RESIDUALS FOR HYDROGENATION OF
ISODODECENES AT 303 K
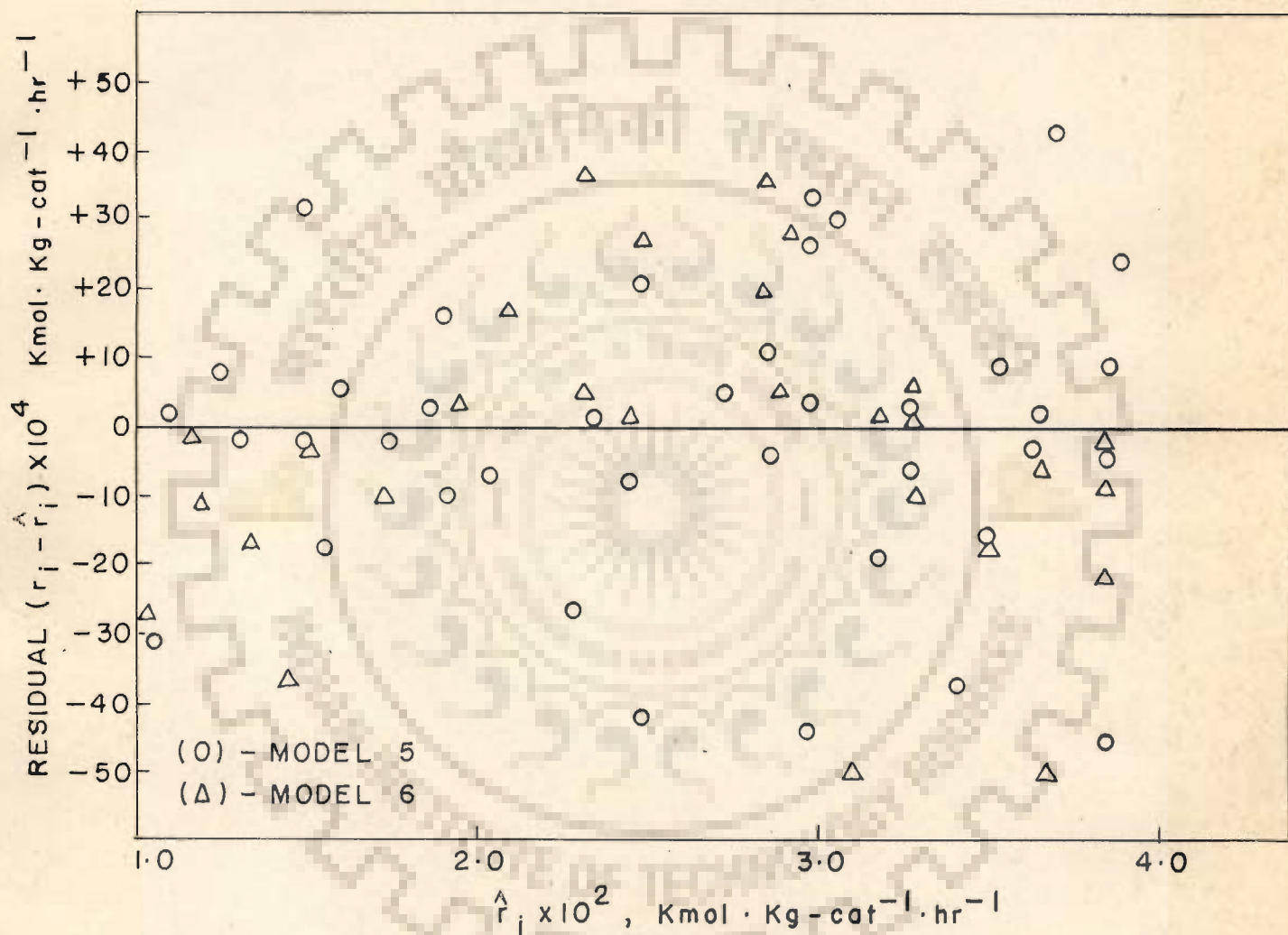
FIG. 4·36 — PLOT OF CALCULATED REACTION RATE Vs
RESIDUALS FOR HYDROGENATION OF n-OCTENE
AT 313 K

Isooctene:

$$k = 1.21 \times 10^{10} \exp(-16640/RT) \qquad \ldots\ldots (4.43\ a)$$

$$K_A = 1.673 \times 10^{-4} \exp(8.785/RT) \qquad \ldots\ldots (4.43\ b)$$

$$K_B = 0.9299 \exp(2137/RT) \qquad \ldots\ldots (4.43\ c)$$

Isododecene:

$$k = 1.006 \times 10^{9} \exp(-15398/RT) \qquad \ldots\ldots (4.44\ a)$$

$$K_A = 4.49 \times 10^{-4} \exp(8260/RT) \qquad \ldots\ldots (4.44\ b)$$

$$K_B = 5.32 \times 10^{-2} \exp(4015/RT) \qquad \ldots\ldots (4.44\ c)$$

n-octene:

$$k = 1.20 \times 10^{10} \exp(-16227/RT) \qquad \ldots\ldots (4.45\ a)$$

$$K_A = 1.707 \times 10^{-4} \exp(8788/RT) \qquad \ldots\ldots (4.45\ b)$$

$$K_B = 1.037 \times 10^{-2} \exp(4956/RT) \qquad \ldots\ldots (4.45\ c)$$

Mechanism of reaction

From the statistical and intrinsic view points for all the three olefins, model 5 represented the experimental data well. The derivation of this model is based on the addition of hydrogen to the olefin in two steps; in the first step a half hydrogenated intermediate is formed to which another hydrogen atom adds to form a saturated product molecule. The sequence of mechanistic steps involved are as follows:

Step I

Equilibrium of hydrogen in liquid phase and catalyst:

$$A^{(1)} \rightleftharpoons A^{(p)} \qquad \qquad \cdots\cdots (4.46 \text{ a})$$

Step II

$$A + 2S_1 \xrightleftharpoons{K_A} 2AS_1 \quad \text{(dissociative adsorption of hydrogen onsites } S_1) \qquad \cdots\cdots (4.46 \text{ b})$$

Step III

$$B + S_2 \xrightleftharpoons[K_{-1}]{\overset{K_B}{k_1'}} BS_2 \quad \text{(associative adsorption of olefin on sites } S_2) \qquad \cdots\cdots (4.46 \text{ c})$$

Step IV

$$BS_2 + AS_1 \xrightleftharpoons[k_2]{k_1} BAS_2 + S_1 \quad \text{(addition of 1st hydrogen atom)} \qquad (4.46 \text{ d})$$

Step V

$$BAS_2 + AS_1 \xrightleftharpoons[k_4]{k_3} CS_2 + S_1 \quad \text{(addition of 2nd hydrogen atom)} \qquad (4.46 \text{ e})$$

Step VI

$$CS_2 \xrightleftharpoons{K_C} C + S_2 \quad \text{desorption of products} \qquad \cdots\cdots (4.46 \text{ f})$$
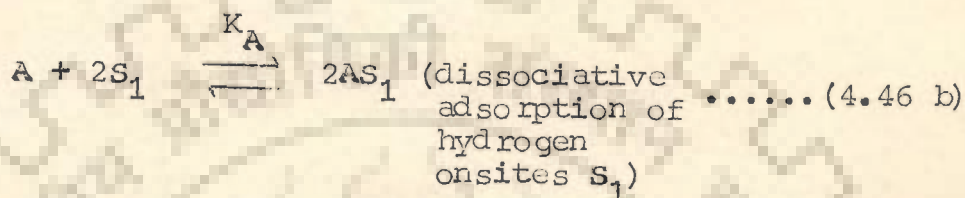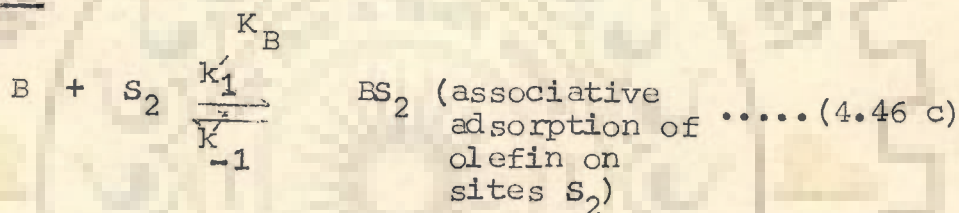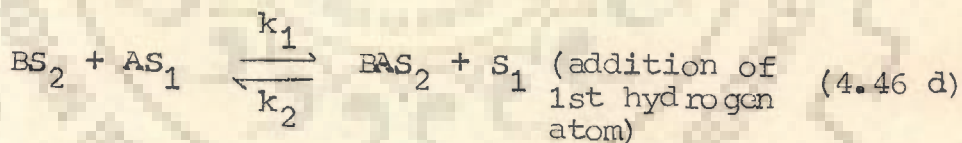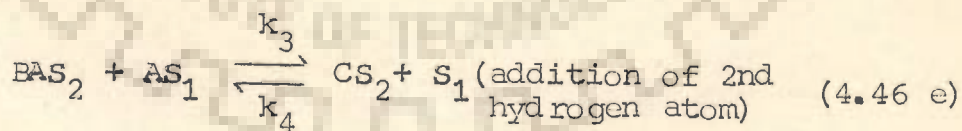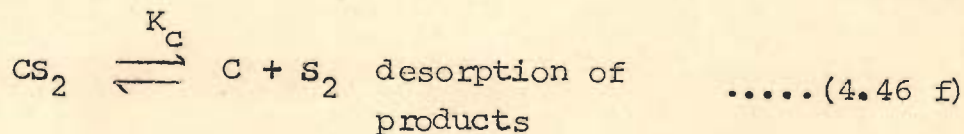
Discussion of Mechanistic steps

It has been observed[160] that when unsaturated hydrocarbon is reacted with (a) equilibrated and (b) non-equilibrated hydrogen - deuterium mixtures, the deuteroalkane distributions are identical. Such observations indicate that the direct addition of a hydrogen molecule across the olefinic bond does not occur and provide a strong evidence for the formation of a half hydrogenated state , i.e. an adsorbed alkyl radical, first suggested by Horiuti and Polanyi[161] as a relatively stable intermediate. Hence the addition of H_2 to the olefin molecule may be regarded as a two step process.

The adsorption of alkenes, hydrogen and alkanes on noble metal catalysts at ambient temperatures follows the sequence[162] alkenes $>$ hydrogen $>$ alkanes. Kemball[162] further stated that under the conditions normally used for olefin hydrogenation, the alkane once formed, is unreactive and its re-adsorption on the catalyst surface can be neglected. From the thermodynamic calculations described earlier, it can be seen that under the pressure and temperature conditions employed in this work, the reverse reaction of dehydrogenation of alkanes is negligible. When the hydrogenation was carried out in the presence or absence of large quantity of

alkane product, the rates were almost identical. On the basis of absence of deuterium exchange reactions Burwell[163] also showed that alkanes do not chemisorb on metals at temperatures around 300 K. Thus the product alkane does not seem to play any important role in the hydrogenation reaction and that the addition of hydrogen atom (step IV) can be regarded as irreversible.

As stated earlier, with this palladium catalyst, the proportion of olefin isomers remained almost in thermodynamic equilibrium. This suggests that the formation of half-hydrogenated state (step III) is reversible. This is also supported by extensive deuterium exchange under similar conditions[164]. Further, it is well established that the adsorption of hydrogen on such catalysts is reversible and dissociative[163-165]. We are thus left only with the questions- (i) whether adsorption of olefin is reversible or not and, (ii) whether olefin and hydrogen compete with one another in the adsorption process.

The apparent order of reaction with respect to olefin was found to be almost zero upto a fairly high degree of conversion; such zero order kinetics requires that the catalyst in effect, remains saturated with chemisorbed olefin throughout the

hydrogenation of the 9 kinetic models tested only model 5 represented the kinetic data well. The next best fitting model is model 6. In both of these models, non-competitive adsorption of hydrogen and olefin was assumed. This indicates that the adsorption of hydrogen and olefin may probably occur non-competitive on different sites. In other words, the catalyst surface is almost covered by olefin molecules and very small number of specified sites, among the bulky olefin molecules, are available for non-competitive adsorption of hydrogen. To further check the occurrence of reversible olefin adsorption and non-competitive adsorption of hydrogen the rate equation for model 5 was re-arranged in the following form:

$$\frac{C_B}{r} = \frac{(1 + \sqrt{K_A C_A})^2}{k\, K_A K_B C_A} + \frac{(1 + \sqrt{K_A C_A})^2}{k\, K_A C_A}\, C_B \quad \ldots\ldots(4.47)$$

Thus, for a given pressure and temperature, a plot of C_B / r Vs. C_B should be a straight line with slope different for reversible and irreversible olefin adsorption; the value of this slope depends upon the value of K_B $(\simeq \dfrac{k'}{k'_{-1}})$, for irreversible olefin adsorption k'_1 k_{-1} i.e. K_B is very large making the intercept nearly zero. On the other hand, if the

olefin adsorption is reversible k'_{-1} will be finite and the intercept will be positive. For the non-competitive adsorption of olefin and hydrogen, the straight line at various pressures should extrapolate to a common intercept with the abscissa axis, indicating that the olefin and hydrogen concentration on the catalyst surface are independent of each other. This behaviour is very well observed with all the three olefins used in this study.

