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A KINETIC STUDY OF THE CATALYTIC LIQUID PHASE HYDROGENATION OF CYCLOHEXENE

A dissertation submitted to the

Graduate School of Arts and Sciences

of the University of Cincinnati

in partial fulfillment of the

requirements for the degree of

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ABSTRACT

A study was made of the kinetics of the liquid phase hydrogenation of cyclohexene in the presence of a platinum catalyst in a stirred semi-flow system. The effects of catalyst concentration, hydrogen flow rate, reactor pressure, stirring rate, agitator and reactor design upon the observed rate of reaction were evaluated experimentally, and are qualitatively explained by the hydrodynamics of the stirred system.

It is shown that the reaction rate is independent of the cyclohexene concentration, and in the major portion of the work is controlled by the mass transfer of hydrogen to the catalyst surface. Duo control is achieved at the limits of obtainable stirring rates, indicating chemical control might be reached with proper operating conditions. The criterion that reaction rate be independent of the stirring rate for chemical control is found to be a necessary, but not sufficient condition.

The semi-flow system is compared to the autoclave type reactor, and shown to present greater mixing efficiencies. It is questioned that mass transfer effects can be eliminated in the latter equipment under normal operation.

Areas requiring further study for the formulation of fundamental theory with engineering utility are discussed.

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TABLE OF SYMBOLS

A	surface area
A	frequency factor in Arrhenius equation
a	numerical constant
B	path of diffusion, film thickness
b	numerical constant
C	numerical constant
c	solution concentration
c_i	concentration at solid-liquid interface
D	diffusion coefficient
E	apparent energy of activation
j	mass transfer rate per unit area
k	specific velocity constant
l	characteristic length
N	molecules diffusing per unit area per unit time
N	stirred speed
ν	kinematic viscosity
p	pressure
R	gas constant
Re	Reynolds number, dimensionless group
r	process rate
Sc	Schmidt number, dimensionless group
Sh	Sherwood number, dimensionless group
T	absolute temperature
t	time
θ	concentration on catalyst surface

U	characteristic velocity
u	velocity component on x axis
V	volume of solution
v	velocity component on y axis
w	velocity component on z axis
x	axis coordinate
y	axis coordinate
z	axis coordinate

Subscripts

A, B	molecular species
C	cyclohexene
c	chemical control
d	duo control
f	final value
H	hydrogen
i	solid-liquid interface
l	active site
o	initial value
t	mass transfer control
1	initial state
2	final state

INTRODUCTION

The economic advantage of the continuous process and its introduction into a rapidly expanding chemical industry, has necessitated an entirely new approach to an old and classical subject, chemical kinetics. In order to intelligently design reactors, the engineer must have tools available with which to relate and predict the effect of all variables in a flow system which are likely to be encountered in the industrial process. The concept of mass transfer, virtually unrecognized by the chemist, has become a major factor to the engineer in dealing with heterogeneous systems.

Most of the emphasis in this new field of applied kinetics has been placed on vapor phase catalytic reactions, because of their great utility to continuous processes. Since the formulation of the first correlation for such kinetic data a little over ten years ago, numerous vapor phase studies have been made and reported in the literature. And yet the fundamental concepts of such reactions are just being exposed at the present time.

This concentration of study on vapor phase reactions has somewhat limited the extension of applied kinetics to other types of heterogeneous systems. The literature is almost completely barren of engineering investigations of

reactions between two liquids, or a liquid and a gas, over a solid catalyst, yet such systems are being used industrially. The fundamental kinetic considerations of such heterogeneous systems should be of equal importance, and perhaps of greater challenge, to the engineer in the field of applied kinetics.

The purpose of this work was to study and evaluate the variables affecting the kinetics of such a reaction, the hydrogenation of cyclohexene in the presence of a platinum catalyst. A semi-flow system was employed, whereby the reactant gas was bubbled through a solution of the cyclohexene in cyclohexane, and the catalyst suspended in the solution by mechanical agitation. This type of process represents a compromise between the old batch autoclave type reactor used for kinetic studies by the chemist in the laboratory for many years, and a completely continuous flow system which up to the present time has received meager attention, even in academic studies.

Due to the pioneering nature of the work, and the complexities involved, it was not intended that the investigation should be overly specific on any one phase of the problem. It is hoped that the work will be the foundation for future study of the problem, by indicating those areas warranting more fundamental investigation from the viewpoint of applied chemical kinetics.

THE KINETIC THEORY OF HETEROGENEOUS REACTIONS IN SOLUTION

The present state of the theory regarding the kinetics of heterogeneous reactions in solution is very unsatisfactory. It is somewhat comparable to the theory for gaseous reactions prevailing fifteen years ago. Although they had been known for many years, only the recent concentration of study on vapor phase catalytic reactions in this interval has revealed new fundamental concepts for engineering utility.

While heterogeneous reactions in solution have also been the object of investigation by chemists for decades, no real attempt has been made to develop useful tools for the engineer in the design of industrial processes. Thus the investigator in the field of applied solution kinetics has yet to cross the barrier, where most of his effort is not of a probing and empirical nature. The present author has found no report in the literature of a kinetic study concerned with a semi-flow system such as is of interest in this work.

It is true that the complexities of liquids and solutions themselves, being less understood, have to some degree retarded the work in this field. However, certain analogies do exist between gaseous and liquid systems. With

the fundamentals of gaseous reactions now being better defined, the exploration of solution kinetics becomes a logical extension of this knowledge.

In any heterogeneous system, the role of the catalyst is to reduce the positive free energy change accompanying the formation of activated reactants, thereby increasing their concentration. The reactant molecules are provided with a path of less resistance between themselves and the product molecules than that which must be followed when the catalyst is not present. The theory of absolute reaction rates (6) permits prediction of this path of least resistance by the potential energy surface of the system.

When a chemical reaction occurs in a heterogeneous system, there are superimposed onto specific chemical effects certain interfacial factors which operate at the boundary of the phases, and which influence the observed rate of reaction. The steps required for a reactant in the main fluid phase to be converted catalytically to a product in the main fluid stream have been often enumerated:

1. Transfer of reactants from the bulk of the fluid phase to the catalyst-fluid interface
2. Adsorption of reactants on the catalyst surface
3. Reaction between the adsorbed reactants, or between adsorbed reactants and other reactants in the fluid phase

4. Desorption of products from the catalyst surface

5. Transfer of products from the catalyst-fluid interface to the bulk of the fluid phase

Of these steps, 2 and 4 are generally characterized by interaction between catalyst and reactant, and along with step 3 are classified as chemical processes, although the adsorption may be of so-called physical nature.

For the particular type of system studied in this work in which one of the reactants is a gas, an additional step preceding all of the above is required. If the catalyst is wetted with the solution containing the liquid reactant, the gas must dissolve in the solution before it can reach the catalyst interface. For this case then, the solution of the gas is the initial step in the overall process.

Under steady state conditions, the slowest step will determine the rate of all the steps, as well as that of the overall reaction. Van Name and Hill (26) were the first to propose a classification of heterogeneous reactions on the basis of the rate determining step:

I Mass Transfer Control - the rate of chemical processes at the interface are much faster than the rate of mass transfer of the reactants or products.

II Chemical Control - the rates of mass transfer of the reactants and products are much faster than the chemical processes at the interface, or on the catalyst surface.

III Duo Control - both the rates of mass transfer and the chemical processes are of the same order of magnitude, and the observed rate of reaction is some function of the two.

As would be expected, the distinction between the possible types of systems is not sharp, and heterogeneous reactions show a graduation between the limiting cases of chemical and mass transfer control. The third class is probably the general case. Many investigators have tried to construct suitable criteria for diagnosing reaction types (13)(30).

Mass Transfer Control

The recognition that the observed rate of reaction in a heterogeneous system may be determined by the rate of mass transfer of either the reactants or products is one of the major contributions to the field of kinetics. There seems to be some doubt at the present time if this effect is ever entirely eliminated in gaseous systems flowing through granular catalyst beds (12). In liquid systems where diffusion is much slower and relative velocities generally much lower, it is probable that mass transfer control can be eliminated only under very extreme conditions. The rates of reactions observed in batch rocking-type autoclaves must be questioned on this basis, and in many cases the reported temperature dependence of the rate clearly indicates the effect of mass transfer.

The theory of diffusion in liquids is not so well developed as for gases, principally because much less is

known of the structure of liquids themselves. The closer packing of molecules in the condensed state increases the importance of molecular attraction, and the present equations of state for liquids are limited in their application. There are few reliable experimental values of diffusion coefficients in liquids, and the available equations for their computation are difficult to use.

Since diffusion is a rate process, the net rate of diffusion of a material through a liquid at a point may be expressed in the familiar terms of a driving force and conductance. According to Fick's Law:

$$N = -D \frac{\partial c}{\partial B} \qquad (1)$$

where N = number of molecules diffusion per unit area per unit time

D = diffusion coefficient, area per unit time

c = concentration, mols per unit volume

B = path of diffusion.

In applying the rate expression to the case of a reactant diffusion to the interface of a solid catalyst, the relationship between D and c must be known if it is to be integrated. Such a relationship is not generally known, and since it has been reported that D varies little with c (7), it must suffice to assume that they are independent.

Attempts to provide a rigorous integration based upon analogy with gaseous diffusion have resulted in expressions of such complexity that they cannot be evaluated (22).

The number of molecules diffusion per unit time in a unit volume will be a measure of the decrease of their concentration in the bulk of the solution. Hence, the integrated form of equation 1 may be written as:

$$-\frac{dc}{dt} = \frac{D\ A\ (c - c_i)}{V\qquad B} \qquad (2)$$

where c_i = concentration of material at the solid liquid interface, mols per unit volume

V = volume of solution

This is the general form for any diffusion process.

A further simplication may be made for the case where the adsorption onto the catalyst at the interface is very rapid, and c_i may be considered essentially zero. Then

$$-\frac{dc}{dt} = k_t \frac{A\ c}{V} \qquad (3)$$

The "constant" k_t is composed of D and B, and is of fundamental importance in kinetic studies. The first order nature of diffusion processes has been generally recognized.

Previous kinetic studies of heterogeneous liquid systems have been confined primarily to solid-liquid reactions consisting of a solid in contact with a dilute solution. The existing theory of heterogeneous reactions in solution

was developed by Nernst (19) based upon an analogy of the dissolution of solids in liquids. He postulated that if the chemical reaction is rapid at the surface of the solid, equilibrium is established almost instantaneously at the interface between phases. He pictured the reactant molecules reaching the surface by diffusion through a thin layer of stationary solution, of thickness B, adhering to the solid surface. Nernst assumed the concentration gradient varied linearly across this film, and arrived at equation 2. This classical theory has been tested by many investigators to test its validity and found to be generally applicable, although it has also been severely criticized (20)(28).

The "film" concept has been explored in great detail for heterogeneous gaseous systems, and it should be even more applicable to solid-liquid interfaces. However, Nernst's concept of a stationary film is erroneous, for fluid motion has been shown to persist up to points very close to such an interface (20). Studies in the dynamics of fluid flow have shown that such a layer is more correctly defined as the normal distance from the surface to the point where the normal velocity component of turbulence (convection) is equal to the velocity of diffusion. This distance then is the true value of B in equation 2, and may be thousands of molecules thick, a fact untenable to the stationary layer concept (17). The gaseous films enveloping granular catalyst in flow

reactors have been shown to be in motion, although under viscous conditions while the main body of the fluid is in turbulence.

The normal velocity components generally increase exponentially with the normal distance, and the concentration in the "apparent" film B would increase likewise. The above definition of the film thickness implies that it is dependent on the diffusion coefficient (and thus viscosity), although this is not indicated in equation 2. However, the complexities in determining either D or B are so great that generally they are treated as a unit in the form of k_t.

A rigorous quantitative treatment of mass transfer in liquid phase requires solution of the relationship:

$$\frac{\partial c}{\partial t} = D\left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right] - u\left[\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} + w\frac{\partial c}{\partial z}\right] \quad (4)$$

where for a given point in solution, the velocity components parallel to the x, y, and z axes are u, v, and w respectively, and $\partial c/\partial t$ the rate of change of concentration at that point due to both diffusion and convection. In general, a solution has been possible only for those cases where the equations of fluid motion can be reduced to a simple form, and the relationship has been solved for only several systems. Levich (16) solved it for a flat disc of very large area rotating in an infinite volume of liquid in viscous flow.

His solution when applied with simplifications to a system of finite size reduced essentially to equation 2.

Dimensional analysis, used successfully for vapor phase catalytic reactions, has been applied by Agar (1) to mass transfer in forced convection in solution. It was found by the usual procedures of the method that:

$$Sh = C\ Re^a\ Sc^b \qquad (5)$$

where Sh is the Sherwood number ($j \cdot l/D \cdot \Delta c$), Re the Reynolds number ($U\ l/\nu$), Sc the Schmidt number (ν/D), and C, a, and b constants. The physical significance of these dimensionless groups has been given for other mass transfer processes (12)(4).

While this development is of academic interest in comparison with similar relationships for heat transfer, it is of little utility at the present time for stirred systems. The characteristic velocity appearing in the Reynolds number is not clearly defined in such systems, but it must be in the nature of a "relative" velocity, i.e. motion of the solution relative to that of the solid. In systems where the catalyst is suspended by stirring, the relative motion is only partially related to the actual speed of the stirrer, and depends on other factors such as the size and shape of the containing vessel, shape of the paddle, and similar effective boundry surfaces. While these factors may all be

grouped together as a stirring "efficiency", there is evidence in this work that the interrelationship between them and the stirring speed is not consistant over a range of stirring speeds.

In view of this evidence, the characteristic length appearing in the dimensionless groups is also in question for even a given physical system. For equation 5 to apply to other physical systems, further dimensionless groups defining characteristic lengths must be included, and at present these are only speculative.

One of the most easily recognizable properties of a mass transfer controlled system is the great effect of stirring rates, or relative fluid motion, on the observed rate of reaction. Hixson and his co-workers have made detailed studies of the characteristics of stirred systems (8). Generally the reaction velocity constant k_t has been found for heterogeneous reactions to be a function of agitator speed:

$$k_t = aN^b \qquad (6)$$

where N is the characteristic stirrer speed (RPM) and a and b are constants. When the reaction taking place is mass transfer controlled, the value of b is approximately 1, since according to the Nernst theory, the "effective" film thickness would be generally dependent on the relative motion of

the solution and solid. For reactions controlled by the rate of the surface reaction, the value of b is usually taken as 0, although the present work disputes this criterion. For cases of duo control, intermediate values of b are found.

Another criterion of mass transfer controlled reactions is their low apparent energies of activation, generally 3 to 6 kcal. per mol. It must be observed, however, that chemical reactions having apparent activation energies of this order or less are known.

Chemical Control

The control of the observed reaction rate by the chemical processes previously enumerated is of great interest in applied kinetic studies, since it is only under this condition that the true mechanism of the reaction may be determined. When the chemical steps determine the overall rate, the condition exists where the concentration of reactants is uniform throughout the fluid body, adsorption layers being considered negligible. In a catalytic process, the reactant molecules migrate to the surface of the catalyst much faster than they can be utilized, and there is no "effective" diffusion film.

Taylor's well known theory of active centers or areas due to the inhomogeneity of catalyst surface (23) is still very controversial, although the present evidence seems to indicate general acceptance of the concept. Only a portion

of the catalyst surface is regarded as being effective in lowering the activation energy of the reaction. The exact nature of such sites is inconsequential in most kinetic studies, so long as the catalyst employed is effective.

The rate of reactions controlled by the chemical processes may be described by the law of mass action as:

$$r = k\, f(c_A)\, f(c_B) \ldots\ldots f(c_1) \qquad (7)$$

where r is the observed rate, c_A, c_B, ...the bulk concentrations of the reactants, c_1 the number of available active areas, and k a constant. The number of active sites, their geometric arrangement, their relative individual ability to catalyze the reaction, and other such factors can at present only be arbitrarily assumed, and $f(c_1)$ is generally combined with k, which then becomes the observed reaction velocity constant, k_c.

The nature of f(c) may be determined by any of the chemical steps in the process, i.e. adsorption of reactants desorption of products, or the chemical reaction itself. The specific form of the function may vary with each reactant or product. The simplest case is that where the observed rate is determined by the molecularity of the chemical reaction. Thus, for the reaction

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

The rate of reaction would be written as:

$$r = k_c \quad c_A^a \, c_B^b \ldots\ldots \qquad (8)$$

the exponents a, b, ... being the stoichiometric proportions. In the general case, the order of the reaction is complicated by one of the adsorption steps, by competitive adsorption of the reactants, etc. The reaction may occur between two adjacently adsorbed molecules of the reactant, an adsorbed molecule and one at the interface from the bulk of the solution, or various combinations of these possibilities.

