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May 21, *19* 52

I hereby recommend that the thesis prepared under my supervision by Richard Francis Kayser

entitled "Mass Transfer Effects and Variable Productive Area in Fixed Bed Catalytic Converters"

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy in Chemical Engineering.

Approved by:

Harold E. Hoelscher

William Licht

[illegible]

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MASS TRANSFER EFFECTS AND VARIABLE PRODUCTIVE AREA IN FIXED BED CATALYTIC CONVERTERS

A dissertation submitted to the
Graduate School
of the University of Cincinnati
in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1952

by

Richard F. Kayser
B.S. in Ch. E., University of Notre Dame, 1948
M.S. in Ch. E., University of Notre Dame, 1949

Letter of Transmittal

Cincinnati, Ohio

May 1, 1952

Faculty of the Graduate School
University of Cincinnati
Cincinnati, Ohio

Gentlemen:

Herewith is submitted a thesis entitled, "Mass Transfer Effects and Variable Productive Area in Fixed Bed Catalytic Converters", in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

This study is regarded to be a critical survey of many of the theories presently used in the application of chemical kinetics to vapor phase heterogeneous catalysis.

In the present work the author has developed the following in particular:

(1) a method of deriving the basic equations expressing the coefficients of heat and mass transfer in gases flowing through packed beds in terms of the analogy between heat, mass and momentum transfer;

(2) the physical significance of the factors involved in these equations and the physical quantities upon which they depend;

(3) the concept of variable productive area on the surface of an active catalyst;

(4) a method of determining the rate expression defining a process over a range of compositions, temperatures and flow rates in which the productive area of the catalyst is a function of the velocity of the gas flowing through the bed;

(5) the application of (4) above to the hydrogenation of propylene.

The results of this study lead to the conclusion that several factors which are important in the interpretation of kinetic data from vapor phase heterogeneous reactions and in the derivation of the rate expressions for these processes have been neglected by other workers in the field.

Respectfully submitted,

Richard F. Kayser

Richard F. Kayser

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The author wishes to express his gratitude to Dr. H. E. Hoelscher for his many efforts in the capacity of thesis advisor and wishes to thank him for his guidance and counsel during the work.

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For his knowledge of the basic nature of fluid flow and heat, mass and momentum transfer, the author is indebted to the teaching of Professor R. S. Tour who gave his time in hours of discussion on the subject.

Thanks also are due Dr. R. H. Price who was consulted many times during the course of the study.

TABLE OF SYMBOLS

The scope of this study is so broad that nomenclature is a difficult problem. To eliminate confusion many symbols are defined as they occur in the text. In order to use the nomenclature commonly employed it has been necessary in some instances to use the same symbol several times for entirely different quantities. Thus F denotes free energy in one section, feed rate in another and force in a third. This does not lead to confusion within any one section but does present difficulties in constructing a table of symbols. For this reason the table of symbols is divided into two parts, the first applying to the section "Theory of Catalysis" and the second to the remainder of the work.

(A) Symbols for "Theory of Catalysis"

$\bar{a}$ activity of any component in a multicomponent mixture

A frequency factor in Arrhenius' equation, a proportionality factor characteristic of the system

c concentration (moles per unit volume)

$c^{\ddagger}$ total concentration of activated complexes

$c^{\ddagger'}$ total concentration of activated complexes at top of energy barrier

E 1) energy of activation in Arrhenius' equation
or 2) internal energy

F free energy

h Planck's constant = 6.6240×10^{-27} (erg)(sec) per molecule

H enthalpy

k Boltzmann constant = 1.3805×10^{-16} erg/(^{o}K)(molecule)

k specific reaction rate constant for the forward reaction

k' specific reaction rate constant for the reverse reaction

K_a k/k' = equilibrium constant for the reaction

P total pressure

R gas law constant

r reaction rate, moles/unit time

S entropy

T temperature

V total volume

π numerical constant, 3.1416

subscripts

A and B molecular species

superscripts

o standard state

$\ddagger$ activated complex

$\ddagger^o$ activated complex in its standard state

(B) Symbols for all Sections except "Theory of Catalysis"

a numerical constant

a activity

A area

b numerical constant

c concentration, moles/unit volume

c and c_p specific heat at constant pressure

c numerical constant

c_v specific heat at constant volume

c_1 moles empty sites or patches for propylene adsorption per unit catalyst area

c_u moles propylene adsorbed per unit catalyst area

C_H heat transfer number

C_M mass transfer number

D moles per unit area seen by the catalyst

D diameter of any conduit

D_p diameter of catalyst pellet

D coefficient of diffusion

f Fanning friction factor

F feed rate, moles per unit time

$\bar{f}$ fugacity of a component in a multicomponent mixture

f° fugacity of a component in its standard state

G mass velocity, mass per unit area per unit time

h heat transfer coefficient through a single film, $\frac{\text{heat transferred}}{(\text{unit time})(\text{unit area})(\text{unit driving force})}$

j_h heat transfer factor

j_d mass transfer factor

J, J_1, J' proportionality constants

k thermal conductivity

k_G mass transfer coefficient through a single film, $\frac{\text{mass transferred}}{(\text{unit time})(\text{unit area})(\text{unit driving force})}$

k_1 specific reaction rate constant for the forward reaction

k_2 constant dependent on temperature and Reynolds number

L total moles of active sites or patches for propylene adsorption at a given temperature

M molecular weight

N total number of moles

N_B modified Reynolds number for a packed bed; $N_B = \frac{D_p G}{\mu}$

p partial pressure of a component in a multicomponent mixture

q rate of heat transfer, heat transferred per unit area per unit time

r_{Aa} rate of mass transfer through a single gas film, $\frac{\text{moles}}{(\text{unit time})(\text{unit area})(\text{unit driving force})}$

r rate of reaction, moles per unit time per unit catalyst area

t thickness of gas film

u mean velocity of a fluid in a conduit

u' deviating velocity parallel to x axis

v' deviating velocity parallel to y axis

W weight of catalyst

x conversion, moles per mole of feed

x an axis in the heat, mass and momentum transfer section

y mole fraction of a component in a multicompound mixture

y an axis in the heat, mass and momentum transfer section

Y functional notation for the resistance to the reaction on the surface of the catalyst

Greek symbols

τ shear stress occurring in an arbitrary plane perpendicular to the y axis; or, in other words, the total momentum transferred in the y direction by molecular and turbulent exchange

μ coefficient of viscosity

ρ density

ϵ coefficient of turbulent exchange

ν kinematic viscosity μ/ρ

π total pressure

subscripts

A	a molecular species or hydrogen
B	a molecular species or propylene
C	propane
f	average film conditions
F	feed
H	hydrogen
i	catalyst-gas interface
m	unit mass
P	product
U	propylene
S	propane

superscripts

*	gas-catalyst interface

TABLE OF CONTENTS

INTRODUCTION

The study of the kinetics of heterogeneous catalysis is in the same status as fluid flow and heat transfer were forty years ago. At the present time fundamental theories are just beginning to emerge and much of the time researchers are only feeling their way along. In short not only is the horizon of practical use of heterogeneous catalysis just beginning to appear, but also the fundamentals of the field are becoming apparent. Thus most of the kinetic formulations developed to date by pioneers in the field may be viewed with skepticism partly because of the lack of necessary tools and partly because of the lack of a fundamental approach. Relatively few examples of successful application of kinetic principles to the design of reactors have been recorded in the literature. In general, dimensions and optimum operating conditions of reactors are decided by pilot plant experiments or by empirical rules. The reason for this is again, lack of necessary tools, and in many instances lack of a fundamental approach. The published work to date has not begun to unravel all of the factors involved.

It seems to the writer that at the present time no really new ideas are being presented and that much time is lost trying to make assumptions work which are initially incorrect. Thus the basic need in kinetics and catalysis today is a fresh viewpoint.

This does not imply antagonism toward the published work in the field, rather it underscores the desirability of a new, fresh clear thinking outlook in the field of vapor phase heterogeneous catalysis.

THE FACTORS INFLUENCING THE RATE OF REACTIONS IN HETEROGENEOUS SYSTEMS CONSISTING OF SOLID CATALYSTS AND A FLUID PHASE FURNISHING REACTANTS AND CARRYING AWAY PRODUCTS.

As a basis for developing equations which quantitatively express the rate of reactions catalyzed by a solid, it is assumed that the chemical reaction occurs entirely on the surface of the catalyst and involves reaction between two molecules or atoms, of which one, at least, is chemically adsorbed on the catalyst surface. The term chemically adsorbed signifies that definite electron bonds corresponding to the formation of a chemical compound exist between adsorbate and the catalyst.

In order that the reactants in the bulk of the fluid phase may be converted to the product in the bulk of the fluid phase, they must undergo the following processes (which have been enumerated often):

(1) The reactants must travel from their positions in the bulk of the fluid phase to the catalyst-fluid interface.

(2) The reactants at the interface must be chemically adsorbed on the catalyst surface.

(3) The reaction must occur between the adsorbed molecules themselves or between the adsorbed molecules and other reactants in the fluid phase.

(4) The product formed must be desorbed from the catalyst.

(5) The desorbed product must travel from the fluid-catalyst interface to the bulk of the fluid phase.

It is evident that steps (1) and (5) involve similar principles as do steps (2) and (4). It is obvious that processes (1) and (5), processes (2) and (4) and process (3) depend upon entirely different factors. Any experimenter studying heterogeneous catalytic reactions must understand thoroughly the physical and chemical factors involved in each of the five processes above if he is to make an intelligent analysis of his data. Each of these processes will be discussed separately in the following sections.

(A) The Theory of Catalysis

In this section the following will be discussed:

(1) Arrhenius' equation and its fundamental weaknesses

(2) The theory of absolute reaction rates with special reference to

(a) the most favorable reaction path,

(b) the significance of the frequency factor A,

(c) the role of free energy in determining the rate of a reaction.

(3) The action of a catalyst as determined by the reduction of the free energy of activation necessary for reaction and the increase of the concentration of activated complexes at the top of the potential energy barrier.

The equation

$$\Delta F^{o} = -RT\ln K_a;\ K_a = e^{-\Delta F^{o}/RT} \qquad (1)$$

is probably the most important fundamental relationship in the field of chemical equilibrium. In the reaction

$$aA + bB + \ldots \rightleftharpoons lL + mM + \ldots\ldots$$

K_a is given as

$$K_a = \frac{k}{k'} = \frac{(\bar{a}_L)^l(\bar{a}_M)^m}{(\bar{a}_A)^a(\bar{A}_B)^b} \qquad (2)$$

In 1889 the Swedish chemist Arrhenius proposed that the variation of the specific rate of a reaction with temperature could be expressed by an equation of the form

$$k = Ae^{-E/RT} \qquad (3)$$

Arrhenius reasoned that in order to react, two molecules must not only collide, but also must possess an energy larger in amount than that common to the bulk of the molecules. Thus he included a term A in his empirical formula to define the frequency of collision and the term E to define the energy of activation necessary for reaction. His formula holds qualitatively for many reactions and quantitatively for many others. His basic ideas are similar but not so precise as those expressed by H. Eyring[4] in the "theory of absolute reaction rates". It is one of the purposes of this section to give the term A a precise meaning and to show that E is not of the nature of an internal energy.

Arrhenius' equation has an essential weakness which can be shown by considering a reversible reaction. Let us assume E to

be an internal energy. The specific rate of the forward reaction as expressed by the Arrhenius formula is given as

$$k_1 = A_1 e^{-E_1/RT} \tag{4}$$

where E_1 is the internal energy required for the forward reaction. Since E_1 is greater than the internal energy E possessed by the bulk of the molecules, E_1-E has been termed $\Delta E^{\ddagger}$ the "activation energy" possessed by the reacting molecule. The specific rate of the reverse reaction is

$$k_2 = A_2 e^{-E_2/RT} . \tag{5}$$

Consequently $\frac{k_1}{k_2}$, the equilibrium constant of the system, may be written

$$K = \frac{k_1}{k_2} = e^{-(E_1-E_2)/RT} . \tag{6}$$

The ratio $\frac{A_1}{A_2}$ cannot vary significantly from unity since A_1 and A_2 each represent the number of collisions between the molecules. Also

$$E_1 = H_1-P_1V_1$$

$$E_2 = H_2-P_2V_2$$

but $P_1V_1 = P_2V_2$, since each product represents the system at the same instant. Therefore

$$-(E_1-E_2) = H_2-H_1$$

$$\Delta E = \Delta H \tag{7}$$

where

ΔE = the change in internal energy for the reaction, the difference between the activation energies for the forward and reverse reactions

ΔH = difference in enthalpy of the products and reactants.

So Arrhenius' simple collision theory leads to the conclusion that

$$K = e^{-\Delta H^{\circ}/RT}. \tag{8}$$

Ultimately all values of free energy of reaction go back either to equilibrium measurements (equation 1) or to the equation

$$\Delta F = \Delta H - T\Delta S . \tag{9}$$

Thus equation (8) can be true only if T is absolute zero or if the reversible reaction involves no entropy change.

Since the equilibrium constant K, which is equal to the ratio of the specific reaction rates of the forward and reverse reactions, is equal to $e^{-\Delta F^{\circ}/RT}$, where ΔF° is the standard free energy change of the reaction, it would seem more reasonable to write,

$$k = Ae^{-\Delta F^{\ddagger}/RT} = Ae^{-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R} \tag{10}$$

where $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the free energy, enthalpy and entropy of activation respectively.

From the above it is seen that the factor deciding the "activation energy" of the reaction is the free energy function. The frequency factor A is also necessary but as given in the Arrhenius equation is of little exact meaning. The theory of absolute reaction rates gives A a simple, precise and universal significance.

Whatever the mechanism of catalysis, the prediction of rates of heterogeneous catalytic reactions will ultimately come through

the use of the theory of absolute reaction rates or some form of it. Because of the limitations of present day knowledge, the application of this method is difficult although the underlying assumptions are extremely logical and not particularly complex. The theory (hereinafter called the Eyring theory) is developed from the principles of statistical mechanics. It permits calculation of reaction velocity constants from a knowledge of chemical structures and energy distributions of the molecules reacting. Hampered by the lack of present knowledge and tools, reaction rates calculated by this method may be in error by factors of 10 to 100. In the light of the deficiencies of the tools used, this furnishes confirmation of the theory, although it confirms it no less than does the logic of the theory itself. However, the degree of accuracy is not sufficient for the Eyring theory to serve as a basis for process design calculations.

Since the author believes that, in theory, the rate of heterogeneous reactions can be predicted by the Eyring theory, the bulk of this section will be devoted to the application of this theory to heterogeneous reactions. It is understood that, as would be expected, the Eyring theory has been applied to many rate processes and is not limited to the rates of chemical reactions. It has been applied with much success to homegeneous and heterogeneous gas phase reactions, reactions in solution, diffusion and viscosity, the passage of electricity through a solution and the deposition of material on the electrodes in that solution. In general, it applies to any rate process.

The Eyring theory is based on the assumption that any rate process will follow the most favorable reaction path (called the reaction coordinate) on the potential energy diagram applying to the given rate process. The potential energy must be defined. The potential energy between two molecules is the energy which must be expended if it is desired to separate the molecules by an infinite distance. It contains two terms: (1) the coulombic energy due to classical electrostatic forces between electrons and protons and (2) the resonance or exchange energy. This latter has a formal resemblance to the state of affairs existing when two strings vibrating with the same frequency are coupled together; the combined system then vibrates with two new frequencies, one being greater and the other less than the original value for the uncoupled systems. The potential energy of the two molecules interchanging energy analogously has two different values, one higher than the other. The resonance energy is extremely difficult to calculate. For any particular process the potential energy of the reacting system has the appearance along the reaction coordinate shown in Figure 1.

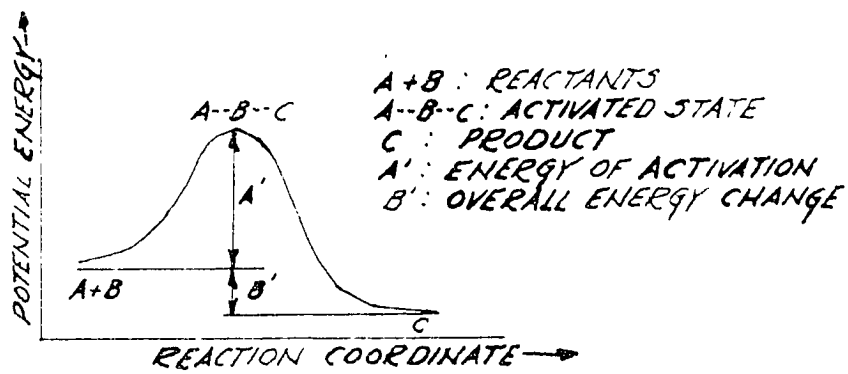


FIGURE 1. A TYPICAL POTENTIAL ENERGY DIAGRAM.

For any given process there are several paths having the same general appearance as that in Figure 1 but varying quantitatively from it. The collection of these paths into one diagram produces a potential energy surface. As a general rule such a diagram usually indicates only one possible path although in any rate process some paths of higher resistance are taken by whatever fundamental elements are involved in the process.

The calculation of the potential energy surface is complex in itself and even for simple processes, approximations must be made. This is the main difficulty in the application of the theory.

Eyring's theory is based on the idea that a chemical reaction or other rate process is characterized by an initial configuration which passes over by continuous change of the coordinates on the potential energy diagram into the final configuration. (A good physical picture can be obtained by studying one of the potential energy diagrams for a chemical reaction such as H_2 + HD presented in most modern physical chemistry texts.) There is, however, always some intermediate configuration which is critical for the process, in the sense that if this configuration is attained, there is a high probability that the reaction will continue to completion. This critical configuration is called the "activated complex" of the reaction and it is, in general, situated at the highest point of the most favorable reaction path on the potential energy surface. In chemical reactions the activated complex is to be regarded as an ordinary molecule, possessing all the

thermodynamic properties, with the exception that motion in one direction i.e., along the reaction coordinate, leads to decomposition at a definite rate. Using these assumptions and statistical mechanics it is possible to derive the concentration and frequency at which the activated complexes pass through the activated state, the product of these quantities is equal to the reaction rate.

Consider a process involving the reactants A, B, etc., which form the activated complex $M^{\ddagger}$ in the reaction

$$A + B + \ldots \rightleftharpoons M^{\ddagger} \longrightarrow \text{products.}$$

The rate of reaction is equal to the concentration of activated complexes at the top of the barrier multiplied by the frequency of crossing the barrier. If $c^{\ddagger}{}'$ is the number of activated complexes in unit volume lying in a length δ representing the activated state at the top of the barrier, and $\bar{v}$ is the mean velocity of crossing, then $\bar{v}/\delta$ is the frequency at which activated complexes pass over the barrier, and hence

$$\text{Rate of reaction} = c^{\ddagger}{}'\frac{\bar{v}}{\delta} = r \qquad (11)$$

The activated complexes differ from normal molecules in the respect that one of the degrees of vibrational freedom is replaced by translational motion along the reaction coordinate; these complexes can, however, be treated as normal molecules by writing their concentration at the top of the barrier as

$$c^{\ddagger}{}' = c^{\ddagger} \cdot \frac{(2\pi m^{*}kT)^{\frac{1}{2}}\delta}{h}$$

where m^{*} is the effective mass of the activated complex in the

coordinate of reaction. The factor $\frac{(2\pi m^* kT)^{\frac{1}{2}}\delta}{h}$ is the partition function for translation in the reaction path and represents the probability of the occurrence of the activated complex at the top of the barrier. By the use of classical methods the mean velocity ($\bar{v}$) of crossing the barrier in one direction, i.e., in the direction of decomposition, is found to be $(kT/2\pi m^*)^{\frac{1}{2}}$, and hence Eq. (11) becomes

$$r = c^{\ddagger}\frac{(2\pi m^* kT)^{\frac{1}{2}}\delta}{h}\left(\frac{kT}{2\pi m^*}\right)^{\frac{1}{2}}\left(\frac{1}{\delta}\right) \qquad (12)$$

$$r = c^{\ddagger}\frac{kT}{h}. \qquad (13)$$

The important consequence of the foregoing treatment is that the effective rate of crossing the energy barrier by the activated complexes is equal to kT/h, which is a universal frequency, dependent only on temperature and independent of the nature of the reactants and the type of reaction.

In the foregoing derivation, it has been assumed that all systems passing over the energy barrier proceed to decomposition; however, there is a possibility that some of these systems will be turned back to the initial state after having passed through the activated state. It is necessary, therefore, to introduce a factor K, known as the "transmission coefficient", to allow for this possibility. Although K is less than unity in reactions involving two atoms and in certain processes accompanied by a change of electron multiplicity and in many unimolecular reactions, it is probably close to unity in most other cases. For the present it will be assumed that every activated

complex reaching the top of the barrier proceeds to decomposition with a frequency kT/h and that the transmission coefficient is unity.

The reaction under consideration is

$$A + B + \ldots \rightleftharpoons M^{\ddagger} \longrightarrow \text{products.}$$

If k is the specific reaction rate constant, the equilibrium between the reactants and the activated complex is given as

$$kc_Ac_B = k'c^{\ddagger} \tag{14}$$

or $$c^{\ddagger} = \frac{k}{k'}c_Ac_B = K^{\ddagger}c_Ac_B$$

but from Eq. (13)

$$r = c^{\ddagger}\frac{kT}{h}$$

$$r = \frac{kT}{h}K^{\ddagger}c_Ac_B$$

$$r = \frac{kT}{h}c_Ac_B(e)^{-\Delta F^{\ddagger o}/RT} \tag{15}$$

This expression quantitatively relates the rate of a reaction with a universal frequency term, the concentration of reactants and the free energy of activation.

The rate of reaction is also given, in the familiar manner, as

$$r = kc_Ac_B \tag{16}$$

combining (15) and (16):

$$k = \frac{kT}{h}K^{\ddagger} \tag{17}$$

where $K^{\ddagger}$ is the constant for the equilibrium, viz.,

$$A + B + \ldots \rightleftharpoons M^{\ddagger},$$

which is assumed to exist between the reactants and the activated complex, assuming, for the present, that the system is ideal so that concentrations may be used in place of activities. The

constant $K^{\ddagger}$ is exactly analogous to any other equilibrium constant, and hence it may be related to $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, the standard free-energy, enthalpy and entropy changes, respectively, accompanying the formation of the activated state from the reactants, by means of the familiar thermodynamic relationships. In this manner, Eq. (17) can be written in the forms

$$k = \frac{kT}{h} e^{-\Delta F^{\ddagger o}/RT} \tag{18}$$

$$= \frac{kT}{h} e^{-\Delta H^{\ddagger o}/RT} e^{\Delta S^{\ddagger o}/R}, \tag{19}$$

which may be compared with Eq. (10), previously considered. It is seen that Eqs. (18) and (19) require that the reaction rate is determined by the free energy of activation, and that they are an improvement over the earlier relationships in the respect that they give a precise and simple significance to the frequency factor.

In the equation

$$k = \frac{kT}{h} K^{\ddagger} = \frac{kT}{h} e^{-\Delta F^{\ddagger o}/RT}$$

we see that $\frac{kT}{h}$ is equal to A as given in Eq. (10). A was termed the frequency factor by many workers and was construed primarily as a function of the number of molecular collisions. The first important consequence of Eyring's treatment is that the frequency factor A is actually $\frac{kT}{h}$, which is the effective rate of activated complexes crossing the energy barrier <u>along the most favorable reaction path</u> as defined by the potential energy surface. The second, and most important, consequence of Eyring's theory is that at a given temperature and concentration of reactants, the free energy of activation determines the rate of a reaction.