A series of such plots using the experimental data of hydrogenation of isooctene, n-octene and iso-dodecene, collected in this study are given in Figs. 4.37-4.39. These plots clearly show that the intercept is positive and the straight-lines for various pressures extrapolate to a common intercept with the abscissa. Hence olefin adsorption on the catalyst surface is reversible (step III) and that olefin and hydrogen are adsorbed non-competitively.

On the basis of above observations and discussion, the hydrogenation process occupying on this Pd-Al$_2$O$_3$ catalyst may finally be envisaged as follows:

On the catalyst surface, which is almost completely saturated with hydrocarbon species, a small number of unspecified sites located among the bulky hydrocarbon species are accessible for hydrogen chemisorption. Hydrogen from the gas phase
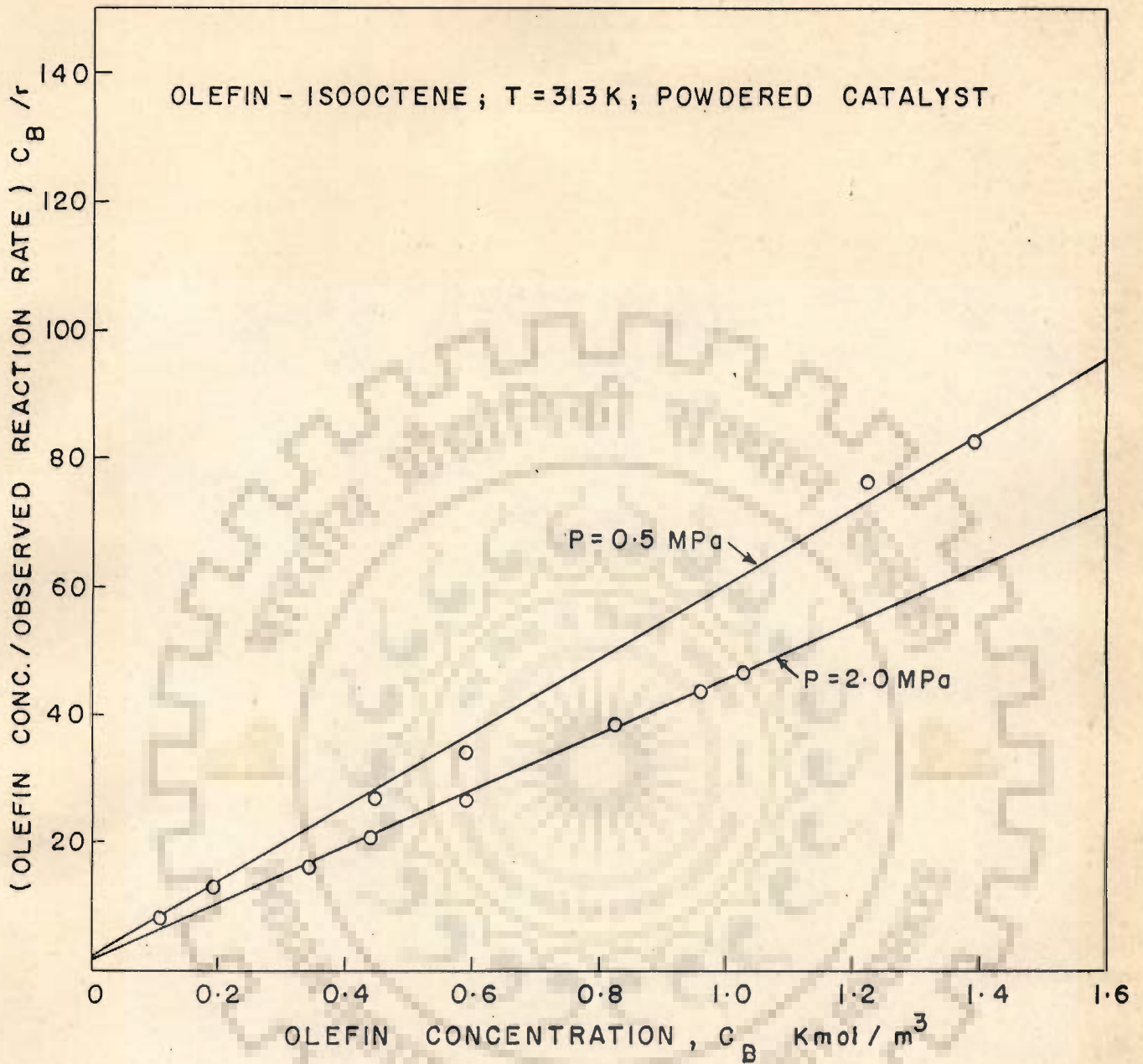
FIG. 4.37- PLOT OF OLEFIN CONCENTRATION IN LIQUID PHASE
Vs RATIO OF OLEFIN CONCENTRATION AND OBSERVED
REACTION RATE (ACCORDING TO EQUATION 4.47)
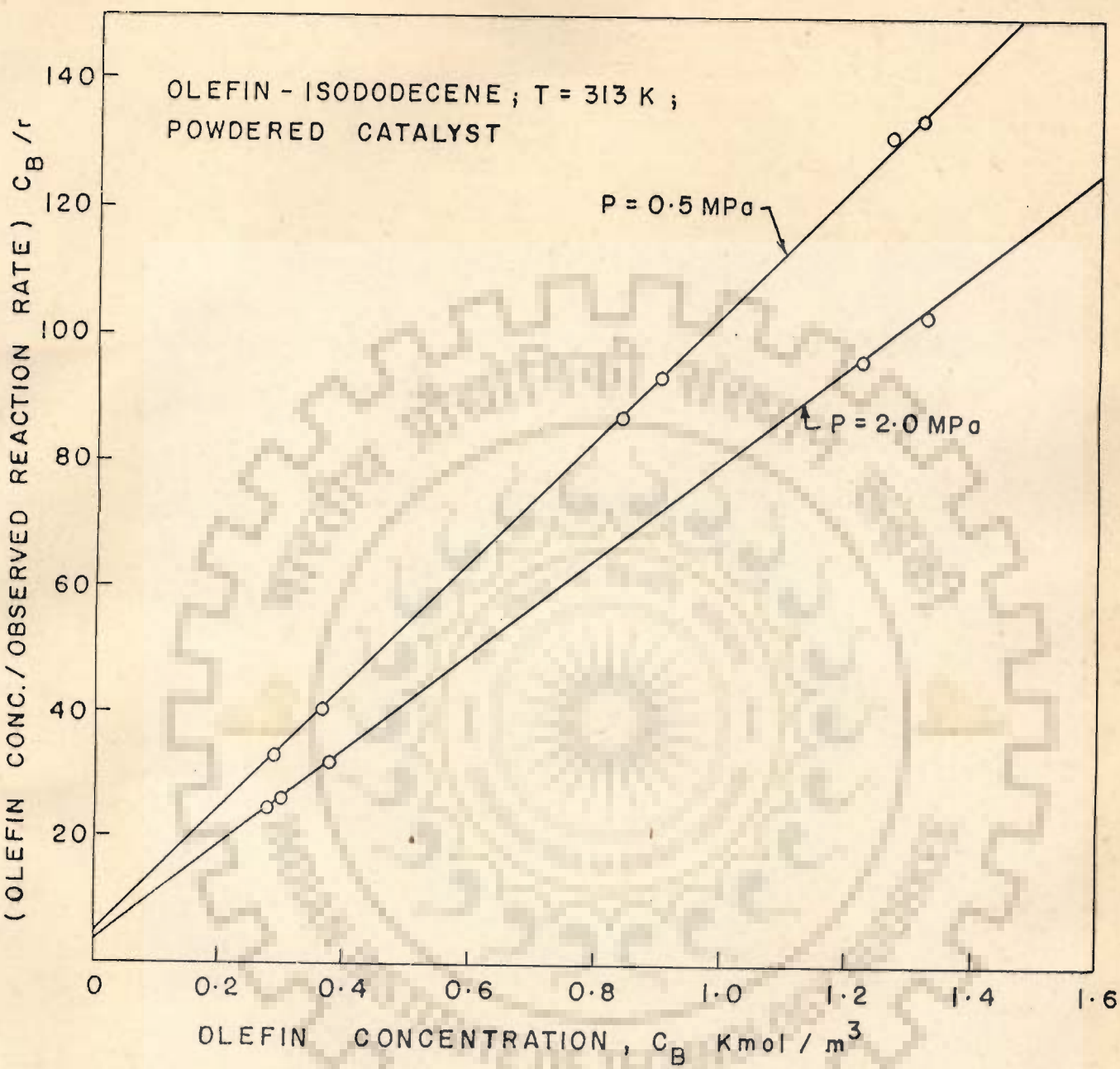
FIG. 4·38 — PLOT OF OLEFIN CONCENTRATION IN LIQUID PHASE Vs RATIO OF OLEFIN CONCENTRATION AND OBSERVED REACTION RATE (ACCORDING TO EQUATION 4:47)
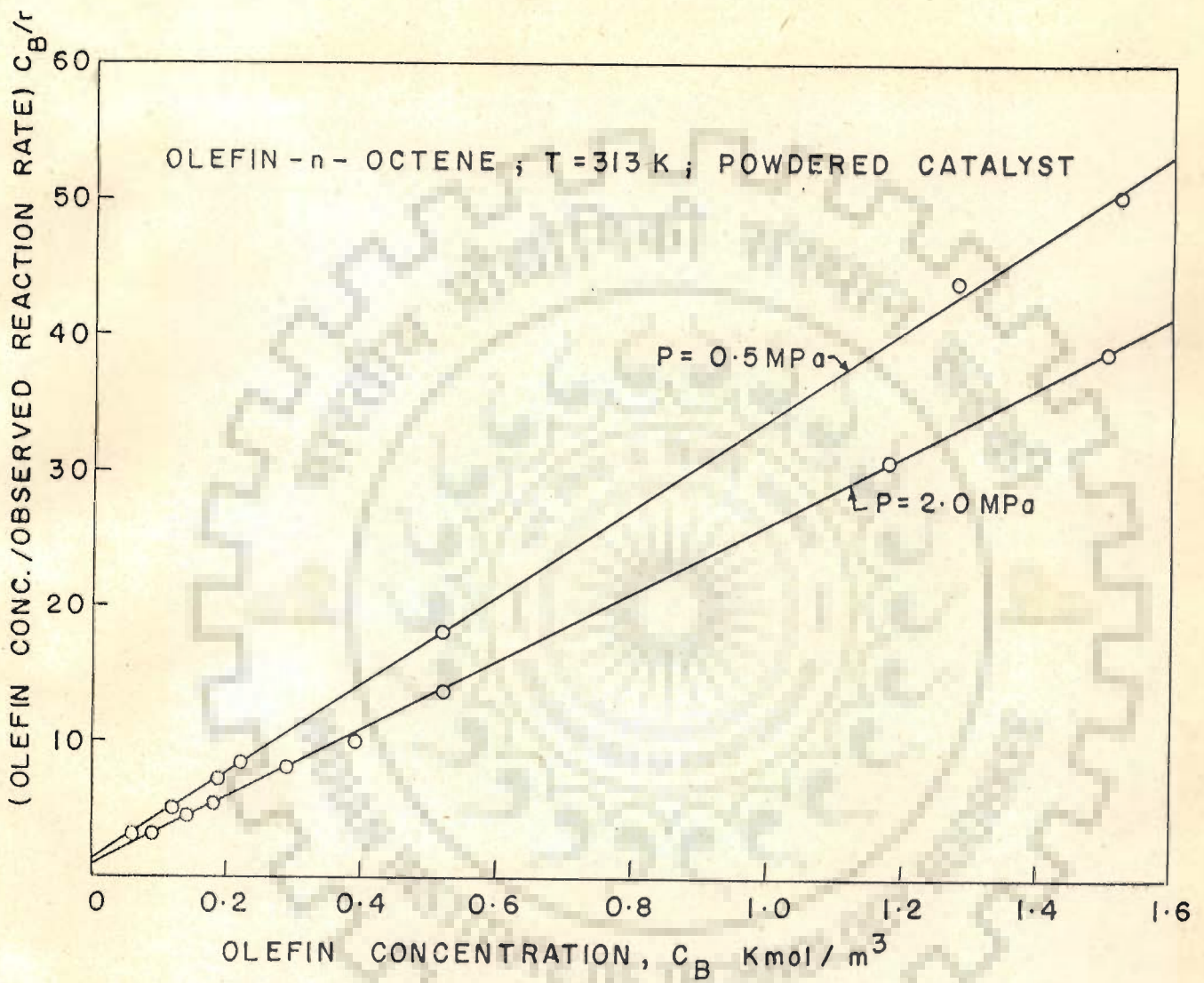
FIG. 4·39- PLOT OF OLEFIN CONCENTRATION IN LIQUID PHASE
Vs RATIO OF OLEFIN CONCENTRATION AND OBSERVED
REACTION RATE (ACCORDING TO EQUATION 4·47)

is first dissolved in the liquid and then diffuses
through the stagnant liquid film surrounding the
catalyst particle to reach the catalyst surface, where
it is chemisorbed in dissociated form.   This is then
followed by the surface reaction which involves the
independent addition of two hydrogen atoms.