Hougen and Watson (10) have pioneered in applied kinetics and developed generalized kinetic equations which permit the determination of the mechanism for chemically controlled reactions. They have considered uni- and bi-molecular reactions, both with and without reverse reaction. Relationships have been developed for control of the chemical process by the surface reaction, adsorption of the reactants, and desorption of the products. These equations have been applied only to vapor phase kinetic studies and have been very successful. They are much too cumbersome to summarize here, although it is thought that with some modification the relationships may eventually be applied to reactions in solution controlled by the chemical processes (2). Wynkoop and Wilhem have proposed an alternate approach to the determination of the reaction mechanism, but it has been found too complicated mathematically for utility even in gaseous systems (29).

Laidler and Socquet (15) have used the Langmuir isotherm in developing expressions for the rate of catalyzed reactions controlled by the adsorption step for the case (a) non-competitive adsorption of reactant molecules on neighboring active sites, (b) competitive adsorption of reactant molecules, and (c) competitive adsorption in which one substrate is the solvent. By analyzing the relationships mathematically, the effect of catalyst and reactant concentrations may be predicted for each case. These expressions have been applied to only very limited experimental data.

While the procedure has yet to be definitely developed for heterogeneous reactions in solution controlled by the chemical processes, the mechanism of such reactions may be determined by the proper choice and accumulation of experimental data taken under the proper conditions. In many cases, a stepwise elimination process of the possible modes leads to the physical mechanism.

As for mass transfer control, the effect of stirring rate, or relative fluid velocity, has been taken as a criterion, for the rate of chemically controlled reactions should be independent of a change in this factor. Chemically controlled reactions also generally have high apparent activation energies (above 8 kcal. per mol), although this is not always reliable.

Duo Control

Reactions where both the mass transfer and chemical processes affect the observed rate of reaction are probably the general case, yet the most difficult to analyze. Unfortunately, they have received very little study. The condition exists where the concentration of solute at the interface is neither the same as that in the bulk of the solution, nor equal to the equilibrium concentration. The only reported work on duo controlled reactions is for gas-solid systems, such as the combustion of carbon spheres (25).

A procedure for deriving an expression for the rate of reaction when both types of control are effective has been proposed by Bircumshaw and Riddiford (4). It is one of essentially obtaining the rate expressions for each case of "pure" control, and equating them. It may be illustrated by considering the simplest case of a unimolecular reaction:

$$A \rightleftharpoons R$$

For the mass transfer steps, the rate is expressed according to equation 2:

$$-\frac{dc_A}{dt} = k_t \frac{A(c_A - c_{A_i})}{V} \qquad (9)$$

and for the surface reaction according to equation 8:

$$-\frac{dc_A}{dt} = \frac{k_c\ A\ c_{A_i}}{V} \qquad (10)$$

At steady state conditions, the two rates must be equal:

$$k_c\ c_{A_i} = k_t\ (c_A - c_{A_i}) \qquad (11)$$

and

$$c_{A_i} = \frac{k_c\ c_A}{(k_t + k_c)} \qquad (12)$$

Substituting this into equation 9, the overall rate expression becomes:

$$-\frac{dc_A}{dt} = \left[\frac{k_c\ k_t}{k_t + k_c}\right] \frac{A}{V}\ c_A = k_d \frac{A}{V}\ c_A \qquad (13)$$

where k_d is the observed reaction velocity constant. Obviously if $k_t > k_c$, the rate will be determined solely by the chemical processes, and if $k_c > k_t$, the opposite will be true.

The observed temperature dependence of k_d and the apparent activation energy for duo controlled reactions will also be a composite of that found for the cases of pure control. Expressing the temperature dependence of k_d, k_t, and k_c in the form of the Arrhenius equation, it may be shown that:

$$E_d = \left[\frac{k_c/k_t}{1 + k_c/k_t}\right] E_t + \left[\frac{1}{1 + k_c/k_t}\right] E_c \qquad (14)$$

and in general, the variation of E_d with a shift in control is governed by the variation of the ratio k_c/k_t. It is the usual case that $E_c > E_t$; at low temperatures the observed rate will be chemically controlled, whereas at high temperature the observed rate will be mass transfer controlled.

This procedure becomes more complex when the chemical reaction at the interface is of higher order, and the equations derived are extremely cumbersome. However, this type of treatment for duo controlled reactions would seem to have some merit.

While the above discussion is somewhat lengthy, it presents only a limited survey of the previous work, which is pertinent only in a qualitative manner to the type of kinetic study under investigation here. The concepts undoubtedly have a degree of bearing upon the studied system, but they have not as yet been formulated into any concrete structure so as to be useful to the engineer. Nor is it thought that such theory is possible at the present time. This work is intended to furnish some of the experimental basis for development of concepts more pertinent and more fundamental to the viewpoint of applied kinetics.

EXPERIMENTAL APPARATUS

A schematic diagram of the apparatus used in this work is presented in Figure 1, while a photograph of the actual operating unit is shown in Figure 18 (Appendix). It was a semi-flow system in which the reactant gas was purified, dried, metered, and passed into a batch reactor containing the reactant liquid and suspended catalyst. The apparatus was constructed entirely of Pyrex glass, 8 mm. tubing being used for all flow lines, and 12/5 ball-socket joints for all connections. The stopcocks were of 4 mm. bore.

Reactor

A three-neck 1000 ml. Morton flask was used as a reactor for the majority of the experimental work. This flask is a regular round bottom flask in which four equally spaced perpendicular indentations have been made, and a small section of the bottom curved concavely inward. It was used because of its demonstrated ability to aid the mixing efficiency of the stirrer paddle (18). As is noted in a later section, a round bottom flask was also employed as a reactor, but only in an isolated portion of the study. Both flasks are pictured in Figure 15 (Appendix).

The center neck of the reactor flask was a S 45/50 joint. Through an adapter, a metal pressure gland with a 29/42 ground joint, purchased from the Ace Glass Co., was

fitted to the reaction flask, and through it passed the stirrer rod. Asbestos cord impregnated with graphite, Garlock No. 117, was used as a packing material for the gland.

Both side necks of the Morton flask were S 29/42 ground joints. One was used for delivery of the hydrogen and withdrawal of the sample. This neck was fitted with a ground joint in which were sealed three tubes. Onto the tube extending into the flask used for hydrogen delivery was sealed a sintered glass disc 20 mm. in length, which dispersed the hydrogen in the reacting solution. The sample withdrawal tube was open in the flask but a 1 mm. bore stopcock attached to it outside the flask prevented escape of the gas or solution during a run. The third tube was used as a thermocouple well. All three tubes extended to the bottom of the flask, and were always in the same fixed position.

The other side neck of the reactor was used as the exit passage for the excess hydrogen. To it was connected an Allihn condenser, through which was continuously circulated ice water. Immediately following the condenser was a manometer tap, for measuring the pressure in the reactor.

A minimum amount of Dow-Corning High Vacuum Silicone Grease was used on all ground joints connecting the reaction flask to the system. In addition, constant spring tension

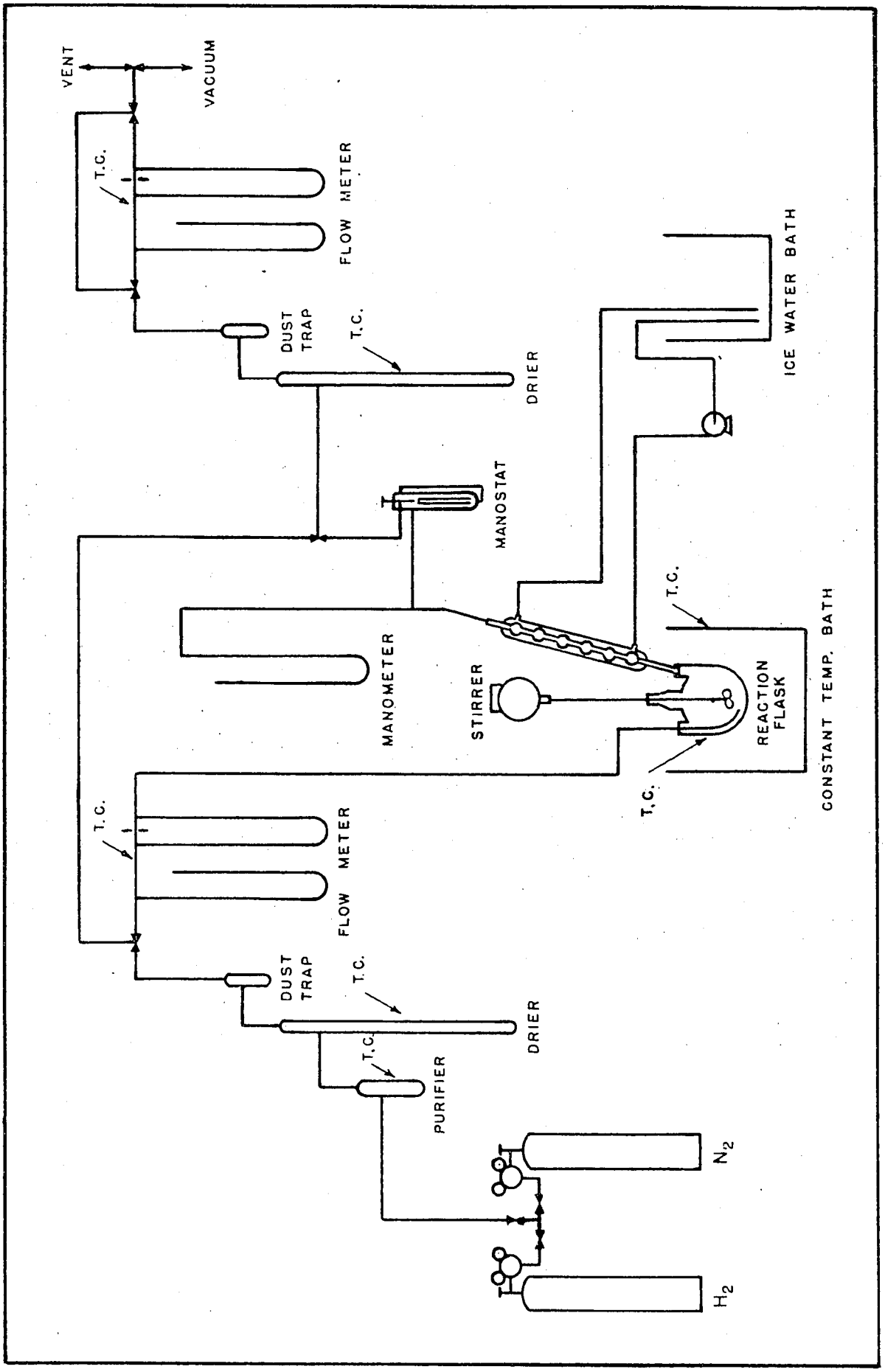


FIGURE I LAYOUT OF EXPERIMENTAL APPARATUS

was applied on all flask connections to insure pressure or vacuum seals.

The entire reaction flask was almost totally immersed in a constant temperature bath maintained at the desired temperature, with only the center and side necks protruding. Thus the level of the reacting solution was always considerably below that of the water level in the bath. The bath temperature was controlled by a mercury regulator through a 1000 watt blade heater, and a cooling coil through which ice water was circulated. The bath elements were so connected by a mercury switch that their action did not conflict with each other, i.e. when the heater was in operation, no water was circulated through the cooling coil, and vice versa. The bath was stirred by an air actuated stirrer. Figure 17 (Appendix) pictures the reaction flask and the constant temperature bath.

Tests on the constant temperature bath indicated the desired temperature was maintained to $\pm$ 0.1°C. Despite this control and the comparative volumes of the bath and reacting solution, a temperature rise in the reactor was noted during most runs due to the exothermic nature of the reaction. The magnitude of this rise was constant for a given run, and depended generally upon the rate of reaction observed. Attempts to reduce the temperature rise in the reactor by increasing the mixing velocities in the bath failed; since no variation in the temperature of the bath

could be detected, the air stirrer was used for the bulk of the work.

The stirrer was turned by an adjustable speed 115 volt Bodine motor, with an electrical governor. Shaft speeds of the motor were variable from 1500 to 7500 RPM, with two gear reduction shafts of ratios 3 to 1 and 18 to 1. The governor action was able to maintain constant speed under variable load conditions as found on this equipment. The stainless steel stirrer shaft extended through the packing gland and was equipped with a threaded chuck, which held the glass stirrer paddles, which are shown in Figure 16 (Appendix).

Purification Units

Experience had shown that bottled hydrogen contained some trace of both oxygen and water vapor. Because of the adverse effects of these impurities on the catalytic effect of platinum, it was necessary to remove them before metering and feeding the gas to the reactor.

Oxygen was removed by passing the hydrogen from the tank through a bed of copper shot maintained at 150°C. This purifier was fabricated from 20 mm. Pyrex tubing, and a thermocouple sealed into the unit gave continuous indication of the temperature of the bed. Nichrome resistance wire was wrapped around the outside of the unit to provide the heating effect. The copper oxide formed was reacted with hydrogen to form water, and regenerate the copper.

The water vapor from both the hydrogen tank and the purifier was removed from the gas stream by passing it through a bed of 8-10 mesh activated alumina. To remove any desiccant dust from the gas stream and prevent abrasive action on the flow meters, the hydrogen was then passed through a glass wool filter before metering.

An alumina drying unit and filter were also placed in the exit lines from the reactor before the exit meters. These units were primarily intended to remove solvent vapor from the gas which may have escaped through the condenser.

The driers were constructed from 15 mm. tubing and wrapped with nichrome resistance wire. The alumina beds were regenerated in place at a temperature of 200-225°C while passing a stream of nitrogen through them, the nitrogen first passing through the purifier. A by-pass was placed in the system permitting exclusion of the reaction flask from the flow system during the process.

Very little water was observed during the regeneration of the entrance desiccant bed, except for the initial use of a new tank of hydrogen. The exit desiccant bed picked up somewhat more solvent, but it was generally not necessary to regenerate the beds after each run. Regeneration was made after about every third run, depending primarily on the flow rates employed at the time.

Flowmeters

The hydrogen flow rate was measured with capillary orifices (27). The orifices were 0.75 mm. in diameter and about 12 cm. in length. The pressure drop across the orifices was measured using dibutyl phthalate as a manometer fluid. The pressures and temperatures immediately preceding the orifices were measured respectively with a mercury manometer, and thermocouples sealed into the delivery lines.

A capillary orifice was placed in the flow system both at the entrance and exit of the reaction flask. The entrance meter was of principle use for determining the flow, while the exit meter was used primarily for a check device to insure an excess of reactant gas was flowing to the reactor at all times.

The orifice meters were calibrated in place with a wet test meter, and both orifices followed the same calibration. The wet test meter itself was calibrated by the water weight displacement method, and found to be accurate within 1%. The calibration curve for the flowmeters is given in Figure 10 (Appendix).

Pressure Regulation

Since it was desirous that all experimental runs be made at constant pressure, a Cartesian Manostat #7, purchased from the Emil Greiner Co., was installed in the flow system following the reactor condenser. This model was constructed of Pyrex glass and was provided with pressure clamps.

Operating on the principle of the Cartesian diver, the manostat was found to give excellent control of pressures below that of the atmosphere. In such cases, the system was maintained in vacuum by a mechanical vacuum pump attached to the exit vent. No variation in reactor pressure was observed during a run.

For operation at pressures above atmospheric, less successful control was obtained with the manostat, although the reactor pressure never varied more than 1%. For runs at atmospheric pressure the manostat was not used, the gas flow by-passing the control diver although flowing through the unit.

Stirrer Speed Measurement

The measurement of stirrer speed was accomplished by the use of a "Strobotac", Type 631-BL, a commercial stroboscope manufactured by the General Radio Company. This instrument has two scales, 600 to 3600 RPM and 2400 to 14400 RPM, and has provision for adjusting the internal oscillator frequency in terms of the AC line frequency in order to compensate for differences in the calibration. When properly standardized for the power line frequency, the Strobotac has a rated accuracy of $\pm$ 1% for the range in which it was used in this work.

To measure the stirrer speed, measurements were taken regularly during the run on the stirrer shaft at a

point immediately above the pressure gland.

Analytical Procedure

The rate of reaction for a given run was determined by withdrawing small samples (5 ml.) from the reactor at measured time intervals, and analyzing the samples for their concentration of cyclohexene. The sample withdrawn were representative of the solution in the reactor, including the suspended catalyst, but were of sufficiently small volume so as to not disturb the mixing efficiency. Since the suspended catalyst in solution was withdrawn along with the sample, the catalyst concentration in the reactor was not altered.

Upon withdrawing a sample, the catalyst was immediately removed by filtering, and the cyclohexene concentration determined by the bromination of the double bond, and subsequent titration with thiosulfate. Greater detail of the analytical procedure is presented in the appendix. A typical concentration-time curve is shown in Figure 2.