By definition a catalyst is a substance which influences the rate of a reaction. From Eq. (15) it is evident that catalytic action is the result of two factors:

(1) A catalyst chemically adsorbs one or more of the reactant molecules in such a way that the reactants are physically aligned along a favorable reaction path. This alignment is thus always along a coordinate requiring a low free energy of activation.

(2) On a catalyst the concentration of molecules physically aligned along a favorable reaction coordinate is very great.

A catalyst often is defined as a substance which influences the rate of a reaction, but is not one of the original reactants or final products. In past years a great accumulation of evidence has shown that in most homogeneous reactions, the catalyst is a reactant but is continually regenerated with the product and thus appears on neither side of the over-all equation representing the reaction. A physical picture of heterogeneous catalysis likewise demands that the catalyst be a reactant. The physical picture conceived is that by reacting with the product molecules, a catalyst reduces the positive free energy changes accompanying the intermediate steps between reactants and products and thus by decreasing the height of the energy barrier between the products and reactants, the rate of the reaction is greatly increased while the over-all free energy change accompanying the reaction

remains the same. The catalyst functions by reducing the length of path between the two point functions $F_{products}$ and $F_{reactants}$.

It is imperative to believe that a catalyst physically or chemically affects the reactant molecules; in fundamental thinking it is impossible to distinguish "physical" from "chemical". It is not the purpose of this work to delve into the many theories of the mechanism of heterogeneous catalysis, but it is of the utmost importance to realize that a mechanism must be postulated for any rate process before the rate corresponding to that mechanism can be calculated. It is then understood that the mechanism of heterogeneous catalysis must be known before its absolute rate can be predicted.

The theory of heterogeneous catalysis is then that the catalyst reduces the positive free energy change accompanying the formation of the activated reactants and increases the concentration of the activated reactants. Because of the action of the catalyst, the reactant molecules in a heterogeneous system are provided a path of less resistance between themselves and the product molecules than the path which must be followed when the catalyst is not present. The path of least resistance can be predicted by the potential energy surface of the system. Some mechanism of reaction must be postulated before this surface can be calculated.

(B) Mass, Heat and Momentum Transfer Through Gases Flowing In Granular Beds

The transfer of reactants and products between the catalyst-fluid interface and the bulk of the fluid stream, are mass transfer operations. Consideration of the basic concepts of mass transfer shows that heat, mass and momentum transfer each involve the movement of mass at some velocity, and therefore they are interrelated by their very nature.

In 1874 Osburne Reynolds suggested that an analogy should exist between the transfer of momentum, heat and mass in a fluid stream. This analogy now bears his name. Although it was known that heat, mass and momentum transfer were fundamentally related, the relationship was not defined for practical use until the middle 1930's when von Kārmān began his series of papers on the nature of turbulent flow and the analogy between heat, mass and momentum transfer in fluid streams.*

Using the logical approach von Kārmān[2] developed in his analysis of the Reynolds analogy, it is possible to demonstrate the physical significance of several concepts presently used to express the rate of heat, mass and momentum transfer through gases flowing in granular beds. Such a demonstration is desirable

*R. S. Tour had independently arrived at the conclusions of von Kārmān at least two years before von Kārmān published his paper [von Kārmān Am. Soc. Mech. Engrs., 61, 705 (1939)]. Tour had derived Nusselt's equation in its basic form using the nature of the quantitative expression between heat and momentum transfer arrived at by von Kārmān. Although Tour's work is thought to be a significant step in the practical application of the Reynolds analogy, it was not made available in the literature.

because the published work in this field has indicated some lack of appreciation of the basic concepts involved and the factors affecting the problem.

The relationship between heat and momentum transfer in gases will be derived in detail because it provides an excellent three-dimensional picture of the transfer operations and is somewhat less complex than the relationship between mass and momentum transfer. It is understood that the relationship between mass and momentum transfer can be derived in essentially the same manner. Although these derivations are somewhat long, many of the concepts they define will be needed later for interpetative purposes.

The Concept of Turbulent Flow

Consider the momentum transferred (per unit area) perpendicular to the direction of flow of a fluid in laminar flow. If the velocity of the fluid is increased, the momentum transferred perpendicular to the direction of flow is increased and thus the stress on any arbitrary plane increases. However in accordance with the principle of Le Chatlier, the plane will move in such a manner as to nullify this increase in stress, i.e., the plane deflects as does a beam supported at both ends when it is subjected to a force between the supports. This deflection reduces the stress to a value lower than it would have been had deflection not occurred. Fluid flow can thus be considered in a manner analogous to any stress-strain problem. When the velocity of the fluid is

increased to a point where the momentum transferred to the plane parallel to the direction of flow creates a stress in excess of that which the viscosity will allow, the plane inelastically buckles and finally breaks.

The molecules carrying sufficient momentum to rupture the plane perpendicular to them then proceed through the rupture, encounter the next plane and, if possible, rupture it. These molecules lose some of their momentum at each plane and are deflected in the direction of flow at each plane until they reach the wall where they undergo an elastic collision and start back through the fluid. Returning through the fluid the molecules lose additional momentum so that when they return to the plane originally ruptured, their momentum is less than it was initially. This difference of momentum in the direction perpendicular to the basic direction of flow when coupled with the difference of momentum on planes parallel to the direction of flow generates the eddies characteristic of turbulent flow. The eddies change in size, shape and position according to the fluctuations of velocity characteristic of turbulent flow.

The Relationship Between Heat, Mass and Momentum Transfer In Gases

Using the above concepts it is seen that in turbulent flow, the shear stress on any arbitrary plane parallel to the direction of flow is equal to the sum of the total momentum transferred by molecular exchange and that transferred due to the velocity

fluctuations. The momentum transferred by molecular exchange is given by the classical law $\tau = \mu \frac{du}{dy}$. The momentum transferred by velocity fluctuations has the magnitude $\tau = -\rho u'v'$ where u' and v' are the fluctuations of the velocity components in the x and y direction respectively. Since distance is measured from the wall and the mean of v' is a velocity toward the wall, the quantity u'v' is negative. Thus the shear stress due to velocity fluctuations has a positive value. The total momentum transferred by molecular and turbulent exchange on an arbitrary plane perpendicular to the y axis is:

$$\tau = \tau_M + \tau_T \tag{20}$$

where τ = shear stress unit area

τ_M = shear stress due to molecular exchange

τ_T = shear stress due to velocity fluctuations.

But $\tau_M = \mu \frac{du}{dy}$

and $\tau_T = -\rho u'v'$

therefore $\tau = \frac{du}{dy} - \rho u'v'$ (21)

The transfer of heat across the arbitrary plane perpendicular to the y axis can be expressed in an analogous manner:

$$q = -k\frac{d\theta}{dy} + c\rho v'\theta' \tag{22}$$

Because a temperature gradient exists in the y direction, $v'\theta'$ does not have a mean value of zero and $c\rho v'\theta'$ is the heat transferred due to the turbulent fluctuations of flow. The

relation between v' and θ' and v' and u' is

$$v'u' = -\epsilon\frac{du}{dy}$$

$$v'\theta' = -\epsilon\frac{d\theta}{dy}$$

The numerical value of ϵ is approximately the same in both expressions and ϵ is called the coefficient of turbulent exchange. Introducing the kinematic viscosity ν, ($\nu = \mu/\rho$) and the {thermometric conductivity (thermal diffusivity)} β, ($\beta = k/c\rho$) into equations (21) and (22):

$$\frac{\tau}{\rho} = (\nu + \epsilon)\frac{du}{dy}$$

$$\frac{q}{c\rho} = -(\beta + \epsilon)\frac{d\theta}{dy} \qquad (23)$$

Thus a direct proportionality between shearing stress and heat transfer can be expected if

(a) ν and β are negligible compared to ϵ

or (b) ν and β are numerically equal.

In the case of turbulent flow (a) is generally satisfied with the exception of a relatively narrow range near the walls of the conduit, i.e., in the film. Condition (b) is closely satisfied for gases, hence for gases the Reynolds analogy can be shown easily. It is important to note that $\frac{\nu}{\beta}$ is the Prandtl number. It will be seen that $\nu \cong \beta$ only for gases.

Coefficients of Friction and Heat Transfer

The term τ/ρ in (23) has dimensions of velocity squared, hence $\frac{\tau}{\rho\frac{U^2}{2}}$, where U is a velocity of reference of the physical set-up, is a dimensionless quantity; in general it is used as a

coefficient of friction and is denoted as f, ($f = \frac{\tau}{\rho \frac{U^2}{2}}$ can also be obtained from Fanning's equation). The term $q/c\rho$ in (23) has dimensions of velocity times temperature, hence if θ_r denotes a reference temperature, the term $\frac{q}{c\rho U\theta_r}$ is dimensionless and will be denoted by C_H, which will be called the heat transfer number. Thus

$$\tau = \frac{f}{2}\rho U^2$$
$$q = C_H \rho c U \theta_r \qquad (24)$$

So f is seen to be the ratio between the momentum transferred per unit area in the y direction (toward the wall) and the momentum carried by the fluid per unit area in the x direction of the stream (in the direction of flow). C_H is the ratio between two heat flows, the heat flow per unit area per unit time, q, in the y direction, and the heat carried in the x direction per unit cross sectional area by a fluid of reference temperature θ_r and velocity U, which is obviously $\rho c U \theta_r$. The concept of the coefficients $\frac{f}{2}$ and C_H appears to be analogous.

The Reynolds Analogy

As has been seen, ν and β are negligible compared to ϵ in the case of fully developed turbulent flow. This condition can be utilized, but for the heat transfer analogy, since ν and β are nearly equal, condition (b) can be imposed.

For an ideal gas ν and β are proportional to the product of the mean free path and the mean velocity of the molecules of the gas. According to the kinetic theory of gases, $\frac{\nu}{\beta}$ depends only on the number of degrees of freedom. Eucken gives

empirically

$$\frac{\nu}{\rho} = \frac{4\frac{c_p}{c_v}}{9\frac{c_p}{c_v} - 5}$$

$\frac{\nu}{\rho} = 0.66$ for monoatomic gases

$\frac{\nu}{\rho} = 0.74$ for diatomic gases

For most gases McAdams[3] recommends that the Prandtl number, $\frac{\nu}{\rho}$, be taken as independent of temperature and pressure. For many real gases (air, CO_2, SO_2, C_2H_4, H_2S, steam) $\frac{\nu}{\rho}$ is close to 0.8 and increases with complexity of the gas. Thus it is justifiable to assume for most cases that $\frac{\nu}{\rho}$ is unity. Equations (23) become

$$\frac{\tau}{\rho} = (\nu + \epsilon)\frac{du}{dy}$$

$$\frac{q}{c\rho} = -(\nu + \epsilon)\frac{d\theta}{dy} \qquad (25)$$

Assume that τ and q are constant with y (or at worst vary in a similar way). Let

u_o = velocity at the wall

θ_o = temperature at the wall

u = velocity at an arbitrary point in the fluid

θ = temperature at an arbitrary point in the fluid.

Integrating (25):

$$\frac{\tau}{\rho}\int_{y=y_o}^{y}\frac{dy}{\nu+\epsilon} = \int_{u=u_o}^{u} du = u - u_o = U$$

$$\frac{q}{c\rho}\int_{\theta=\theta_o}^{\theta}\frac{dy}{\nu+\epsilon} = -\int_{\theta=\theta_o}^{\theta} d\theta = \theta_o - \theta = \Delta\theta \qquad (26)$$

It follows that, if U is the mean velocity of the fluid at y relative to that at the wall, and if $\Delta\theta$ is the difference between the mean temperature of the fluid and that at the wall, then

$$\frac{\tau c}{q} = \frac{U}{\Delta\theta} \qquad (27)$$

or c.f. equation (24)

$$\frac{f}{2} = C_H \qquad (28)$$

In like manner, for mass transfer, it can be shown that

$$C_M = \frac{f}{2} \qquad (29)$$

The mass transfer number C_M, is the ratio between two mass flows, the mass transferred per unit area per unit time in the y direction (toward the wall) and the mass carried in the x direction per unit time per unit area (in the direction of flow).

Relations (28) and (29) imply two very important conclusions which can be used to test the concepts defining rate of heat and mass transfer. It is well-known that in laminar flow the shear stress τ is proportional to the first power of the velocity and that in purely turbulent flow τ is proportional to

the square of the velocity. Since momentum transfer by molecular exchange always exists even in very turbulent flow, τ actually varies as a power of the velocity slightly less than 2. Thus

(1) if the shear stress per unit area is proportional to the nth power of the velocity, U, the heat or mass transfer rates q or m are proportional to the (n - 1) power of U, where n is somewhat less than 2.

(2) roughness increases the friction and heat or mass transfer in the same ratio.

Applications of the Equation $f/2 = C_H = C_M$

(1) Derivation of the Equation Defining the Heat Transfer Factor j_h.

The quantities $\frac{f}{2}$, C_H and C_M were regarded as the ratios of two perpendicular flows (therefore tangents of an angle) and were thought to be proportional to one another before von Kārmān published his conclusion that the proportionality constant is unity:

$$\frac{f}{2} = (1)(C_H) = (1)(C_M) = C_H = C_M.$$

The basic concept of the ratio of two perpendicular flows was used to develop Nusselt's equation as follows:*

Consider a fluid flowing in a turbulent manner through a circular conduit of uniform diameter throughout its length. The momentum being carried axially down the conduit at any arbitrary point is $\rho \frac{U^2}{2}$, while the momentum transferred radially will be denoted as γ. The heat being carried axially down the pipe at the same point is $c\rho U$, while that transferred radially is q. Now

$$C_H = \frac{f}{2} = \frac{q}{c\rho U} = \frac{\frac{q}{}}{c\rho U} \qquad (30)$$

$$\frac{q}{} = \frac{f}{2} c\rho U = \frac{f}{2} cG \qquad (31)$$

The fraction of the amount of heat q/ transferred through the film on the wall of the pipe is the heat transfer coefficient h.

*The procedure for this derivation is due to R. S. Tour who developed it in 1937 using ratios of perpendicular flows. His final expression was

$$\frac{hD}{k} = J\left(\frac{DG}{\mu}\right)^{0.8}\left(\frac{c\mu}{k}\right)^{n}.$$

Using von Kārmān's conclusion that $C_H = \frac{f}{2}$ the author has shown J to be 0.023.

Coefficient h is different from $q/\Delta\sigma$ because the actual conductance of heat through the film is different from the total theoretically possible by the ratio of actual to theoretical thermal conductivity k/κ, where k is actual thermal conductivity of the fluid film and κ is the theoretical thermal conductivity of the film. From the kinetic theory of gases, $\kappa = c\mu$.

Therefore $$h :: \frac{q}{\Delta\sigma} \tag{32}$$

$$h = J\frac{q}{\Delta\sigma} = J\frac{f}{2}cG \tag{33}$$

But as seen above, J is a function of $\frac{k}{c\mu}$ only, and it is rigorous to write

$$J = J_1\left(\frac{k}{c\mu}\right)^n .$$

If the quantity $\left(\frac{k}{c\mu}\right)$ is unity, the actual conductance of the film is equal to the theoretical, n is indeterminate but J_1 is seen to be unity.

Hence $$J = \left(\frac{k}{c\mu}\right)^n = \left(\frac{k}{\kappa}\right)^n$$

So $$h = J\frac{f}{2}cG$$

but $$c = \frac{\kappa}{\mu}$$

and $$\kappa = \frac{k}{J^{1/n}}$$

therefore $$c = \frac{k}{\mu J^{1/n}}$$

$$h = J\frac{f}{2}\frac{k}{\mu J^{1/n}}G = J^{1-\frac{1}{n}}\frac{f}{2}\frac{kG}{\mu}$$

but $$J = \left(\frac{k}{c\mu}\right)^n$$

so $$h = \left(\left[\frac{k}{c\mu}\right]^n\right)^{\frac{n-1}{n}}\frac{f}{2}\frac{kG}{\mu} = \left(\frac{k}{c\mu}\right)^{n-1}\frac{f}{2}\frac{kG}{\mu} \tag{33a}$$

Over the limited range of Reynolds numbers from 5000 to 200,000,

it has been shown[4] experimentally that

$$f = \frac{0.046}{\left(\frac{DG}{\mu}\right)^{0.2}} \tag{34}$$

Substituting in 33a:

$$h = \left(\frac{k}{c\mu}\right)^{n-1} (0.023)\left(\frac{DG}{\mu}\right)^{-0.2}\frac{k}{\mu}G$$

$$\frac{hD}{k} = 0.023\left(\frac{DG}{\mu}\right)^{0.8}\left(\frac{c\mu}{k}\right)^{1-n} \tag{35}$$

Experimentally n has been determined as (-0.6) so equation (35) becomes

$$\frac{hD}{k} = 0.023\left(\frac{DG}{\mu}\right)^{0.8}\left(\frac{c\mu}{k}\right)^{0.4} \tag{36}$$

Equation (36) is Nusselt's equation for heat transfer through gases.

Returning to equation (33):

$$h = \frac{Jq}{\Delta t} = J\frac{f}{2}cG = \frac{f}{2}cG\left(\frac{k}{c\mu}\right)^{n}$$

$$\frac{f}{2} = \left(\frac{h}{cG}\right)\left(\frac{c\mu}{k}\right)^{n} \tag{37}$$

Equation (37) can be generalized and expressed in a form relating the heat transfer coefficient to the ratio of momentum transferred perpendicular to the direction of flow (by both molecular and eddy viscosity) to the momentum carried in the direction of flow. Thus:

$$\frac{f}{2} = \frac{1}{2}\left(\frac{\tau}{\rho\frac{U^2}{2}}\right) = \left(\frac{h}{cG}\right)\left(\frac{c\mu}{k}\right)^{n} \tag{38}$$

Define

$$j_h = \frac{1}{2}\left(\frac{\tau}{\rho\frac{U^2}{2}}\right) = \left(\frac{h}{cG}\right)\left(\frac{c\mu}{k}\right)^{n} \tag{39}$$

Equation (39) derived on the basis of the Reynolds analogy is Colburn's[5] equation for the heat transfer factor but further clarifies j_h by giving it the significance of $\frac{1}{2}\left(\frac{\tau}{\rho\frac{U^2}{2}}\right)$.

As previously discussed, heat and momentum transfer are in reality operations involving only the movement of mass. Equation (39) quantitatively relates the shear stresses generated by momentum transfer, the momentum carried by the fluid in its direction of flow and the coefficient of heat transfer through the film on the wall of the conduit. This equation, derived from first principles, is applicable to heat transfer in any conduit. Factor j_h has the physical significance of the ratio of momentum perpendicular to the direction of flow (which is detected as the shear forces per unit area resulting from resistance to flow) to the momentum carried by the fluid in its direction of flow. Since this ratio depends on Reynolds number and is affected by roughness and shape of the conduit, j_h will be a function of those variables.

(2) Derivation of the Equation Defining the Mass Transfer Factor j_d.

This derivation is, of course, identical with that for j_h except that a different function effects the efficiency of the film in the transfer of mass. Consider any section of a gas in turbulent flow in a circular conduit:

p_A = partial pressure of component A in the turbulent stream

π = total pressure

N_T = total number of moles in the section

V = volume of the section

M_A = molecular weight of component A

u = mean axial velocity

ρ_A = density A

k_G = film coefficient,

$$\frac{\text{moles A transferred}}{(\text{unit time})(\text{unit area})(\text{unit partial pressure diff.})}$$

μ = viscosity

D = diffusion coefficient, $\frac{\text{area}}{\text{unit time}}$

Then

$$\frac{p_A N_T M_A}{\pi V} = \frac{\text{mass A}}{\text{unit volume}}$$

$$\frac{p_A N_T M_A u}{\pi V} = \frac{\text{mass A going axially downstream}}{(\text{unit time})(\text{unit area})}$$

$$\frac{C_M p_A N_T M_A u}{\pi V} = \frac{\text{mass A going radially toward the wall}}{(\text{unit time})(\text{unit area})}$$

but

$$\frac{N_T M_A}{V} = \rho_A = \text{density of A in the fluid stream}$$

$$\frac{C_M p_A \rho_A u}{\pi} = \frac{\text{mass A going radially toward the wall}}{(\text{unit time})(\text{unit area})}$$

$$\frac{C_M \rho_A u}{M_A \pi} = \frac{\text{moles A going radially toward the wall}}{(\text{unit time})(\text{unit area})(\text{unit partial pressure A})}$$

The fraction of $\frac{C_M \rho_A u}{\pi M_A}$ transferred through the film on the wall of the conduit is the mass transfer coefficient k_G. Coefficient k_G is different from $C_M \rho_A u / \pi M_A$ because the actual conductance of mass through the film is different from the total theoretically possible by the ratio of actual to theoretical viscosity (viscosity is the measure of mass transfer). In the appendix the significance of viscosity and the coefficient of diffusion are demonstrated by means of "descriptive dimensional analysis". It is shown that for gases, the theoretical viscosity is related to the density and the

diffusion coefficient by the following equation:

$$\mu :: \rho D$$

Therefore the efficiency of the gas film in conducting the quantity of mass $C_M \rho_A u / \pi M_A$ is a function of $\frac{\mu}{\rho D}$ only, where μ is the actual viscosity.

Then $$k_G :: \frac{C_M \rho_A u}{\pi}$$

$$k_G = J' \frac{C_M \rho_A u}{\pi}$$

But J is a function of $\frac{\mu}{\rho D}$ only, and it is rigorous to write

$$J' = J_2 \left(\frac{\mu}{\rho D}\right)^m$$

If $\frac{\mu}{\rho D}$ is unity, the actual conductance of the film is equal to the theoretical, n is indeterminate, but J_2 is seen to be unity.

Hence $$J' = \left(\frac{\mu}{\rho D}\right)^m$$

So $$k_G = \frac{C_M \rho_A u}{M_A \pi} \left(\frac{\mu}{\rho D}\right)^m$$

But $$C_M = \frac{f}{2}$$

Therefore $$\frac{f}{2} = \left(\frac{k_G \pi}{\frac{G}{M_A}}\right) \left(\frac{\mu}{\rho D}\right)^m \qquad (40)$$

Equation (40) can be generalized and expressed in a form relating the mass transfer coefficient with the ratio of momentum transferred perpendicular to the direction of flow (by both molecular and eddy viscosity) to the momentum carried in the direction of flow. Thus since $\frac{f}{2} = \frac{1}{2}\left(\frac{\tau}{\rho \frac{U^2}{2}}\right)$

$$\frac{1}{2}\left(\frac{\tau}{\rho \frac{U^2}{2}}\right) = \left(\frac{k_G \pi}{\frac{G}{M_A}}\right) \left(\frac{\mu}{\rho D}\right)^m = j_d \qquad (41)$$

Equation (41), derived on the basis of the Reynolds analogy, is seen to be Chilton and Colburn's[4] expression for the mass transfer factor but gives the factor the significance of $\frac{1}{2}\left(\frac{f}{f\frac{U^2}{2}}\right)$.

Equation (41), derived from first principles, is applicable to mass transfer in gases flowing in any conduit. Factor j_d has the same physical significance as does j_h and one would expect their values to be identical. This is the case. Factor j_d depends on the same variables as does j_h i.e., it depends upon Reynolds number, roughness and shape of the conduit.

Heat Transfer Factor j_h, Mass Transfer Factor j_d and the Variables Affecting Their Numerical Value In Packed Beds

From the physical significance of $f/2$, j_d and j_h it is obvious that for heat transfer in pipes $f/2 = j_h$ and for mass transfer in pipes $f/2 = j_d$.