4.5   HYDROGENATION WITH CATALYST PELLETS

        Experiments were also carried out to see the
effect of pore-diffusion on the rate of hydrogenation
of isooctenes, n-octenes and isododecenes, using
catalyst pellets in the stirred autoclave fitted with
rotating basket impeller.   The catalyst pellets were
held in four baskets, each containing about 1.0×10^{-3} kg
catalyst.   The agitation in the reactor was provided
by the rotation of impeller baskets; this was kept
constant corresponding to an agitator speed of 800 rpm.
It has already been mentioned earlier, in sec.4.1,
that at such turbulence in this system, the external
mass transfer did not influence the reaction rate;
therefore, the effect of pore diffusion only would
be reflected in the conversion rate.   For isooctenes,
the hydrogenation experiments were carried out at
0.5 MPa pressure, varying the initial isooctene
concentration and temperature in the ranges of
$0.5572 - 1.423$ kmol/m^3 and $303 - 333$ K respectively.
In case of n-octenes and isododecenes, the runs were

conducted at 313 K and 0.5 MPa pressure; the initial
concentration of n-octenes and isododecenes were varied
in the ranges of 0.5128 - 1.520 kmol/m^3 and 0.373 -
1.325 kmol/m^3 respectively.

4.5.1. Hydrogenation of isooctenes

Table 4.13 shows the variation of initial reaction
rates with temperature at a fixed initial isooctene
concentration of 0.5572 kmol/m^3. The rate of reaction
increased with increase of temperature, but these
were much lower than those obtained with powdered
catalyst under similar operating conditions. These
low values of the reaction rates with catalyst pellets
can be attributed to the diffusional resistance
inside the catalyst pores. The results obtained on
varying the initial iso-octene concentration are
given in Table 4.14. In the narrow concentration
range studied, the rate of hydrogenation was found to
have almost zero order dependence on the initial
concentration of isooctenes.

The values of effectiveness factor, η expt
were estimated by the ratio of reaction rate with
pellets to the reaction rate with powdered catalyst;
the values of η expt thus calculated are given in
the last line of Tables 4.13 and 4.14. It can be
observed that the effectiveness factor of the
catalyst pellet decreased with increase in tempera-
ture (Table 4.13). This is due to the fact that the

TABLE 4.13

HYDROGENATION OF ISOOCTENES ON CATALYST PELLETS[a]:
EFFECT OF TEMPERATURE

Temperature, K	303	313	333
Pressure, MPa	0.5	0.5	0.5
Agitator speed, rpm	800	800	800
Initial rate of reaction $kmol \cdot (kg-cat)^{-1} \cdot (hr)^{-1}$			
- with catalyst pellets	2.89×10^{-3}	4.633×10^{-3}	10.25×10^{-3}
- with powdered catalyst	6.293×10^{-3}	16.12×10^{-3}	54.20×10^{-3}
Effectiveness factor, η expt.	0.46	0.287	0.19

Notes (a): Initial isooctene concentration = 0.5572 $kmol/m^3$

TABLE 4.14

HYDROGENATION OF ISOOCTENE ON CATALYST PELLETS:
EFFECT OF INITIAL OLEFIN CONCENTRATION

Initial conc. of isooctene, $kmol/m^3$	0.5572	1.025	1.423
Temperature, K	313	313	313
Pressure, MPa	0.5	0.5	0.5
Agitator speed, rpm	800	800	800
Initial rate of reaction, $kmol \cdot (kg-cat)^{-1} \cdot (hr)^{-1}$			
- with catalyst pellet	4.633×10^{-3}	4.549×10^{-3}	4.886×10^{-3}
- with powdered catalyst	16.12×10^{-3}	16.35×10^{-3}	16.74×10^{-3}
Effectiveness factor, η expt	0.287	0.278	0.292

rate of reaction at 333 K was about 9 times higher than that of 303 K with powdered catalyst whereas this increase was less than 4-fold with the powdered catalyst. It may be noted that the increase in temperature increases reaction rate rapidly but its effect on mass transfer rate is only marginal. Isooctene concentration in the liquid feed, however, did not significantly affect the values of η expt showing very little or negligible gradients in isooctene concentration inside the catalyst pores at bulk isooctenes concentrations of 0.5572 kmol/m^3 and above since the bulk concentration of the other reactant, hydrogen, is extremely low $\simeq$ 0.03 kmol/m^3.

4.5.2. Hydrogenation of n-octenes

The initial rates of hydrogenation of n-octenes with catalyst pellets at 313 K and 0.5 MPa pressure varied negligibly with the initial concentration of n-octenes in the feed (Table 4.15); the reaction rate increased only by 4.93 % with an increase in n-octene concentration from 0.5128 to 1.520 kmol/m^3. Thus, with catalyst pellets, the rates of hydrogenation of n-octenes at initial n-octene concentration in the range of 0.5128 - 1.52 kmol/m^3 followed almost zero order dependence with initial n-octenes concentration. The values of catalytic effectiveness factor, η expt for n-octene hydrogenation were a little lower than those for isooctenes.

TABLE 4.15

HYDROGENATION OF n-OCTENES OVER CATALYST PELLETS

Initial concentration of n-octenes, $kmol/m^3$	0.5218	1.109	1.520
Temperature, K	313	313	313
Pressure, MPa	0.5	0.5	0.5
Agitator speed, rpm	800	800	800
Initial rate of reaction, $kmol.(kg\text{-}cat)^{-1}.(hr)^{-1}$			
- with catalyst pellets	6.522×10^{-3}	6.974×10^{-3}	7.383×10^{-3}
- with powdered catalyst	28.60×10^{-3}	29.49×10^{-3}	30.01×10^{-3}
Effectiveness factor, η_{expt}	0.23	0.236	0.246

5.3. Hydrogenation of isododecenes

The results of hydrogenation of isododecenes over catalyst pellets at 313 K and 0.5 MPa pressure are given in Table 4.16. In this case also, the reaction rates showed an almost zero order dependence on isododecene concentration in the feed. The experimental values of catalytic effectiveness factor were in the range of 0.296 - 0.329; these were a little higher than those obtained for

TABLE 4.16

HYDROGENATION OF ISODODECENES OVER CATALYST PELLETS

Initial concentration of isododecenes, $kmol/m^3$	0.3730	0.9402	1.325
Temperature, K	313	313	313
Pressure, MPa	0.5	0.5	0.5
Agitator speed, rpm	800	800	800
Initial rate of reaction, kmol. $(kg\text{-}cat)^{-1}.(hr)^{-1}$			
- with catalyst pellets	2.561×10^{-3}	2.362×10^{-3}	2.419×10^{-3}
- with powdered catalyst	7.785×10^{-3}	7.951×10^{-3}	8.175×10^{-3}
Effectiveness factor, η expt.	0.329	0.297	0.296

n-octenes and isooctenes under similar operating conditions.

These data show that when catalyst pellet is used, the effect of pore diffusional restriction is more pronounced for the faster intrinsic reaction rate obtained with powdered catalyst. The reaction rates with powdered catalyst were in the order n-octene >

iso-octene $>$ isododecene; with catalyst pellets;
under similar operating conditions, the effectiveness
factors are in the order iso-dodecene $>$ isooctenes
$>$ n-octene.

4.5.4. Theoretical analysis (Rigorous Model)

As described earlier, in liquid phase hydrogena-
tion, both the reactants, hydrogen and olefin, have to
diffuse first through the bulk liquid phase and
catalyst pores, chemisorb on the active sites of the
catalyst and then react to form the products. After
the surface reaction the products are desorbed and
diffuse back to the bulk liquid phase. The pores of
the catalyst pellets remain filled with liquid. To
evaluate the mass transfer effects on such a system,
model equations were derived and solved numerically.
In the development of the model equations the
following assumptions were made:

1.   No temperature gradients exist inside the
     catalyst pellet - i.e. the pellets are iso-
     thermal.

2.   The diffusivities of the reactants and the
     products remain constant throughout the pellet.

3.   A diffusional steady-state exists inside the
     catalyst pellet.

4.   By visual inspection of the broken catalyst pellet under microscope, the pellet was found to have two distinct portions - the first of about 0.04 cm thickness on the outer periphery of the pellet and second the inside core.   The palladium metal was observed to be concentrated towards the outer peripheral part of the pellet. For analysis of the results, described below, the pellet geometry was, therefore, approximated by a slab of thickness L = 0.04 cm with uniform distribution of active sites.

Derivation of equations

Under steady-state conditions, the molal mass flux of hydrogen and olefin inside the catalyst pores is equal, i.e.

$$J_A = J_B = - J_P \qquad \dots (4.48)$$

Or

$$-D_{eff,A} \frac{dC_A}{dx} = - D_{eff,B} \frac{dC_B}{dx}$$

$$= D_{eff,P} \frac{dC_P}{dx} \qquad \dots (4.49)$$

Integrating equation 4.42 under steady state gives:

$$C_B = C_{AS} \left[E_B - (1-f) / D_B \right] \qquad \dots (4.50\ a)$$

and

$$C_P = C_{AS} \left[E_P + (1-f) / D_P \right] \qquad \dots (4.50\ b)$$

where

$$E_B = C_{BS} / C_{AS} \qquad \dots\dots\dots\dots (4.50\ c)$$

$$E_P = C_{PS} / C_{AS} \qquad \dots\dots\dots\dots (4.50\ d)$$

$$D_B = D_{eff,B} / D_{eff,A} \qquad \dots\dots\dots\dots (4.50\ e)$$

$$D_P = D_{eff,P} / D_{eff,A} \qquad \dots\dots\dots\dots (4.50\ f)$$

$$f = C_A / C_{AS} \qquad \dots\dots\dots\dots (4.50\ g)$$

Reactant A (hydrogen) has been taken as a reference substance.

The steady-state mass balance for hydrogen over a differential thickness in the catalyst pellet, gives

$$D_{eff,A}\ \frac{d^2 C_A}{dx^2} = r \qquad \dots\dots (4.51)$$

or

$$D_{eff,A}\ \frac{d^2 C_A}{dx^2} = \frac{k\ K_A K_B C_A C_B}{(1 + \sqrt{K_A C_A})^2 (1 + K_B C_B)} \qquad \dots\dots (4.52)$$

with boundary conditions at

$$x = 0, \quad C_A = C_{AS} \qquad \dots\dots (4.53)$$

$$x = L, \quad \frac{dC_A}{dx} = 0 \qquad \dots\dots (4.54)$$

r being the reaction rate given by Equation 4.47. Converting Equations 4.52-4.54 into dimensionless form, these equations become:

$$\frac{d^2 f}{dx^2} = \frac{\phi^2 f\ [E_B - (1-f)/D_B]}{(1 + \psi \sqrt{f})^2 [1 + K_B C_{AS} \{E_B - (1-f)/D_B\}]} \qquad \dots (4.55)$$

$$X = 0, \qquad f = 1 \qquad\qquad \cdots\cdots (4.56)$$

$$X = 1, \qquad df/_{dX} = 0 \qquad\qquad \cdots\cdots (4.57)$$

where $X = x/L$; $\quad \psi = \sqrt{K_A C_{AS}}$; $\quad = L\sqrt{\dfrac{k\, K_A K_B C_{AS}}{D_{eff,A}}}$

From the definition, the effectiveness factor can be written as

$$\eta = \frac{-(df/dX)_{X=0}}{(\phi^2 E_B / D_B)/\left[(1+\psi)^2(1+K_B C_{AS} E_B / D_B)\right]} \quad\cdots (4.58)$$

Numerical integration of Eq.4.55 gives f and $\dfrac{df}{dX}$ as a function of X and Eq. 4.58 then gives the values of effectiveness factor as a function of the following parameters:

$$\eta = \eta(\phi, \psi, E_B, D_B) \qquad\qquad \cdots\cdots (4.59)$$

For the given values of D_B, E_B, ψ, the Eqs. 4.55-4.58 were solved numerically and the values of effective diffusivity of hydrogen, $D_{eff,A}$ was estimated to match the experimental data. The numerical integration of Eq. 4.55 was performed by Fourth-order Runge Kutta method. The values of effective diffusivity of hydrogen thus obtained are summarized in Table 4.17. It can be seen that the values of $D_{eff,A}$ varied negligibly with type of the three olefins studied.