MATERIALS

Hydrogen

Bottled electrolytic hydrogen was purchased from the Air Reduction Company. The gas was oil-pumped. The rated purity of the hydrogen was 99.7% and the guaranteed purity 99.5% with oxygen as the only known impurity.

Nitrogen

Bottled water-pumped nitrogen was also purchased from the Air Reduction Company. The rated purity was 99.7% with a guaranteed purity of 99.5%. Oxygen, argon, and krypton were the known impurities.

Cyclohexene

Cyclohexene used as the reactant liquid was purchased in one-kilogram quantities from Distillation Products Industries, with a boiling point range of 82.5 - 83.5°C. The principle impurity in this material was an alcohol, which was removed by refluxing the cyclohexene for 10-12 hours over a 3% sodium amalgam. The resultant product was filtered and distilled in a 10 mm. x 50 cm. packed column. The constant boiling fraction collected had a head temperature of 82.0°C at 744 mm. mercury pressure. Infrared analysis of the material indicated the presence of no hydroxyl or carbonyl groups.

As is discussed in a later section, the cyclohexene so purified could not be stored, due to autoxidation, but was distilled fresh before usage.

Cyclohexane

Practical grade cyclohexane, purchased from Matheson Coleman-Bell, was used as solvent. This material contained considerable amounts of unsaturables, which were removed by dispersing concentrated sulfuric acid for 24 hours in the cyclohexane. The acid phase was then separated and discarded, while the solvent phase was washed and then dried over calcium chloride. It was then distilled with a 10 mm. x 70 cm. packed column, the fraction with a head temperature of 79.6°C at 744 mm. mercury pressure collected. This product showed no trace of unsaturable material.

Cyclohexane used in the reaction was recovered by this same treatment, redistilled, and re-used.

Catalyst

The catalyst used was a 5% deposit of platinum on powdered activated-alumina carrier which was less than 300 mesh. The catalyst was prepared by Baker and Co. of Newark, N. J., and supplied for this work by Schenley Distillers, Inc.

Before use the catalyst was dried for at least 48 hours in an oven maintained at a temperature of 120°C. The dried material was stored in a closed weighing bottle which in turn was kept in a dessicator.

The catalyst was recovered after each experimental run by filtration from the reaction solution. This material was washed with distilled cyclohexane and c.p. acetone, and re-dried. No change in catalyst activity with this treatment was observed.

INTERPRETATION OF EXPERIMENTAL RESULTS

The major portion of this work consisted of experimental determination of the effect on the observed rate of reaction of those variables thought to be important in the semi-flow system. While the studies of earlier investigators previously described gave some qualitative knowledge of these factors, the direction of the study was not clearly defined, and the work was governed by the results of preceding runs. The apparatus was designed to be as flexible as possible, in order to cover a range of each variable, although, of course, laboratory equipment has definite limitations.

The hydrogenation of cyclohexene was choosen for study because it is representative of the types of reactions that might be carried out under semi-flow conditions, and because of its utility to this type of work. The reaction was easily conducted at normal temperatures and pressures, presented no possibility for side reactions, and has an equilibrium constant such that the reverse reaction can be considered negligible. The analytical procedures required were also of an elementary nature.

The work was divided into "series" of runs, each series being intended to study a single variable. The experimental data taken are presented in their entirety in the Appendix.

The series are recorded in the chronological order in which they were made, while the individual runs in each series are generally arranged according to an increasing magnitude in the variable under consideration.

The units chosen for expressing the observed rate were somewhat arbitrary. Since the rate was actually determined from analysis of cyclohexene in the reaction solution expressed in normality, the units of mols per liter per second are employed throughout this work to represent the observed rate. However, it must be remembered that only about half a liter of solution was actually used, and that the weight of catalyst specified for each run refers to this volume.

At the beginning of the experimental work it was deemed advisable to purify a sufficient quantity of cyclohexene to supply the entire study, to eliminate any variation in its purity. This material was stored in a dark bottle, but under the normal atmosphere. As is discussed in detail in the Appendix, this procedure partially defeated its purpose due to the autoxidation of the cyclohexene. The data taken with this material (Series 000 to Series 600) are labeled as "stored cyclohexene".

The failure to anticipate and recognize this important factor was in part due to the author's own lack of advanced training in organic chemistry, although no specific reference

to it had been made by other investigators who used the material for kinetic studies. The products of the autoxidation do have a marked effect on the observed rate of reaction. While it is most unfortunate that this factor was not recognized until considerable data had been taken, it is not thought to completely invalidate the data for the purpose of this work.

As later discussion will indicate, the observed rate of reaction was greatly dependent upon the hydrodynamics of the stirred system, which in turn is determined by the physical arrangement of the reaction flask, stirrer paddle, gas dispersion tube, etc. Thus, it is primarily the qualitative aspects of the variables and their implications that are of importance in this work, since reproduction of specific values of the data would only be possible by close duplication of the apparatus. For this reason, only the more pertinent data were retaken using freshly distilled cyclohexene, and only these data have been treated quantitatively.

The following discussion will consider each of the variables in turn, as they were found to affect the observed rate of reaction.

Effect of Cyclohexene Concentration

It has been previously indicated that the rate of

reaction for a run was determined by measuring the cyclohexene concentration in the solution at given time intervals. A typical plot of such data is shown in Figure 2. Since the relationship of cyclohexene concentration with time was found to be linear, the observed rate could be determined directly from the slope of such a plot.

The straight line relationship represents the steady-state portion of the run, i.e. a constant rate of reaction. Since the solution was saturated with hydrogen before beginning the run, no initial period wherein the rate gradually built up to the steady-state value was observed, as has been mentioned by some investigators (14). In some cases, a falling rate period at the end of the run at very low cyclohexene concentrations was found, as might be expected as subsequent discussion will show. Several runs were made using higher initial concentrations of cyclohexene, but no deviations from the linearity were observed.

Aside from facilitating the determination of the steady-state rate, the linear relationship between cyclohexene concentration and time has fundamental implications in determining the control of the observed rate. The rate of reaction during a run remained constant, while the cyclohexene concentration continuously decreased. For this to be true, the observed rate must have been independent of the cyclohexene concentration in the bulk of the solution, or according to

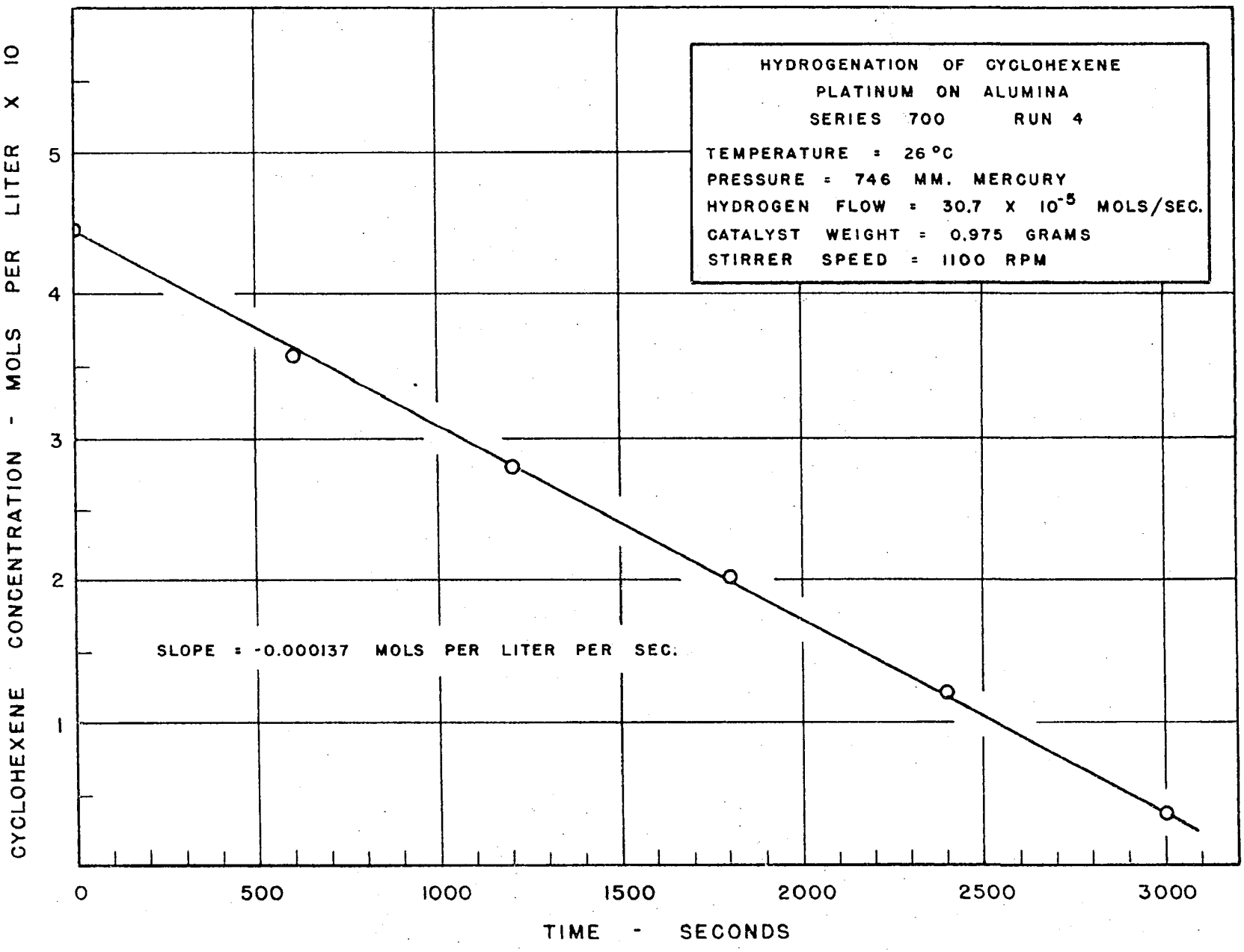


FIGURE 2 TYPICAL CONCENTRATION - TIME RELATIONSHIP FOR EXPERIMENTAL RUNS

classical kinetics, is "zero order" with respect to this factor. This has been found to be the case for many hydrogenation reactions (24).

Indications are then, that under the experimental conditions of this work, the observed rate was not controlled by the diffusion of cyclohexene, since such a rate would be affected by the bulk concentration. For this same reason the rate of adsorption of this reactant cannot be considered the controlling step. The rate of desorption of the product is an unknown factor, although the fact that the product is a saturated compound, and the same as the solvent, would seem to render this step unimportant.

The independence of the observed rate from cyclohexene concentration has been attributed by some workers to the "strong" adsorption of the reactant on the catalyst surface. That is, the concentration of cyclohexene on the catalyst surface remains essentially constant, independent of the bulk concentration, and the surface is always "satisfied" with respect to the hydrogen acceptor. Consider the Langmuir type adsorption isotherm:

$$\theta_C = \frac{b\ a\ c_C}{1 + a\ c_C} \qquad (15)$$

where θ_C is the surface concentration of the adsorbed material, c_C the concentration in the bulk of the solution

and a and b constants dependent only on temperature. If a is very large so that ac_C is not significantly different from $(1 + ac_C)$ even at low values of c_C, θ_C will appear to be a constant independent of c_C.

Subsequent discussion will show that the rates of reaction observed in this work were controlled by the mass transfer of the hydrogen. Under these conditions, the data cannot verify that the cyclohexene is strongly adsorbed, or that the reaction even takes place between adsorbed cyclohexene and hydrogen. It is possible that the reaction could be between adsorbed hydrogen molecules and cyclohexene in the bulk of the solution at the interface. So long as the mass transfer of hydrogen controls the observed rate, the rate will appear independent of the cyclohexene concentration. If this independence were observed when the chemical steps controlled the reaction, then the "strong" adsorption assumption would appear to be true. Indications of the present data are that this is probably the case.

Effect of Catalyst Concentration

Previous studies of hydrogenation reactions have generally indicated that the increase in observed reaction rate was linear with addition of catalyst in a constant volume of solution. This effect, however, was usually studied over a very limited range of catalyst concentrations.

Figure 3 shows the results of the investigation of this factor in the present work.

It will be observed that the rate increases rather rapidly with increased amounts of catalyst, and that the relationship is linear for only a very small range. The observed rate approaches a limiting value within a fairly small change in catalyst concentration.

Visual observation of the reaction flask during this series of runs leads to the conclusion that for a given stirrer speed, the mixing effects have a definite limit in their ability to hold the catalyst in suspension. At the very low catalyst concentrations, it was found that all the solid was suspended in the swirling solution, and that the mixture appeared to be completely homogeneous. With additional amounts of catalyst, it was quite evident that some of the solid was deposited on the bottom of the flask, and at the higher concentrations, on the sides of the flask.

It is concluded therefore, that the limiting value of the observed rate was due to the inability of the stirrer to hold more than a limited amount of the catalyst in suspension. The "settled" material did not seem to be a stagnant quantity, but rather in a kind of "dynamic" equilibrium. Some of the solid on the bottom of the flask was continuously being swept into the fluid, while other catalyst was constantly being deposited, and a fairly constant inventory maintained.

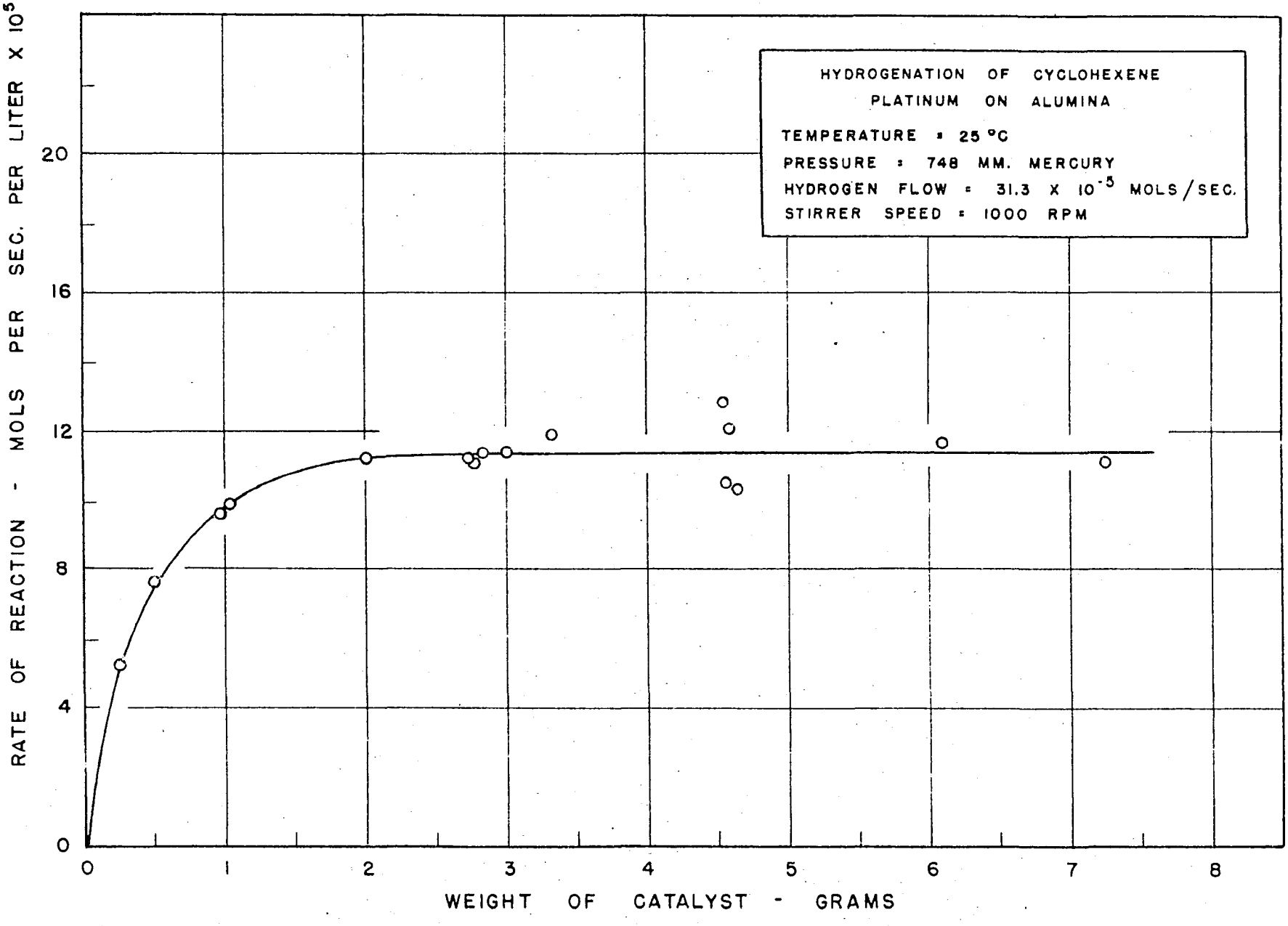


FIGURE 3 EFFECT OF CATALYST WEIGHT ON RATE OF REACTION

If the limiting effect of catalyst concentration is due to the restricted ability of the stirrer to suspend all the solid, then it must follow that only the catalyst in suspension was effective in determining the observed rate. Undoubtedly this is true generally, for the catalytic effect of solid several layers deep surrounded by a comparatively stagnant envelope of solution would seem to be negligible. However, some question must be raised concerning the top layer of catalyst settled on the bottom of the flask. It would seem the relative velocity of the solution to this material would be greater than that to suspended catalyst which itself was in motion. This top layer of catalyst then would have less effective "film" surrounding it, and it should be more active for the reaction.