For heat and mass transfer in granular beds, j_h equals j_d for any given bed but j_h does not equal the friction factor for the bed. The friction factor for a packed bed involves the loss of momentum in shear forces due to viscous and eddy transfer of momentum and also the loss of momentum in internal turbulence resulting from expansions and contractions of the gas as it flows through the passages of the bed. The loss of momentum in shear forces due to viscous and eddy momentum transfer is that part of the total momentum lost which corresponds to j_h or j_d. The loss of momentum in internal turbulence plays no part in the Reynolds analogy except insofar as it affects the shear stresses on any plane

and the corresponding transfer of momentum by molecular and eddy viscosity. Since the loss of momentum in internal turbulence due to expansions and contractions in a packed bed is very large, j_d and j_h can be very different in value from the friction factor for the bed.

Heat and mass transfer depend on the momentum transferred toward the film and not upon that lost in internal turbulences. Since the j factors depend solely on the momentum transferred per unit area toward the film divided by the total momentum carried per unit area in the direction of flow $j = \frac{1}{2}\left(\frac{\tau}{\rho\frac{U^2}{2}}\right)$ then according to the conclusions of von Kārmān, if τ varies as the nth power of the velocity, h and k_G must vary as the (n - 1) power. The experimental work done has verified this in every case. If j varies as the nth power of velocity, h and k_G vary as the (n - 1) power.

For a gas flowing in a pipe, the friction factor $f/2$ represents a constant ratio of τ to $\rho\frac{U^2}{2}$. Consider, however, a gas flowing around the particles of a packed bed. The ratio of τ to $\rho\frac{U^2}{2}$ at any point will depend on the velocity and basic direction of flow at that point; further the basic direction and velocity of flow will vary from point to point around any particle. Hence j_d or j_h measured in any experiment is an average of the ratio of τ to $\rho\frac{U^2}{2}$ at all points in the bed. Since the basic direction of flow at any point in a packed bed depends on the shape and arrangement of the particles, j_h and j_d will be functions of these variables in addition to being a function of Reynolds number.

In the first measurements of j_h and j_d in a packed bed, the

work of Gamson, Thodos and Hougen[7] indicated that for spheres and cylinders, j_d and j_h were independent of shape and packing arrangement of the particles. In 1950 Gamson[8] published work showing the dependence of the j factors on particle shape. No work has been done to define the relation of j_h and j_d on packing arrangement or fraction void.

Mass, Heat and Momentum Transfer Through Liquids

It is of the utmost importance to realize that the above use of the Reynolds analogy and the derivation of the equations defining the j factors are valid only for gases.

In liquids viscosity is no longer a measure of mass transfer because of the interactions between the molecules. Thus the efficiency factors $k/c\mu$ and $\mu/\rho D$ are no longer applicable.

Further, in gases von Kārmān[2] has shown that

$$\frac{f}{2} = C_H .$$

But in liquids he has found that

$$\frac{1}{C_H} = \frac{2}{f} + 5\left(\frac{2}{f}\right)^{\frac{1}{2}}\left\{\frac{\nu}{\beta} - 1 + \log_e\left[1 + \frac{5}{6}\left(\frac{\nu}{\beta} - 1\right)\right]\right\} \qquad (42)$$

Hence in liquids the expression of the Reynolds analogy becomes more complex. This coupled with the uncertainties of the efficiency factors make the expressions ~~defining~~ permitting the calculation of j for gases merely crude approximations when applied to liquids.

(C) The Effect of Turbulent Fluid Flow in Catalytic Beds

In the preceding section it was shown that turbulent flow is the result of the rupture of lamina, or streamlines of flow, under a stress exceeding that which the viscosity of the fluid will permit. The rupture results in eddies which greatly increase mass, momentum and heat transfer through the fluid by the addition of eddy diffusivity, eddy viscosity and eddy conductivity to the molecular transport properties. Whenever streamlines of flow are ruptured or caused by any mechanism to break into eddies, the transfer of mass, heat and momentum is greatly increased in the region where the eddy exists.

The Variation of Area Covered by Turbulent Flow with Velocity of Fluid Flowing

Consider a fluid flowing through a packed bed in such a manner that laminar flow exists in all passages. At a sufficiently low velocity none of the streamlines of flow are broken as the result of excessive shearing forces, or as the result of direct impingement either on surfaces partially blocking the path, or on surfaces jutting like jagged peaks into the fluid. If the velocity is increased but laminar flow maintained in all passages of the bed, some streamlines of flow are ruptured and converted into eddies at those irregular parts of the bed jutting into and blocking the moving fluid. The areas of the points scoured with the eddies formed are furnished with much greater mass, momentum and heat transfer than are those areas over which the flow is viscous. If the velocity of the fluid is further increased, the eddy on, for

example, a jagged peak, increases in intensity and length, covering more area on that peak not only by spreading out, but also by lengthening on the downstream side thus enabling it to scour that side and to reach lower peaks in that vicinity. Furthermore, the increase in velocity uncovers new peaks and impinges on new surfaces so that the area scoured by eddies increases rapidly as the velocity is increased. During this time the remaining area is covered by viscous fluid through which heat, mass, and momentum transfer is accomplished by molecular, not eddy, movement.

If the velocity of the fluid is now raised until the large diameter passages break into turbulent flow, the total area scoured by eddies increases very greatly. However, when turbulent flow begins in the larger passages, further increases in fluid velocity do not so greatly increase the eddy scoured areas. As more of the passages break into turbulent flow, this area increases less rapidly with velocity, until finally the eddy covered area ceases to vary with changes in velocity.

The Importance of the Variation of Area Scoured by Turbulent Flow with Velocity

To demonstrate the importance of the variation of the catalyst area scoured by turbulent flow, two limiting types of catalysts will be considered:

(1) A very poor catalyst which uses the reactants adsorbed on its surface so slowly that in comparison, the furnishing of new reactants, even by fluid in viscous flow, is exceedingly rapid.

(2) A very active catalyst which uses the reactants adsorbed on its surface so rapidly that in comparison the furnishing of new reactants from the fluid phase is exceedingly slow.

Case (1). A "Poor" Catalyst

It is immediately obvious in the case of the "poor" catalyst that even where only a part of the catalyst area is covered by turbulent fluid and the remainder covered by viscous flow of the fluid, all parts of the catalyst area are equally productive. A change in velocity of the fluid does not change the productive area of the catalyst, or the amount of product formed. The amount of turbulence in the gas flowing through the bed is of no importance.

Case (2). An "Active" Catalyst

In this case, the catalyst changes the reactants into products much faster than the fluid phase can deliver them. Thus the rate of production of product molecules depends almost entirely on the rate at which the fluid phase delivers reactants to the surface of the catalyst.

The experimental work of this study has shown that the area of catalyst covered by turbulent flow or eddies is a function of the velocity of the fluid flowing through the bed. The areas covered by turbulent flow are furnished with reactants very much more rapidly than are the areas covered by viscous flow because of the addition of eddy - to molecular - diffusivity on those areas. Therefore, the areas scoured by eddies are more productive than those which are not. Since in the lower ranges of velocity the

areas scoured by turbulence increase rapidly in size and number with velocity of the fluid flowing, the productive areas of the catalyst surface increase rapidly in size and number with fluid velocity.

In the case of a very active catalyst, the amount of turbulent flow in the catalyst bed is of extreme importance in determining the rate of production of product molecules.

Because all catalysts lie somewhere between the two cases discussed above, this concept of variable productive area must be used in the interpretation and correlation of data. As seen from the above discussion its relative importance becomes greater as the activity of a catalyst increases.

The Material Balance Equation

For the correlation of kinetic data obtained during vapor phase studies in a fixed bed catalytic converted, Hougen and Watson have discussed the following equation:

$$rdW = Fdx \qquad (42)$$

This equation has been utilized almost universally in treating kinetic data obtained from such studies. The assumption involved in the derivation of this equation aside from the obvious implication of constant feed rate and steady state conditions, is that the rate of reaction, the conversion, and the active weight of catalyst are constant over any horizontal plane. This implies that:

(1) the temperature and pressure are uniform over any horizontal plane,

(2) the rate of fluid flow per unit area of horizontal plane is uniform (no channeling),

(3) the composition of gas phase is uniform over any horizontal plane,

(4) the activity of catalyst and available active catalyst area are uniform per unit area of any horizontal plane,

(5) the factors determining the mechanism of the reaction are the same over any horizontal plane.

The Effect of Variable Productive Area on the Material Balance $rdW = Fdx$

The assumption underlying the material balance and its five dependent assumptions are seen to be satisfied for a very poor catalyst, however they are not all satisfied for an active catalyst. For these and other reasons equation (42) cannot be applied to an active catalyst without modification.

Consider an "active" catalyst with the velocity of the gas stream such that some areas of the catalyst are covered by fluid in viscous flow and the others by turbulent eddies. The rate of reaction (moles product formed per unit time per unit area) on surfaces covered by the viscous stream depends almost entirely on the transfer of reactants and products to and from the surface by molecular motion. Since this transfer is extremely slow, the rate of reaction will be low on these areas. The rate of reaction on areas scoured by turbulent eddies, even though a thin viscous film covers these areas, is very much greater than that on the viscous areas. In the present study it was found that at sufficiently low flow rates, the conversion was not measurable (no change in the feed composition) in the fourth decimal place of mole fractions.

Only when some turbulence was introduced with increasing feed rate was the conversion measurable. Therefore the dW of equation (42) refers only to that portion of the catalyst scoured by turbulent eddies, and, since an area, not a weight is the effective portion, it is more significant to use the term dA instead of dW, where dA is the productive area, namely that scoured by turbulent eddies.

Any rate expression must satisfy the requirement that the rate is the quotient of driving force and resistance. In any catalytic reaction if one assumes that the adsorption offers negligible resistance to the process then the two resistances determining the total resistance to the process are: (1) transfer of reactant and product molecules through the film covering the most productive areas and (2) resistance to the reaction on the catalyst surface.

As has been seen, the major resistance to the formation of product molecules on an active catalyst is the transfer of reactant molecules through the viscous film on the surface of those areas scoured by turbulent eddies. This resistance is directly proportional to the thickness of the film which in turn depends on the velocity of the fluid through the bed passages. Thus the rate (i.e., reaction rate) of the process is a function of feed rate. In addition, the reaction rate depends on the resistance to the reaction on the surface of the catalyst. Therefore in the case of a very active catalyst, equation (42) is written more correctly, in functional notation:

$$r(F,Y)dA(F) = Fdx \qquad (43)$$

where r(F,Y) indicates the rate to be a function of the resistance to the reaction on the surface of the catalyst, indicated by Y, and of the resistance of the viscous film covering the productive area dA(F). Area dA(F) is the area scoured by turbulent eddies, the "most productive" area. The area dA(F) is indeterminate and varies rapidly with feed rate in the range of feed rates where most academic studies are made. In these ranges it is not permissable to calculate and correlate rates from the equation $r = Fdx/dA$ where dA is the total area of catalyst in the differential bed unless the catalyst is a poor catalyst for the reaction. If the catalyst is at all active this equation cannot be applied because

(1) the assumptions underlying it are not satisfied, and

(2) the active area dA(F) on which the measurable conversion dx is produced is far different from the total area dA.

Because the active area dA(F) is indeterminate, rates of reaction at different velocities in a bed of an active catalyst cannot be correlated unless they are obtained at identical active areas.

Effect of Variable Productive Area on the Use of j Factors in Predicting "Mass Transfer Controlling" in Catalytic Beds

In vapor phase catalytic kinetic studies to date, the assumption has been almost universally made that the resistance to mass transfer through the fluid film surrounding each catalyst particle is negligible in comparison with the resistance to the

reaction on the surface. However, most investigators have failed to experimentally evaluate the validity of this assumption, and have considered it satisfactory to make a calculation of the partial pressure drop through the film. In the case of an active catalyst used in the regions of flow where most academic studies are made, this calculation is meaningless if the total area is assumed to be equally productive. The best method of accurately determining the effect of mass transfer in the bed is to study the variation of reaction rate with flow rate. If mass transfer is a negligible resistance, the reaction rate will be independent of flow rate; and, similarly, the converse is true.

The method whereby the partial pressure drop through the film may be calculated is based on the equations presented by Yang and Hougen.[9] Essentially, they write:

$$r_{Aa} = k_G(p_A - p_{Ai})A_m \tag{44}$$

for $N_B < 350$: $$j_d = \frac{k_G M_m p_f}{G}\left(\frac{\mu}{\rho D_{Am}}\right)_f^{2/3} = 1.82 N_B^{-0.51} \tag{45}$$

therefore $$p_A - p_{Ai} = \Delta p = \frac{r_{Aa} N_B^{0.51}\left(\frac{\mu}{\rho D_{Am}}\right)_f^{2/3}}{1.82 A_m\left(\frac{G}{M_m p_f}\right)} \tag{46}$$

In the above equations, the term A_m signifies the area on which the conversion is measured. All workers to date have assumed A_m to be the total area per unit mass of catalyst, an assumption which is incorrect. A_m has been seen to be far different from the most productive area. The use of this procedure leads to

results which are meaningless and always indicates that mass transfer does not "control" when the catalyst used is an active catalyst and the flow rates through the bed are low. In the present study, assuming the total area to be active, the partial pressure drop through the film assumed to cover the entire catalyst (although in most passages the entire flow was laminar), was calculated to be $\frac{0.043}{A_m}$ atm. This, if true, would justify the conclusion that mass transfer is of negligible importance as a resistance to the process since A_m is in the range 1×10^4 cm^2/g for active catalysts. Despite this calculation, the interpretation of the experimental data demonstrates that the resistance of the film is by far the major resistance to the process. It should be noted that the basic concepts of the method of Yang and Hougen and the j factors are not at fault. Their method yields incorrect results in many cases because it is incorrectly applied.

If the true active area per unit mass i.e., the most productive area on an active catalyst, were known and set equal to A_m and r_{Aa} was calculated on this area, then the Δp calculated from equation (46) would be the true pressure drop across the film. Equation (46) is seen to be applicable when a "poor" catalyst is being used so that the entire area is equally productive or when an active catalyst is used with turbulent flow in all passages of the bed. It is not applicable to an active catalyst with flow in the transition region.

Effect of Variable Productive Area on the Rate of Reaction

Assume for the moment that the total area of the active catalyst used in this study is equally productive. Then from Figure 6 at $N_B = 40$ and $N_B = 38$ at $y_H = 0.4$ it is seen that

$$r(F,Y) = \frac{F\delta x}{\delta A} = \frac{250}{\delta A} \text{ @ } N_B = 40$$

$$r(F,Y) = \frac{F\delta x}{\delta A} = \frac{182}{\delta A} \text{ @ } N_B = 38$$

Thus between $N_B = 38$ and $N_B = 40$ the rate would appear to vary by 37.4 percent based on $\frac{182}{\delta A}$. For a unit increase in Reynolds number the rate increases by 18.7 percent. Since the composition is constant and a unit increase in Reynolds would not decrease by 18.7 percent the film thickness covering the catalyst, there is no apparent reason for this increase in rate. Since the resistances to the process are substantially unchanged by a unit change in Reynolds number, the rate must remain substantially unchanged. But the rate based on total catalyst area increased 18.7 percent. Thus, the assumption that the total catalyst area is equally productive is incorrect, and, in fact, the productive area increased approximately 18.7 percent for a unit change of Reynolds number in this case. Thus $\delta A_{N = 40}$ is 1.187 times as large as $\delta A_{N = 39}$ or is 1.374 times as large as $\delta A_{N = 38}$.

As can be easily shown most, if not all, academic studies of reaction kinetics in gas phase heterogeneous catalysis have been done with Reynolds numbers of less than 80. Under such conditions, with a reasonably active catalyst, the variation of area with flow rate is a major factor in the interpretation of data.

EXPERIMENTAL WORK AND ITS INTERPRETATION

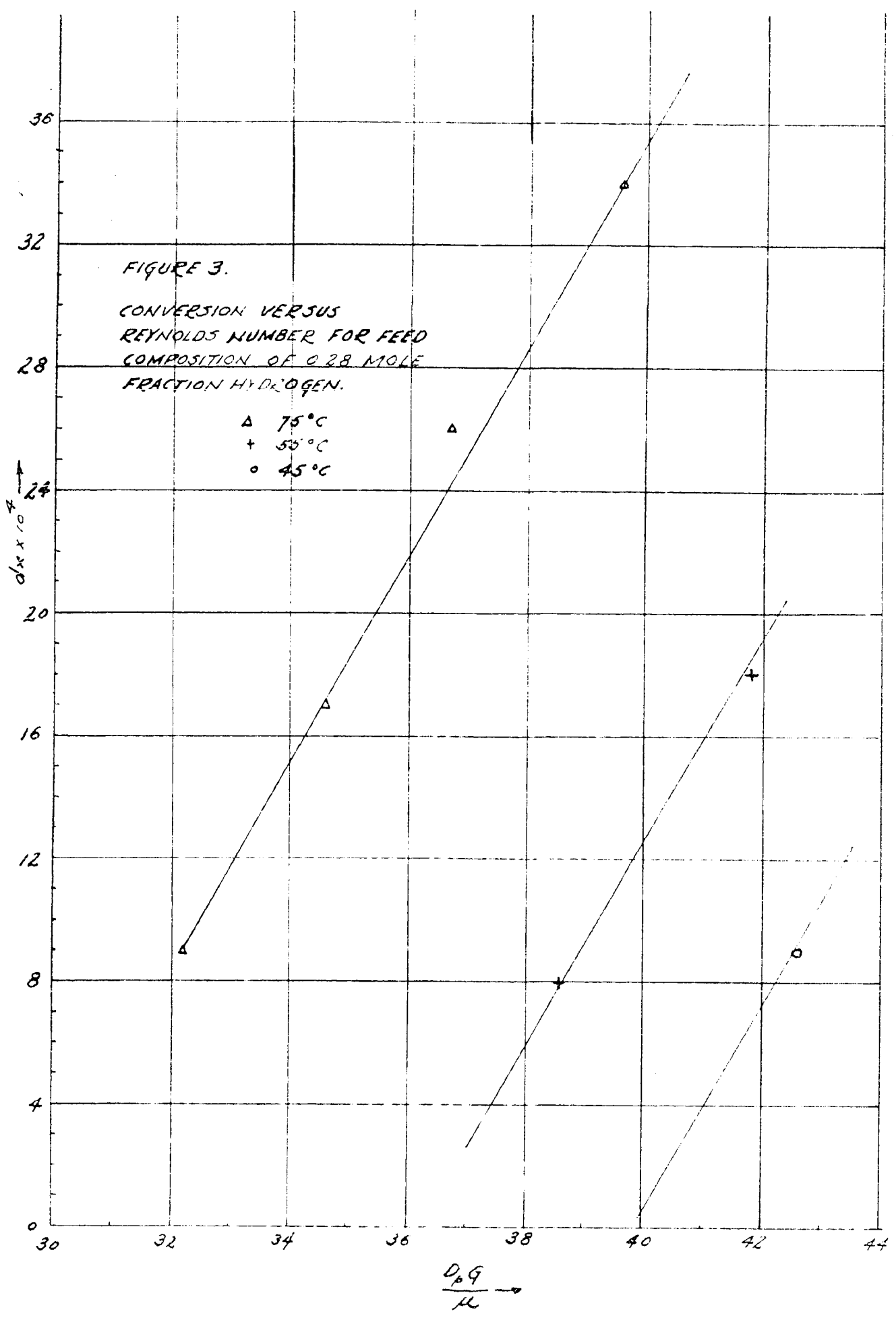
The experimental problem of this study was to obtain data from which the rate of the reaction chosen could be determined and interpreted with the use of the theories previously stated.

The process chosen was the hydrogenation of propylene on 0.5% Pd carried on tabular alumina. Because an accurate method of chemical analysis was available it was possible to use a differential reactor. The conversions obtained were so small that they were termed differential, written as dx, and substituted in the equation $r(F,Y)dA(F) = Fdx$.

For reasons which will be established in this section, the following data were taken: the differential conversion, dx, was measured at three constant feed compositions, 0.28, 0.50 and 0.65 mole fraction hydrogen. In each of the three series the Reynolds number was varied from approximately $N_B = 30$ to $N_B = 42$; the temperatures studied in each series were 45°C., 55°C. and 75°C. The data obtained are given in Figures 3, 4 and 5.

Reproducibility and Accuracy of the Data

The data were exactly reproducible in every case and it was possible to duplicate any given conversion. Thus the entire apparatus and the analytical apparatus i.e., gas density balance, were highly precise instruments. The accuracy of the gas density