TABLE 4.17

EFFECTIVE DIFFUSIVITIES OF H_2 COMPUTED USING RIGOROUS MODEL

Eqs. 4.49 – 4.52

Olefin	Temp. K	Modulus ϕ	$\eta = \sqrt{K_A C_A}$	$K_B C_B$	$D_{eff,A}$ cm^2/s
isooctene	313	17.32	2.80	37.82	3.52×10^{-5}
n-octene	313	22.52	2.79	31.19	3.87×10^{-5}
isododecene	313	14.78	2.87	31.52	3.73×10^{-5}

4.5.5. Simplified Model for Limiting case of hydrogen diffusion
controlling

Further simplification of the foregoing equations
were made on the basis of the following considerations:

(1)   For olefin concentrations much higher than those of
       hydrogen, the experimental effectiveness factor,
       η expt, for the three olefins did not change
       significantly with olefin concentration in bulk
       liquid phase. The global rate for such a case was
       almost zero order in olefin concentration.

(2)   Under the reaction conditions, the liquid olefin
       remain uniformly distributed in the solvent. The

pores of the catalyst remain filled with the liquid containing solvent, liquid olefin and also the products when formed. The surface and interior concentrations may be quite different for hydrogen but differ little in the case of olefins when the ratio of surface concentrations of olefins to hydrogen is ten or more. In earlier studies on liquid phase hydrogenation of unsaturated compounds like styrene, α-methyl styrene and cyclohexene, several authors[6,7,112] have observed that diffusion of hydrogen through the liquid filled pores of the catalyst is rate limiting under the hydrogenation conditions when bulk olefin concentrations are much higher than those of hydrogen.

Under these conditions, Eqs. 4.55-4.58 can be simplified to give,

$$\frac{d^2 f}{dx^2} = \frac{\phi_P^2 f}{(1 + \gamma \sqrt{f})^2} \qquad \ldots (4.60)$$

$$X = 0, \quad f = 1 \qquad \ldots (4.61)$$

$$X = L, \quad df/dx = 0 \qquad \ldots (4.62)$$

where $f = C_A / C_{AS}$; $X = x/L$; $\gamma = \sqrt{K_A C_{AS}}$;

and $\phi_P = L \left[\dfrac{k_v K_A K_B C_B}{(1 + K_B C_B) D_{eff,A}} \right]^{\frac{1}{2}} \qquad \ldots (4.63)$

The results of numerical computation on Equations 4.60-4.62 for this simplified case are shown in Figure 4.40 in which the catalytic effectiveness factor η is plotted against the modulus, ϕ_p with parameter ψ_1. Using this η vs ϕ_p chart, the effective diffusivity of hydrogen, $D_{eff,A}$ was estimated by the following procedure:

First the experimental value of catalytic effectiveness factor, η expt was obtained taking the ratio of the observed reaction rate with the catalyst pellet to the intrinsic reaction rate obtained with powdered catalyst. Knowing η expt and the parameter ψ_1 —which is specified by the temperature and the hydrogen pressure, the corresponding modulus ϕ_p was read on the abscissa in Figure 4.40. The values of $D_{eff,A}$ were then calculated from ϕ_p (Eq. 4.63) for all experimental data; these are summarized in Table 4.18. The tortuosity factors were also calculated from the commonly used Equation 4.64.

$$D_{eff,A} = \frac{D_A \theta}{\tau} \qquad \ldots\ldots (4.64)$$

The values of $D_{eff,A}$ thus computed are summarized in Table 4.18. From Tables 4.17 and 4.18 it can be seen that when the olefin is in excess, hydrogen diffusion through the pores can be assumed to control the reaction rate; the catalytic effectiveness factor and effective diffusivity of H_2 can be estimated using the simplified model described above. The rigorous model
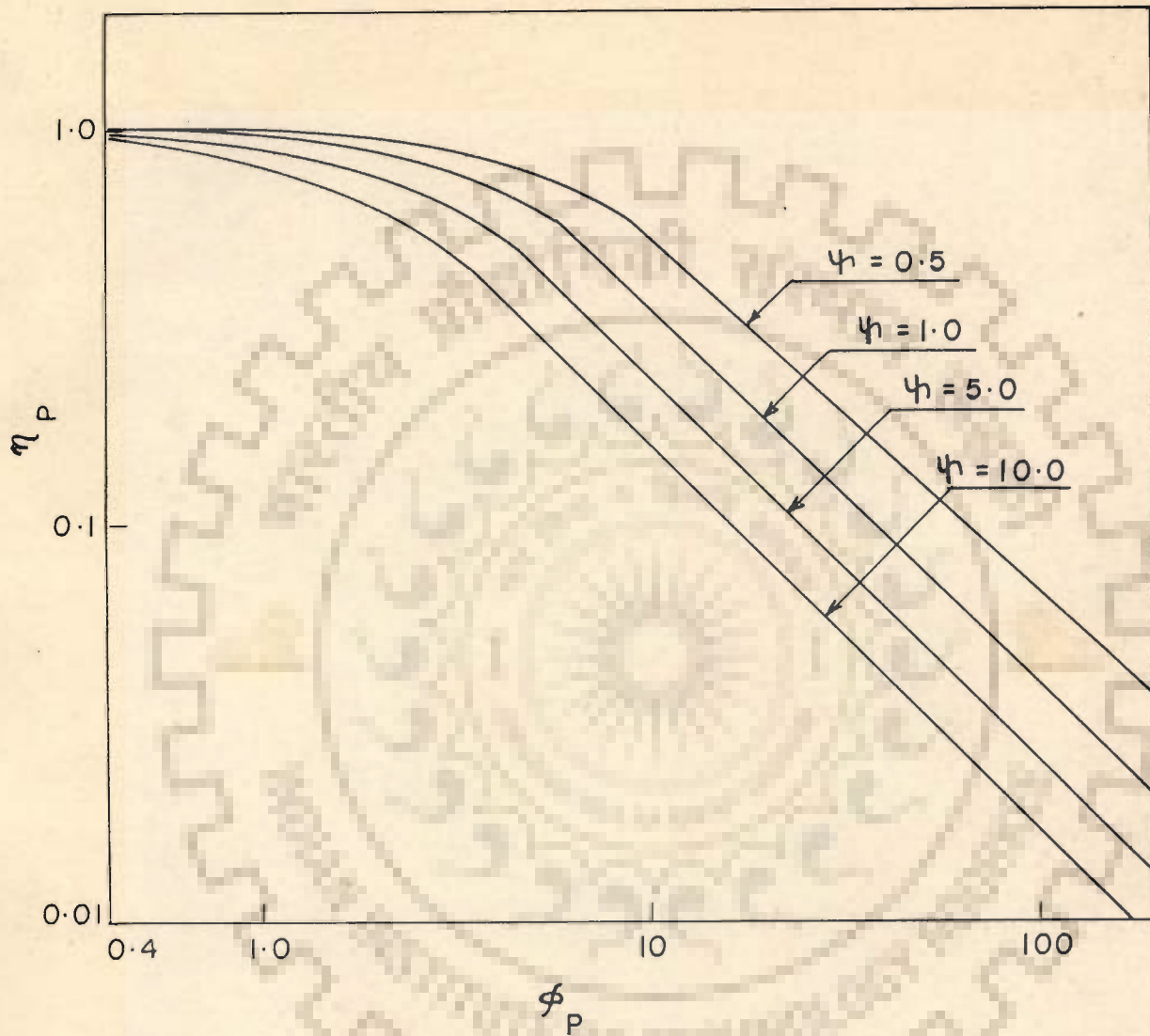
FIG. 4·40 – CATALYTIC EFFECTIVENESS FACTOR η_P Vs
THIELE MODULUS ϕ_P SIMPLIFIED MODEL ;
HYDROGEN DIFFUSION CONTROLLING.

TABLE 4.18

EFFECTIVENESS FACTORS, DIFFUSIVITY OF HYDROGEN AND TORTUOSITY FACTORS FOR THE HYDRO-
GENATION OF OLEFINS ON Pd-Al_2O_3 CATALYST (4 mm x 4 mm size): COMPUTED FROM SIMPLIFIED
MODEL EQUATIONS 4.60-4.63

Olefin	Temp. K	Effective-ness factor, η_{expt}	Modu-lus ϕ_P	$\psi = \sqrt{K_A C_{AS}}$	$K_B C_{BS}$	$D_{eff,A}$ cm^2/s	Tortuosity factor $\tau = D_j\Theta/D_{eff,j}$
Isooctene	313	0.2874	12.0	2.80	14.81	3.88×10^{-5}	2.27
	313	0.278	11.5	2.80	27.24	4.35×10^{-5}	2.03
	313	0.2924	12.5	2.80	37.82	3.72×10^{-5}	2.37
	303	0.46	9.5	3.10	19.0	2.91×10^{-5}	2.56
	333	0.19	13.0	1.74	13.47	5.60×10^{-5}	1.95
n-octene	313	0.23	15.0	2.79	14.67	4.36×10^{-5}	2.02
	313	0.236	15.5	2.79	31.19	4.38×10^{-5}	2.01
	313	0.246	14.0	2.79	42.75	5.28×10^{-5}	1.67
isododecenes	313	0.329	9.6	2.87	12.50	3.69×10^{-5}	2.39
	313	0.297	10.8	2.87	31.52	3.30×10^{-5}	2.67
	313	0.296	10.8	2.87	44.42	3.06×10^{-5}	2.88

can, however, be used for whole of the ranges of olefins and hydrogen concentrations, but it requires computer calculations.

4.6 SUMMARY OF CHAPTER 4

Higher olefins like isooctenes, n-octenes and isododecenes were hydrogenated using a supported palladium catalyst (0.5 % Pd-Al$_2$O$_3$) in stirred slurry and stirred basket reactors between 303 and 333 K at 0.5 - 2.0 MPa pressure; n-heptane was used as a solvent. The effects of agitator speed, catalyst loading, temperature, pressure and initial concentration of olefin on the conversion of olefin feed were determined.

The rate of hydrogenation of these olefins in slurry reactor increased with agitator speed from 200 rpm onward and levelled off at about 600 rpm and above. Further experimental work was, therefore, carried out at 800 rpm which ensured that mass transfer was not restricting the reaction rate. The reaction rate in all the three cases however, varied linearly with the catalyst loadings in the range of 8.8 - 19.0 kg/m^3.

Experimental evidence and suitable calculations showed that mass transfer resistances to the outside of catalyst particles in this apparatus were not

significant, provided the agitation speed is above
700 rpm and catalyst loading remains less than 19.0
kg/m^3. The effectiveness factor in the intrinsic
kinetic study, using powdered catalyst was shown to
be essentially unity; Thiele parameter being in the
range of 0.07 - 0.30.