Such a phenomenon is a complex problem in hydrodynamics, but perhaps may be partially explained by the observed fact that the catalyst was never completely stationary in the settled layer, thus reducing the magnitude of this factor. While this question of the effectiveness of catalyst on the bottom and sides of the flask requires further study, the overall effectiveness would seem to depend upon that held in suspension.

Although the data on Figure 3 are rather scattered because this was one of the earlier series made before all operating difficulties had been eliminated, it is not thought

that a maximum in the curve is indicated. Such a maximum has been postulated by some investigators (15), who contend that it is possible to present so much surface that the reactants will be widely separated on it, and the chance of reaction reduced. Such a postulate assumes that the reaction is between adsorbed molecules of both reactants. A simple calculation employing an estimated adsorption area of the cyclohexene and the total catalyst surface can be made to determine the amount of reactant required to completely cover the surface. Such a computation is presented in another section of this thesis for a compound of comparable structure, and it is indicated that the amount of cyclohexene used in this work was sufficient to cover the surface many times. Further, if the reactants were too widely separated on the surface, the observed rate of a single run should decrease as the reaction proceded, an effect which was not observed.

Effect of Flow Rate

One of the primary purposes for using a semi-flow system in this work was to maintain the concentration of the gaseous reactant constant in the reaction solution, thereby essentially reducing the number of variables for a given run. From an engineering viewpoint, a flowing system also would seem to

be an efficient method for contacting the two phases. The effect of the hydrogen flow rate on the observed rate of reaction, as shown in Figure 4, may be due to two factors, namely, the effect of the bubbling gas on the stirring efficiency, and the effect of contact surface on the steady state value of the gas concentration. Unfortunately, these two effects cannot be separated in the present work.

The effect of the flow rate on the stirring efficiency is easily pictured. When no gas is flowing, the solution in the flask will be in motion with probably some degree of a regular pattern. With the gas flowing, the stream of bubbles disrupts this pattern of motion, and the turbulence is increased. At lower flow rates, some of the bubbles are carried along in the solution for a short distance, and as they rise to the surface, also interrupt the regular flow of the fluid. Such an effect could be observed in the reaction flask. As the flow rate is increased, however, the bubbles issue from the disperser with greater velocity and rise to the surface faster, thereby fewer bubbles proportionately are carried through the solution any distance. At high flow rates of hydrogen, the gas stream has an effect very similar to a solid tube extending into the fluid pattern; it has a fixed interruptive influence, and further increases in flow rates have no effect on the stirring efficiency. If such a mechanism is true, then the

limiting effect of flow rate on the observed reaction rate such as found in Figure 4 would be expected.

In this connection, it might be mentioned that the single dispersion tube used in the apparatus is probably not the most efficient method for distributing the gas, although necessitated in this work due to fabrication problems. A study of mixing efficiences in a reactor with various types of dispersion nozzles, located in different positions in the reactor, would prove interesting for engineering considerations.

The effect of an increase in contact area between the gas and liquid phases, as presented by increasing gas flow rates, on the steady-state concentration of hydrogen is much more difficult to evaluate. As a bubble of the gas rises to the surface of the solution, solvent will be evaporating into it, and gas will be diffusing from it. Under such conditions, it is possible that the rate of solution of the hydrogen is increased, and the concentration of the gas more nearly approaches the equilibrium value, thereby increasing the rate of transfer to the catalyst surface. In this case, a limiting value of the observed rate would also be obtained, wherein the actual concentration of the gas in the solution would correspond closely to the equilibrium value. However, it is also possible that this factor, if present, would be partially nullified by a decrease in contact time of bubbles, since they issue at higher velocities.

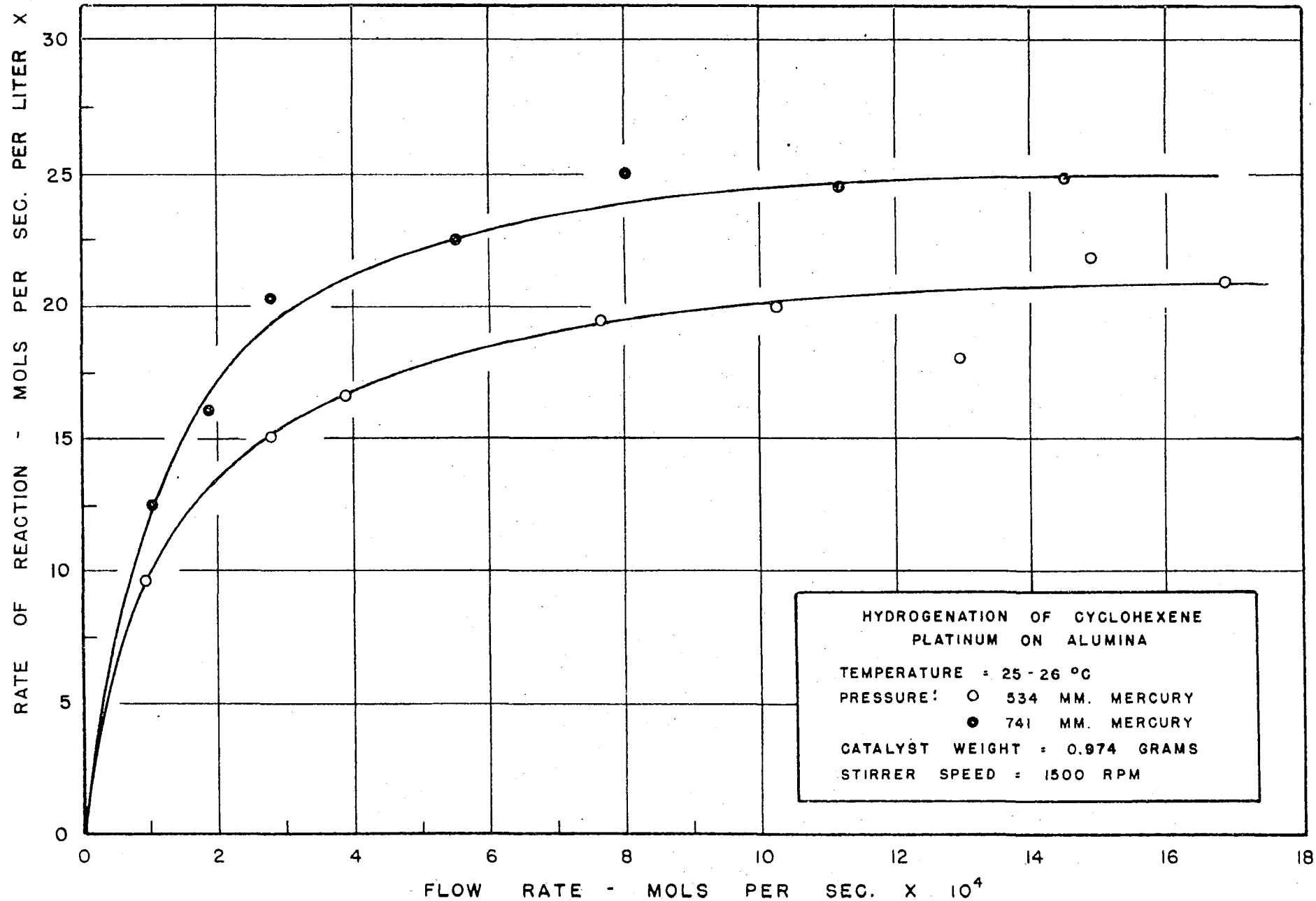


FIGURE 4 EFFECT OF RATE OF HYDROGEN FLOW ON RATE OF REACTION

In this work, these two effects cannot be separated and any decision as to their relative importance would be purely speculative. They are probably both in effect. The two curves presented in Figure 4 correspond to two different pressures. The limiting value of the observed reaction rate at the higher pressure is 20% greater than that at the lower pressure. Calculation of the solubility of hydrogen in cyclohexane by Henry's Law from data in the literature (5) indicates a 24% increase in hydrogen concentration for the same increase in partial pressure of the gas. While these values may be considered about equal within experimental error, they do not support or deny either effect, and further study into both of these factors would seem to be of fundamental interest.

Effect of Pressure

A change in the total pressure in the reaction flask was found to affect the observed rate of reaction linearly, as shown in Figure 5. Since the vapor pressure of the solvent is determined only by the temperature, which was maintained constant for this series of runs, a change in the total pressure on the system corresponded to a change in the partial pressure of the hydrogen over the solution, provided equilibrium was established. The range of pressures studied was somewhat limited, due in part to the construction of the apparatus.

The effect of the hydrogen pressure would appear to be solely that of a change in the equilibrium, or more correctly, the steady-state concentration of the gas in the solution, as provided by Henry's law. It is also found, however, that the linear relationship of Figure 5, if continued to zero pressure, indicates a finite rate of reaction. This, of course, cannot be the case. This discrepancy is further evidenced by the fact that between the limits of pressure studied, the observed rate of reaction increased 54%, while according to Henry's law, the equilibrium hydrogen concentration would increase almost 80%.

If it is to be assumed that the steady-state hydrogen concentration is proportional to the equilibrium concentration, and that this is the major effect of the reactor pressure on the observed rate of reaction, then the slope of the plot of Figure 5 must be in error. That is, if the slope were about 10% greater, the line would pass through the origin, and correspond closely to the linear relationship of the equilibrium hydrogen concentration and pressure.

The size of the bubbles in the gas stream at reduced pressures would seem to offer a plausible explanation of this observed discrepancy. The mass rate of gas flow was held constant during this series of runs, which means the volume rate of flow increased as the pressure on the system was decreased. According to the discussion of the previous

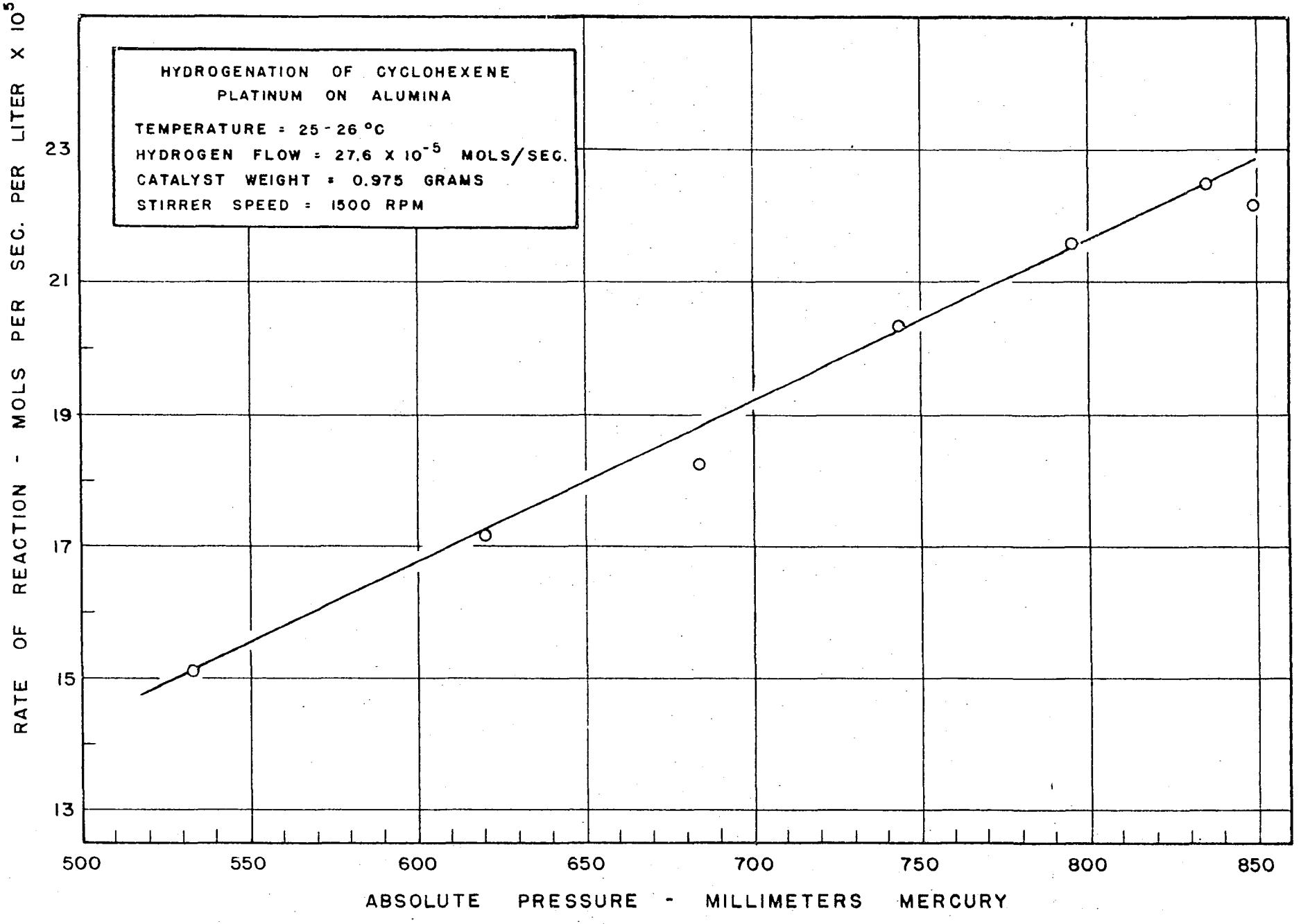


FIGURE 5 EFFECT OF PRESSURE ON RATE OF REACTION

section, an increase in the bubble size would increase the observed reaction rate, due to either the increase in mixing efficiency caused by greater disruptive action of the gas stream, or the increase in contact area, or both. Thus, the observed rates at lower pressures are probably somewhat greater than they should be for comparison on the same basis of contact area and stirring efficiency. Therefore the slope of the plotted line is decreased, although the linear relationship is still found, since gas volume is inversely proportional to the pressure.

The effect of pressure on the observed rate of reaction could have been determined much more effectively by maintaining the volume rate of flow constant, rather than the mass rate, thereby eliminating the above factor. Further study of the effect with this change in experimental procedure would be of value, although it is thought that the single effect of reactor pressure previously proposed would be verified. In such a study, the relationship at much lower pressures should be investigated, which would probably necessitate employing a different solvent. The lowest total pressure that could be used in this work was limited by the relatively high vapor pressure of cyclohexane at 25°. The capacity of the ice water condenser was exceeded at the lowest pressure studied in this series, as indicated

by the considerably increase in the vapor adsorbed in the exit drier.

Effect of Stirring Rate

One of the most important phases of the present work was intended to be a thorough exploration of the influence of the stirring rate on the observed rate of reaction. Recent studies on vapor phase catalytic reactions have indicated that mass transfer effects may never really be eliminated for such systems. If this is true, then these effects should be multiplied many times for reactions in the liquid state, and are worthy of considerable investigation. The author has been particularly disturbed by studies reported in the literature of heterogeneous reactions in batch-type equipment, where the data presented clearly indicates mass transfer effects, but no recognition was made of this factor.

The experimental equipment used in this work was designed particularly for study of the effects of the stirring rate. The Morton type flask was used because of its high mixing efficiency, and the stirrer motor purchased for the work had a wide range of speeds. Since the semi-flow system appears to offer considerable industrial utility, knowledge of mass transfer effects in such a system was thought desirable, and this fact in part determined its selection for study.