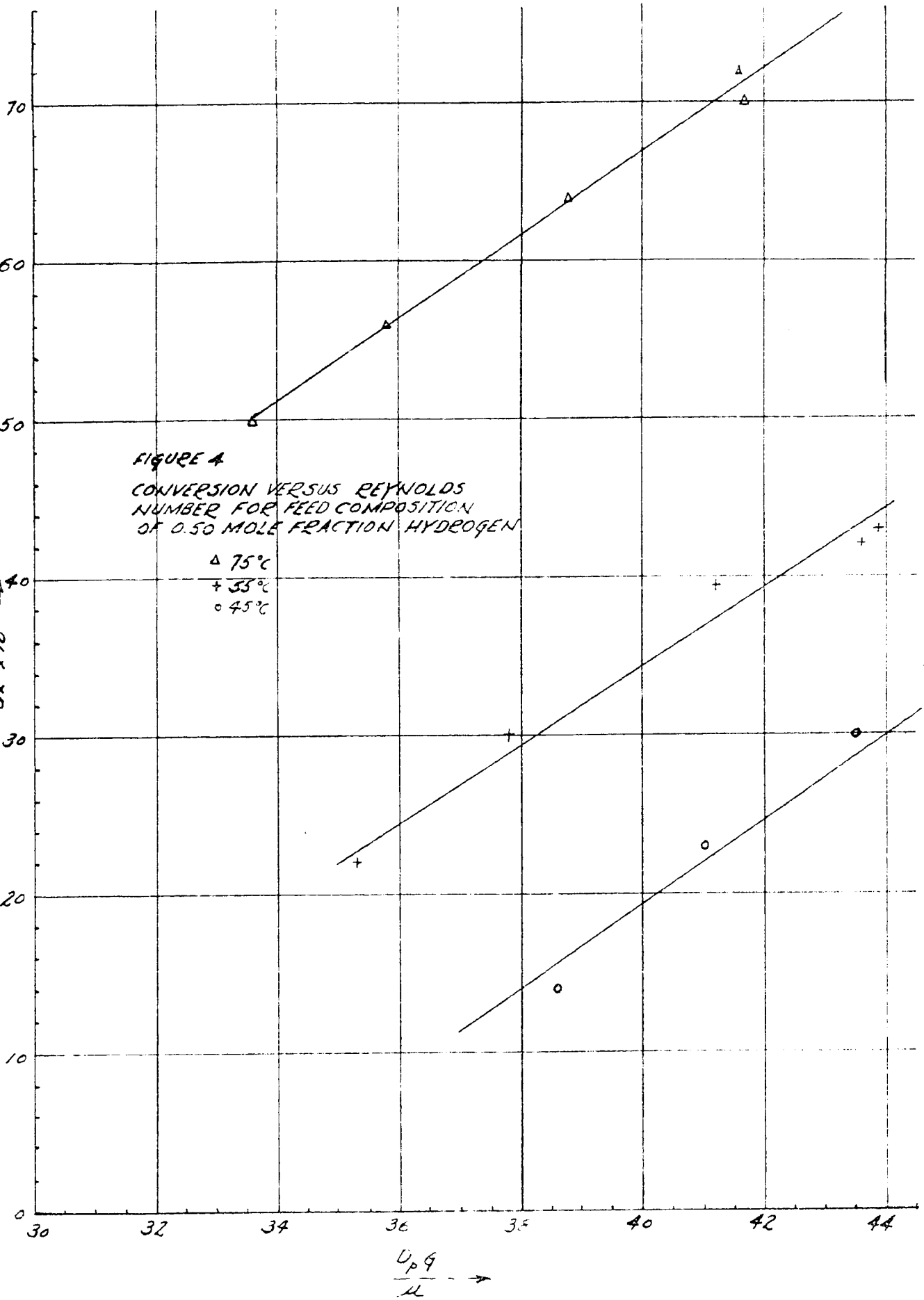


FIGURE 4

CONVERSION VERSUS REYNOLDS NUMBER FOR FEED COMPOSITION OF 0.50 MOLE FRACTION HYDROGEN

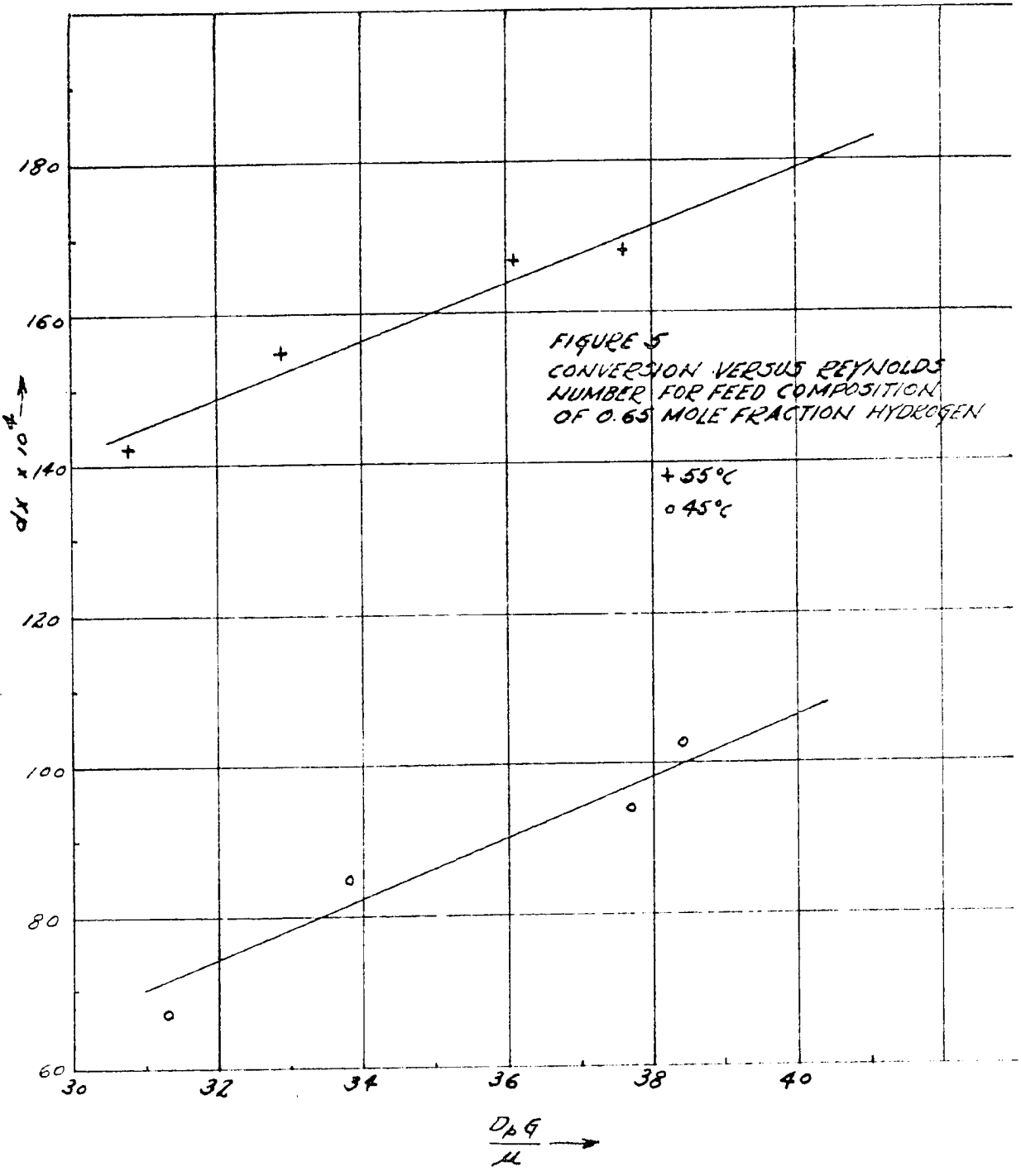


FIGURE 5
CONVERSION VERSUS REYNOLDS NUMBER FOR FEED COMPOSITION OF 0.65 MOLE FRACTION HYDROGEN

balance was limited by the accuracy with which the pressure could be measured. In the Appendix data are given showing that the density of the feed and product stream was measured accurately to 1 part in 10,000.

The heat transfer in the reactor was a major problem in obtaining adequate data. For the purposes of this study, it was desirable that the fluid flow be in the transition region (this term will be defined shortly). In this region heat transfer is poor. At 75°C. the experimental work was conducted at the highest temperature at which the catalyst was stable in activity. Even at this temperature a feed composition of greater than fifty mole percent hydrogen caused a rapid decrease in catalyst activity, finally killing the catalyst. Thus 75°C. was chosen as the maximum temperature to be studied. This was not completely satisfactory in all details. It is believed that the catalyst was at some temperature appreciably higher than 75°C. due to poor heat transfer and the exothermicity of the reaction. As will be seen the interpretation of the data clearly indicates this.

The lower temperature limit was dictated by the lowest conversions which could be accurately measured. This temperature was taken at 45°C. Although the conversions measured at this temperature are small, they are not believed to contain significant error.

The major factor contributing to inaccurate data was not the accuracy of analysis but the control of reaction temperature. In the section entitled "Experimental Apparatus and General

Experimental Procedure", it will be seen that the major disadvantage of the reactor was the inadequacy of temperature measurement and control in the bed. The adsorption isotherms and of course reaction rate and, thus, the conversion depended greatly upon temperature. Thus any apparent inaccuracy in the measurement of conversion is believed to be the result of inadequate temperature measurement and control.

It was not possible to exceed approximately 0.70 mole fraction of hydrogen without causing catalyst activity to fall off. Since the gases were pure and free of poisons, the decrease in activity was attributed to sintering caused by high surface temperatures. Catalyst activity did not decrease at 0.65 mole fraction of hydrogen at reaction temperatures of 45° and 55°C. but did decrease at 75°C. On this basis 0.65 mole fraction hydrogen was used as the upper limit of hydrogen concentration. However because of the exothermic character of the reaction and the poor heat transfer in the reactor this concentration of hydrogen raised the reaction temperature above that desired and the data taken at this concentration may be used only for qualitative interpretation.

Summarizing, only the data at 45°C. and 55°C. between 0.0 and 0.50 mole fraction hydrogen can be regarded as exact. The data at 75°C. and 0.65 mole fraction hydrogen can be used only in a qualitative sense.

Interpretation of the Data

At first sight, the most remarkable aspect of the data is the fact that the conversion (i.e., moles of propane formed per mole of feed) increases very rapidly with increasing gas velocity or Reynolds number. This is apparently in contradiction to all fundamental principles until the condition of the fluid flowing through the bed is considered. In academic work it is somewhat difficult to design a reactor of sufficient diameter to eliminate channeling (wall) effects and at the same time raise the feed rates to those necessary for most of the passages in the bed to be in turbulent flow. Thus most, if not all, academic reaction rate studies have been done in a region that may be defined as the transition region of flow where some points of the bed are in turbulent flow, others in viscous. As discussed in the previous sections, the regions covered by turbulent flow are vastly more productive than those covered by viscous flow, providing the catalyst is active. Further it was proposed that the productive areas increase very rapidly with increase in velocity in the low Reynolds number ranges of flow.

Thus the conversion increased with increased velocity because the area covered by turbulent flow increased.

Conversion was not measurable unless the velocity was sufficient to produce turbulent flow on some points of the catalyst. On these points measurable conversion was produced. Thus in the rate, moles of propane formed per unit area per unit time, the unit

area refers to the area covered by turbulent flow. This does not infer that the remainder of the catalyst was inactive. It only means that on this catalyst, the points covered by turbulent flow were provided with reactants so much more rapidly than were the catalyst sections which were covered with viscous flow, that the production of product on viscous covered areas was negligible in comparison with the production of product on the turbulent areas.

It is immediately obvious that if the total surface area of the catalyst is not measurably productive and if the most productive area increases rapidly with velocity then the rates expressed in terms of total area of catalyst will increase rapidly with velocity. Such a rate expression is meaningless. The rate must be expressed per unit of area on which the measured conversion occurs; unfortunately this area is indeterminate.

One is thus faced with the problem of correlating rate data obtained at varying velocities over different and unknown productive areas with gases of various composition. The assumption made in this study is that at any single Reynolds number, the ratio of the amount of turbulent flow to the amount of viscous flow is a constant, and at any single Reynolds number, the area covered by turbulent flow is a constant. Thus rates obtained at a constant Reynolds number are assumed to be based on identical areas and can be compared with one another. For this reason all the experimental data, ranging over varying gas compositions and temperatures,

was taken over the same range of Reynolds numbers, and only the rates obtained at the same Reynolds number are correlated in defining the resistances and driving forces in the rate expression.

In Tables I and II are given the data used to determine the expression defining the rate of the process. The conversion, dx, is read from Figures 3, 4 and 5 and the feed rate, F, is calculated from the Reynolds number and the properties of the gas stream. Sample calculations are given in the Appendix.

Table I Experimental Values Obtained at 45°C. for Fdx

N_B	y_H	dx x 10^4	F x 10^4	Fdx x 10^8
42.6	0.28	9	9.77	87.9
42.6	0.50	26.4	13.69	361
42.6	0.65	116	19.0	2200
41	0.28	4	9.41	37.6
41	0.50	22	13.2	290
41	0.65	110	18.3	2010

Table II Experimental Values Obtained at 55°C. for Fdx

N_B	y_H	dx x 10^4	F x 10^4	Fdx x 10^8
37	0.28	2.55	8.77	22.37
37	0.50	26.9	12.29	330.6
37	0.65	168	17.04	2860
40	0.28	12.5	9.48	118.7
40	0.50	34.5	13.3	458
40	0.65	179.2	18.4	3295
41	0.28	15.8	9.72	153.8
41	0.50	36.9	13.61	502
41	0.65	183	18.9	3460
38	0.28	6	9.01	54.06
38	0.28	29.4	12.50	367
38	0.65	171.8	17.47	2995

Since all runs were at atmospheric pressure, y_H is equal to p_H. For each N_B, Fdx is plotted against y_H or p_H on an

isothermal plot. These plots are given in Figures 6, 7 and 8 and are represented by the solid lines. The indicated points are calculated from the rate expression theoretically derived and do not represent the experimental data.

Derivation of the Rate Equation

One of the most important relationships in chemical engineering is the equation

$$\text{rate} = \frac{\text{driving force}}{\text{resistance}} . \qquad (47)$$

In order to determine the rate expression fitting the data, many different mechanisms were chosen and rate expressions derived. Table III lists the mechanisms tested. As expected none of these would fit the data.

Table III Mechanisms Which Fail to Fit the Data

Mechanism (Assuming Film Resistance Negligible)	Equation Expressing the Mechanism
I Reaction between molecularly adsorbed H_2 and adsorbed C_3H_6:	
a) adsorption of hydrogen "controlling"	$\frac{p_H}{r} = a + bp_U + cp_S$
b) adsorption of propylene "controlling"	$\frac{p_U}{r} = a + fp_H + cp_S$
c) surface reaction controlling	$\sqrt{\frac{p_H p_U}{r}} = a + fp_H + bp_U + cp_S$
II Reaction between atomically adsorbed H_2 and adsorbed C_3H_6:	
d) adsorption of H_2 controlling"	$\sqrt{\frac{p_H}{r}} = a + bp_U + cp_S$
e) adsorption of C_3H_6 "controlling"	$\frac{p_U}{r} = a + f\sqrt{p_H} + cp_S$
f) surface reaction controlling	$\sqrt[3]{\frac{p_H p_U}{r}} = a + f\sqrt{p_H} + bp_U + cp_S$

III	Reaction between C_3H_6 in the gas phase and molecularly adsorbed hydrogen	
	g) adsorption of H_2 controlling	$\frac{p_H}{r} = a + cp_S$
	h) surface reaction controlling	$\frac{p_H p_U}{r} = a + fp_H + cp_S$
IV	Reaction of C_3H_6 in the gas phase and atomically adsorbed hydrogen	
	i) adsorption of hydrogen controlling	$\sqrt{\frac{p_H}{r}} = a + cp_S$
	j) surface reaction controlling	$\sqrt{\frac{p_H p_U}{r}} = a + f\sqrt{p_H} + cp_S$
V	Reaction between H_2 in the gas phase and adsorbed C_3H_6	
	k) impact of hydrogen upon adsorbed C_3H_6 controlling	$\frac{p_H p_U}{r} = a + bp_U + cp_S$
	l) adsorption of C_3H_6 controlling	$\frac{p_U}{r} = a + cp_S$

Most of the mechanisms proposed in Table III are those suggested by Hougen and Watson.[10] They are of invaluable assistance when reaction rate studies are being made on very poor catalysts (c.f. "The Importance of Turbulent Flow etc." in the preceding sections). However many, possibly most, catalysts industrially used are excellent catalysts for the reaction they catalyze and, in such cases as previously discussed, the transfer of reactants and products to and from the catalyst offers a substantial resistance to the rate of the process.

Thus far no one has provided a really adequate tool for defining rates of reactions in which the major resistance is in

the transfer of reactants (mass transfer) through the viscous film covering areas scoured by turbulent flow. The following development takes this resistance into account, regarding it as being "in series" with the resistance to the reaction on the catalyst surface. The entire development is based on equation (47).

Adsorption characteristics of hydrogen, propylene and propane have been established on several palladised carriers by Reyerson and Cines.[44] Their work is of considerable importance to this study and demonstrates the following points:

(1) Hydrogen is not adsorbed on palladised carriers.

(2) Propane is adsorbed very weakly on palladised carriers.

(3) Propylene is adsorbed very strongly on palladised carriers.

The palladium is so strong an adsorbent for propylene that at any constant temperature greater than 35°C. the palladium adsorbs all the propylene it can hold at a very low partial pressure of propylene i.e., at approximately 200mm. mercury pressure. At partial pressures above 200mm. the amount of propylene adsorbed is substantially independent of partial pressure. This effect begins at approximately 35°C. and becomes more pronounced as the temperature increases, that is, the catalyst adsorbs the maximum quantity at lower partial pressures. On this basis one can write at constant temperature:

$$c_l = L - c_U = 0$$
$$c_U = L \qquad (48)$$

where L is a constant dependent on temperature.

On the basis of these adsorption characteristics, the following mechanism of reaction is assumed: propane molecules are formed by the impact of hydrogen molecules from the gas phase on propylene molecules adsorbed on the catalyst surface. Thus the rate of reaction on the surface of the catalyst is:

$$r = k_1 a_H^* c_U = \frac{a_H^* c_U}{\frac{1}{k_1}} = \frac{\text{driving force}}{\text{resistance}} \qquad (49)$$

$$r = \frac{a_H^* L}{\frac{1}{k_1}} \qquad (50)$$

The rate of transfer of hydrogen through the film is:

$$r = k_g \frac{(D_H - D_H^*)}{t} = \frac{D_H - D_H^*}{\frac{t}{k_g}} = \frac{\text{driving force}}{\text{resistance}}$$

But
$$\text{rate} = \frac{\text{total driving force}}{\text{total resistance}}$$

$$= \frac{D_H - D_H^* + a_H^* L}{\frac{t}{k_g} + \frac{1}{k_1}} = r(F,Y) \qquad (51)$$

Now
$$\frac{\text{moles hydrogen}}{\text{unit volume}} = \frac{p_H}{RT}$$

$$D_H = \frac{\text{moles hydrogen}}{\text{unit area}} = \frac{\alpha p_H}{RT}$$ where α is a constant having units of length

$$a_H = \frac{\bar{f}_H}{f_H^\circ} = \bar{f}_H = p_H$$ by choice of the standard state

Equation (51) may be written

$$r(F,Y) = \frac{\alpha' p_H - \alpha' p_H^* + p_H^* L}{\frac{t}{k_g} + \frac{1}{k_1}} = \frac{\alpha' \Delta p_f + (p_H - \Delta p_f) L}{\frac{t}{k_g} + \frac{1}{k_1}} \qquad (52)$$

where $\alpha' = \alpha/RT$

but, driving force = (rate)(resistance)

$$D_H - D_H^* = r\frac{t}{k_g} = \frac{\alpha}{RT}\Delta p_f = \alpha'\Delta p_f \; ; \; \Delta p_f = \frac{rt}{\alpha' k_g} \qquad (53)$$

Substituting in equation (52):

$$r(F,Y) = \frac{r\frac{t}{k_g} + (p_H - \frac{rt}{\alpha' k_g})L}{\frac{t}{k_g} + \frac{1}{k_1}} \qquad (54)$$

$$r(F,Y) = \frac{Lp_H}{\frac{L}{\alpha' k_g}t + \frac{1}{k_1}}$$

let $L/\alpha' = B$, B is a constant, dependent on temperature only, then

$$r(F,Y) = \frac{Lp_H}{B\frac{t}{k_g} + \frac{1}{k_1}} \qquad (55)$$

The film resistance $\frac{t}{k_g}$ can be defined using the theories developed in the section on heat, mass and momentum transfer:

$$R_F = \frac{t}{k_g} = \frac{f(N_B)}{j_d c u \left(\frac{\mu}{\rho D}\right)_f^{2/3}} \qquad (56)$$

But at a constant Reynolds number, $f(N_B)$ and j_d are constants, u is equal to $\frac{N}{D_p}\frac{\mu}{\rho}$ and c is p_H/RT so that in beds where D_p is constant,

$$R_F = \frac{k_2}{p_H\left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}} = \frac{1}{p_H A} \text{ at constant } N_B \qquad (57)$$

where $$A = \frac{1}{k_2}\left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}$$

k_2 = a constant dependent on temperature

Equation (55) becomes

$$r(F,Y) = \frac{Lp_H}{\frac{B}{p_H A} + \frac{1}{k_1}} \qquad (58)$$

In testing this equation it was found that $\frac{1}{k_1}$ was negligible in comparison to $\frac{B}{p_H A}$. Hence it will be dropped at this point. Thus the only important resistance to the rate process is the mass transfer resistance of the film. Dropping $\frac{1}{k_1}$:

$$r(F,Y) = \frac{L}{B} p_H^2 A \tag{59}$$

Now $$r(F,Y) = \frac{Fdx}{dA(F)}$$

At a constant Reynolds number the area covered by turbulent flow is assumed to be the same for all gas composition so that

$$A(F) = A(N) = A_N .$$

So at a constant N_B

$$Fdx = \frac{(dA_N)L}{B} p_H^2 \frac{1}{k_2} \left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}$$

or $$Fdx = Z_N p_H^2 \left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3} \tag{60}$$

Equation (60) is the final form of the rate equation. The quantity Z_N is a constant dependent on temperature and Reynolds number.

Application of the Derived Rate Equation to the Data

The Schmidt number, or efficiency factor, in equation (60) represents the average efficiency of the film and should be evaluated at true average film conditions. A knowledge of these conditions presupposes the answer to the problem, hence at best the average film condition can only be estimated.

Initial testing of the data with equation (58) demonstrated that the resistance to the reaction on the catalyst surface was

negligible compared to the resistance of the gas film. Since the rate in each of these resistances is identical and is equal to the quotient of individual driving force and resistance, it is obvious that the driving force through the reaction resistance is small. Since this driving force involves the partial pressure of hydrogen, which is zero after reaction, it is seen that nearly all the partial pressure of hydrogen in the gas phase is dropped across the film. Thus the average pressure of hydrogen in the film is approximately $p_H/2$. Since the total pressure is one atmosphere, the average partial pressure of propylene in the film is $1 - p_H/2$ if the very small partial pressure of the differential amount of propane formed is neglected. The Schmidt number was calculated on this basis.

The quantity $\left(\frac{\mu}{\gamma}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}$ can be expressed in terms of p_H but the resulting equation is too complex to be feasible for ordinary use. Since in everyday practice values for this quantity would be plotted and obtained from a graph, the author prepared these graphs at 45° and 55°C. for varying mole fractions (partial pressures) of hydrogen. These plots are given in Figure 9 and the calculated points are given in the Appendix.

The experimental data are represented by solid lines in Figures 6, 7 and 8. The quantity Z_N as previously mentioned is dependent on temperature and Reynolds number. Thus on the isothermal plots (Figures 6, 7 and 8), Z_N will be a constant for any one Reynolds number. Values of Z_N were chosen which best fit

the data. Sample calculations are given in the Appendix. Table IV below summarizes the values of Z_N obtained.

Table IV Values of Z_N

$t^{\circ}C$	N_B	$Z_N \times 10^{-5}$
55°	41	58
55	40	51
55	38	39.4
55	37	36.15
45	42.6	46.2
45	41	33.5

In order to calculate the value of Fdx at a desired reaction temperature, partial pressure of hydrogen and Reynolds number, the value of Z_N is selected from Table IV, $\left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}$ is read from Figure 9 and Fdx calculated.