The rate of hydrogenation for all the three
olefins increased non-linearly with increasing olefin
concentration and hydrogen pressure; hydrogen pressure
influenced the rate to a greater extent than olefin
concentration. Under similar operating conditions
n-octenes reacted at a faster rate than isooctenes and
isododecenes; the rates of hydrogenation followed the
order:

n-octenes $>$ isooctenes $>$ isododecenes

The hydrogenation of these olefins followed almost
zero and fractional order behaviour with respect to
olefin and hydrogen concentration respectively. The
experimental data in the kinetic regime were analysed
to determine the most probable kinetic model to
represent the reaction rate for each olefin feed.
Power law model gave good fit of data in the low
temperature range only. Using non-linear least square
analysis, the following kinetic model was found to
correlate the data, for all the three olefin feeds,

satisfactorily over the temperature (303 - 333 K) and
pressure ranges (0.5 - 2.0 MPa) studied:

$$r = \frac{k \, K_A \, K_B \, C_A \, C_B}{(1 + \sqrt{K_A C_A})^2 (1 + K_B C_B)}$$

The average error between the calculated and observed
reaction rates were $\pm$ 1.32 %, $\pm$ 1.69 % and$\pm$3.01 % for
isooctenes, n-octenes and isododecenes respectively.
The parameters k, K_A and K_B followed Arrhenius
behaviour and the values of activation energies for
hydrogenation of isooctenes, n-octenes and isododecenes
were found to be 69.65, 67.94 and 64.42 kJ./mole
respectively. This good fit of the model suggests
that the broad mechanism of hydrogenation of the three
olefins remained the same and that olefin and hydrogen
are adsorbed non-competitively on the catalyst surface;
the olefin adsorbed reversibly in molecular form and
hydrogen adsorbed in dissociative form on different
sites and the reaction occured through a semihydrogena-
ted state as suggested by Horuity and Polanyi.[161]   Even
though the broad mechanism remains the same, n-octenes
reacted at a faster rate than isooctenes; this may
probably be due to the ease in adsorption of n-octenes
on the catalyst surface.

With pellets the rates of hydrogenation was
influenced by pore diffusion; the absolute rates were

about 1/5 th to 1/3 rd of the rates obtained with powdered catalyst under similar operating conditions. The effective diffusivities of hydrogen were estimated using a simplified theoretical analysis assuming a quasi-steady-state.

Typical values of effective diffusivity of H_2 were found to be in the range of $3.06 - 4.38 \times 10^{-5}$ cm^2/s at 313 K. Using these effective diffusivities, the tortuosity factors of the catalyst were also determined and found to lie in the range of $1.67 - 2.88$; these values are very close to the range of previously published values[6,7] estimated in the liquid phase hydrogenation of various unsaturated compounds and appear to be reasonable for the pore diffusion within a liquid-filled catalyst.

. . . . .

C H A P T E R   5

CONCLUSIONS

Hydrogenation of C_8 -C_{12} olefins, namely, n-octene, iso-octene and iso-dodecene, was studied in the liquid phase using a 0.5% Pd on alumina catalyst at 303-333 K temperature and 0.5 to 2.0 MPa pressures in stirred slurry and rotating basket reactors. n-heptane was used as solvent. The results obtained were evaluated for kinetic parameters including intrinsic reaction rate, rate model, mechanism and the effectiveness factor when the catalyst is used as pellet. These evaluations were done applying generally accepted methods and correlations which have been developed in recent times. Wherever felt necessary, the results have been explained or correlated in mathematical form deduced from basic concepts. Calculations for fitness of results with rate model by non-linear regression was done by using a IBM 370/145 computer.

The experimental results and their evaluation led to the following conclusions:

1. The rate of hydrogenation, in general, increased initially with increasing speed of the agitator and then levelled off at about 600 r.p.m. and above. The influence of agitation on the rate

of reaction was more pronounced with n-octene than with isooctene and isododecene; the trend, however, remained similar.

2. For the catalyst concentrations used in these studies (5.56 - 19.50 kg/m^3) the rates of hydrogenation increased linearly with increase of catalyst concentration. Using powdered catalyst suspended as slurry, the reaction was in kinetic regime at stirrer speed of 600 r.p.m. and above.

3. The hydrogen pressure influenced the rate of hydrogenation more pronouncedly than the olefin concentration. The apparent orders of reaction with respect to both hydrogen and olefin showed an increasing trend with increase in temperature of the reaction.

4. The intrinsic rates of hydrogenation were slightly different for the 3 olefin-feeds used. The hydrogenation rate was much faster for n-octene than those of isooctene and isododecene; the rate decreased in the order:

$$n\text{-octene} > \text{isooctene} > \text{isododecene}$$

5. For the three olefins studied, the power-law rate model could fit the experimental data well only for the lower temperature around 303 K. At 333 K, the deviations were large.

6.   The broad mechanism of the hydrogenation of all the three olefins was found to be similar. The rate data could be correlated well with the reaction rate equation,

$$r = \frac{k\,K_A\,K_B\,C_A\,C_B}{(1 + \sqrt{K_A C_A}\,)^2\,(1 + K_B C_B)}$$

based on Modified Huority Polanyi mechanism which suggests that olefin and hydrogen adsorb non-competitively on the catalyst surface and hydrogen is adsorbed dissociatively. The parameters k, K_A and K_B followed Arrhenius behaviour.

7.   The energies of activation were found to be 67.94, 69.65 and 64.42 kJ/mol for n-octene, iso-octene and isododecene respectively.

8.   When catalyst pellets were used in rotating baskets, the rate of hydrogenation was found to be sufficiently lower than with the powdered catalyst; obviously the reaction rate was affected by the diffusions of reactants, particularly hydrogen through the pores. Under the reaction conditions, the catalyst pores remain filled with the liquid and precise analysis of diffusion of components is difficult. The catalytic effectiveness factor was dependent upon the type of olefin and decreased in the order:

isododecene > isooctene > n-octene.

The effective diffusivity of hydrogen, however, remained almost unaffected by the structural differences of these olefins.

9. The rates of reaction for the hydrogenation of the three olefins were clearly found to be different. The three olefins differ in their molecular structure and linear chain length. In industrial practice, mixed olefinic feeds are often required to be hydrogenated. It would, therefore, be interesting if some approximation could be made about the hydrogenation reaction rate from the knowledge of structure or other properties of such olefin molecule.

The general structure of the three olefin molecules studied, their standard heat and entropies of formation and properties related to hydrogenation, namely, the equilibrium constant and the heat of reaction are shown in Table 5.1; the respective reaction rates are given in Table 5.2.

Broad comparison of the reaction rates show that:

(i) The rate of hydrogenation decreased with increasing chain length and methyl group branching in the olefin molecule.

TABLE 5.1

CHARACTERISTICS OF OlEFIN MOLECULES

Olefin	Molecular dimensions			Heat of formation	Heat of reaction	Equilibrium constant, K at 298 K
	no. of carbon atoms	C-atoms in linear chain	CH_3-group branching	$\Delta H_{f,298K}$, kJ/mol.	ΔH_{298K}, kJ/mol	
n-octene	8	8	0	92.96 – 93.76	133.5	2.44×10^{15}
isooctene	8	5	3	98.37 –109.04	126.5	3.7×10^{13}
isododecene	12	7	5	210.38	118.2	4.0×10^{12}

TABLE 5.2

ENERGETIC FACTORS AND RATES OF REACTION

Olefin	Adsorption Equilibrium const. K_B, $m^3.mol^{-1}$	Energy of activation kJ, mol^{-1}	Entropy of formation, S^o_{298K} $J.mol^{-1}.K^{-1}$	Difference in standard entropy of olefin and paraffins, $J.mol^{-1}.K^{-1}$	Relative rate of reaction at 313 K and 0.5 MPa.
n-octene	28.13	67.94	460.33[a]	4.186[b]	1 (0.2866 x 10^{-1})
isooctene	26.87	69.65	428.10[a]	4.772[b]	0.56 (0.1612 x 10^{-1})
isododecene	31.88	64.42	622.83[a]	5.818[b]	0.32 (0.7785 x 10^{-2})

Notes- The bracketted figures in column 6 are the absolute reaction rates.

a- The entropy is expressed as an average of all isomers taken together.

b- 2,4,4- TMP-1, octene-1, 4-methylene, 2,2,6,6-tetramethyl heptane, 2,4,4-TMP, n-octane and isododecane were taken as model compounds.

(ii) The decrease in the reaction rate with increasing
molecular dimensions of the olefin molecule showed
some correspondence with standard heat of formation
of the olefins, heat of hydrogenation and
equilibrium constant; the rate decreased with
increase in heat of formation of the olefin, while
it increased with increase of the standard heat of
reaction and the equilibrium constant.

(iii) The rate of hydrogenation did not show any trend,
or relationship in respect of adsorption equili-
brium constant of the olefin molecules on the
catalyst surface, energy of activation or
standard entropy of formation. When the difference
in standard entropies of formation of the olefin
and the corresponding paraffin is compared with
the rate of hydrogenation, there appears to be
some possible trend; when this difference in the
entropy values are higher the reaction rate was
lower.

The data available here are only with 3 olefins;
when more data with many olefins are available,
some generalised relationship may possibly be
established. It can, however, be stated that
the variations of the reaction rates with molecular
configuration of the olefins may be attributed to
both geometrical as well as energetic factors
involved.

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A P P E N D I X -1

CALCULATIONS OF DIFFUSIONAL RESISTANCES

A. Calculations for Diffusivity of Hydrogen:

Basis:

Temperature, $T = 333$ K

Molal volume at N.B.P., $V_b = 14.3$ cm^3/gmol

Molecular weight of solvent n-heptane, $M = 100$

Viscosity of solvent, $\mu = 0.274$ C.P.

Association parameter for n-heptane, $\emptyset = 1.0$

Substituting these values in Eq. 4.1, one gets the

diffusion coefficient of H_2 in n-heptane at 333 K =

$$1.825 \times 10^{-4} \text{cm}^2/\text{s}$$

B. Calculations for Liquid/solid Mass Transfer
Coefficients, K_{ls} :

Basis: Temperature 313 K; olefin isooctene

$D_A = 1.437 \times 10^{-4}$ cm^2/s; $d_p = 80 \times 10^{-4}$ cm

$\mu = 0.35$ C.P.; $\rho_a = 1.638 + 0.60 \times 0.668$

$(= 2.038$ g/cm^3); $\rho_l = 0.668$ g/cm^3; $g = 981$ cm/s^2

substituting these values in Brain and Hales correlation

(Eq. 4.6) the value of liquid-solid mass transfer

coefficient, K_{ls} obtained is $\simeq 327$ cm/hr.

C. Estimation of Thiele Parameter and Effectiveness
factor:

Basis: Hydrogenation of isooctene at 313 K and

0.5 MPa.

Thiele Parameter is given by the correlation,

$$\emptyset = \frac{d_p^2}{D_A \Theta} \cdot \frac{-r_A \rho_p}{m} \cdot \frac{1}{C_A} \quad \ldots\ldots\ldots (A)$$

Catalyst particle diameter, $d_p = 75 \times 10^{-4}$ cm

Particle density, $\rho_p = 1.633$ g/cm^3 (Table 3.3)

Porosity, $\Theta = 0.60$ (Table 3.3)

Diffusivity of H_2 in n-heptane at 313 K

$$D_A = 1.437 \times 10^{-4} \text{cm}^2/\text{s} \quad \text{(Table 4.1)}$$

Solubility of H_2 in n-heptane at 313 K

$$C_A = 3.020 \times 10^{-5} \text{ gmol/cm}^3 \quad \text{(Table 4.2)}$$

Amount of catalyst, m = 7.81 g

Reaction rate at 313 K and 0.5 MPa,

$$-r_A = 0.1612 \times 10^{-1} \text{ gmol/gcat/hr}$$

$$= 0.03643 \times 10^{-3} \text{ gmol/s}$$

substituting the above values in Eq. A, the value of $\emptyset$ was obtained to be $\simeq 0.165$; this shows that effectiveness factor, $\eta = 1.0$ (Ref. 131).