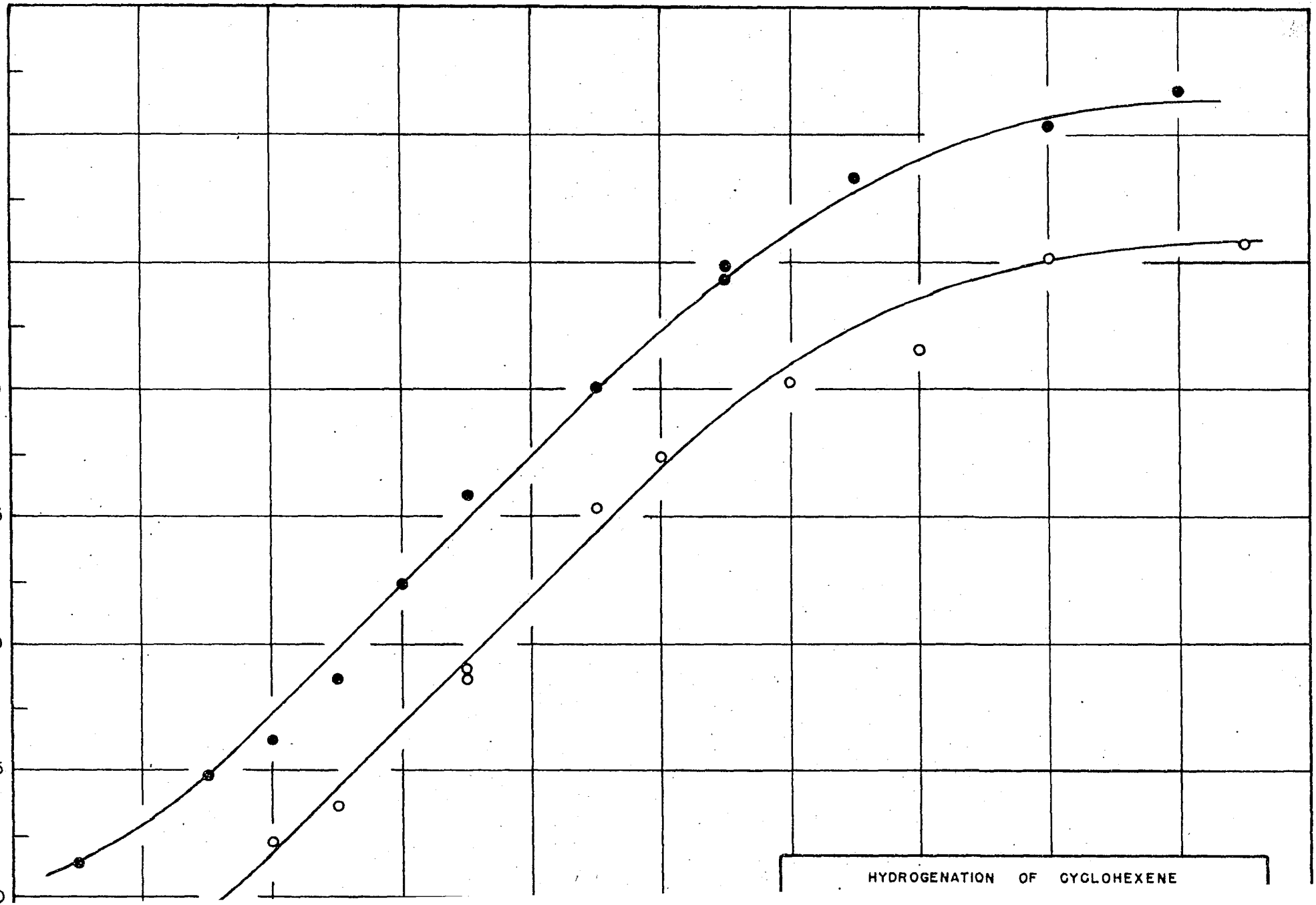
The effect of the stirring rate on the observed rate of reaction as found in this work are best shown graphically in Figure 6. The two curves presented represent two different hydrogen flow rates, all other variables being the same.

The two plotted curves shown are seen to be similar to each other in practically every detail, and displaced from each other by essentially an equal increment of rate. The scattering of points about the curves is apparently inherent in the experimental system, but it is thought that sufficient data are presented to justify the plots as drawn. The reaction rate corresponding to the curve for the higher flow rate is about 22% greater than that for the lower flow rate, at a stirrer speed of 1500 RPM. Comparison with Figure 4 indicates the given increment in flow rate produced about 23% increase in the observed rate, at this same speed. The higher flow rate simply adds a given amount of stirrer efficiency or contact area over the range of stirrer speeds employed.

The expected dependancy of the observed rate on the stirring rate has been previously discussed, and was expressed as:

$$k_t = a\, N^b \qquad (6)$$

where b is equal to 1 for the mass transfer controlled



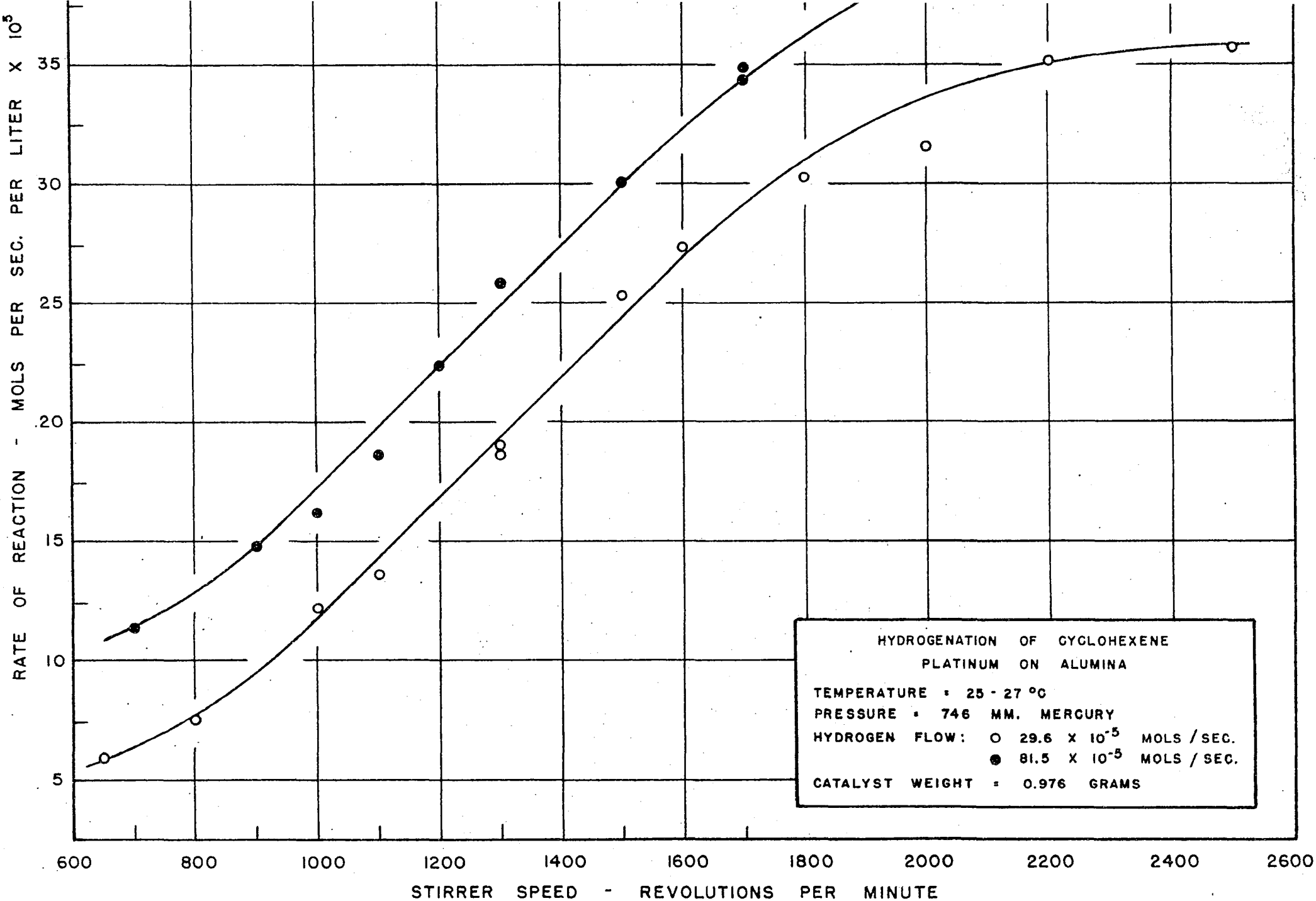


FIGURE 6 EFFECT OF STIRRING ON RATE OF REACTION

reaction, equal to 0 for chemical control, and variable between these two values in the duo-control region. The experimental curves presented would seem to possess all these characteristics.

The lower portion of the curves which give them their "S" shape indicates that the observed rate was approaching some minimum value (in which case b would also be 0). This effect where the reaction rate is linear with stirrer speed only after a certain speed is obtained has been previously reported (11). Since the minimum rates would appear to differ for the two flow rates by the same increment observed over the higher portions of the curves, they must represent the agitation effects of the flow rates themselves or the effect of increased contact area as previously discussed. Apparently at low stirring rates, the mixing caused by the stirrer paddle is negligible compared to the turbulence created by the bubbling gas. This turbulence caused by the gas steam apparently is additive to that caused by the stirrer paddle.

For both flow rates the linear dependence of the observed rate on the stirrer speed is found in the range of 1000 to 1700 RPM. Such dependence is one of the most obvious criterion for recognizing mass transfer controlled reactions, and inherently implies that the effective "film" thickness is inversely proportional to the stirrer speed in

this range. It also follows that the relative motion of the fluid phase to the solid surface of the catalyst is linear with respect to the stirring rate. The observed rate of reaction in this linear portion of the curves may be expressed as:

$$r = 25.2 \times 10^{-8} (N - 1000) + C \qquad (16)$$

where C is a function of the flow rate.

Previous discussion has suggested that the mass transfer of cyclohexene to the catalyst surface did not control the observed rate of reaction. In the linear portion of the curves, therefore, the rate must correspond to the rate of diffusion of the hydrogen. That is, the mass transfer rate of one of the reactants must control the observed rate since none of the other steps in the overall process would be so affected by the stirrer speed. The validity of this postulate can be determined by simple calculation. According to equation 3, the rate of mass transfer for one component is given as:

$$-\frac{dc}{dt} = \frac{D\,A}{V\,B}\,c$$

Levich (16) has shown from purely theoretical considerations that:

$$B \propto D^{1/3} \qquad (17)$$

Assuming all the other variables to be the same:

$$\frac{r_H}{r_C} = \frac{D_H^{2/3} c_H}{D_C^{2/3} c_C} \qquad (18)$$

The rates of mass transfer for the two reactants will be equal when this ratio is unity, or

$$c_C = \frac{D_H^{2/3}}{D_C^{2/3}} c_H \qquad (19)$$

Experimental data for the diffusion coefficients of hydrogen and cyclohexene in cyclohexane are not available. Arnold (3) has proposed a method for estimating the coefficients based upon molar volumes. Using this method, the diffusion coefficients at 25°C are:

$$D_H = 15.2 \times 10^{-5} \text{ cm.}^2/\text{sec.}$$
$$D_C = 1.83 \times 10^{-5} \text{ cm.}^2/\text{sec.}$$

Frolich and co-workers (5) give the solubility of hydrogen in the cyclohexane at 25°C and 646 mm. Hg. as 0.00348 mols per liter. Using these values in equation 19:

$$c_C = 0.0143 \text{ mols per liter}$$

This is the concentration of cyclohexene in solution when the rates of mass transfer of the two reactants are equal.

Such a concentration of cyclohexene was generally less than that of the last sample taken in an experimental run. Thus it suffices to say that the rate of diffusion of the cyclohexene was always much greater than that of the gas, and that the mass transfer of the hydrogen controlled the reaction, at least in the linear portion of the curves.

If consideration is made only of the curve representing the lower flow rate, it would seem that above 2200 RPM the observed rate of reaction was controlled by chemical processes, for certainly it is approaching a limiting value, i.e. $b = 0$. Since the curve for the higher flow rate is found to also approach a limiting value, and one higher than the first, chemical control is indicated only if the effect of an increase in flow rate is solely that of increasing the steady-state hydrogen concentration. While this possibility has been previously discussed, it does not seem likely that agitation effects of the gas stream could have been entirely eliminated at these speeds. In any case, the classical criterion that $b = 0$ for the chemical control of a reaction must be modified. It is a necessary, but not sufficient, condition to determine the control of the observed rate.

The experimental curves presented are in actuality graphical evidence of the mixing efficiencies of the reaction flask and stirrer paddle. Apparently for a given

set of operating conditions, the relative motion which they create between the solid catalyst and solution has a definite maximum, which can only be altered by a change in another variable, such as the flow rate. Further increases in the stirring rate will not affect this maximum.

It must be pointed out that the depth of the stirrer paddle below the solution surface was carefully held constant throughout all the experimental work, the bottom of the paddle being about 5/8" from the flask bottom. Early work indicated that this factor has some effect on the stirring efficiency. The factor was not studied in this work, but could be of very fundamental nature to the hydrodynamics of the system.

In essence then, it is seen that in this work, it was impossible to shift entirely out of the range where the mass transfer of the hydrogen controlled the observed rate of reaction. There is some evidence, as will be discussed later, that at the very high stirring rates, the observed rate was perhaps duo-controlled. It is not thought that increasing the flow rate would have altered the upper curve appreciably, since from Figure 4 it is seen that the higher flow rate employed gives about the maximum effect on the observed rate.

An attempt was made to eliminate the mass transfer effects by reducing the amount of catalyst used. The data

of Series 900 indicates that this was unsuccessful, as an appreciable difference in the observed rate at the different flow rates is found even at the high stirring speeds.

The foregoing discussion has attempted to emphasize that a conscientious effort was made in this study to create maximum turbulence in the reaction flask. While high stirring efficiencies were obtained, the mass transfer effect could not be eliminated. This fact increased the author's suspicion concerning the importance of mass transfer in kinetic studies reported in the literature.

In this regard, particular reference is made to the batch type autoclave, which has been almost a universal tool of the chemist in studying the kinetics of reactions. The form of this equipment consists of a reaction bottle connected to a large gas reservoir, provision being made to mix the contents of the bottle by a reciprocating motion. The progress of the reaction is usually followed by the decrease in the pressure of the system.

For purposes of comparison, a set of data was taken on the reaction in the standard low-pressure Parr hydrogenation apparatus. A smaller volume of solution had to be used than for the flow system, but proportionate quantities of the materials were used, i.e. 1/5 of the weight of catalyst and solvent, and of cyclohexene volume. The reactor bottle was shaken at a rate of 350 cycles/minute. In order that the values of the specific reaction constant calculated be on the

same basis for both systems, it was necessary that the rate of the reaction be determined from the cyclohexene concentration in solution, rather than by the hydrogen pressure, since the latter depends on the reservoir volume. The data of this run are presented below.

Table I

Time min.	Pressure psia	$(p - p_f)$ psi	$\frac{(p - p_f)}{(p_o - p_f)}$	Concentration mols/liter
0	45.3	4.0	1.000	0.543
2	44.4	3.1	.775	0.421
4	43.6	2.3	.575	0.321
7	42.6	1.1	.275	0.149
8	42.0	.8	.200	0.109

A plot of the concentration against the time yields a straight line whose slope is the observed rate of reaction, and equal to the mass transfer rate of hydrogen. Actually the plot should show some slight curvature, since the hydrogen concentration is decreasing along with the gas pressure. However, since the total pressure drop was only 4 psi, this effect has been neglected and the hydrogen concentration considered constant. Once the rate has been established, a "specific velocity constant" k_t may be calculated from equation 3:

$$k_t = \frac{1}{c_H}\frac{dc_H}{dt} = \frac{\text{rate}_{obs.}}{c_H} \qquad (20)$$

Table II summarizes typical values of k_t for the flow system

taken from Figure 6, along with those calculated for the batch system.

Table II

	obs. rate mols/liter sec.	c_H mols/liter	k_t sec.$^{-1}$
Parr Apparatus	0.000390	0.0122	0.0762
Run 701 650 RPM $R_f = 2.76 \times 10^{-4}$.	0.000060	0.00348	0.0172
Run 812 2400 RPM $R_f = 8.08 \times 10^{-4}$	0.000418	0.00348	0.120

Run 701 represents the lowest stirring efficiency exhibited in Figure 6, and it is seen that the velocity constant for the batch system is considerably larger than that of the flow system. On the other hand, Run 812 is the maximum rate observed in this work, and its velocity constant is almost double that of the Parr data.

Inspection of the plotted curve for the lower flow rate indicates that the velocity constants of the two systems are equal at a stirring rate between 1500-1600 RPM. This has previously been shown to be a region where mass transfer of hydrogen definitely controls the observed rate of reaction. In general, the upper half of the curves in Figure 6 represent stirring efficiencies greater than those obtained in the Parr apparatus, and even in this region mass transfer effects predominate.

It is true that the rate of the chemical processes themselves in part determine the relative importance of mass

transfer. If such processes were very slow, it is plausible that the diffusional effects could be eliminated or rendered negligible. This would be the case for very poor catalysts, but the common catalysts used for hydrogenation reactions certainly cannot be so classified. As found in this study, cognizance of mass transfer rates would seem to be essential in kinetic investigations of heterogeneous reactions in the liquid phase.