It is seen from the coordinates calculated and shown in Figures 6, 7 and 8 that the fit of the experimental data is excellent up to 0.55 mole fraction hydrogen. The curves are not shown above the value 0.55 because as discussed in a previous section it is felt that the highly exothermic character of the reaction coupled with poor heat transfer raised the temperature above that of the isothermal plot. This conclusion substantiated by the fact that the equation $Fdx \text{ ~~x 10}^{8}~~ = Z_N p_H^2 \left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}$ fits the data so well between hydrogen mole fractions of 0 and 0.55 and continues to be of the correct form above y_H of 0.55 that there is no doubt that it represents a correct interpretation of the mechanism of the process. Further, research has shown that above 0.65 mole fraction hydrogen the catalyst activity was no

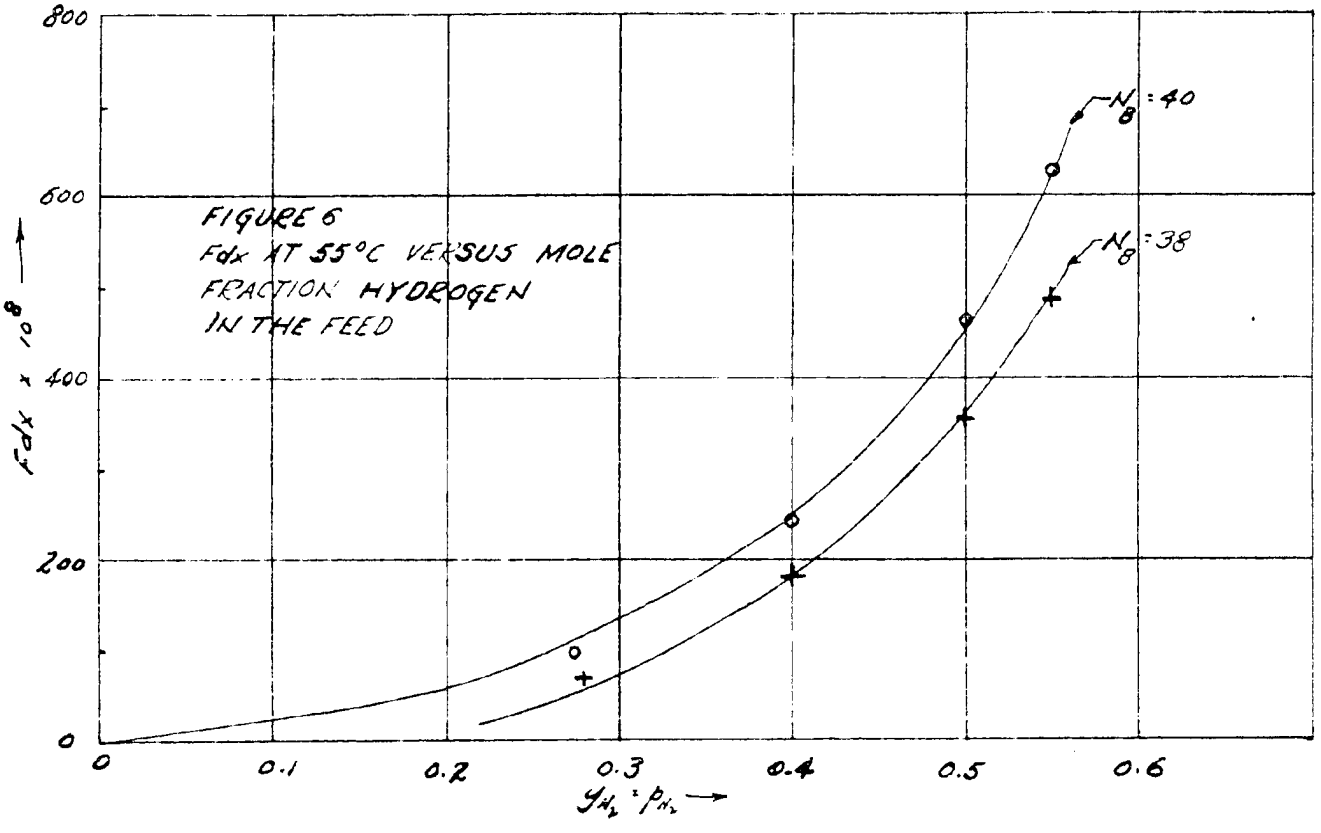


FIGURE 6
f_{dx} AT 55°C VERSUS MOLE FRACTION HYDROGEN IN THE FEED

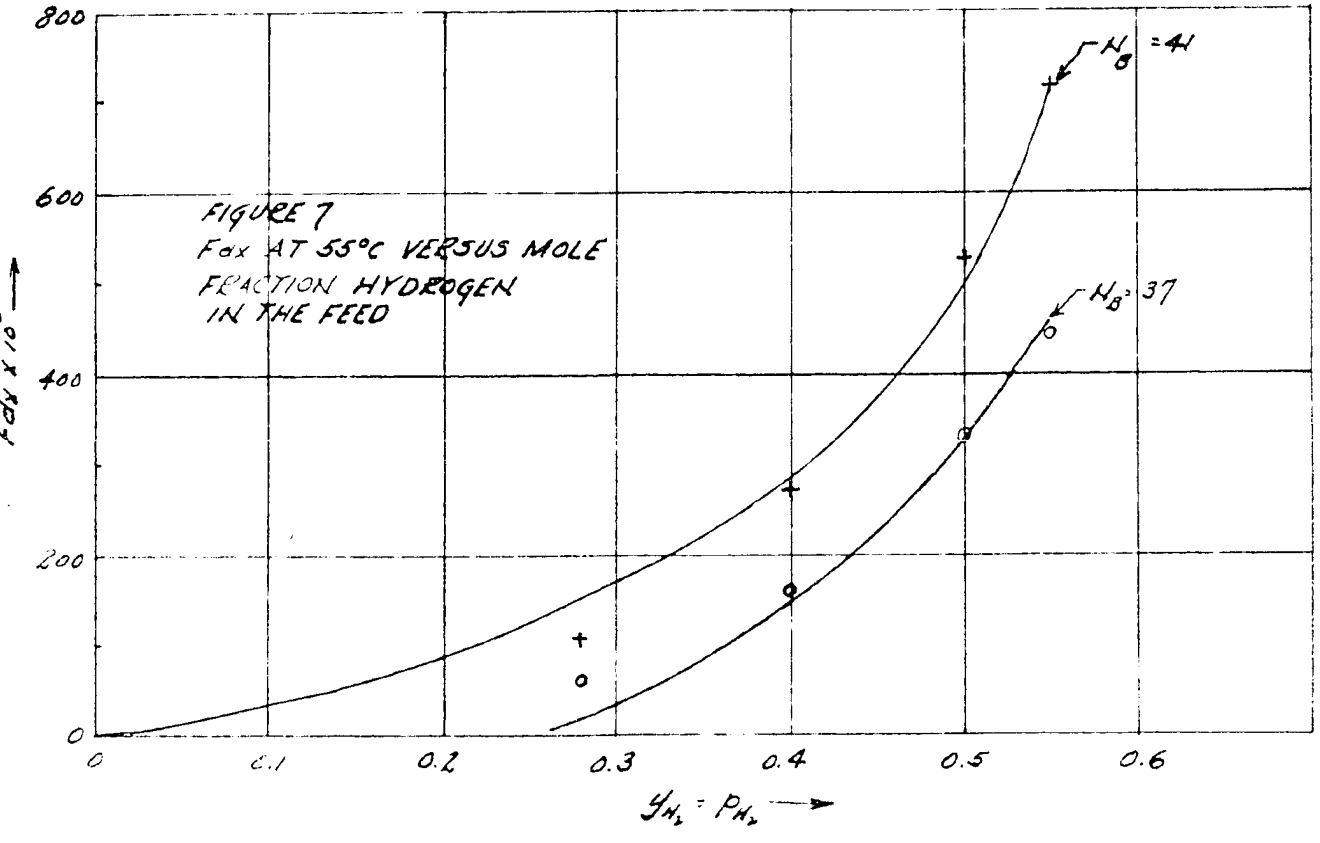


FIGURE 7
f_{dx} AT 55°C VERSUS MOLE FRACTION HYDROGEN IN THE FEED

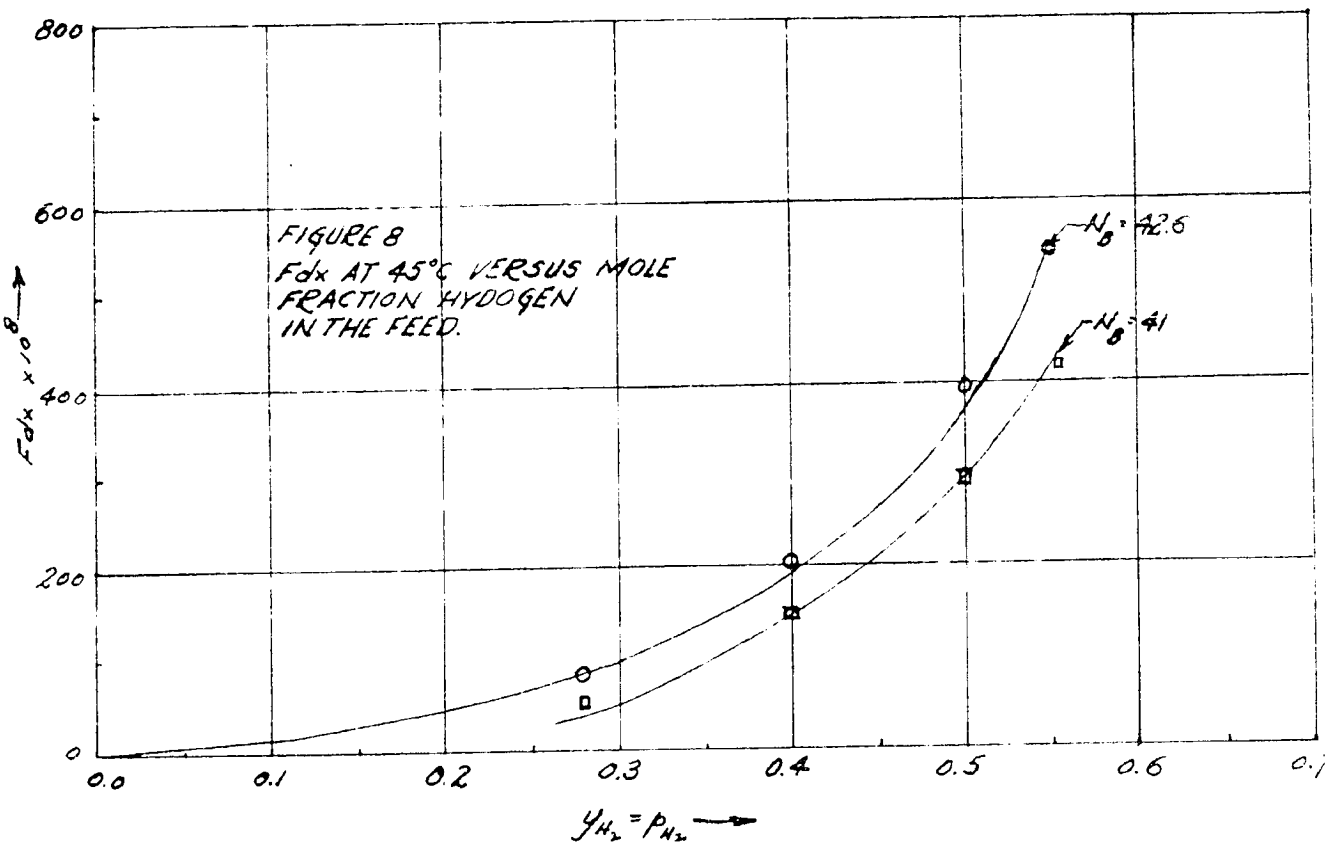


FIGURE 8
F_{dx} AT 45°C VERSUS MOLE FRACTION HYDOGEN IN THE FEED.

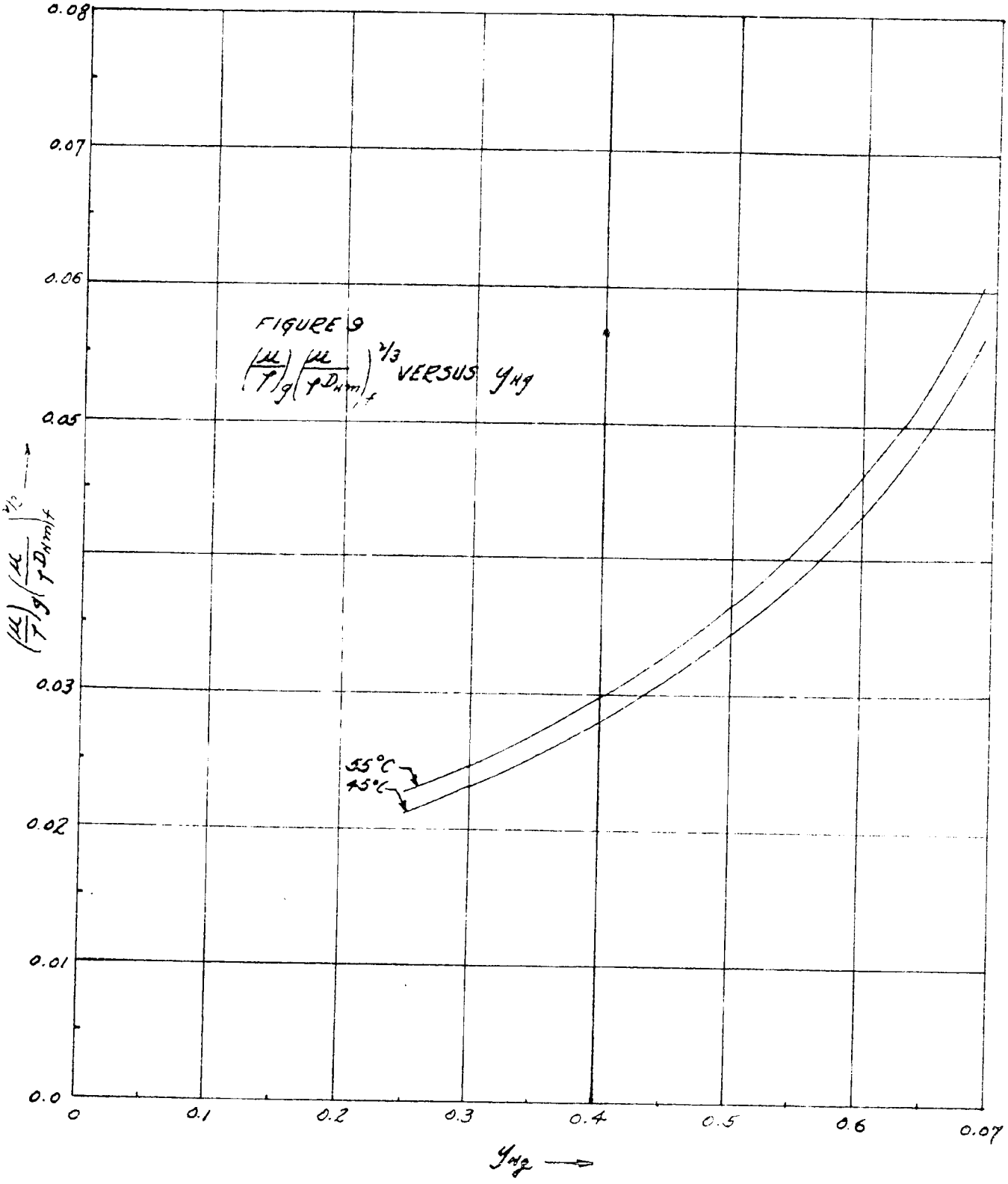


FIGURE 9
$\left(\frac{\mu}{\rho}\right)_g\left(\frac{\mu}{\rho D_{Hm}}\right)_f^{2/3}$ VERSUS y_{Hg}

longer stable. Since this phenomenon is attributable only to sintering of the catalytic structure, it is logical to believe that the data obtained at 0.65 mole fraction hydrogen is unreliable because the unremoved heat of reaction resulted in a reaction temperature much higher than that obtained at lower hydrogen compositions. Thus the data at 0.65 mole fraction hydrogen does not fit on an isothermal plot of conversions obtained at lower hydrogen compositions.

EXPERIMENTAL APPARATUS

The apparatus used in this investigation is diagrammatically shown in Figure 10. It was constructed entirely of pyrex glass. For the most part 6 and 8mm. pyrex was used. The stopcocks were 2mm. bore.

Reactant Gases

Hydrogen and propylene were purchased from the Matheson Co. Inc. Water pumped hydrogen and propylene (c.p. grade) were the gases used. Both gases were found to contain water vapor and the hydrogen contained oxygen as an additional impurity.

Purification Units

Because of the adverse effects of oxygen on the catalyst and of water vapor on both the catalyst and the analytical procedure, these impurities were removed from the gas streams before they were metered, analyzed and fed to the reactor.

Oxygen was removed from both gases by passing them through beds of spherical copper shot maintained at 150°C. The hydrogen reacted with the copper oxide formed to form water and regenerate the copper. The propylene did not regenerate copper from the oxide formed and a freshly reduced copper bed was inserted in the propylene stream before each run.

Water in both gases was removed in dessicant beds freshly activated before each run. The hydrogen was dessicated with activated alumina and the propylene with drierite.

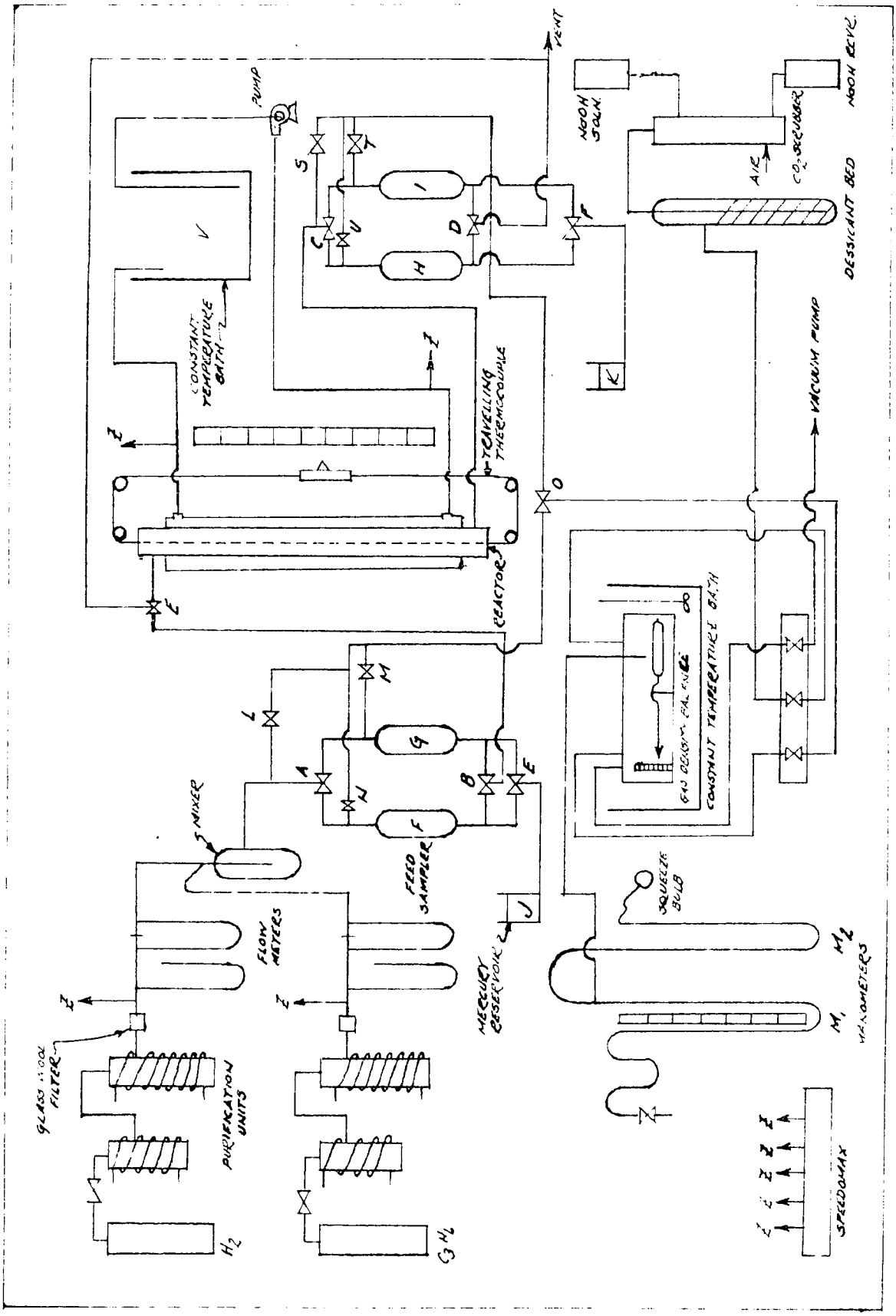


FIGURE 10. EXPERIMENTAL APPARATUS.

Each dessicant was activated in place by heating it to 200-225°C. while passing a stream of nitrogen through it. The nitrogen was purchased from Linde Air Products. Activated alumina was found to be unsuitable as a dessicant for propylene because it irreversibly adsorbed propylene to form a liquid product. This product eventually rendered the activated alumina inactive as a dessicant.

Metering Devices

The flow rates (moles per unit time) were determined by capillary orifices[62]. Each gas was passed through a glass wool filter immediately following the purification beds. These filters removed any fines from the dessicant beds which could have altered the roughness and diameter of the capillary orifices and thus changed their calibration. The pressure and temperature of the gas immediately preceding the capillary orifices were measured with a mercury manometer and Leeds and Northrup Speedomax respectively.

The orifices were calibrated with a wet test meter. In order to determine the accuracy of the calibrations, mixtures of the metered gases were analyzed in the gas density balance. The composition of mixtures calculated from the calibration curves never varied by more than 1% from the analytical determination. This accuracy of metering was maintained during the entire experimental schedule of eleven months.

The orifices were 0.75mm. in diameter. The hydrogen orifice was 11cm. long and the propylene orifice was 9cm. long. The manometer fluid was dibutyl phthalate.

Feed and Product Stream Sampling Devices

A photograph of these devices is shown in the Appendix. They are shown diagrammatically in Figure 10. These devices permitted instantaneous and simultaneous sampling of feed and product streams without affecting the rate of flow through the catalyst bed for more than one or two seconds. A complete description of the construction and operation of these units is given in the Appendix.

The Preheater and Reactor

The preheater and reactor were preceded by three way stopcock E through which the gases sweeping out the system in the beginning of the run were shunted around the catalyst bed.

This procedure allowed the purification beds to be heated to operating temperatures before the gases were introduced to the preheater and catalyst by opening valve E. In this manner only pure gases were passed over the catalyst so that it was never subjected to oxidants or poisons.

The reactor and preheater units were integral as is seen in Figure 10. Tabular alumina was chosen as the heating media in the preheater because it was inert as a catalyst or adsorbent. The preheater was $1\frac{1}{2}$ feet long. The inside diameter of the unit was 10mm. and a 3mm. tube ran along its axis. Thus the catalyst chamber and preheater were annular in cross-section. Both the preheater and reactor were jacketed and water from thermostatically controlled bath (V in Fig. 10) was pumped through the jacket. A travelling thermocouple in the 3mm. tube measured temperatures

along the axis of the unit.

Upon leaving the reactor, the product gases passed through the product sampling system and were vented to the atmosphere.

The reactor was designed so that the physical assumptions underlying the material balance rdA = Fdx were satisfied. The most important assumptions controlling design of reactors from which kinetic data are to be obtained are (1) a nearly isothermal bed must be obtained and (2) there must be no channeling of gases.

Since the reaction was exothermic, it is obvious that an isothermal bed is unobtainable. However, to prevent any "hot spots" in the bed, and to produce as nearly a constant temperature bed as possible, the catalyst particles were intermixed with small pellets of tabular alumina. This procedure was effective. Without the alumina there was an axial temperature gradient of two or three degrees Fahrenheit. With the alumina diluent, it was not possible to measure any gradient with an instrument which measures temperatures accurately to $\pm\frac{1}{2}^{\circ}$F.* This does not mean that no gradient existed. The disadvantage of the reactor was that conduction of heat through the three millimeter axial glass rod containing the travelling thermocouple leveled out the temperature gradient which existed axially. The major problem in reactor design was to remove the heat of reaction from the catalyst surface. In this study with most of the fluid in viscous flow, this removal was not possible at higher temperatures and this factor lends uncertainty to the data taken at high temperatures

*Leeds and Northrup Six Point Recording "Speedomax".

and high hydrogen composition.

Channeling had to be avoided since the amount of channeling varies with velocity and this study involved velocity effects.

Furnas[13] did the first and most reliable study on this effect and his work resulted in the empirical rule that the ratio of catalyst pellet diameter to reactor diameter should be at least 1 to 10. The diameter of the alumina pellets and the catalyst particles was 0.0563 centimeters, hence the diameter of the reactor must be at least 0.563 centimeters. The equivalent diameter of the annular shaped reaction chamber used was 0.742 centimeters, a ratio of approximately 13:1. Thus it is felt that channeling effects were negligible.

Analytical Method

The composition of the feed and product streams was determined by the use of a gas density balance. This instrument was capable of measuring the density of a gas accurately to 1 part in 10,000. The theory and accuracy of gas density balances has been comprehensively studied by Edwards.[14] The operation and construction of the gas density balance used is given in detail in the Appendix. This discussion includes operational procedure, standard gas, accuracy etc.

Catalyst

The catalyst chosen was 0.5 percent palladium on non porous alumina. It was prepared by Baker and Co., Inc., Newark, New Jersey. This catalyst needed no activation. The alumina was

prepared in a jaw crusher and was carefully screened so that although the particles were irregular in shape, they would not pass a 16 mesh Tyler screen. The pellets were 12 to 16 mesh in size. The activity of the catalyst was found not to vary in the ranges of temperature and composition used in the experiments.