A P P E N D I X 2

EXPERIMENTAL DATA

Explanatory Notes

1. Initial volume of liquid reactants in each run= $0.450 \times 10^{-3} m^3$

2. The 1st row of data for each Run represents the following variables in order:

   Run No./Feed stock/ Temp, K/ Pressure, MPa/ Catalyst weight, kg x 10^3/ Agitator speed, rpm/

3. Symbols: t = time, minutes; BR = Bromine number of reacting mixture; C_B = Olefin concentration; r_i= reaction rate, kmol. $(kg\text{-}cat)^{-1}.hr^{-1}$; IO-F1 = isooctene feed 1; IO-F2 = isooctene Feed 2; Io-F3 = isooctene feed 3; ID = isododecene; NO = n-octene.

t	BR	C_B	$r_i x 10^2$	BR	C_B	$r_i x 10^2$

EXPERIMENTS WITH POWDERED CATALYST

Run 1 Io-F1/313/0.5/7.81/800/   **Run 3** Io-F1/313/0.5/3.88/800/

t	BR	C_B	$r_i x 10^2$	BR	C_B	$r_i x 10^2$
0	12.9702	0.5572	1.6173	12.9702	0.5572	1.4797
15	12.2351	0.5256	-	12.6233	0.5423	-
30	11.4850	0.4934	-	12.2392	0.5258	-
45	10.7682	0.4626	-	11.8715	0.5100	-
60	10.0302	0.4309	-	11.5502	0.4962	-
75	0.2900	0.3991	-	11.1429	0.4787	-
90	8.5125	0.3657	-	10.7728	0.4628	-

Run 2 Io-F1/313/0.5/4.67/800/   **Run 4** Io-F1/313/0.5/5.92/800/

t	BR	C_B	$r_i x 10^2$	BR	C_B	$r_i x 10^2$
0	12.9702	0.5572	1.5639	12.9702	0.5572	1.6875
15	12.5302	0.5383	-	12.4068	0.5330	-
30	12.0810	0.5190	-	11.8552	0.5093	-
45	11.6573	0.5008	-	11.2942	0.4852	-
60	11.2127	0.4817	-	10.7495	0.4618	-
75	10.7448	0.4616	-	10.1838	0.4375	-
90	10.3119	0.4430	-	9.5949	0.4122	-

Run 5   Io-F1/313/0.5/4.50/800/

0	12.9702	0.5572	1.6191
15	12.5465	0.5390	-
30	12.1322	0.5212	-
45	11.7062	0.5029	-
60	11.1801	0.4803	-
75	10.7565	0.4621	-
90	10.3305	0.4438	-

Run 6   Io-F1/313/0.5/5.41/800/

12.9702	0.5572	1.6472
12.4534	0.5350	-
11.9483	0.5133	-
11.4455	0.4917	-
10.8705	0.4670	-
10.3770	0.4458	-
9.9161	0.4260	-

Run 7   Io-F1/313/0.5/6.43/1200/

0	12.9702	0.5572	1.6240
15	12.3601	0.5310	-
30	11.7503	0.5048	-
45	11.1265	0.4780	-
60	10.5678	0.4540	-
75	9.9300	0.4266	-
90	9.3155	0.4002	-

Run 8   Io-F1/313/0.5/6.99/800/

12.9702	0.5572	1.5833
12.3252	0.5295	-
11.6804	0.5018	-
11.0333	0.4740	-
10.3769	0.4458	-
9.6879	0.4162	-
9.1037	0.3911	-

Run 9   Io-F1/323/0.5/7.23/800/

0	12.9702	0.5572	2.7930
15	11.7945	0.5067	-
30	10.5981	0.4553	-
45	9.4272	0.4050	-
60	8.2680	0.3552	-
75	7.0949	0.3048	-
90	5.7006	0.2449	-

Run 10   ID/313/0.5/3.97/800/

8.6687	0.3730	0.7435
8.4889	0.3682	-
8.2978	0.3570	-
8.1179	0.3493	-
7.9250	0.3410	-
7.7251	0.3324	-
7.6159	0.3277	-

Run 11   ID/323/0.5/7.13/800/

0	8.6687	0.3730	1.4100
15	8.0830	0.3478	-
30	7.4997	0.3227	-
45	6.9024	0.2970	-
60	6.3237	0.2721	-
75	5.7450	0.2472	-
90	5.1594	0.2220	-

Run 12   ID/313/0.5/7.33/800/

8.6687	0.3730	0.7735
8.3364	0.3587	-
8.0017	0.3443	-
7.6787	0.3304	-
7.3440	0.3160	-
7.0140	0.3018	-
6.6677	0.2869	-

Run 13   ID/313/0.5/4.26/800/

0	8.6687	0.3730	0.7584
15	8.4781	0.3649	-
30	8.2806	0.3563	-
45	8.0877	0.3480	-
60	7.9413	0.3417	-
75	7.7484	0.3334	-
90	7.5741	0.3259	-

Run 14   ID/313/0.5/6.01/800/

8.6687	0.3730	0.8490
8.3666	0.3600	-
8.0668	0.3471	-
7.7925	0.3353	-
7.4811	0.3218	-
7.2022	0.3099	-
6.9140	0.2975	-

Run 15   ID/313/0.5/7.88/1200/

0	8.6687	0.3730	0.7610
15	8.3201	0.3580	—
30	7.9692	0.3429	—
45	7.6113	0.3275	—
60	7.2929	0.3138	--
75	7.1604	0.3081	—
90	6.5422	0.2815	—

Run 16   ID/313/0.5/6.85/800/

5.9266	0.2550	0.6240
5.6776	0.2443	.—
5.4267	0.2335	—
5.1826	0.2230	—
4.9247	0.2119	—
4.6830	0.2015	—
4.4227	0.1903	—

Run 17   ID/313/0.5/7.69/460/

0	8.6687	0.3730	0.7594
15	8.3294	0.3584	—
30	7.9878	0.3437	—
45	7.6577	0.3295	—
60	7.3184	0.3149	—
75	6.9768	0.3002	—
90	6.6421	0.2858	—

Run 18   ID/333/0.5/6.47/800/

5.9266	0.2550	3.1600
4.7364	0.2038	—
3.5233	0.1516	—
2.3519	0.1012	—
1.0970	0.0472	—
0.4881	0.0210	—
—	—	—

Run 19   ID/313/0.5/8.20/200/

0	8.6687	0.3730	0.4520
15	8.4526	0.3637	—
30.	8.2271	0.3540	—
45	8.0133	0.3448	—
60	7.7786	0.3347	—
75	7.5903	0.3266	—
90	7.3696	0.3171	—

Run 20   No/323/0.5/7.33/800/

12.1497	0.5218	5.4330
9.8282	0.4221	—
7.5347	0.3236	—
5.1947	0.2231	—
2.0732	0.1234	—
0.5588	0.0240	—
—	—	—

Run 21   ID/313/0.5/7.79/300/

0	8.6687	0.3730	0.5422
15	8.4014	0.3615	—
30	8.1806	0.3520	—
45	7.9413	0.3417	—
60	7.7017	0.3314	—
75	7.4579	0.3209	—
90	7.2115	0.3103	—

Run 22   No/313/0.5/7.11/1200/

12.1497	0.5218	2.9480
10.9202	0.4690	—
9.7071	0.4169	—
8.4777	0.3641	—
7.2646	0.3120	—
6.0492	0.2598	—
4.6778	0.2009	—

Run 23   No/313/0.5/6.82/460/

0	12.1497	0.5218	2.7580
15	11.0553	0.4748	—
30	9.9586	0.4277	—
45	8.8736	0.3811	—
60	7.7699	0.3337	—
75	6.6639	0.2862	—
90	—	—	—

Run 24   No/313/0.5/6.77/200/

12.1497	0.5218	1.4448
11.5745	0.4971	—
11.0064	0.4721	—
10.4173	0.4474	—
9.9027	0.4253	—
9.3020	0.3995	—
9.1972	0.3950	—

Run 25   No/313/0.5/6.95/300/

0	12.1497	0.5218	2.2038
15	11.3231	0.4863	–
30	10.0480	0.4501	–
45	9.6606	0.4149	–
60	8.8479	0.3800	–
75	8.0237	0.3446	–
90	7.2297	0.3105	–

Run 26   No/313/0.5/5.29/800/

12.1497	0.5218	2.9250
11.2462	0.4830	–
10.3707	0.4454	–
9.4254	0.4048	–
8.5453	0.3670	–
7.6779	0.3276	–
6.7361	0.2893	–

Run 27   No/333/0.5/2.71/1200/

0	12.1497	0.5218	10.0520
15	10.5617	0.4536	–
30	8.9738	0.3854	–
45	7.4160	0.3185	–
60	5.8190	0.2499	–
75	4.2377	0.1820	–
90	2.6590	0.1142	–

Run 28   No/313/0.5/3.6/800/

12.1497	0.5218	2.9660
11.5250	0.4950	–
10.8946	0.4679	–
10.2660	0.4409	–
9.6303	0.4136	–
9.0645	0.3893	–
8.4079	0.3611	

Run 29   No/333/0.5/2.55/460/

0	12.1497	0.5218	9.6200
15	10.7153	0.4602	–
30	9.0645	0.3892	–
45	7.8258	0.3361	–
60	6.1097	0.2624	–
75	4.7755	0.2051	–
90	3.1154	0.1338	–

Run 30   No/313/0.5/2.52/800/

12.1497	0.5218	2.9100
11.7166	0.5032	–
11.2952	0.4851	–
10.8411	0.4656	–
10.4430	0.4485	–
10.0704	0.4325	–
9.6629	0.4150	–

Run 31   No/313/0.5/4.94/800/

0	12.1497	0.5218	3.0454
15	11.2742	0.4842	–
30	10.3615	0.4450	–
45	9.4883	0.4075	–
60	8.7316	0.3750	–
75	7.7420	0.3325	–
90	6.9271	0.2975	–

Run 32   No/333/0.5/2.98/800/

25.7585	1.1090	9.9700
24.4880	1.0350	–
22.4830	0.9670	–
20.5688	0.8865	–
18.8865	0.8140	–
17.1117	0.7375	–
15.3854	0.6631	–

Run 33   No/303/0.5/7.40/800/

0	4.3524	0.1863	0.7734
15	4.0110	0.1721	–
30	3.6778	0.1578	–
45	3.3468	0.1436	–
60	2.9832	0.1280	–
75	2.6849	0.1152	–
90	2.3104	0.0991	–

Run 34   Io–F1/303/0.5/6.98/800

12.9702	0.5572	0.6293
12.7165	0.5463	0.6263
12.4651	0.5355	0.6247
12.2114	0.5246	0.6235
11.9553	0.5136	0.6197
11.7086	0.5030	0.6134
11.4595	0.4923	0.6145

Run 35   Io–F1/303/2.0/7.04/800/

0	12.9702	0.5572	0.8048
15	12.6467	0.5433	0.8016
30	12.3254	0.5295	0.7985
45	12.0019	0.5156	0.7953
60	11.6806	0.5018	0.7931
75	11.3571	0.4879	0.7913
90	11.0801	0.4760	0.7910

Run 36 Io-F1/303/1.0/6.9/800/

0	12.9702	0.5572	0.7087
15	12.6039	0.5449	0.7083
30	12.4022	0.5328	0.7078
45	12.1103	0.5206	0.7074
60	11.8320	0.5083	0.7070
75	11.5480	0.4961	0.7065
90	11.2663	0.4840	0.7061

Run 37 Io-F1/303/0.5/6.83/800

23.7838	1.0250	0.6414
23.5280	1.0140	0.6407
23.2727	1.0030	0.6400
23.0198	0.9921	0.6393
22.7669	0.9812	0.6387
22.5140	0.9703	0.6380
22.2611	0.9594	0.6370

Run 38 Io-F1/303/1.5/7.31/800

0	12.9702	0.5572	0.7572
15	12.6490	0.5434	0.7566
30	12.3371	0.5300	0.7559
45	12.0042	0.5157	0.7553
60	11.6830	0.5019	0.7546
75	11.3617	0.4881	0.7539
90	11.0475	0.4746	0.7533

Run 39 Io-F1/303/0.5/6.51/800/

32.9225	1.4230	0.6469
32.6911	1.4130	0.6461
32.3903	1.4000	0.6458
32.2052	1.3920	0.6454
31.9507	1.3810	0.6452
31.7194	1.3710	0.6450
31.4649	1.3600	0.6445

Run 40 Io-F1/303/0.5/7.12/800

0	4.4823	0.1920	0.5699
15	4.2536	0.1822	0.5673
30	4.0271	0.1724	0.5646
45	3.8006	0.1628	0.5619
60	3.5765	0.1532	0.5493
75	3.5882	0.1537	0.5466
90	3.1283	0.1340	0.5440

Run 41 Io-F1/313/1.5/6.55/800

12.9702	0.5572	1.9780
12.2044	0.5243	1.9760
11.4525	0.4920	1.9740
10.7193	0.4605	1.9730
9.9581	0.4278	1.9710
9.1923	0.3949	1.9690
8.4567	0.3633	1.9680

Run 42 Io-F1/303/0.5/7.69/800

0	8.6240	0.3700	0.6120
15	8.3513	0.3583	0.6097
30	8.0809	0.3467	0.6075
45	7.8059	0.3349	0.6055
60	7.5355	0.3233	0.6043
75	7.3747	0.3164	0.6037
90	7.1369	0.3062	0.6045

Run 43 Io-F1/313/2.0/7.03/800

12.9702	0.5572	2.0920
12.1113	0.5203	2.0770
11.2826	0.4847	2.0630
10.4097	0.4472	2.0500
9.5996	0.4124	2.0370
8.7593	0.3763	2.0260
7.9330	0.3408	2.0150

Run 44 Io-F1/313/0.5/7.0/800

0	12.9702	0.5572	1.6120
15	12.3138	0.5290	1.6080
30	11.6597	0.5009	1.6030
45	11.0079	0.4729	1.5990
60	10.3562	0.4449	1.5950
75	9.7067	0.4170	1.5910
90	9.0596	0.3892	1.5880