Effect of Temperature

The influence of temperature on the observed rate of reaction has long been used as a criterion for determining the controlling step in the overall process. Diffusional processes generally have been found to require much lower apparent energies of activation than either surface reactions or adsorption. The temperature dependence of the specific velocities of all rate processes may be expressed in the general form of the Arrhenius equation:

$$k = A\, e^{-\frac{E}{RT}} \qquad (21)$$

The constants A and E have been given physical significance by the theory of absolute reaction rates (6). The factor E is not the true energy of activation, but contains a entropy term to account for configuration changes, and is referred to as the "apparent" energy of activation.

The specific velocity constants for the experimental

data of Series 1000 and 1100 could be calculated from equation 20, provided the change in hydrogen concentration with temperature was known. Experimental data for hydrogen solubility in cyclohexane were available only at 25°C (5) and 35°C (21). Using a Clausius-Clapeyron type of relationship, the heat of solution of hydrogen in cyclohexane was calculated from these two sets of data and found to be -1538 cal./mol. Assuming this value constant, solubilities at other temperatures were estimated using the equation:

$$\ln \frac{c_1}{c_2} = \frac{-1538}{R} \left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad (22)$$

It might again be pointed out that the actual hydrogen concentrations in the reaction solution were probably somewhat smaller than the equilibrium values, but steady-state concentrations were unknown, and could not be reasonably estimated.

Taking the natural log of both sides of equation 22:

$$\ln k = \frac{-E}{RT} + \ln A \qquad (23)$$

and a plot of ln k versus 1/T should be a straight line with a slope equal to - E/R. The data used to prepare such a plot is given in Table III, and the plots are shown in Figure 7.

Table III

T °C	1/T	rate mols/l. sec.	c_H mols/l.	k $sec.^{-1}$
Series 1000 1300 RPM				
10.2	0.003532	0.000118	0.00398	0.0296
13.4	0.003492	0.000141	0.00387	0.0364
17.3	0.003445	0.000162	0.00373	0.0434
22.7	0.003382	0.000179	0.00355	0.0504
26.6	0.003338	0.000191	0.00344	0.0555
33.4	0.003264	0.000214	0.00324	0.0660
41.1	0.003184	0.000248	0.00304	0.0816
Series 1100 2500 RPM				
10.2	0.003532	0.000132	0.00398	0.0332
14.0	0.003484	0.000169	0.00385	0.0439
18.2	0.003434	0.000251	0.00370	0.0678
23.0	0.003378	0.000275	0.00354	0.0778
23.0	0.003378	0.000269	0.00354	0.0760
27.0	0.003333	0.000358	0.00342	0.1047
31.6	0.003284	0.000374	0.00329	0.1137

The influence of temperature was studied at two different stirring rates to give further evidence of the controlling process. Mass transfer was known to determine the observed rate at 1300 RPM, and it was thought that perhaps a shift in control might be found at the maximum stirring speed. The lower flow rate was used since it was found an increase in temperature would make the observed rate too rapid to measure accurately at 2500 RPM with the higher flow rate. This was unfortunate, as data at the maximum stirring efficiency would have given further insight

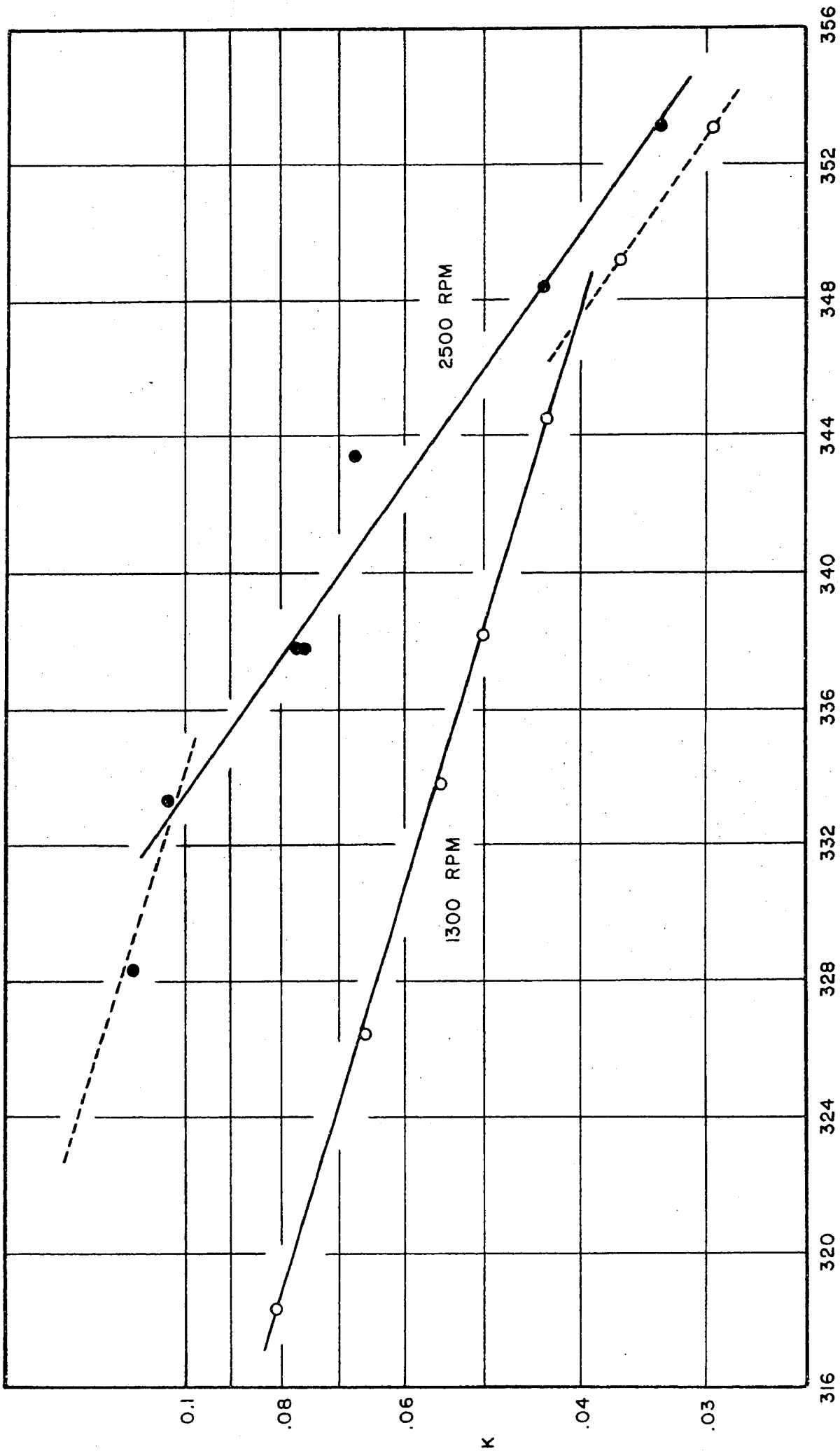


FIGURE 7 EVALUATION OF APPARENT ENERGIES OF ACTIVATION

of the controlling step.

The plots of k versus 1/T are presented in Figure 7. The data for 1300 RPM fall on a straight line very well except at lower temperatures, where the deviation strongly suggests a shift in control to the chemical processes which are influenced more by temperature changes. The points for the higher stirrer speed are somewhat scattered, due to the apparent instability of the stirring efficiency at that rate, and the plot as drawn is not definite. If the observed rate is duo controlled at 2500 RPM as has been proposed, it would be expected that at higher temperatures, the control would be shifted to mass transfer, and the plot should become paralled to that at the slower speed. It was not possible to obtain data to confirm this, and the dotted line drawn is only suggestive of this expectation. The experimental data do not dispute this possibility, although they are hardly conclusive. Whether or not the two plots become parallel at the lower temperatures cannot be determined from the limited data, although again this would be expected.

From the slopes of the plots, the following results were obtained:

1300 RPM $E_{obs.}$ = 4,790 cal./mol

2500 RPM $E_{obs.}$ = 12,790 cal./mol

The value of the apparent activation energy at 1300 RPM

merely confirms that the observed rate is mass transfer controlled in this region, for it corresponds to that generally reported for diffusional processes. The value at 2500 RPM gives a good indication that the observed rate is in duo-controlled region. Since the apparent activation energies for the chemical processes are not known, it cannot be determined just how far into the transition range, or how close to chemical control, the observed rate actually was at the higher stirring rates.

Inspection of the data shows that the observed rate of reaction at a stirring speed of 2500 RPM, 32°C, and the lower flow rate was still less than that at the same speed, 25°C, and the higher flow rate. Thus the maximum observed rates at 25°C (Runs 810-812) were certainly in the duo-controlled region, and perhaps even close to chemical control. It is not, therefore, impossible to approach conditions where mass transfer effects are negligible, if not by increasing the stirring efficiency, then by lowering the temperature of the reaction. The experimental work was limited somewhat in this respect as the cyclohexane used as solvent has a solidification point of 6.5°C.

The influence of temperature on the observed rate of reaction seems to substantiate the contention that mass transfer effects predominated in the data taken in this work, although at higher stirring rates at least the

transition range was reached. With appropriate changes in the magnitude of some of the operating variables, it is thought that it would be possible to obtain chemical control, whereby the mechanism of the chemical combination could be studied.

Effect of Stirrer Design

When it became apparent that mass transfer effects could not be eliminated by stirring speed alone in this apparatus, an attempt was made to increase the mixing efficiency of the system by altering the design of the stirrer itself. A single paddle stirrer with four equally spaced blades was used in the majority of the work. For the runs of Series 1200, this stirrer was replaced by one constructed of two such paddles, so situated on the stirrer shaft that the blades of one lay between (and above) the other. An end view of this stirrer would show eight blades equally placed around the shaft, although on two different planes. About one-eighth of an inch separated the two paddles, and all the blades were at an angle of about 10° to the vertical. Figure 16 (Appendix) shows this stirrer in detail.

The variance in observed rate of reaction with stirring rate with this stirrer was determined for the same operating conditions as for the single paddle stirrer, and can be

compared with the latter at the higher flow rate (Series 800) as is shown in Figure 8. It is seen that up to stirrer speeds of about 1400 RPM, the double paddle stirrer is more efficient, i.e. the mass transfer rates are increased due to higher relative velocities and smaller "effective" film thicknesses. However, about this speed the stirrer rapidly loses its efficiency and its maximum is considerably below that of the single paddle stirrer.

Visual observation of the reaction solution during these runs permitted some explanation of this effect. At the lower stirring rates, the surface of the solution appeared to be in much more turbulence than previously observed. The degree of surface turbulence increased with stirrer speed, and practically reached "foam" characteristics at the high speeds. Along with this surface turbulence, the formation of vortices behind the trailing edges of the blades also appeared to increase with stirring rate. At very high speeds, vortices were observed about the shaft itself, and extended almost the full depth of the stirrer in the solution.

The effect of vortex formation on mixing efficiencies has been previously observed (9), and this phenomenon would seem to explain the decrease in observed reaction rate at higher stirrer speeds. When the gaseous vorticies become so large so as to envelop the shaft, the paddles are in a sense revolving in the gas rather than the solution, and the

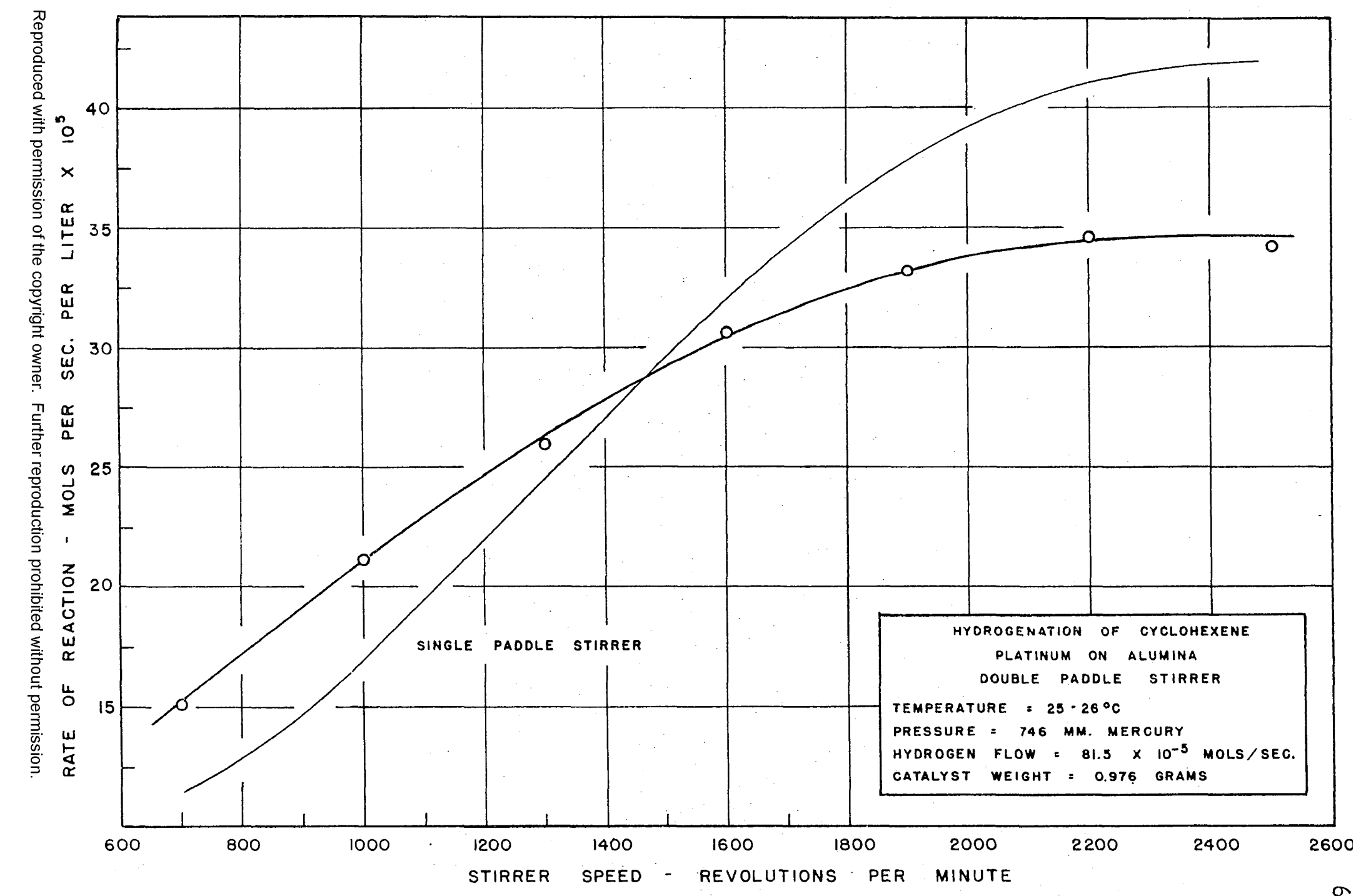


FIGURE 8 EFFECT OF STIRRER DESIGN ON RATE OF REACTION

net effect is that the vortices and shaft act as a solid revolving unit. The effective action of the blades is thereby lost, and the relative motions produced lessened.

This effect for the double paddle stirrer of course cannot be generalized for all shapes and designs of stirrers. A study of the effectiveness of the common stirrer designs on mixing efficiency in the semi-flow system would be of real benefit to the engineer. The work that has been done in this connection is of limited scope, and employed rather idealized conditions (9). A reaction such as studied in this work affords a good means of determining mixing efficiency.

Effect of Reaction Flask Shape

Mixing efficiency has long been of interest to the engineer, for process time is an important economical factor in all industrial operations. The use of baffles in tanks to obtain better mixing may now be regarded as standard practice. The Morton flask used in this work with its indented sides corresponds somewhat with a baffled tank.

To show the effect of reactor design, a series of runs were made using an ordinary round bottom flask as the reaction flask. As was expected, the results, shown in Figure 9, when compared to those obtained in the Morton flask for the same operating conditions indicated much lower mixing efficiency. With only the gas dispersion and

sampling tube to interfere with the fluid motion, the reaction solution moved in almost unbroken flow about the flask. The surface of the solution showed practically no turbulence, even at very high stirring rates.

This streamlined flow then effectively dampened the stirring action of the paddle, and a change in relative motion between the solid and solution obtained with difficulty. It is seen from the plot that the observed reaction rate approached a minimum at low stirring speeds which corresponds closely to that obtained in the other flask, and represents as before the turbulence created by the gas stream alone. From this minimum the linear dependence of observed rate with speed is gradually approached. A linear relationship is found for a much smaller range of stirring rates than previously, and the maximum efficiency reached was considerably lower than in the Morton flask.