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APPENDIX

A) Tables of Experimental Data

B) Sample Calculations

C) Detailed Experimental Procedures and Apparatus

D) Effect of Reverse Reaction

E) Descriptive Dimensional Analysis

F) Calculation of $\left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}$, D and D_p

G) Properties of Hydrogen, Propylene, and Propane

H) Pictures of Equipment

(A) Experimental Data

Throughout this section p and Δp refer to centimeters of mercury pressure in the gas density balance. R refers to manometer reading in inches of dibutyl phthalate.

(1) Variation of Catalyst Activity with Time

One run was specifically made to test the variation of catalyst activity with time. The data from this run are given in Table V.

Table V Variation of Catalyst Activity with Time

reactor temperature: 55°C.
feed composition: 0.50 mole fraction H_2
Reynolds number: 43 (approximately)

		H_2 flow meters		C_3H_6 flow meters		Gas Density Analysis		
time	sample	p"Hg	R	p"Hg	R	p_F	p_P	p
10:25	1	7.78	2.00	7.62	4.00	28.45	28.33	0.12
11:20	2	7.74	2.00	7.57	4.00	28.48	28.36	0.12
12:20	3	8.10	2.00	7.86	4.00	28.49	28.37	0.12
1:30	4	7.85	2.00	7.67	4.00	28.46	28.34	0.12
2:20	5	8.02	2.00	7.81	4.00	28.45	28.33	0.12

Since the change in pressure between the feed and product samples necessary to balance the gas density beam is exactly proportional to change in density of the two samples which is in turn directly proportional to the amount of reaction, it is obvious that the activity of the catalyst is invariant at least over the time used for each run. In addition the variation of catalyst activity was checked periodically by duplicate samples as will be seen in the remaining data.

The kinetic data taken are as follows:

Table VI Series II Data ($y_H = 0.50$)

run	sample	H_2 meters p"Hg	H_2 meters R	C_3H_6 meters p"Hg	C_3H_6 meters R	t_{meters} °K	$t_{reactor}$ °C	π_{mm}	Analysis p_F	Analysis p_p	Analysis p_a
A	1					300	45	733	27.75	27.67	21.34
A	2	7.87	1.99	7.56	4.00	300	55	733	28.45	28.33	21.34
A	3	8.02	2.00	7.86	4.00	300	55	733	28.13	28.01	21.34
A	4	8.49	1.99	8.33	3.99	300	75	733	28.11	27.91	21.34
A	5	8.43	2.00	8.27	4.00	300	75	733	27.83	27.63	21.34
A*	6	8.94	2.00	8.79	4.00	300	95	733	27.75	27.53	21.34
A*	7	8.94	1.99	8.79	4.00	300	95	733	27.83	27.75	21.34
A*	8	10.10	1.99	9.92	3.99	300	95	733	27.80	27.80	21.34
B	1	5.81	1.61	5.71	3.00	300	55	753	27.50	27.44	21.14
B	2	6.45	1.60	6.31	3.00	300	75	753	27.30	27.16	21.14
B*	3	6.71	1.60	6.62	3.00	300	95	753	27.30	27.30	21.14
D	1	6.39	1.69	6.32	3.25	300	45	735	27.33	27.29	21.10
D	2	7.33	1.69	7.27	3.25	300	55	735	27.35	27.27	21.10
D	3	7.09	1.69	7.03	3.26	300	75	735	27.33	27.17	21.10
E	1	6.82	1.75	6.59	3.54	300	45	737	26.10	26.04	20.24
E	2	8.50	1.78	8.26	3.62	300	55	737	26.36	26.25	20.24
E	3	9.01	1.74	8.80	3.54	300	75	737	26.22	26.04	20.24

Table VIII Series III Data ($y_H = 0.65$)

run	sample	H_2 meters p	H_2 meters R	C_3H_6 meters p	C_3H_6 meters R	^oC t_{meters}	^oC $t_{reactor}$	π_{mm}	Analysis p_F	Analysis p_P	Analysis pa
A	2	8.90	2.94	8.26	2.88	27	45	730	26.82	26.56	14.87
A	3	9.97	2.80	9.44	2.88	27	45	730	25.89	25.62	14.87
A	4	10.10	2.80	9.55	2.88	27	55	730	25.89	25.45	14.87
A	5	10.98	2.94	10.35	2.88	27	55	730	26.82	26.36	14.87
A*	6	10.10	2.66	9.59	2.78	27	75	730	24.88	24.50	14.87
B	1	6.79	2.62	6.34	2.26	27	45	743	26.57	26.39	14.45
B	2	7.34	2.61	6.90	2.26	27	55	743	26.59	26.21	14.45
B*	3	8.44	2.60	7.98	2.26	27	75	743	26.55	26.17	14.45
C	1	7.32	2.65	6.92	2.51	27	45	744	25.40	25.18	13.98
C	2	8.61	2.64	7.25	2.51	27	55	744	25.36	24.96	13.98
C*	3	8.80	2.65	8.42	2.54	27	65	744	25.32	24.94	13.98

Table VIII Series IV Data ($y_H = 0.28$)

run	sample	H_2 meters p	H_2 meters R	C_3H_6 meters p	C_3H_6 meters R	^oC t_{meters}	^oC $t_{reactor}$	π_{mm}	Analysis p_F	Analysis p_P	Analysis pa
A	1	3.81	0.60	4.04	3.02	27	45	744	24.22	24.22	26.13
A	2	4.58	0.61	4.75	3.02	27	55	744	24.30	24.30	26.13
A	3	5.11	0.60	5.25	3.02	27	75	744	24.22	24.20	26.13
B	1	5.47	0.73	5.95	3.93	27	45	740	23.96	23.94	25.66
B	2	6.13	0.73	6.35	3.95	27	55	740	23.94	23.90	25.68
B	3	6.41	0.73	6.64	3.95	27	75	740	23.80	23.72	25.68
C	1	4.09	0.66	4.31	3.66	27	45	746	23.26	23.26	25.18
C	2	4.93	0.66	5.14	3.66	27	55	746	23.24	23.22	25.18
C	3	5.56	0.66	5.76	3.66	27	75	746	23.30	23.24	25.18
C	4	5.13	0.63	5.42	3.37	27	75	746	23.28	23.24	25.18

In Tables VI, VII and VIII the runs marked with an asterisk (*) are those in which catalyst activity was not constant. The decay of catalyst is illustrated nicely by Series II runs A6, A7 and A8. It is interesting to note that catalyst activity dropped off more slowly in these runs than it did in run IIB3. Since the Reynolds number is lower in IIB3, the assumption that sintering due to poor heat transfer is causing catalyst decay is further substantiated.

The calibration curves of the hydrogen and propylene meters are given in Figures 12 and 13. With these curves and Tables VI, VII and VIII any of the calculated data may be obtained as shown in the "Sample Calculations".

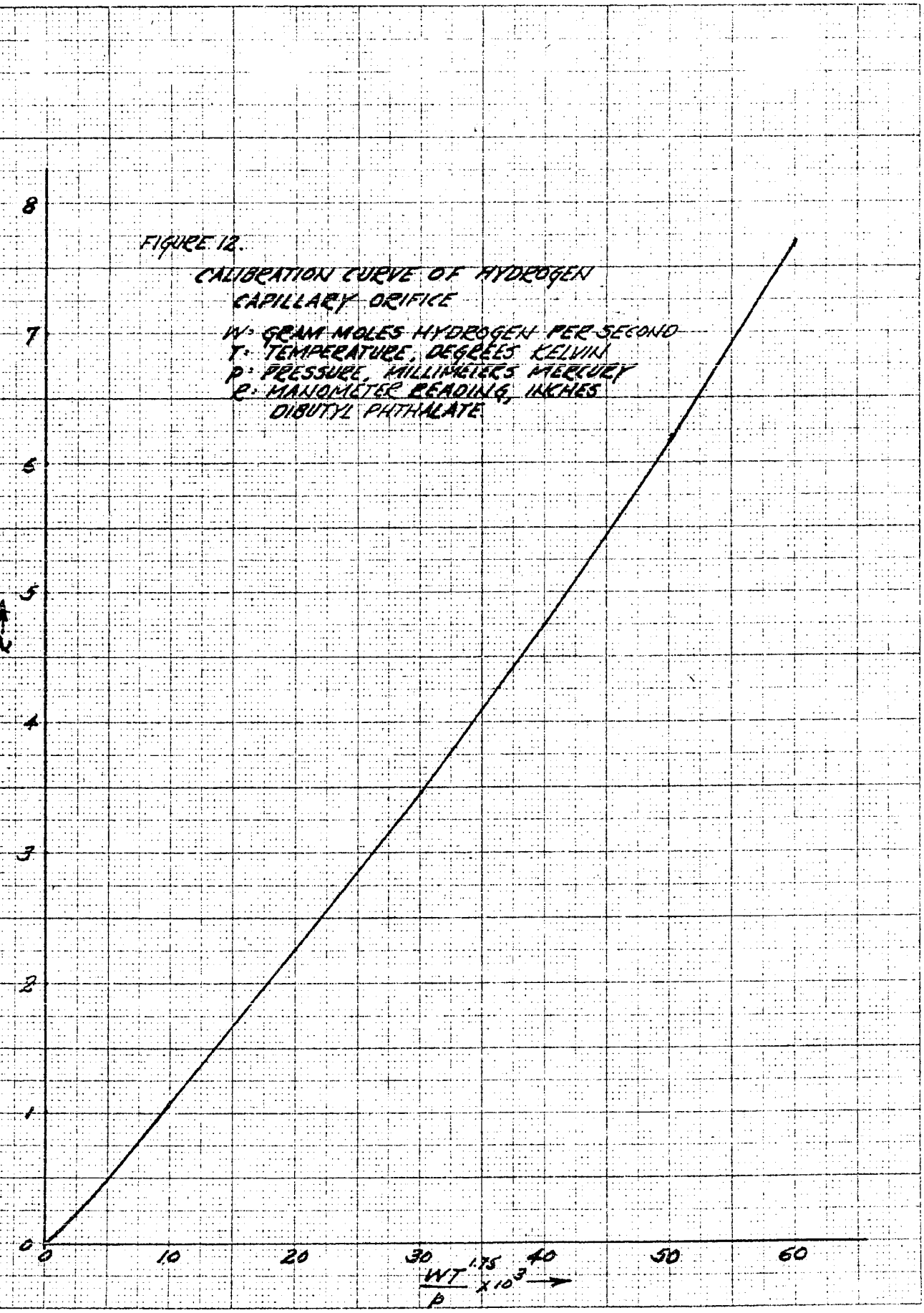
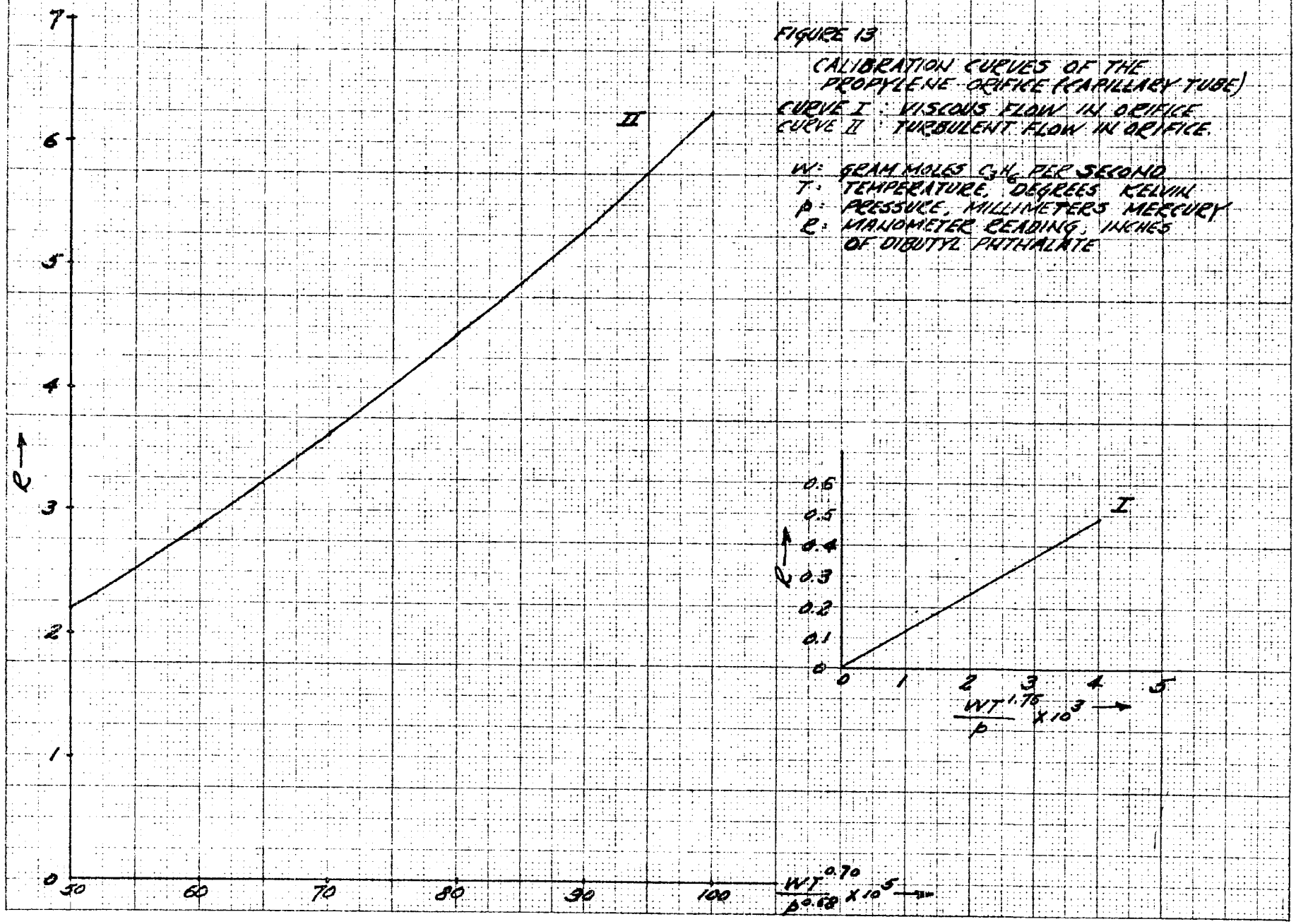


FIGURE 12.

CALIBRATION CURVE OF HYDROGEN CAPILLARY ORIFICE

W: GRAM MOLES HYDROGEN PER SECOND
T: TEMPERATURE, DEGREES KELVIN
P: PRESSURE, MILLIMETERS MERCURY
ℓ: MANOMETER READING, INCHES DIBUTYL PHTHALATE



(B) Sample Calculations

(1) Calculation of F (g moles feed/sec) and N_B

This calculation is for Run IIA2.

H_2 meters		C_3H_6 meters		π	$T^{\circ}K$ meters
p	R	p	R		
7.87	1.99	7.56	4.00	733	300

p_{H_2}	$T^{1.75}$	$\frac{WT^{1.75}}{p} \times 10^3$	W_{H_2}	$p_{C_3H_6}^{0.58}$	$T^{0.7}$	$\frac{WT^{0.7}}{p^{0.58}} \times 10^5$	$W_{C_3H_8} \times 10^4$	$F \times 10^4$
933	22000	17.7	7.50	52.5	54.1	75	7.27	14.77

$$y_{H_2} = \frac{7.50}{14.77} = 0.508$$

$F \times 10^4$	M	$G \times 10^4$	D_p	$\mu \times 10^6$	$\frac{D_pG}{\mu} = N_B$
14.77	21.6	738	0.0563	95.2	43.6

(2) Calculation of Feed and Product Stream Composition and the Conversion, dx

This calculation is also for Run IIA2. The symbols used are:

a = air
A = H_2
B = C_3H_6
C = C_3H_8
F = feed
p = pressure, cm. Hg.
P = product
y = mole fraction
N = total moles
d = density
x = conversion

The reaction is A + B ⟶ C.

$d_a = d_{air}$ @ $0^{\circ}C$ and 760mm. = 1.293 g/l

$d_B = d_{C_3H_6}$ @ $0^{\circ}C$ and 760mm. = 1.910 g/l

$d_C = d_{C_3H_8}$ @ $0^{\circ}C$ and 760mm. = 2.020 g/l

$d_A = d_{H_2}$ @ $0^{\circ}C$ and 760mm. = 0.0899 g/l

$d_a p_a = d_F p_F$

$d_a p_a = d_P p_P$

$(1.293)(21.34) = d_F(28.45)$; $d_F = 0.9699$ g/l

$(1.293)(21.34) = d_P(28.33)$; $d_P = 0.9740$ g/l

Composition of Feed

$$\begin{cases} d_B y_{BF} + d_A y_{AF} = d_F \\ y_{BF} + y_{AF} = 1 \end{cases}$$

$$\begin{cases} 1.910 y_{BF} + 0.0899 y_{AF} = 0.9699 \\ y_{BF} + y_{AF} = 1 \end{cases}$$

$y_{AF} = 0.5165$

$y_{BF} = 0.4835$

Composition of the Product

On the basis of one mole of feed:

$N_{BP} + N_{CP} = y_{BF}$

$N_{AP} + N_{CP} = y_{AF}$

$$\frac{N_{BP} + N_{CP}}{N_{AP} + N_{CP}} = \frac{y_{BF}}{y_{AF}}$$

$$\frac{\frac{N_{BP} + N_{CP}}{N_P}}{\frac{N_{AP} + N_{CP}}{N_P}} = \frac{y_{BP} + y_{CP}}{y_{AP} + y_{CP}} = \frac{y_{BF}}{y_{AF}}$$

then
$$\begin{cases} y_{AP} + y_{BP} + y_{CP} = 1 \\ 0.0899y_{AP} + 1.910y_{BP} + 2.020y_{CP} = d_P \\ \frac{y_{BP} + y_{CP}}{y_{AP} + y_{CP}} = \frac{y_{BF}}{y_{AF}} \end{cases}$$

$$\begin{cases} y_{AP} + y_{BP} + y_{CP} = 1 \\ 0.0899y_{AP} + 1.910y_{BP} + 2.020y_{CP} = 0.9740 \\ \frac{y_{BP} + y_{CP}}{y_{AP} + y_{CP}} = \frac{0.4835}{0.5165} \end{cases}$$

solving:

$$y_{AP} = 0.5145$$

$$y_{BP} = 0.4813$$

$$y_{CP} = 0.0042$$

let x = moles A in the feed reacting, then

$$\begin{cases} (y_{AF} - x) + (y_{BF} - x) + x = N_P \\ \frac{y_{AF} - x}{N_P} = y_{AP} \end{cases}$$

$$\begin{cases} (0.5165 - x) + (0.4835 - x) + x = N_P \\ \frac{0.5165 - x}{N_P} = 0.5145 \end{cases}$$

$$x = 0.0042 \quad \frac{\text{moles propane formed}}{\text{mole feed}}$$

$$Fdx = 14.77 \times 0.0042 \times 10^{-4} = \frac{620}{\cancel{608}} \times 10^{-8}$$

These calculations for each run are given in Table IX.

(3) Sample Calculation of the Data with the Equation

$$Fdx = Z_N p_H^2 \left(\frac{\mu}{\gamma}\right)_G \left(\frac{\mu}{\gamma D}\right)_f^{2/3}$$

This calculation is for $N_B = 40$ and $t = 55^{\circ}C$. From Table IV $Z_{40} = 51 \times 10^{-5}$.

p_H	p_H^2	$\left(\frac{\mu}{\gamma}\right)_G \left(\frac{\mu}{\gamma D}\right)_f^{2/3}$	$Fdx \times 10^8$ calculated	$Fdx \times 10^8$ experimental
0.28	0.0784	0.0238	95.2	118
0.40	0.1600	0.0296	242	250
0.50	0.2500	0.0365	465	458
0.55	0.3025	0.0409	631	630

$\left(\frac{\mu}{\gamma}\right)_G \left(\frac{\mu}{\gamma D}\right)_f^{2/3}$ is obtained from Figure 9.

Table IX Calculated Data

A = H_2; B = C_3H_6; C = C_3H_8; y = mole fraction; P = product; F = feed; d = density; dx = conversion.

run	sample	d_F	d_P	y_{AF}	y_{BF}	y_{AP}	y_{BP}	y_{CP}	dx	F x 10^4	Fdx x 10^8
IIA	1	.9943	.9972	.5031	.4969	.5017	.4953	.0030	.0030	14.00	420.0
IIA	2	.9699	.9740	.5165	.4835	.5145	.4813	.0042	.0042	14.77	620.3
IIA3	3	.9809	.9851	.5105	.4895	.5804	.4873	.0043	.0043	14.89	640.3
IIA	4	.9816	.9886	.5101	.4899	.5066	.4863	.0071	.0070	15.00	1050
IIA	5	.9915	.9986	.5047	.4953	.5011	.4917	.0072	.0072	15.00	1080
IIB	1	.9940	.9961	.5033	.4967	.5022	.4956	.0022	.0022	11.79	259.4
IIB	2	1.0012	1.0064	.4993	.5507	.4967	.4982	.0051	.0050	11.94	597.0
IID	1	.9983	.9997	.5009	.4991	.5002	.4984	.0014	.0014	12.40	173.6
IID	2	.9975	1.0005	.5014	.4986	.4999	.4971	.0030	.0030	12.65	397.5
IID	3	.9983	1.0041	.5009	.4991	.4980	.4963	.0057	.0056	12.63	707.3
IIE	1	1.0027	1.0050	.4985	.5015	.4973	.5004	.0023	.0023	13.07	300.6
IIE	2	.9928	.9970	.5039	.4961	.5019	.4941	.0040	.0039	13.72	535.1
IIE	3	.9981	1.0050	.5009	.4991	.4976	.4959	.0065	.0064	13.71	877.4
IIIA	2	.7169	.7239	.6555	.3445	.6522	.3353	.0095	.0094	17.0	1598
IIIA	3	.7426	.7505	.6419	.3586	.6377	.3519	.0104	.0103	16.9	1741
IIIA	4	.7426	.7555	.6414	.3586	.6353	.3478	.0169	.0167	16.9	2822
IIIA	5	.7169	.7294	.6555	.3445	.6497	.3333	.0170	.0168	17.8	2990
IIIB	1	.7032	.7080	.6631	.3369	.6608	.3324	.0068	.0067	14.45	968.2
IIIB	2	.7027	.7129	.6634	.3366	.6586	.3270	.0144	.0142	14.61	2075
IIIC	1	.7117	.7179	.6584	.3416	.6555	.3359	.0086	.0085	15.07	1281
IIIC	2	.7128	.7242	.6578	.3422	.6524	.3319	.0157	.0155	15.46	2396
IVA	1	1.3950	1.3950	.2830	.7170	.2830	.7170	.0000	.0000	7.97	0.0
IVA	2	1.3904	1.3904	.2855	.7145	.2855	.7145	.0000	.0000	8.13	0.0
IVA	3	1.3950	1.3961	.2830	.7170	.2824	.7167	.0009	.0009	8.18	73.62
IVB	1	1.3858	1.3870	.2880	.7120	.2874	.7117	.0009	.0009	9.86	88.74
IVB	2	1.3870	1.3893	.2874	.7126	.2861	.7121	.0018	.0018	10.00	180.0
IVB	3	1.3951	1.3998	.2829	.7171	.2805	.7161	.0034	.0034	10.04	341.4
IVC	1	1.3997	1.3997	.2804	.7196	.2804	.7196	.0000	.0000	9.07	0.0
IVC	2	1.4009	1.4021	.2797	.7203	.2791	.7201	.0008	.0008	9.22	73.76
IVC	3			.2817	.7183	.2798	.7176	.0026	.0026	9.34	242.8
IVC	4	1.3985	1.4009	.2810	.7190	.2798	.7185	.0017	.0017	8.78	149.3

(C) Details of the Experimental Procedure and Apparatus

(1) Loading the Catalyst Chamber

In order to obtain a constant temperature bed, the catalyst pellets (12 to 16 mesh) were mixed with tabular alumina pellets (28 to 32 mesh). In every run 0.315g. of catalyst and 1.369g. of tabular alumina were used. These two weighed quantities were vary carefully mixed together in a nitrogen atmosphere and dumped through a funnel through the empty preheater; they came to rest on a bed of tabular alumina (28 to 32 mesh) which filled the bottom part of the preheater-reactor unit. This operation was performed in precisely the same way in each run. With the catalyst bed in place, the preheater was filled with tabular alumina (28 to 30 mesh), the top of the reactor was put on, and the unit was ready for use. Nitrogen was forced up through the reactor-preheater before and during charging.