Run 45 Io-F1/313/0.5/6.12/800

4.4823	0.1920	1.4490
3.9641	0.1698	1.4200
3.4668	0.1485	1.3810
2.9906	0.1281	1.3310
2.5120	0.1076	1.2700
2.0754	0.0889	1.1990
1.6622	0.0712	1.1740

Run 46 Io-F1/313/1.0/8.33/800/

0	12.9702	0.5572	1.8480
15	12.0671	0.5184	1.8440
30	11.1522	0.4790	1.8400
45	10.2933	0.4422	1.8370
60	9.4041	0.4040	1.8330
75	8.5033	0.3653	1.8290
90	7.6211	0.3274	1.8250

Run 47 Io-F1/313/0.5/7.99/800

32.9225	1.4230	1.6740
32.1590	1.3900	1.6720
31.4418	1.3560	1.6740
30.6089	1.3230	1.6670
29.8454	1.2900	1.6510
29.0819	1.2570	1.6260
28.3415	1.2250	1.5930

Run 48	Io-F1/313/2.0/8.14/800/		
0	23.7838	1.0250	2.1630
15	23.0059	0.9915	2.1620
30	22.2332	0.9582	2.1510
45	21.4606	0.9249	2.1400
60	20.6879	0.8916	2.1120
75	19.9199	0.8585	2.1000
90	19.1565	0.8256	2.0970

Run 49	Io-F1/333/1.5/2.52/800/		
	12.9702	0.5572	7.2640
	11.6737	0.5015	7.1950
	10.4260	0.4479	7.1240
	9.1550	0.3933	6.9550
	7.9097	0.3398	6.9470
	6.6667	0.2864	6.8980
	5.4469	0.2340	6.8180

Run 50	Io-F1/313/0.5/6.55/800		
0	4.4823	0.1920	1.5230
15	3.9267	0.1682	1.4420
30	3.3944	0.1454	1.3610
45	2.8855	0.1236	1.2810
60	2.3976	0.1027	1.2000
75	1.9517	0.0836	1.1190
90	1.5478	0.0668	1.0380

Run 51	Io-F1/333/2.0/2.90/800		
	12.9702	0.5572	7.6140
	11.0987	0.4768	7.5480
	9.2458	0.3972	7.4320
	7.4651	0.3207	7.2650
	5.6750	0.2438	7.0480
	3.9758	0.1708	6.7800
	2.3510	0.1010	6.4620

Run 52	Io-F3/333/0.5/7.51/800		
0	12.9702	0.5572	5.4200
15	10.6099	0.4558	5.3050
30	8.2658	0.3551	5.1000
45	5.9637	0.2562	4.8180
60	3.9548	0.1699	4.5140
75	1.8296	0.0786	3.6260
90	0.7030	0.0302	2.1540

Run 53	Io-F1/333/0.5/4.82/800		
	23.7838	1.0250	5.5520
	22.2240	0.9578	5.5510
	20.6763	0.8911	5.5539
	19.1310	0.8245	5.5140
	17.5949	0.7583	5.4770
	16.0659	0.6924	5.4270
	14.5600	0.6275	5.3650

Run 54	Io-F1/333/1.0/3.45/800		
0	12.9702	0.5572	6.5220
15	11.6667	0.5012	6.4930
30	10.3701	0.4455	6.4440
45	9.0689	0.3896	6.3740
60	7.7980	0.3350	6.2830
75	6.5619	0.2819	6.1710
90	5.3282	0.2289	6.0390

Run 55	Io-F1/333/0.5/3.01/800		
	4.4823	0.1920	4.6510
	3.7213	0.1594	4.2880
	3.0489	0.1306	4.2010
	2.4816	0.1063	4.1160
	2.0194	0.0865	3.8660
	1.6832	0.0721	3.6290
	1.4287	0.0612	3.1950

Run 56	Io-F1/333/2.0/3.96/800		
0	32.9225	1.4230	7.9730
15	31.1179	1.3450	7.9900
30	29.2670	1.2650	7.9980
45	27.4392	1.1860	7.9940
60	25.6859	1.1070	7.9800
75	23.8520	1.0280	7.9550
90	22.0267	0.9493	7.9200

Run 57	ID/303/1.5/8.16/800/		
	8.6687	0.3730	0.5371
	8.4199	0.3623	0.5339
	8.1411	0.3503	0.5307
	7.8692	0.3386	0.5276
	7.6391	0.3287	0.5244
	7.3648	0.3169	0.5212
	7.0279	0.3024	0.5203

Run 58	Io-F1/333/2.0/4.23/800/		
0	12.9702	0.5572	7.8810
15	11.7039	0.5028	7.5400
30	10.4516	0.4490	7.3430
45	9.1690	0.3939	7.2900
60	7.9074	0.3397	7.2810
75	6.7784	0.2912	7.2160
90	5.3538	0.2300	7.1940

Run 59	ID/303/2.0/6.50/800/		
	8.6687	0.3730	0.5538
	8.4595	0.3640	0.5490
	8.2387	0.3545	0.5476
	7.9993	0.3442	0.5467
	7.7692	0.3343	0.5453
	7.5368	0.3244	0.5443
	7.3207	0.3150	0.5413

Run 60	ID/3 03/0.5/7.84	800/		Run 61	ID/3 03/0.5/6.60/800	
0	8.6687	0.3730	0.4443	5.9266	0.2550	0.4200
15	8.4687	0.3644	0.4371	5.7636	0.2480	0.4196
30	8.2735	0.3560	0.4369	5.5800	0.2401	0.4177
45	8.0481	0.3463	0.4346	5.4267	0.2335	0.4165
60	7.8389	0.3373	0.4324	5.2593	0.2263	0.4151
75	7.5996	0.3270	0.4314	5.1129	0.2200	0.4134
90	7.4346	0.3199	0.4309	4.9293	0.2121	0.5113

Run 62	ID/3 03/1.0/7.38/800/			Run 63	ID/3 03/0.5/6.97/800/	
0	8.6687	0.3730	0.4958	30.5975	1.3250	0.4650
15	8.4455	0.3634	0.4956	30.4128	1.3170	0.4641
30	8.2317	0.3542	0.4955	30.2281	1.3090	0.4642
45	8.0272	0.3454	0.4953	29.8586	1.2930	0.4641
60	7.7808	0.3348	0.4952	29.8355	1.2920	0.4639
75	7.5322	0.3241	0.4950	29.6508	1.2840	0.4639
90	7.3253	0.3152	0.4919	29.4198	1.2740	0.4638

Run 64	ID/3 03/0.5/7.34/800/			Run 65	ID/3 13/1.5/9.25/800	
0	21.7126	0.9402	0.4600	8.6687	0.3730	0.9355
15	21.5176	0.9318	0.4596	8.1620	0.3512	0.9292
30	21.3236	0.9234	0.4594	7.5810	0.3262	0.9104
45	21.1296	0.9150	0.4592	7.1557	0.3079	0.9079
60	20.9218	0.9060	0.4591	6.7397	0.2900	0.9080
75	20.7463	0.8984	0.4589	6.5119	0.2802	0.9109
90	20.4830	0.8870	0.4584	5.8054	0.2488	0.9066

Run 66	ID/3 03/0.5/7.17/800/			Run 67	ID/3 13/2.0/6.77/800/	
0	11.7000	0.5036	0.4561	8.6687	0.3730	0.9200
15	11.5388	0.4956	0.4460	8.2642	0.3556	0.9190
30	11.2992	0.4862	0.4453	7.8529	0.3379	0.9086
45	11.1205	0.4785	0.4452	7.8947	0.3397	0.9033
60	10.9671	0.4719	0.4444	7.1162	0.3062	0.9012
75	10.7114	0.4609	0.4440	6.7188	0.2891	0.8920
90	10.5836	0.4554	0.4427	6.4515	0.2776	0.8910

Run 68	ID/3 13/0.5/8.66/800/			Run 69	ID/3 13/0.5/7.18/800/	
0	8.6687	0.3730	0.7785	21.7126	0.9042	0.7952
15	8.2317	0.3542	0.7039	21.3097	0.9228	0.7937
30	7.9063	0.3402	0.6980	20.8987	0.9050	0.7920
45	7.5298	0.3240	0.6959	20.5292	0.8890	0.7917
60	7.1324	0.3069	0.6811	20.1366	0.8720	0.7902
75	6.7350	0.2898	0.6773	19.7279	0.8543	0.7901
90	6.4190	0.2762	0.6740	19.3038	0.8394	0.7883

Run 70	ID/3 13/1.0/7.07/800/			Run 71	ID/3 13/0.5/6.38/800/	
0	8.6687	0.3730	0.8982	30.5975	1.3250	0.8175
15	8.2921	0.3568	0.8375	30.2973	1.3120	0.8172
30	7.9482	0.3420	0.8280	30.0203	1.3000	0.8166
45	7.5972	0.3269	0.8273	29.7662	1.2890	0.8160
60	7.2091	0.3102	0.8191	29.6046	1.2820	0.8152
75	6.8061	0.2963	0.8100	29.4198	1.2740	0.8147
90	6.5445	0.2816	0.8010	29.1889	1.2640	0.8134

Run 72	ID/3 13/2.0/7.08/800/			Run 73	ID/333/1.5/4.37/800/		
0	30.5975	1.3250	1.0700	8.6687	0.3730	4.5230
15	30.1819	1.3070	1.0730	7.3695	0.3171	4.2950
30	29.7662	1.2890	1.0630	6.0611	0.2608	4.2000
45	29.3736	1.2720	1.0620	4.7968	0.2064	3.9990
60	28.9580	1.2540	1.0620	3.6069	0.1552	3.7180
75	28.5192	1.2350	1.0600	2.4402	0.1050	3.8180
90	28.1266	1.2180	1.0600	1.4223	0.0612	3.5410

Run 74	ID/3 13/2.0/7.56/800/			Run 75	ID/333/2.0/4.84 800/		
0	8.6687	0.3730	0.9582	8.6687	0.3730	5.0350
15	8.2178	0.3536	0.9550	7.2626	0.3125	5.0130
30	7.8321	0.3372	0.9543	5.9937	0.2579	4.9900
45	7.4090	0.3188	0.9534	4.6713	0.2010	4.9680
60	6.9767	0.3002	0.9490	3.2583	0.1402	4.8460
75	6.5212	0.2806	0.9475	2.0916	0.0900	4.8240
90	6.1099	0.2629	0.9468	1.1086	0.0477	4.9020

Run 76	ID/333/0.5/5.98/800/			Run 77	ID/333/0.5/5.51/800/		
0	8.6687	0.3730	3.2450	21.7126	0.9402	3.4480
15	7.6321	0.3248	3.1200	20.6378	0.8937	3.4430
30	6.4422	0.2772	3.0520	19.5247	0.8455	3.4360
45	5.3708	0.2311	2.9580	18.4486	0.7989	3.4310
60	4.2809	0.1842	2.8110	17.3933	0.7532	3.4250
75	3.3200	0.1432	2.6640	16.1717	0.7003	3.4190
90	2.3240	0.1000	2.4260	15.2133	0.6588	3.4140

Run 78	ID/333/1.0/6.02/800/			Run 79	ID/333/0.5/6.20/800/		
0	8.6687	0.3730	4.1200	30.5975	1.3250	3.5090
15	7.5322	0.3241	4.0050	29.3505	1.2710	3.5040
30	6.4399	0.2771	3.9570	28.1036	1.2170	3.4980
45	5.3453	0.2300	3.8510	26.7873	1.1600	3.4930
60	4.3041	0.1852	3.8080	25.6788	1.1120	3.4870
75	3.2165	0.1384	3.7180	24.2933	1.0520	3.4820
90	2.1892	0.0942	3.6930	23.1156	1.0010	3.4760

Run 80	ID/333/2.0/6.46/800/			Run 81	ID/333/2.0/6.33/800/		
0	30.5975	1.3250	5.0100	8.6687	0.3730	5.4420
15	28.7271	1.2440	4.9670	6.8814	0.2961	4.6580
30	26.7642	1.1590	4.9480	5.1222	0.2204	4.3410
45	24.9399	1.0800	4.9380	3.4674	0.1492	3.7990
60	23.0717	0.9991	4.9030	2.0196	0.0869	3.2570
75	21.3005	0.9224	4.8610	0.7297	0.0314	2.7150
90	19.5293	0.8457	4.8610	0.1441	0.0062	2.1740