Generally, vapor phase catalytic reactions are conducted in tubular reactors, and the hydrodynamic aspects of the process are those of the flow of fluid through packed beds. In a stirred system, the hydrodynamics are much more complex, for both the design of the stirrer and the containing vessel will determine the mixing efficiency. There is a real need for considerable investigation of this problem alone, if the kinetic aspects of the stirred system are to be completely understood.

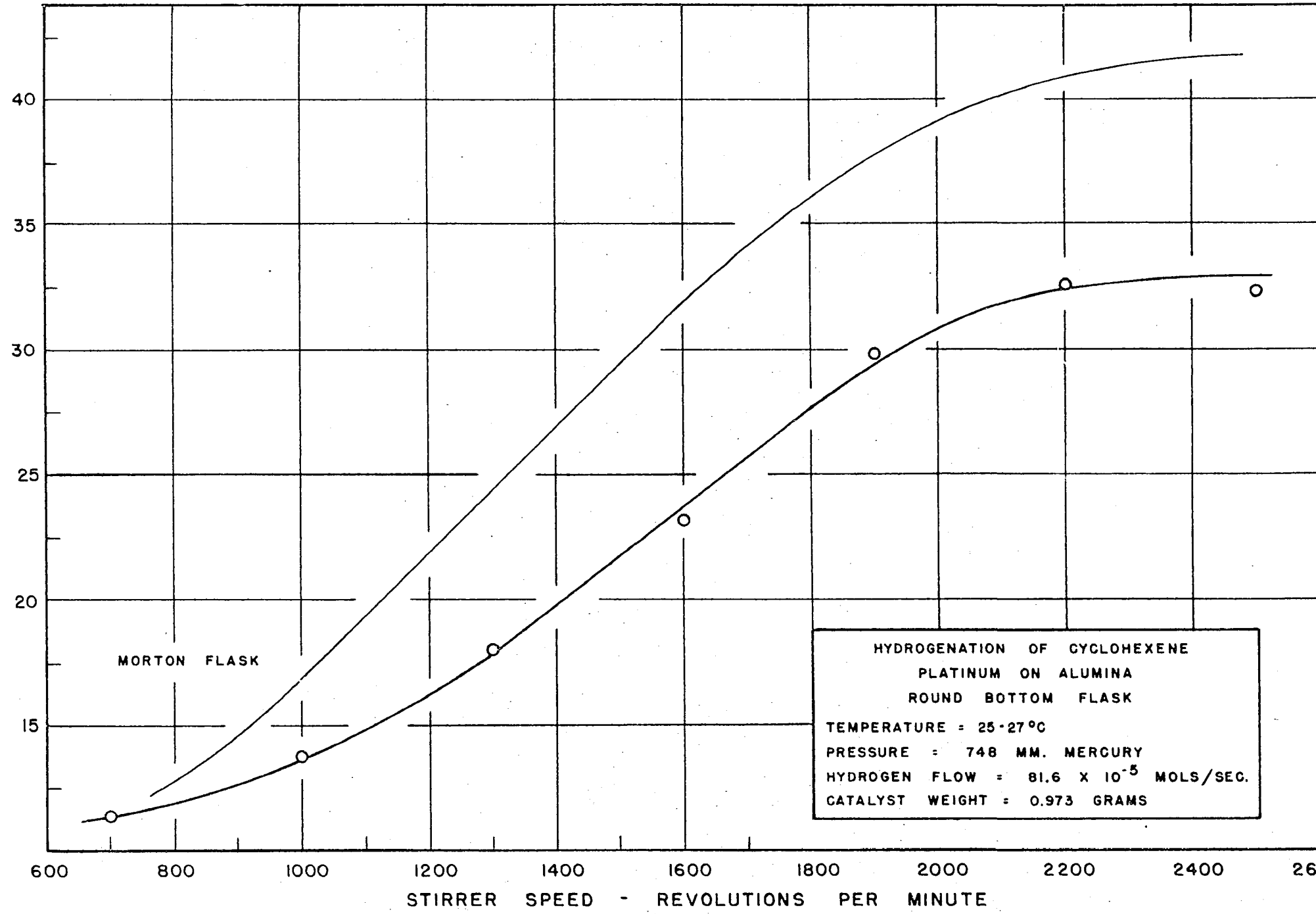


FIGURE 9 EFFECT OF REACTION FLASK SHAPE ON RATE OF REACTION

Mechanism of the Chemical Reaction

The actual mechanism of the catalytic reaction between a molecule of cyclohexene and a molecule of hydrogen in a heterogeneous system can be evaluated only when the experimentally observed rate is controlled by the chemical processes. Any mass transfer effects will obscure the true dependence of the rate on operating variables. In the present work, the control of the rate by the mass transfer of hydrogen to the interface could not be eliminated, and determination of the mechanism is not possible. However, it is of some value to indicate the method by which such a determination could be made using data from the semi-flow system.

When chemical control has been achieved, the observed rate may be that of the adsorption of either of the reactants onto the surface, the rate of desorption of the product (not considered likely in this case), or the chemical combination itself. Regardless of which rate is observed, the actual rate of combination must be in accord with the law of mass action, appropriately expressed as:

$$r = k \text{ (conc. cyclohexene)(conc. hydrogen)} \qquad (24)$$

The mechanism of the reaction determines where these concentrations are to be measured.

Let c_C = concentration of cyclohexene in solution at time t

c_H = concentration of hydrogen in solution at time t

θ_C = concentration of cyclohexene adsorbed on the catalyst surface at time t

θ_H = concentration of hydrogen adsorbed on the catalyst surface at time t

The following rate expressions encompass all possible mechanisms for the reaction, assuming the hydrogen is molecularly adsorbed:

$$\begin{aligned} &\text{(a)} && r = k\ c_C\ c_H \\ &\text{(b)} && r = k\ c_C\ \theta_H \\ &\text{(c)} && r = k\ \theta_C\ c_H \\ &\text{(d)} && r = k\ \theta_C\ \theta_H \end{aligned} \qquad (25)$$

Mechanism (a) is an expression for a non-catalytic reaction. Since no reaction between the cyclohexene and hydrogen could be detected experimentally in the absence of the catalyst in the present work, this mechanism may be discarded immediately. Mechanism (b) represents reaction between cyclohexene in the solution at the interface and adsorbed hydrogen, mechanism (c) that between hydrogen in the solution and adsorbed cyclohexene, and (d) a true surface reaction where both reactants are adsorbed, and the mechanism generally found for hydrogenations.

The elimination of all but one of the above mechanisms should be possible if the proper data are available. However, the procedure is complicated and must be carried out with care. For example, in the semi-flow system the hydrogen concentration remains constant, while that of the cyclohexene continuously decreases. However, even if the observed rate should remain constant for a given run, mechanism (b) cannot be discarded since the observed rate might be that of the adsorption of hydrogen. Likewise for mechanism (c), a constant rate could mean that the solution of the hydrogen was controlling the reaction, or that the cyclohexene was "strongly" adsorbed and not dependent on the concentration in the solution. Thus it would seem that some knowledge of adsorption rates for both cyclohexene and hydrogen would be necessary to determine the mechanism of the reaction. Such rates have received little attention, and are difficult to measure due to mass transfer effects.

An alternate method would seem to be that proposed by Hougen and Watson (10), which to the author's knowledge has never been applied to reactions in solution. Their basic relationships were derived on a perfectly general basis employing activities, and should hold for any system. The ideal gas law has been used exclusively in applying these equations to vapor phase reactions, and similar simplifications could be made appropriately for the liquid phase. The method permits a rate equation to be written for every possible

controlling step for each proposed mechanism. Each equation can then be tested against experimental data to arrive at the proper mechanism.

The present author feels that a real contribution to applied kinetics could be made by a study of the reaction in the chemical controlled region, and comparing the mechanisms as determined by the above methods. The value of the present work is thought to be that of indicating the requirements for achieving chemical control in the semi-flow system. Now that the effect of the pertinent variables have been at least qualitatively exposed, future investigators may more readily establish experimental conditions so that the fundamental aspects of reactions in solution may be studied.

CONCLUSIONS

The kinetics of the liquid phase hydrogenation of cyclohexene in the presence of a platinum catalyst in a stirred semi-flow system have been studied experimentally. It was found that:

1. The observed rate of reaction increases with an increase in catalyst concentration, but reaches a limiting value due to the inability of the stirrer to hold additional amounts of solid in suspension.

2. The flow of hydrogen affects the rate of reaction either by aiding the stirring efficiency in the reaction flask or by changing the contact area of the gas, and the effect is of fixed magnitude at higher flow rates.

3. An increase in the total pressure on the reaction flask affects a linear increase in the reaction rate, corresponding to the change in steady-state hydrogen concentration in the solution.

4. For the major portion of the work, the observed rate of reaction is controlled by the mass transfer of hydrogen from the bulk of the solution to the solid-liquid interface, and is independent of the cyclohexene concentration in solution.

5. At the higher limits of obtainable stirring rates, the reaction rate is duo-controlled and is approaching the chemical control.

6. That the observed rate of reaction be independent of the stirring rate is a necessary, but insufficient, criterion for determining chemical control.

7. The stirred semi-flow system offers greater mixing efficiency than the batch type autoclave, and it is questionable mass transfer effects can be eliminated in the latter equipment.

8. The design of the stirrer and reaction flask together determine the stirring efficiency, and complex hydrodynamic phenomena such as formation of vortices prevent at present prediction of maximum obtainable efficiencies.

9. With the proper choice and control of operating conditions, chemical control of the reaction might be achieved in the semi-flow system, and the reaction mechanism evaluated.

10. Further concentrated study of each of the variables explored is required before fundamental theory of engineering utility for such systems can be developed.

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APPENDIX

EXPERIMENTAL DATA

The following designations are used in the presentation of data:

H	=	flowmeter manometer reading, inches of mercury
H'	=	flowmeter reading, inches of dibutyl phthalate
T_f	=	flowmeter temperature, °C
R_f	=	calculated hydrogen flow rate, mols per second
P_a	=	barometric pressure, millimeters of mercury
P_r	=	reactor pressure, millimeters of mercury
T_i	=	initial reactor temperature, °C
T_r	=	reactor temperature during reaction, °C
R_f	=	calculated reaction rate, mols per second per liter
Time	=	time of sample withdrawal, minutes
Conc.	=	concentration of cyclohexene, normality
RPM	=	stirrer speed, revolutions per minute
Catalyst	=	weight of catalyst, grams

(The reference to "days" for Series 000 is the time of the run from preparation of the Raney nickel catalyst.)

SERIES 000

Stored Cyclohexene - Raney Nickel Catalyst

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
001	0.7247	920	1.57	1.39	28.2	0.000318	734.6	735.0	24.8	25.4	0	0.9192	0.000118
											15	0.7449	
(1 day)											30	0.5285	
											45	0.3111	
											60	0.1121	
											75	0.0069	
002	0.7206	920	0.66	1.34	31.6	0.000312	743.5	743.9	24.6	25.0	0	0.9342	0.000083
											15	0.7866	
(27 days)											30	0.6328	
											45	0.4840	
											60	0.3393	
											75	0.2200	
											90	0.1179	
003	0.7238	930	0.63	1.33	29.8	0.000309	745.4	745.7	24.2	25.0	0	0.9329	0.000105
											15	0.7583	
(28 days)											30	0.5497	
											45	0.3602	
											60	0.1770	
											75	0.0515	

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
004	0.7119	910	1.17	1.25	27.8	0.000291	739.8	740.1	30.4	30.8	0	0.9274	0.000079
											15	0.8041	
(51 days)											30	0.6518	
											45	0.4972	
											60	0.3597	
											75	0.2223	
											90	0.1104	
005	0.7198	920	1.22	1.30	24.4	0.000309	737.0	737.3	29.8	31.0	0	0.9335	0.000073
											15	0.7849	
(52 days)											30	0.6735	
											45	0.5477	
											60	0.4072	
											75	0.2835	
											90	0.1720	
006	0.7228	910	1.52	1.36	23.6	0.000331	749.8	750.2	25.4	25.2	0	0.9279	0.000061
											15	0.8386	
(56 days)											30	0.7252	
											45	0.6039	
											60	0.5002	
											75	0.3979	
007	0.7243	910	1.55	1.36	23.6	0.000324	743.5	743.9	25.0	25.4	0	0.8946	0.000069
											15	0.7893	
(59 days)											30	0.6759	
											45	0.5379	
											60	0.4196	
											75	0.2939	

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
008	0.7199	940	1.90	1.27	25.4	0.000299	740.8	741.2	24.6	25.0	0	0.9372	0.000053
											15	0.8645	
(68 days)											30	0.7738	
											60	0.5749	
											90	0.3905	
											120	0.2208	
009	0.7191	930	1.72	1.29	27.2	0.000307	743.0	743.4	24.6	25.0	0	0.9421	0.000060
											15	0.8588	
(79 days)											30	0.7543	
											60	0.5322	
											90	0.3160	
											120	0.1324	
010	0.7205	950	1.93	1.31	23.8	0.000318	745.3	745.8	24.8	25.0	0	0.9417	0.000049
											15	0.8909	
											30	0.7977	
											60	0.6099	
											90	0.4593	
											120	0.2717	

SERIES 100

Stored Cyclohexene

Run No.	Catalyst	RPM	Flowmeter				P_a	Reactor			Time	Conc.	R_r
			H	H'	T_f	R_f		P_r	T_i	T_r			
101	0.2467	1000	2.02	1.39	25.0	0.000348	740.8	751.5	25.0	25.4	0	0.8805	0.000053
											15	0.8066	
											30	0.7228	
											60	0.5379	
											90	0.3432	
											120	0.1523	
102	0.5039	1000	1.81	1.31	24.8	0.000327	738.5	743.1	25.0	25.4	0	0.8813	0.000077
											15	0.7668	
											30	0.6340	
											60	0.3579	
											90	0.0734	
103	0.9718	1000	2.74	1.05	24.6	0.000271	724.0	747.1	25.0	25.6	0	0.8731	0.000097
											15	0.6989	
											30	0.5280	
											50	0.3000	
											60	0.1798	
104	1.0303	1000	1.10	1.25	26.0	0.000305	743.5	747.8	25.0	25.6	0	0.8802	0.000099
											15	0.7159	
											30	0.5374	
											45	0.3678	
											60	0.1807	
											70	0.0414	

Run No.	Catalyst	RPM	Flowmeter				P_a	Reactor			Time	Conc.	R_r
			H	H'	T_f	R_f		P_r	T_i	T_r			
105	2.0078	1000	2.15	1.32	22.2	0.000339	735.6	746.5	25.0	25.8	0	0.8657	0.000113
											15	0.6759	
											30	0.4750	
											45	0.2719	
											60	0.0660	
106	2.7388	1000	2.42	1.30	24.2	0.000333	744.0	748.3	25.0	25.8	0	0.8767	0.000113
											15	0.6815	
											30	0.4826	
											45	0.2761	
											60	0.0739	
107	2.7633	1000	2.36	1.13	24.6	0.000293	742.0	747.8	25.0	25.8	0	0.8215	0.000111
											15	0.6342	
											30	0.4341	
											45	0.2299	
											55	0.1003	
108	2.8346	1000	2.15	1.18	23.4	0.000303	746.0	748.8	25.0	25.8	0	0.8638	0.000114
											15	0.6616	
											30	0.4511	
											45	0.2522	
											60	0.0439	
109	3.0060	1000	2.05	1.20	24.6	0.000307	745.5	748.8	25.0	25.8	0	0.8718	0.000114
											15	0.6746	
											30	0.4700	
											45	0.2637	
											60	0.0596	

Run No.	Catalyst	RPM	Flowmeter				P_a	Reactor			Time	Conc.	R_r
			H	H'	T_f	R_f		P_r	T_i	T_r			
110	3.3234	1000	2.48	1.33	23.0	0.000343	734.0	748.7	25.2	26.0	0	0.8805	0.000119
											15	0.6710	
											30	0.4028	
											45	0.2440	
											60	0.0241	
111	4.5336	1000	2.82	1.31	25.0	0.000340	745.1	748.9	25.0	25.8	0	0.8738	0.000129
											15	0.6638	
											30	0.4329	
											45	0.2060	
											55	0.0501	
112	4.5781	1000	2.53	1.18	24.4	0.000307	743.2	746.5	25.0	25.8	0	0.8738	0.000121
											15	0.6539	
											30	0.4366	
											45	0.2233	
											55	0.0780	
113	4.5548	1000	2.03	1.14	25.0	0.000290	744.3	747.9	25.2	25.8	0	0.8787	0.000105
											15	0.7058	
											30	0.5156	
											45	0.3300	
											60	0.1373	
114	4.6435	1000	2.51	1.06	25.6	0.000275	733.5	746.7	25.0	25.8	0	0.8738	0.000104
											15	0.6897	
											30	0.5057	
											45	0.3221	
											60	0.1324	

Run No.	Catalyst	RPM	Flowmeter				P_a	Reactor			Time	Conc.	R_r
			H	H'	T_f	R_f		P_r	T_i	T_r			
115	6.0928	1000	2.12	1.22	24.2	0.000310	739.9	745.5	25.0	25.8	0	0.8787	0.000117
											15	0.6613	
											30	0.4539	
											45	0.2411	
											60	0.0242	
116	7.2530	1000	2.88	1.20	23.8	0.000310	729.0	746.5	25.2	25.8	0	0.8645	0.000111
											15	0.6710	
											30	0.4733	
											45	0.2724	
											60	0.0641	

SERIES 200

Stored Cyclohexene

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
201	0.9902	600	2.65	1.09	23.4	0.000293	748.5	753.1	25.0	25.4	0	0.8836	0.000054
											15	0.7873	
											30	0.6811	
											60	0.4930	
											90	0.2966	
202	0.9784	700	4.49	1.07	23.8	0.000294	739.5	749.2	25.0	25.4	0	0.8782	0.000064
											20	0.7556	
											40	0.6089	
											60	0.4525	
											80	0.3024	
203	0.9812	900	2.75	1.18	24.0	0.000306	733.8	745.9	25.0	25.4	0	0.9096	0.000081
											15	0.7676	
											30	0.6194	
											45	0.4786	
											60	0.3263	
204	0.9750	900	4.72	1.05	23.6	0.000294	744.5	748.1	25.2	25.6	0	0.8757	0.000072
											15	0.7619	
											30	0.6270	
											45	0.5069	
											60	0.3787	
											75	0.2435	

(Series 200 cont.)