The catalyst storage hopper was a 35mm. pyrex tube blown on the bottom with a large stopcock of 1/8 inch bore. To this stopcock was blown a 10/30 standard taper male joint. The hopper was purged with nitrogen before and while the catalyst was charged to it and then was sealed off from the atmosphere. The catalyst was kept in this container during the entire experimental part of the thesis.

The catalyst weighing chamber was provided with two female standard taper joints (10/30). It was purged with nitrogen before and during the period when the catalyst was being charged to it.

Every precaution was taken to prevent the contact of water vapor or oxygen with the catalyst since either might alter its activity. Nitrogen was not adsorbed on the catalyst (this adsorption was measured for the author by the Davison Chemical Co.) and because it is a dry gas was used as an atmosphere in the storage, weighing and charging of the catalyst.

(2) Placing the Equipment in Operation; On Stream Operation

The purification units operated efficiently only when up to temperature; in order not to expose the catalyst to impure gases the reactor was bypassed by the initial gases flowing through the system. The initial flow rate of gases was kept low.

Since the conversions were very low at low temperatures, the water flowing in the jacket of the preheater-reactor unit was cooled to 10°C. When the preheater attained this temperature and the purification units came up to their operating temperatures (about 200°C.) the reactant gases were introduced in small quantity to the reactor. This procedure eliminated initial high heats of adsorption or reaction thus protecting the catalyst from sintering. Next, the reactant gases were slowly increased in quantity until the desired feed rate was achieved. The cooling water in the reactor jacket was then slowly heated from 10°C. to 45°C. Twenty minutes after this temperature was reached, feed and product samples were taken. In some cases duplicate samples were made. It was the rule in the early portions of the experimentation to take duplicate samples, later this proved unnecessary.

The reactor temperature was then raised to 55°C. and after analysis of the feed and product at that temperature, the temperature was raised to 65°C. It was the practice to wait twenty and sometimes thirty minutes after reaching a temperature before taking a sample.

(3) Sampling Procedure

As stated in the main body of the thesis in "Experimental Apparatus", the sampling devices permitted instantaneous and simultaneous sampling of feed and product streams without affecting the rate of flow through the catalyst bed for more than one or two seconds.

The construction of the sampling devices was as follows: In Figure 10, valves A, B, C, D, E, F, and O were three way pyrex stopcocks with a mm. bore. All other stopcocks in the entire apparatus except E were two way cocks with a 2mm. bore. Tubes F, G, H, I were 45mm. diameter pyrex of 11 inches length. Mercury reservoirs J and K were normally blocked from the system by means of stopcocks E and F.

The operation of the feed and product sampling devices was identical. Their operation is given in the following paragraph.

Let valves A, B, C, and D be open so that gas is flowing through F, G, H and I. Valves L, M and N and E are normally closed as are S, T, U and F. Turn valves A and C so that gas is flowing only through F and H. The gas in G and I is trapped and by turning valves D and B this trapped gas is isolated from the gas flowing through the system. The isolated gases in G and I

are the feed and product samples respectively.

In actual operation valves A and C and valves B and D were turned simultaneously.

The isolated gas in G was introduced to the gas density balance by means of a technique which completely avoided contamination of the sample by any method. Valves L, M, N and O were left in the closed position, three way valve O was turned so that when P was opened a vacuum was placed on the entire line up to valves L, M and N. An eight mm. vacuum was drawn on this line and then valve P was closed. Any leak in this sampling line was detected on manometer M_1. Because the stopcocks in this line were greased previously to each run, leaks very seldom occurred. Valve M was then opened slowly and the gas allowed to fill the sampling line. Stopcock P was then cracked and a small quantity of the feed sample was allowed to enter the gas density balance until the pressure in the balance raised from eight millimeters to 4 or 5 centimeters. Valve P was then closed and the balance evacuated to a pressure of 2 millimeters of mercury. Valve P was again cracked and the gas allowed to fill the balance so that its density could be measured. If the pressure of the gas in chamber G was insufficient to achieve balance, then valve E was opened and the mercury in reservoir J permitted to rise into G. The reservoir could be manually raised so that the mercury acted as a piston, increasing the pressure of the gas in the balance.

After the gases in G and I had been analyzed it was necessary to restore these chambers to the conditions existing in F

and H. This was done by opening valves L and S slowly, allowing some gas flowing in the main lines to enter these evacuated chambers and slowly force out the mercury pistons (if it was necessary to use them). Valves E and F were closed when the mercury fell below the level of valves B and D. Valves B and D were then turned so as to connect chambers F, G, H and I with the main stream at points B and D. Valves L, and S, M and T were then closed.

The next sample was taken by simultaneously turning cocks A and C and B and D so as to isolate chambers F and H from the system. The sampling procedure was then repeated.

(4) The Gas Density Balance

The gas density balance purchased was the Edwards model whose theory and construction is completely reported in the Technologic Paper of the Bureau of Standards, No. 89. The principle of the gas density balance is given in the following paragraph.

According to Boyle's law the density of a gas is proportional to its pressure; and the buoyant force exerted upon a body suspended in a gas is proportional to the density of the gas and therefore to its pressure. Therefore if the buoyant force exerted upon a body is made the same when suspended successively in two gases, then the densities of the two gases must be the same at these pressures.

Let d_a be the density of air at some standard pressure p_o and d_g the density, at the same pressure p_o, of the gas to be

tested. Also let p_a be the pressure at which the beam balances in air and p_g the pressure at which it balances in the gas.

Then the buoyant effect of the air displaced by the globe equals $kd_a\frac{p_a}{p_o}$ and the buoyant effect of the gas displaced equals $kd_g\frac{p_g}{p_o}$, k being a constant which depends on the difference in external volume of the balance globe and its counterweight. These buoyant effects are equal since the buoyant force must have been the same in the two cases to bring the beam to the same position. Therefore

$$kd_g\frac{p_g}{p_o} = kd_a\frac{p_a}{p_o}$$

and

$$\frac{d_g}{d_a} = \frac{p_a}{p_g}$$

The basic construction and operation of the balance are as follows. The gas density balance consists of a balance beam carrying a sealed globe (usually glass) on one end and a counterweight upon the other. The balance beam fulcrum consisted of two small pins with especially hardened tips which rested in an agate bearing. The bearing support and the beam were mounted in a gas tight chamber to which was attached a mercury manometer, a vacuum pump and inlet gas and air lines. In operation the balance case and manometer connections were evacuated to about a 7 or 8mm. vacuum and then a small amount of dry, CO_2 free air admitted so as to further clean the system. The case was then evacuated to a pressure of 2mm. and dry, CO_2 free air admitted until the beam was balanced about its rest point. Pressure p_a was then read from the manometer. The case was re-evacuated, purged with the gas to be

measured, evacuated again to 2mm. pressure and the gas measured admitted until the beam was balanced about its rest point. Pressure p_g was then read from the manometer.

Edwards did a considerable amount of work in determining the accuracy of his balance. With an ordinary open end manometer, stagnant water in the cooling jacket and metal needle valves for the admittance of gas, air and vacuum, densities measured in his apparatus were accurate to ± 0.0005. Using his balance the author verified this accuracy.

The main disadvantages of the Edwards balance are

(1) the needle valves are sticky in operation, and leak when worn,

(2) slight jars shift the position of the balance beam and change the pressure needed to balance,

(3) once the beam comes to balance there is no way of activating it to test its oscillations around the rest point,

(4) the temperature control with stagnant water in the jacket is poor,

(5) the open end manometer makes the pressure reading subject to changes in atmospheric pressure.

In order to improve these features the author retained the balance beam and its agate support but enclosed them in a 55mm. pyrex tube with a standard taper 55/60 joint on one end. Dr. R. H. Price, Assistant Professor of Chemistry, blew the case

and attached four 10/30 standard taper joints to it so that air, gas, vacuum and manometer lines could be connected. The balance support was fastened to the case by means of beeswax. The female 55/60 joint closing the case was ground and polished so that undistorted vision of the balance beam would be obtained. The entire case was placed in a water bath maintained at 25°C. The stirring action in the bath was gentle. The gas and vacuum lines were constructed of 1mm. capillary tubing and gases and vacuum were admitted to the balance by capillary stopcocks which were firmly mounted on a panel board separate from the main apparatus. These did not become sticky, leak, or in any way necessitate touching of the balance case as did the needle valves.

An absolute barometer was attached to the balance so that the effect of atmospheric pressure was eliminated.

In order to give the beam sufficient oscillation to enable an accurate balance about the rest point, the standard taper joint leading from the manometer into the balance was modified so as to contain a 3mm. pyrex glass tube whose end was just above the glass globe on one end of the balance beam. By inserting a dummy manometer into the system as shown in Figure 9, and attaching a squeeze bulb to its open end, it was possible by squeezing the bulb to force the mercury in the dummy manometer to push the gas in the manometer line causing it to blow with a gentle puff against the globe on the balance arm thus activating it.

These procedures proved exceedingly effective and the author quickly found that the accuracy of the measurement was limited by the accuracy with which the manometer could be read.

In many trials the density of a gas sample was found over and over to be accurate to ±0.0001 and in many cases no error was found. Theoretically the only limits imposed upon the method are those due to the deviation of gases from Boyle's law. In order to eliminate this source of error, the balance was adjusted so that the pressure needed to balance it was never greater than 280mm. At this pressure propylene, hydrogen and propane have negligible deviations from Boyle's law.

The standard gas used was air scrubbed free of CO_2 with NaOH and dessicated with $CaCl_2$. This gas was found to be of remarkably uniform density. Since the final use of the data was to determine the difference in density of feed and product streams, air was a completely satisfactory standard gas.

(D) Over-All Equilibrium Constant

Before the mechanism of this reaction was studied, thermodynamic calculations were made to determine the reversibility of the reaction within the experimental range of pressures and temperatures. The following calculations show that in the range of pressures and temperatures used K_a is so large that the reverse reaction is negligible.

component	$\Delta H_{formation}$ @ 18°C.	$\Delta F_{formation}$ @ 25°C.
C_3H_6	4.55 kg. cal/mole	14.80 kg. cal/mole
C_3H_8	-24.82 kg. cal/mole	-5.61 kg. cal/mole

$c_{pH_2} = 6.88 + 0.000066T$

$c_p\ C_3H_6 = 1.97 + 0.0504T$ } (T in °K)

$c_{pC_3H_8} = 0.41 + 0.0648T$

$\Delta H_{18°C} = -24.82 - 4.55 = -29{,}370$ cal/mole H_2 reacted

$\Delta F_{25°C} = -5.61 - 14.80 = -20{,}410$ cal/mole H_2 reacted

$\Delta c_p = 0.41 - 1.97 - 6.88 + (0.0648 - 0.0504 - 0.00006)T$

$\Delta c_p = -8.44 + 0.0144T$

$\Delta H = \int \Delta c_p dT$

$\Delta H = \int (-8.44 + 0.0144T) dT$

$\Delta H = -8.44T + 0.0072T^2 + H_o$

$-29{,}370 = -8.44(291) + 0.0072(291)^2 + H_o$

$H_o = -27{,}530$

$\therefore$ $\underline{\Delta H = -8.44T + 0.0072T^2 - 27{,}530}$ (T in °K)

$$\frac{d(\ln K_a)}{dT} = \frac{\Delta H}{RT^2}$$

$$R\int d(\ln K_a) = \int \frac{\Delta H dT}{T^2}$$

$$R\ln K_a = \int \left(-\frac{8.44}{T} + 0.0072 - \frac{27,530}{T^2} \right) dT$$

$$R\ln K_a = -8.44\ln T + 0.0072T + \frac{27,530}{T} + C$$

$$RT\ln K_a = -8.44T\ln T + 0.0072T^2 + 27,530 + CT$$

but $\Delta F = -RT\ln K_a$

$$\therefore \Delta F = 8.44T\ln T - 0.0072T^2 - 27,530 - CT$$

$$-20,410 = 8.44(298)(2.303)\log 298 - 0.0072(298)^2 - 27,530 - C(298)$$

$$C = 22.2$$

$$\therefore \Delta F = -RT\ln K_a = 8.44T\ln T - 0.0072T^2 - 27,530 - 22.2T \quad (T \text{ in } {}^{o}K)$$

$$\log K_a = -4.26\log T + 0.00158T + \frac{6,020}{T} + 4.86 \quad (T \text{ in } {}^{o}K)$$

@ $25^{o}C$ $K_a = 9.76 \times 10^{14}$

@ $100^{o}C$ $K_a = 4.16 \times 10^{10}$

(E) Descriptive Dimensional Analysis Applied to the Coefficient of Viscosity and the Coefficient of Diffusion

It is not the purpose of this Appendix to delve into the basis of descriptive dimensional analysis. This tool has been studied in detail by Professor R. S. Tour who has applied it to a wide variety of problems but has not made it available in the literature. The author used descriptive dimensional analysis to arrive at the relationship between viscosity, density and coefficient of diffusion in gases. In essence descriptive dimensional analysis is described in the following paragraph which is an abstracted portion of R. S. Tour's unpublished work.

The system of fundamental units into which any quantity is broken down must have physical significance either as a natural phenomenon or by definition for the problem at hand. Thus length divided by time, $\frac{L}{T}$, is average velocity and may appear only where motion is involved, otherwise it is meaningless. If instantaneous velocities are considered, the definition is $\frac{dL}{dT}$ and the length or time should not be separated from their differential operators if maximum information is desired from a dimensional analysis. The more restrictive the properties of the dimensions used, the more complete will be the analysis. Continuing with the idea of inherent properties of dimensions and the real significance of physical quantities, it is obvious that length squared or cubed is meaningless unless the lengths involved are specified in the proper directions; thus the concept of area

involves the product of two lengths at right angles, and volume implies the product of three orthogonally directed lines. The property of direction of a length in the definition of a physical quantity is an essential attribute and must not be neglected.

With these barest essentials one can apply descriptive dimensional analysis to the coefficient of viscosity and the coefficient of diffusion.

The Coefficient of Viscosity, μ

$$\mu = \frac{F}{\frac{S}{\frac{dV}{dy}}}$$

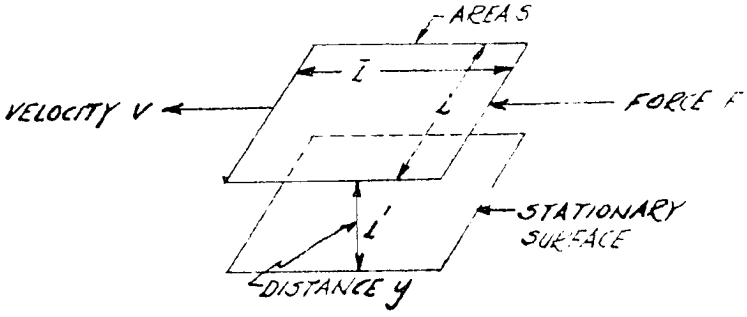


FIGURE 11. QUANTITIES INVOLVED IN THE COEFFICIENT OF VISCOSITY.

physical quantities		descriptive dimensions
F	::	$\frac{M d^2\bar{L}}{dT^2}$
S	::	$\bar{L}\bar{L}$
$\frac{dV}{dy}$	::	$\frac{d\left(\frac{d\bar{L}}{dT}\right)}{d\bar{L}'}$ :: $\frac{d^2\bar{L}}{dT d\bar{L}'}$

$$\mu :: \frac{\frac{M\bar{d^2L}}{dT^2}}{\frac{\bar{L}\bar{L}'}{\frac{\bar{d^2L}}{dTdL'}}} :: \frac{M\frac{dL'}{dT}}{\bar{L}\dot{\bar{L}}}$$

The ordinary dimensional analysis of viscosity ascribes to it the final dimensions of $\frac{M}{LT}$ which is physically meaningless due to the cancellation of differentials and lengths irrespective of direction. Including these properties leads to more information, viz., viscosity is not only a resistance to flow but is the momentum normal to the plates per unit of plate cross-section. For a gas where the molecular velocities $\frac{dL'}{dT}$ are fixed, the viscosity is the measure of the rate of transfer of mass between plates per unit cross-section through unit length. This interpretation will lead directly to $k :: c_p \mu$ where k is thermal conductivity of a gas and c_p its specific heat at constant pressure.

The Coefficient of Diffusion, D

The above application of descriptive dimensional analysis is the work of R. S. Tour. The author has extended the application of this principle to the coefficient of diffusion in the following manner:

$$dm = -DS\frac{dc}{dy}dt$$

where dm = quantity of solute that crosses a boundary of cross-sectional area S in the time dt when the concentration gradient is $\frac{dc}{dy}$, the distance y being measured in the direction of diffusion

D = coefficient of diffusion

physical quantities		descriptive dimensions
dm	::	dM
S	::	$\dot{\bar{L}}L$
dt	::	dT
dc	::	$\frac{dM}{\dot{\bar{L}}LL'}$
dy	::	dL'
D	::	$\frac{dM}{(LL)dT \quad \frac{dM}{\dot{\bar{L}}LL'}}{dL'}$ :: $\dot{\bar{L}}LL' \frac{dL'}{\frac{dT}{\dot{\bar{L}}L}}$

but density = ρ = $\frac{M}{\dot{\bar{L}}LL'}$

so ρD :: $\frac{M}{\dot{\bar{L}}LL'} \cdot \dot{\bar{L}}LL' \frac{dL'}{\frac{dT}{\dot{\bar{L}}L}}$

therefore ρD :: μ

Thus for gases ρD is the measure of the rate of transfer of mass between plates per unit cross-section through unit length. This relationship is of great importance since it defines the rate at which mass may be transferred through a gas. In any actual gas the rate of mass transfer will be somewhat less than this quantity and $\frac{\mu_{actual}}{\rho D}$ gives the fraction of the theoretical rate of mass transfer that is actually attained. This is the physical significance of the Schmidt number as applied to gases.

The same type interpretation applies to the Prandtl number.

(F) Calculation of $\left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}$ and D_p and D

(1) Calculation of $\left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}$

Tables X and XI summarize the calculation of $\left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}$

Table X $\left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}$ at 55°C.

y_H	y_H	$\rho_g \times 10^3$	$\mu_g = \mu_f \times 10^6$	$D_g = D_f$	$\rho_f \times 10^3$	$\left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}$
0.25	0.125	1.211	95.2	0.438	1.401	0.0227
0.40	0.20	0.984	95.2	0.438	1.285	0.0296
0.55	0.275	0.756	95.2	0.438	1.174	0.0409
0.70	0.35	0.531	95.4	0.438	1.060	0.0626

Table XI $\left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}$ at 45°C.

y_H	y_H	$\rho_g \times 10^3$	$\mu_g = \mu_f \times 10^6$	$D_g = D_f$	$\rho_f \times 10^3$	$\left(\frac{\mu}{\rho}\right)_g \left(\frac{\mu}{\rho D}\right)_f^{2/3}$
0.25	0.125	1.248	92.1	0.416	1.444	0.02115
0.40	0.20	1.010	92.1	0.416	1.325	0.0278
0.55	0.275	0.799	92.1	0.416	1.206	0.0382
0.70	0.35	0.547	92.5	0.416	1.088	0.0585

(2) Calculation of D

Curtiss and Hirschfelder [15] have developed equations based on a statistical treatment for predicting diffusion coefficients of a few non polar gases. They further develop equations showing that the coefficient of diffusion of one gas in another is independent of the composition of the binary mixture. Their methods are extremely complex and are not applicable to the gases used in this study. Thus Gilliland's equation was used to predict the diffusion coefficient.

$$D_{ij} = 0.0043 \frac{T^{3/2}}{\pi (v_i^{1/3} + v_j^{1/3})^2} \sqrt{\frac{1}{M_i} + \frac{1}{M_j}}$$

D_{ij} = diffusion coefficient of i in j, cm^2/sec

$T = {}^{o}K$

M = molecular weight

v = molecular volumes obtained from tables

π = total pressure, atmospheres

$v_{H_2} = 14.3 \quad M_{H_2} = 2$

$v_{C_3H_6} = 66.6 \quad M_{C_3H_6} = 42$

$v_{C_3H_8} = 74.0 \quad M_{C_3H_8} = 44$

$$D_{H_2,C_3H_6} = T^{3/2} \frac{0.0043}{\left[(14.3)^{1/3} + (66.6)^{1/3}\right]^2} \sqrt{\frac{1}{2} + \frac{1}{42}}$$

$$= 7.44 \times 10^{-5} T^{3/2}$$

In like manner

$$D_{H_2,C_3H_8} = 7.11 \times 10^{-5} T^{3/2}$$

(3) Calculation of D_p

The catalyst bed was a mixture of particles of different sizes and the formula recommended by Brown[16] was used to calculate average pellet diameter. The catalyst bed consisted of

1.369g. of 0.0213" Al_2O_3 (28-32 mesh, Tyler Screen)

0.315g. of 0.047" catalyst (12-16 mesh, Tyler Screen)

$$D_p = \sqrt{\frac{\sum \frac{M_i}{D_i}}{\sum \frac{M_i}{D_i^3}}} = \sqrt{\frac{\frac{1.369}{0.0213 \times 2.54} + \frac{0.315}{0.047 \times 2.54}}{\frac{1.369}{(0.0213 \times 2.54)^3} + \frac{0.315}{(0.047 \times 2.54)^3}}} = 0.0563 cm.$$

(G) Properties of Hydrogen, Propylene, Propane and Air

The densities (@ 760mm., 0°C.) of H_2, C_3H_6, C_3H_8 and CO_2 free, dry air are as follows:

$d_{air} = 1.293 g/l$	Technologic Paper No. 89, Bureau of Standards
$d_{H_2} = 0.0899 g/l$	Lange's Handbook of Chemistry
$d_{C_3H_6} = 1.910 g/l$	International Critical Tables
$d_{C_3H_8} = 2.020 g/l$	International Critical Tables

The density and viscosity of hydrogen and propylene mixtures are given in Figures 14 and 15.