Run 82	No/3 03/1.5/6.43/800/			Run 83	No/3 03/2.0/6.58/800/		
0	12.1497	0.5218	1.6010	12.1497	0.5218	1.6030
15	11.5653	0.4967	1.5870	11.5164	0.4946	1.6130
30	10.9739	0.4713	1.5730	10.9017	0.4682	1.6240
45	10.3964	0.4465	1.5590	10.2823	0.4416	1.6350
60	9.7771	0.4199	1.5450	9.6606	0.4149	1.6470
75	9.2252	0.3962	1.5310	9.0250	0.3876	1.6580
90	8.6618	0.3720	1.5170	8.3777	0.3598	1.6690

Run 84   No/303/0.5/6.30/800/

0	12.1497	0.5218	1.3180
15	11.6747	0.5014	1.3030
30	11.1765	0.4800	1.2880
45	10.7457	0.4615	1.2730
60	10.2567	0.4405	1.2580
75	9.7934	0.4206	1.2430
90	9.3533	0.4017	1.2280

Run 85   No/303/0.5/6.92/800/

25.7585	1.1090	1.3370
25.2242	1.0860	1.3370
24.6668	1.0620	1.3380
24.1326	1.0390	1.3380
23.5984	1.0160	1.3390
23.0851	0.9939	1.3390
22.5299	0.9700	1.3400

Run 86   No/303/1.0/6.86/800/

0	12.1497	0.5218	1.5170
15	11.5583	0.4964	1.4960
30	10.9646	0.4709	1.4750
45	10.3871	0.4461	1.4550
60	9.7747	0.4198	1.4340
75	9.2345	0.3966	1.4130
90	8.6734	0.3725	1.3920

Run 87   No/303/0.5/7.04/800/

35.2023	1.5200	1.3570
34.6465	1.4960	1.3490
34.0907	1.4720	1.3410
33.5580	1.4490	1.3340
33.0022	1.4250	1.3260
32.4695	1.4020	1.3180
31.9368	1.3790	1.3110

Run 88   No/303/2.0/7.23/800/

0	4.3524	0.1863	1.5680
15	3.7240	0.1594	1.4930
30	3.0979	0.1326	1.4180
45	2.5232	0.1080	1.3430
60	1.9508	0.0835	1.2690
75	1.4391	0.0616	1.1940
90	0.9602	0.0411	1.1880

Run 89   No/313/1.5/6.81/800/

12.1497	0.5218	3.5450
10.7690	0.4625	3.4920
9.3999	0.4037	3.4380
8.0331	0.3450	3.3850
6.6826	0.2870	3.3310
5.4113	0.2324	3.2770
4.1050	0.1763	3.2230

Run 90   No/303/2.0/6.16/800/

0	9.2142	0.3944	1.6160
15	8.6348	0.3696	1.6060
30	8.0554	0.3448	1.5970
45	7.4854	0.3204	1.5880
60	6.9153	0.2960	1.5790
75	6.3499	0.2718	1.5700
90	5.7846	0.2476	1.5600

Run 91   No/313/2.0/6.50/800/

12.1497	0.5218	3.7470
10.7620	0.4622	3.6760
9.3859	0.4031	3.6040
8.0284	0.3448	3.5320
6.7059	0.2880	3.4600
5.3810	0.2311	3.3890
4.1562	0.1785	3.3170

Run 92   No/313/0.5/7.18/800 /

0	12.1497	0.5218	2.8600
15	10.9622	0.4708	2.8310
30	9.7887	0.4204	2.8020
45	8.6152	0.3700	2.7730
60	7.4580	0.3203	2.7440
75	6.3351	0.2721	2.7150
90	5.1924	0.2230	2.6860

Run 93   No/313/0.5/5.70/800 /

35.2023	1.5200	3.0010
34.2480	1.4780	2.9880
33.2338	1.4350	2.9750
32.2611	1.3930	2.9620
31.2652	1.3500	2.9650
30.3157	1.3090	2.9200
29.3430	1.2670	2.8590

Run 94   No/313/1.0/6.95/800/

0	12.1497	0.5218	3.2820
15	10.8272	0.4650	3.2450
30	9.5140	0.4086	3.2080
45	8.2287	0.3534	3.1710
60	6.9550	0.2987	3.1340
75	5.7093	0.2452	3.0970
90	4.4403	0.1907	3.0600

Run 95   No/313/0.5/538/800/

4.3524	0.1863	2.4740
3.5558	0.1522	2.4850
2.7965	0.1197	2.3970
2.0886	0.0894	2.2100
1.4018	0.0600	1.9240
0.8738	0.0374	1.5380
0.4626	0.0198	1.0530

Run 96   No/313/2.0/5.94/800 /

0	35.2023	1.5200	3.8910
15	33.8822	1.4630	3.8730
30	32.5158	1.4040	3.8540
45	31.2421	1.3490	3.8360
60	29.8757	1.2900	3.8180
75	28.6019	1.2350	3.8000
90	27.2818	1.1780	3.7820

Run 97   No/333/1.5/2.11/800 /

12.1497	0.5218	13.7600
10.5035	0.4511	13.3800
8.8480	0.3800	13.0000
7.3159	0.3142	12.6200
5.7885	0.2486	12.2400
4.2447	0.1823	11.8500
2.8779	0.1236	11.4700

Run 98   No/313/2.0/5.99/800/

0	9.2142	0.3944	3.9370
15	7.9283	0.3405	3.7510
30	6.7121	0.2873	3.5650
45	5.2846	0.2262	3.3790
60	4.2777	0.1831	3.1940
75	3.2100	0.1374	3.0070
90	2.1540	0.0922	2.8210

Run 99   No/333/2.0/2.55/800/

12.1497	0.5218	15.4400
10.0402	0.4312	14.4900
7.9516	0.3415	13.5300
5.9841	0.2570	12.5800
4.1539	0.1784	11.6300
2.3843	0.1024	10.6700
1.0897	0.0468	9.7220

Run 100   No/33.3/0.5/ 2.6/800/

0	12.1497	0.5218	9.9680
15	10.6945	0.4593	9.7080
30	9.2066	0.3954	9.4490
45	7.8235	0.3360	9.1900
60	6.4497	0.2770	8.9310
75	5.0760	0.2180	8.6720
90	3.8326	0.1646	8.4120

Run 101   No/333/0.5/2.18/800/

35.2023	1.5200	10.0900
33.9054	1.4640	10.1600
32.5621	1.4060	10.2200
31.3347	1.3530	10.2800
30.0609	1.2980	10.3400
28.7177	1.2400	10.4000
27.3744	1.1820	10.4600

Run 102   No/333/1.0/2.91/800/

0	12.1497	0.5218	13.3200
15	10.1054	0.4340	12.4900
30	8.1611	0.3505	11.6600
45	6.0383	0.2592	10.8300
60	4.2493	0.1825	10.0000
75	2.6368	0.1132	9.1770
90	1.3083	0.0560	8.3490

Run 103   No/333/0.5/2.37/800/

4.3524	0.1863	8.6060
3.2334	0.1384	8.0200
2.2008	0.0942	6.6230
1.3340	0.0571	5.2270
0.7055	0.0302	3.8300
0.2593	0.0110	2.4340
0.1100	0.0035	1.0380

Run 104   No/333/2.0/2.61/800/

0	35.2023	1.5200	14.9300
15	32.9095	1.4210	14.9900
30	30.5704	1.3200	15.0500
45	28.3703	1.2250	15.1100
60	26.1701	1.1300	15.1600
75	23.7616	1.0260	15.2200
90	21.4711	0.9271	15.2800

Run 105   No/333/2.0/2.09/800/

9.2142	0.3944	15.2300
7.4480	0.3188	14.0500
5.8173	0.2490	12.8800
4.3735	0.1872	11.7100
2.9040	0.1243	10.5400
1.6354	0.0700	9.3650
0.7196	0.0308	8.1920

II EXPERIMENTS WITH CATALYST PELLETS

Run 1   Io-F1/303/0.5/4.10/800/

0	12.9702	0.5572	0.2890
15	12.9025	0.5543	~
30	12.8420	0.5517	~
45	12.7582	0.5481	~
60	12.6860	0.5450	~
75	12.6348	0.5428	~
90	12.5510	0.5392	─

Run 2   Io-F1/313/0.5/5.02/800/

32.9225	1.4230	0.4886
32.8776	1.4170	~
32.7220	1.4103	~
32.5886	1.4042	~
32.4460	1.3984	~
32.2996	1.3920	~
32.1792	1.3868	─

Run 3   Io-F1/313/0.5/4.52/800/

0	12.9702	0.5572	0.4633
15	12.8490	0.5520	~
30	12.7302	0.5469	~
45	12.6185	0.5421	~
60	12.4882	0.5365	~
75	12.3671	0.5313	─
90	12.2275	0.5253	─

Run 4   No/313/0.5/5.0/800/

12.1497	0.5218	0.6522
11.9587	0.5136	~
11.7585	0.5050	~
11.5070	0.4942	~
11.3859	0.4890	~
11.2625	0.4837	~
11.0017	0.4725	─

Run 5   Io-F1/333/0.5/4.51/800/

0	12.9702	0.5572	1.0250
15	12.6441	0.5432	~
30	12.3252	0.5295	~
45	11.9784	0.5146	~
60	11.8480	0.5090	~
75	11.3290	0.4867	~
90	10.9984	0.4725	─

Run 6   No/313/0.5/4.34/800/

25.7585	1.1090	0.6970
25.5550	1.1014	~
25.3322	1.0918	~
25.1211	1.0827	~
25.0492	1.0795	~
24.8496	1.0710	~
24.6478	1.0623	─

Run 7   Io-F1/313/0.5/4.99/800/

0	23.7838	1.0250	0.4549
15	23.6501	1.0193	~
30	23.4877	1.0120	~
45	23.3740	1.0074	~
60	23.2603	1.0025	~
75	23.1187	0.9964	─
90	22.9865	0.9907	─

Run 8   No/313/0.5/4.0/800/

35.2023	1.5200	0.7383
35.0981	1.5127	~
34.9264	1.5053	~
34.7051	1.4958	~
34.7663	1.4984	~
34.4020	1.4827	~
34.1573	1.4720	─

Run 9   ID/313/0.5/4.23/800/

0	8.6687	0.3730	0.2561
15	8.6036	0.3702	~
30	8.5571	0.3682	~
45	8.4572	0.3639	~
60	8.4131	0.3620	~
75	8.3550	0.3595	─
90	8.2666	0.3557	─

Run 10   ID/313/0.5/4.85/800/

21.7126	0.9402	0.2362
21.7056	0.9374	~
21.7116	0.9392	~
21.6415	0.9312	~
21.5788	0.9285	~
21.5067	0.9254	~
21.4510	0.9230	─

Run 11   ID/313/0.5/5.00/800/

0	30.5975	1.3250	0.2419
15	30.5816	1.3219	~
30	30.6519	1.3289	~
45	30.5798	1.3158	~
60	30.5194	1.3132	~
75	30.4288	1.3093	~
90	30.3707	1.3068	─

GLC analysis data

Run No. 84

t	Conver-sion mol %	Low boiling	Composition of unreacted olefin mol%			
			Octene-1	Octene-2	Octene-3	Octene-4
0	0.00	0.5	31.7	40.2	17.9	9.7
15	3.90		23.5	41.2	25.3	10.0
30	8.01		15.3	45.4	30.9	8.4
45	11.56		11.9	43.5	28.6	16.0
60	15.58		7.2	44.8	25.4	22.6
75	19.39		4.8	41.6	30.6	23.2
90	23.02		7.53	38.2	25.9	28.4

Run No. 100

t	Conver-sion mol %	Low boiling	Octene-1	Octene-2	Octene-3	Octene-4
0	0.00		31.7	40.2	17.9	9.7
15	11.98		13.4	49.7	25.4	10.5
30	24.22		8.3	52.5	30.2	14.0
45	35.60		7.2	46.6	31.0	15.2
60	46.91		10.4	44.9	29.8	14.9
75	58.22		5.7	44.8	26.9	22.6
90	68.45		5.5	47.0	28.6	21.4

Run No. 52

t	BR	C_B	Conv. mol %	Ratio of TMP-1/TMP-2
0	13.2936	0.5700	0.0	4.10
15	10.9764	0.4713	17.3	4.18
30	8.3943	0.3602	36.8	4.04
45	6.2433	0.2679	53.0	3.87
60	4.2507	0.1824	68.6	3.92
75	2.2442	0.0963	83.1	3.81
90	0.8086	0.0347	93.9	3.96

Run No. 52 A   Io/F2/333/0.5/6.44/800/

t				
0				5.0
15				3.93
30				3.91
45				3.56
60				4.12
75				3.86
90				3.85