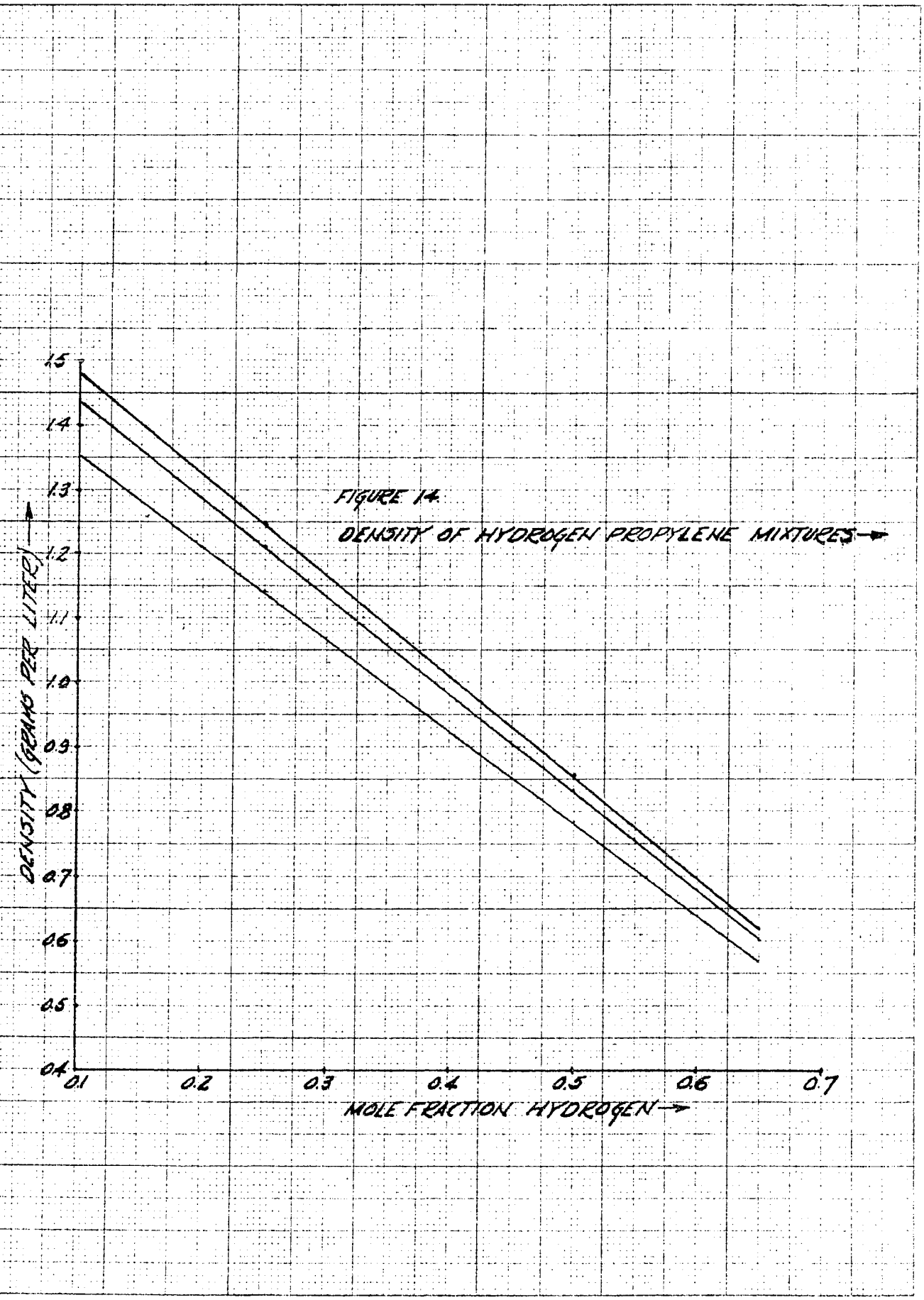


FIGURE 14.
DENSITY OF HYDROGEN PROPYLENE MIXTURES

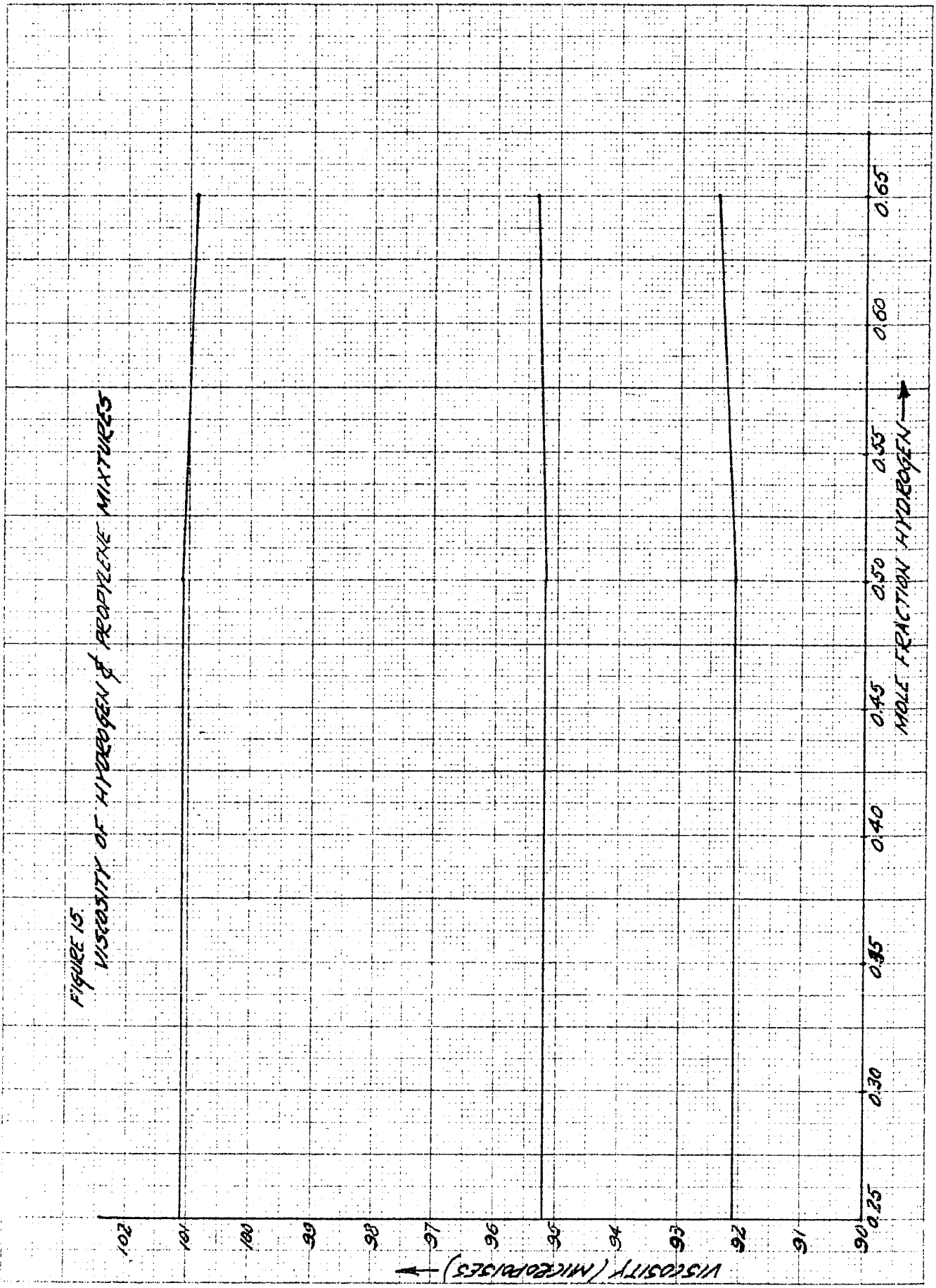


FIGURE 15.
VISCOSITY OF HYDROGEN & PROPYLENE MIXTURES

(H) Pictures of Equipment

In this section several pictures of the experimental apparatus are given:

Figure 16: Feed Sampling Device

Figure 17: Preheater-Reactor Unit

Figure 18: Purification Units

Figure 19: Gas Density Balance

Figure 20: Experimental Apparatus

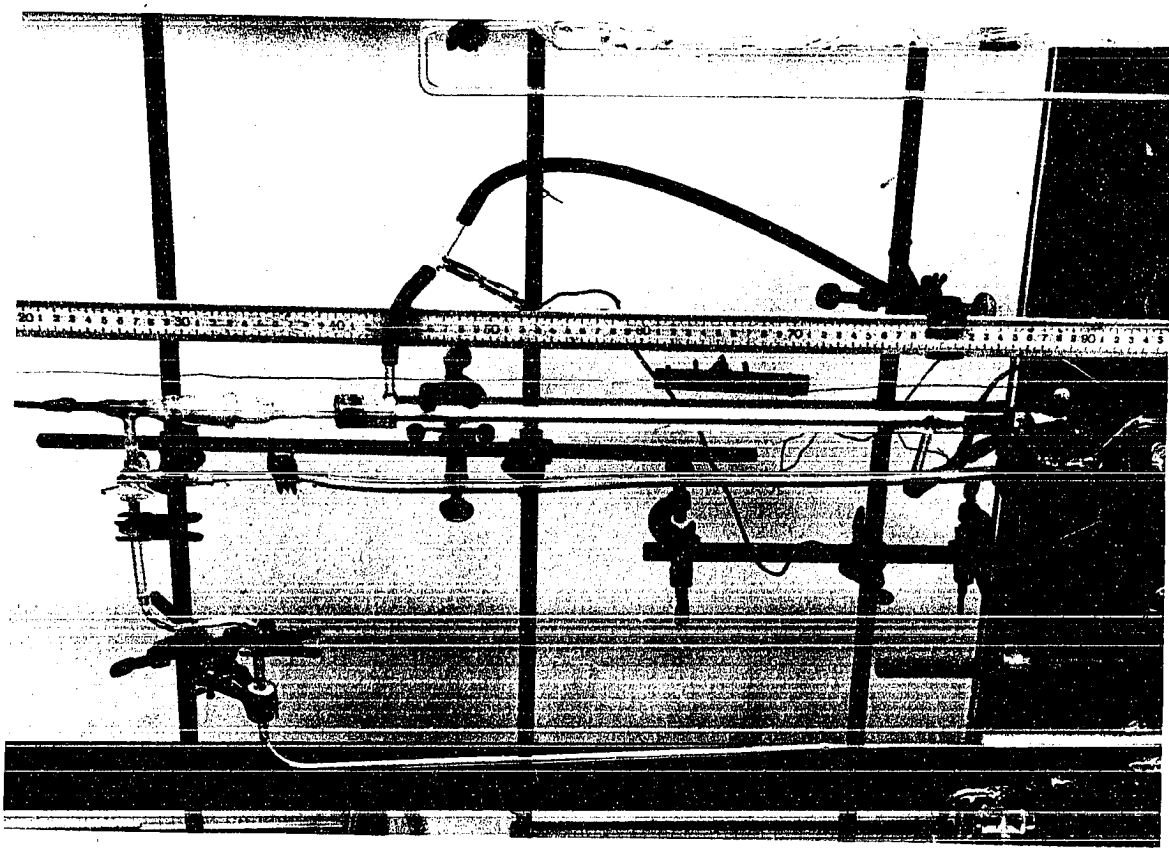


FIGURE 17

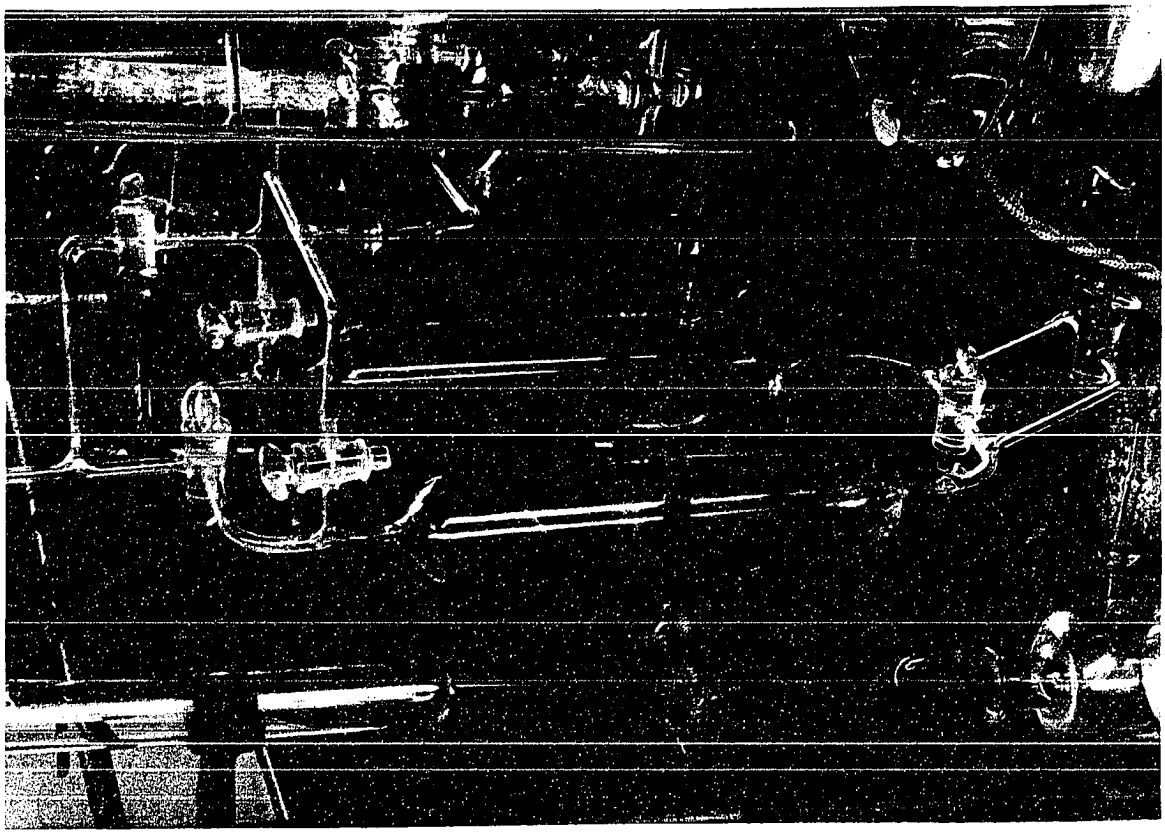


FIGURE 16

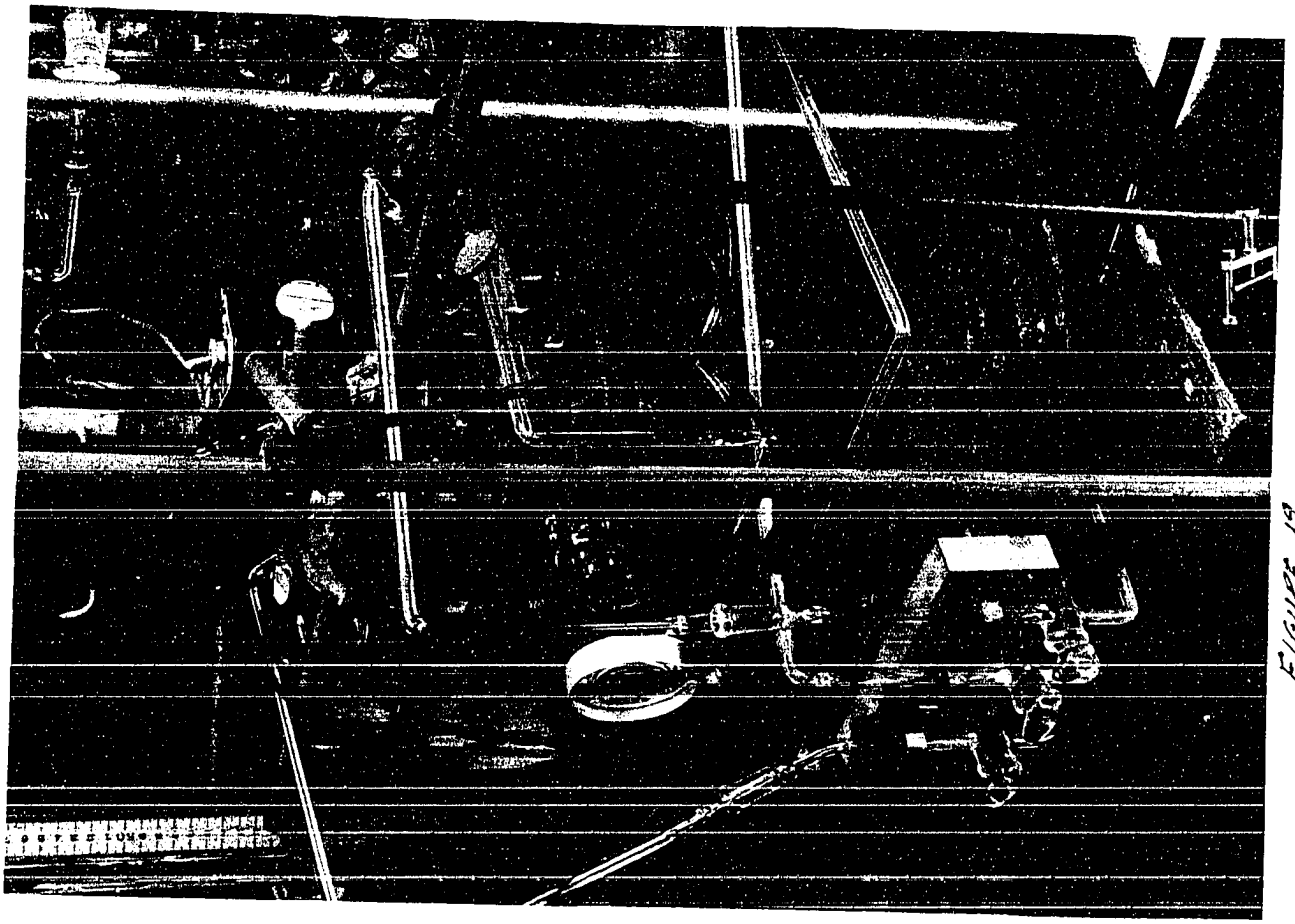


FIGURE 19

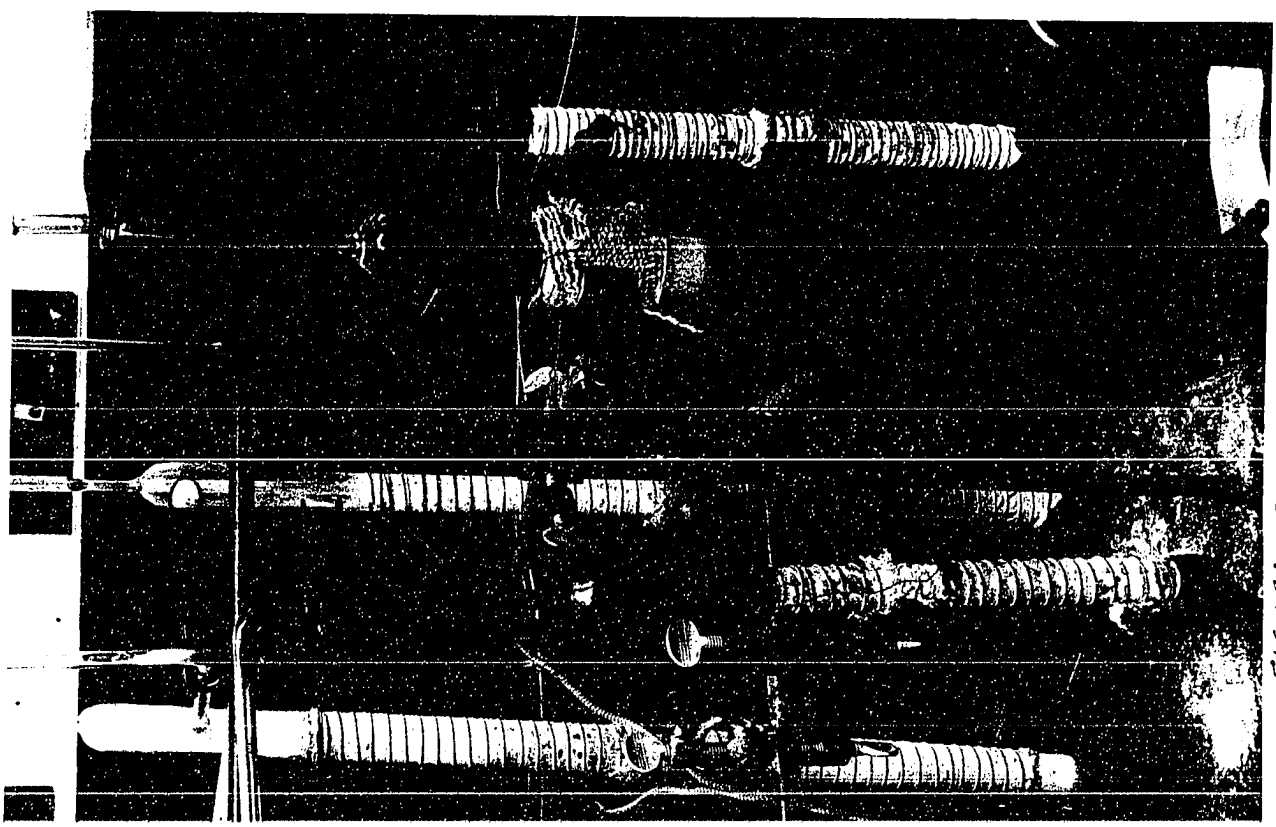


FIGURE 18

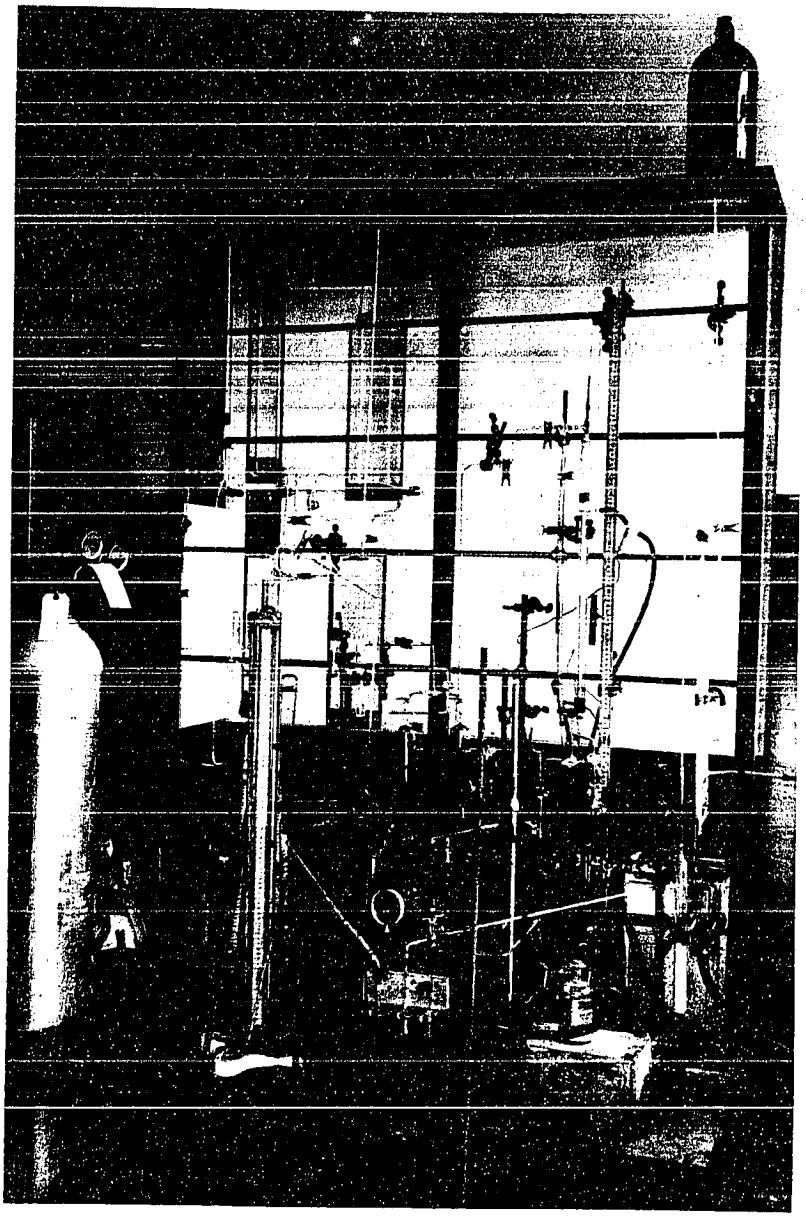


FIGURE 20