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
205	0.9781	1100	2.66	1.20	23.8	0.000310	735.3	746.2	24.8	25.6	0	0.8713	0.000123
											15	0.6638	
											30	0.4341	
											45	0.2139	
											56	0.0496	
206	0.9741	1300	2.91	1.03	24.8	0.000278	749.5	750.3	25.0	26.0	0	0.8718	0.000166
											15	0.5976	
											30	0.3078	
											45	0.0015	
207	0.9757	1500	2.37	1.06	23.8	0.000282	748.5	749.8	25.0	26.4	0	0.8873	0.000231
											15	0.4897	
											25	0.1941	
											35	0.0010	
208	0.9736	1750	2.09	0.91	23.8	0.000234	748.0	749.8	25.0	26.6	0	0.8762	0.000251
											10	0.5687	
											20	0.2737	
											30	0.0000	
209	0.9758	1750	2.71	0.93	22.4	0.000248	748.0	749.8	25.0	26.6	0	0.9256	0.000253
											10	0.6436	
											20	0.3411	
											30	0.0373	

(Series 200 cont.)

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
210	0.9747	2000	2.11	1.03	22.6	0.000278	749.3	751.1	25.0	26.8	0	0.9207	0.000285
											10	0.5769	
											20	0.2349	
											28	0.0089	
211	0.9752	2500	2.04	0.98	23.0	0.000258	748.5	750.3	25.2	27.0	0	0.8817	0.000294
											5	0.7038	
											10	0.5119	
											15	0.3399	
											20	0.1781	

SERIES 300

Stored Cyclohexene

Run No.	Catalyst	RPM	Flowmeter				P_a	Reactor			Time	Conc.	R_r
			H	H'	T_f	R_f		P_r	T_i	T_r			
301	0.9745	1500	6.22	0.48	24.2	0.000092	748.0	530.1	25.0	25.6	0	0.8787	0.000097
											15	0.6984	
											30	0.5230	
											45	0.3485	
											60	0.1798	
302	0.9726	1500	3.75	1.92	24.4	0.000389	742.5	532.4	25.0	26.0	0	0.8817	0.000167
											10	0.6811	
											20	0.4855	
											30	0.2834	
											40	0.0830	
303	0.9722	1500	1.49	3.45	23.6	0.000765	746.0	531.4	24.6	25.8	0	0.8886	0.000194
											10	0.6507	
											20	0.4237	
											30	0.2089	
											37	0.0607	
304	0.9744	1500	0.28	4.72	25.0	0.001024	741.5	536.5	24.6	25.6	0	0.8960	0.000194
											10	0.6544	
											20	0.4168	
											30	0.1793	
											35	0.0756	

(Series 300 cont.)

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	Reactor P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
305	0.9740	1500	0.00	6.08	25.6	0.001292	743.2	537.0	25.0	26.2	0	1.9472	0.000180
											15	1.6187	
											30	1.2924	
											45	0.9676	
											60	0.6465	
											75	0.3452	
											90	0.0682	
306	0.9742	1500	0.73	7.27	24.8	0.001489	747.5	536.7	24.8	26.0	0	0.9330	0.000218
											10	0.6581	
											20	0.3872	
											30	0.1366	
											35	0.0262	
307	0.9737	1500	1.37	8.69	25.0	0.001682	745.7	535.1	24.6	25.8	0	0.9454	0.000209
											10	0.6490	
											20	0.3930	
											30	0.1497	

SERIES 400

Stored Cyclohexene

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
401	0.9747	1500	3.68	1.37	26.0	0.000277	733.5	532.8	25.0	25.8	0	0.8750	0.000151
											10	0.7009	
											20	0.5131	
											30	0.3324	
											45	0.0484	
402	0.9736	1500	1.07	1.24	25.4	0.000277	732.8	620.3	25.0	26.2	0	-	0.000172
											10	0.6613	
											20	0.4539	
											30	0.2509	
											40	0.0435	
403	0.9739	1500	1.40	1.13	24.2	0.000285	751.5	683.8	24.8	26.0	0	0.8693	0.000184
											10	0.6488	
											20	0.4267	
											30	0.2089	
											40	0.0	
404	0.9765	1500	3.13	1.05	24.2	0.000278	740.6	743.6	25.2	26.4	0	0.8750	0.000204
											10	0.6688	
											20	0.4242	
											30	0.1818	

Series 400 (cont.)

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	Reactor P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
405	0.9756	1500	5.75	0.94	23.4	0.000271	752.0	795.4	25.0	26.4	0	0.8762	0.000216
											10	0.6347	
											20	0.3822	
											30	0.1158	
											35	0.0039	
406	0.9736	1500	6.57	0.92	24.6	0.000267	736.0	835.1	25.0	26.4	0	0.8799	0.000225
											10	0.6285	
											20	0.3608	
											30	0.0879	
											35	-	
407	0.9736	1500	8.38	0.91	26.6	0.000275	743.0	848.7	25.0	26.4	0	0.8787	0.000222
											10	0.6119	
											20	0.3473	
											30	0.0824	

SERIES 500

Stored Cyclohexene

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
501	0.9748	1500	2.94	0.39	26.2	0.000101	734.0	739.6	25.2	26.2	0	0.8676	0.000125
											10	0.7275	
											20	0.5754	
											35	0.3473	
											50	0.1077	
502	0.9761	1500	3.36	0.70	25.4	0.000186	739.8	741.6	25.0	26.2	0	0.8664	0.000161
											10	0.6964	
											20	0.5045	
											30	0.3114	
											45	0.0081	
503	0.0726	1500	6.09	1.96	25.4	0.000551	739.0	745.4	25.0	26.4	0	0.8836	0.000225
											10	0.6441	
											20	0.2810	
											30	0.1045	
											36	0.0064	
504	0.9734	1500	6.71	2.89	24.8	0.000800	733.5	742.9	25.0	26.6	0	0.8911	0.000250
											10	0.5922	
											20	0.2695	
											30	0.0027	

(Series 500 cont.)

Run No.	Catalyst	RPM	Flowmeter				P_a	Reactor			Time	Conc.	R_r
			H	H'	T_f	R_f		P_r	T_i	T_r			
505	0.9731	1500	8.35	3.90	26.8	0.001114	746.7	737.0	24.8	26.4	0	0.8940	0.000246
											10	0.6095	
											20	0.3028	
											25	0.1567	
506	0.9735	1500	9.48	5.04	27.0	0.001448	747.5	737.8	24.6	26.2	0	0.8923	0.000249
											10	0.6026	
											20	0.2880	
											25	0.1465	

SERIES 600

Stored Cyclohexene

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
601	0.9753	700	8.09	2.83	25.2	0.000802	732.6	747.1	24.8	25.4	0	0.8828	0.000082
											15	0.7346	
											30	0.5854	
											45	0.4426	
											60	0.3049	
											75	0.1910	
602	0.9757	900	6.87	2.87	25.4	0.000798	744.2	744.2	24.8	25.6	0	0.8935	0.000126
											15	0.6930	
											30	0.4637	
											45	0.2386	
											55	0.0904	
603	0.9772	1100	8.28	2.84	25.8	0.000820	736.8	747.5	24.8	26.0	0	0.8836	0.000175
											10	0.6984	
											20	0.4810	
											30	0.2719	
											40	0.0682	
604	0.9754	1300	7.13	2.86	25.4	0.000803	743.5	743.5	25.0	26.4	0	0.8856	0.000219
											10	0.6663	
											20	0.3971	
											30	0.1423	

(Series 600 cont.)

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
605	0.9787	1750	7.63	2.84	26.2	0.000811	745.0	745.0	25.0	26.6	0	0.9009	0.000260
											10	0.5927	
											20	0.2670	
											25	0.1220	
606	0.9724	2100	7.66	2.81	24.6	0.000800	737.7	747.6	25.0	26.4	0	0.8831	0.000259
											5	0.7668	
											10	0.6134	
											15	0.4574	
											20	0.2995	
											25	0.1470	
607	0.9731	2400	7.10	2.85	24.2	0.000802	737.2	747.6	25.0	26.6	0	0.8812	0.000276
											5	0.7495	
											10	0.5874	
											15	0.4154	
											25	0.0871	
608	0.9747	2400	7.57	2.83	26.0	0.000806	744.0	744.0	25.0	26.8	0	0.8775	0.000296
											10	0.5366	
											15	0.3522	
											20	0.1670	

SERIES 700

Freshly Distilled Cyclohexene

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
701	0.9739	650	4.32	1.00	23.8	0.000276	740.0	743.8	24.8	25.4	0	0.9223	0.000060
											15	0.8078	
											30	0.6929	
											45	0.5919	
											60	0.4883	
702	0.9753	800	4.72	1.00	23.8	0.000277	732.2	745.4	25.0	25.6	0	0.9050	0.000075
											15	0.7755	
											30	0.6421	
											45	0.5057	
											60	0.3740	
											75	0.2314	
703	0.9778	1000	4.11	1.00	23.8	0.000275	741.5	745.3	24.8	25.6	0	0.9112	0.000123
											15	0.6892	
											30	0.4635	
											45	0.2524	
											60	0.0273	
704	0.9751	1100	4.52	1.13	26.0	0.000307	742.1	746.2	25.0	26.0	0	0.8930	0.000137
											10	0.7272	
											20	0.5614	
											30	0.4064	
											40	0.2405	
											50	0.0722	

(Series 700 cont.)

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
705	0.9748	1300	4.47	1.09	23.8	0.000295	732.0	744.2	25.0	26.4	0	0.9050	0.000187
											10	0.6768	
											20	0.4561	
											30	0.2331	
											38	0.0416	
706	0.9755	1300	6.66	1.09	23.8	0.000313	728.3	743.8	25.2	26.6	0	0.9094	0.000191
											10	0.6793	
											20		
											30	0.2128	
											37	0.0615	
707	0.9740	1300	4.43	1.13	26.6	0.000302	734.0	745.9	25.0	26.2	0	0.9000	0.000184
											10	0.6818	
											20	0.4616	
											30	0.2382	
											38	0.0615	
708	0.9745	1500	4.13	1.10	23.8	0.000296	744.0	748.3	25.2	26.8	0	0.9128	0.000253
											10	0.6121	
											20	0.3074	
											28	0.0648	
709	0.9755	1600	4.58	1.10	24.0	0.000300	734.1	745.8	25.2	26.8	0	0.9129	0.000274
											10	0.5707	
											15	0.4164	
											20	0.2616	
											25	0.0920	

(Series 700 cont.)

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
710	0.9742	1600	4.30	1.12	23.8	0.000312	739.3	744.9	24.8	26.6	0	0.9050	0.000275
											10	0.5603	
											15	0.4072	
											20	0.2376	
											25	0.0788	
711	0.9744	1800	4.11	1.10	23.8	0.000299	743.0	746.6	25.0	27.0	0	0.8975	0.000303
											5	0.7078	
											10	0.5181	
											15	0.3368	
											20	0.1639	
712	0.9784	2000	4.39	1.10	23.8	0.000299	734.5	741.4	25.2	27.2	0	0.9000	0.000315
											5	0.7110	
											10	0.5131	
											15	0.3273	
											20	0.1433	
713	0.9806	2200	4.25	1.10	23.8	0.000300	740.2	744.0	25.0	27.2	0	0.9099	0.000352
											5	0.6724	
											10	0.4486	
											15	0.2425	
											20	0.0397	

(Series 700 cont.)

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
714	0.9756	2500	3.97	1.10	23.8	0.000298	743.3	745.6	25.0	27.0	0	0.8975	0.000358
											5	0.6644	
											10	0.4759	
											15	0.2425	
											20	0.0392	
715	0.9735	2500	4.34	1.09	23.2	0.000298	740.2	746.0	25.0	27.2	0	0.9075	0.000358
											5	0.6674	
											10	0.4511	
											15	0.2308	
											20	0.0237	

SERIES 800

Freshly Distilled Cyclohexene

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
801	0.9759	700	6.40	2.93	23.8	0.000813	741.3	746.4	25.2	25.8	0	0.9179	0.000114
											15	0.7036	
											30	0.4913	
											45	0.2976	
											60	0.1136	
802	0.9777	900	6.17	2.94	24.8	0.000812	746.0	746.0	24.6	25.6	0	0.9298	0.000149
											10	0.7239	
											20	0.5404	
											30	0.3616	
											40	0.1904	
803	0.9765	1000	6.54	2.93	23.8	0.000816	740.8	747.2	25.2	26.6	0	0.9273	0.000163
											10	0.7115	
											20	0.5181	
											30	0.3194	
											40	0.1260	
804	0.9763	1100	6.70	2.99	24.8	0.000831	739.3	747.9	24.8	26.0	0	0.9427	0.000187
											10	0.6912	
											20	0.4561	
											30	0.2395	
											35	0.1314	

(Series 800 cont.)

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
805	0.9736	1200	6.52	2.89	24.6	0.000813	747.0	747.0	24.6	26.4	0	0.9169	0.000224
											5	0.7785	
											10	0.6421	
											20	0.3690	
											30	0.1086	
806	0.9739	1300	6.67	2.93	24.0	0.000818	740.1	746.3	25.0	26.6	0	0.9149	0.000259
											10	0.5950	
											20	0.2847	
											30	0.1389	
807	0.9784	1500	6.91	2.88	24.0	0.000809	744.0	748.8	25.0	26.8	0	0.9153	0.000301
											5	0.7396	
											10	0.5557	
											15	0.3804	
											20	0.1985	
											25	0.0128	
808	0.9730	1700	6.77	2.91	24.4	0.000807	733.0	742.1	25.0	27.2	0	0.9161	0.000349
											5	0.7071	
											10	0.4903	
											15	0.2871	
											20	0.0788	

(Series 800 cont.)

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
809	0.9754	1700	6.71	2.93	25.6	0.000814	739.5	748.4	24.8	27.0	0	0.9397	0.000344
											5	0.7115	
											10	0.5057	
											15	0.3020	
											20	0.0937	
810	0.9758	1900	6.18	2.97	24.8	0.000817	742.2	747.5	25.0	27.6	0	0.9050	0.000384
											5	0.6649	
											10	0.4392	
											15	0.2053	
											20	0.0044	
811	0.9744	2200	6.28	2.99	24.8	0.000822	740.2	746.0	24.8	27.2	0	0.9352	0.000404
											5	0.6768	
											10	0.4529	
											15	0.2083	
812	0.9749	2400	6.88	2.89	23.6	0.000808	732.0	740.9	25.2	27.6	0	0.9075	0.000418
											5	0.6520	
											10	0.3869	
											15	0.1557	

SERIES 900

Freshly Distilled Cyclohexene

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
901	0.4998	2200	4.18	1.09	26.4	0.000290	739.5	743.3	25.4	26.4	0	0.9025	0.000169
											10	0.6788	
											20	0.4710	
											30	0.2673	
											40	0.0739	
902	0.4999	2200	7.06	2.89	25.0	0.000813	740.2	745.5	25.0	26.4	0	0.8901	0.000191
											10	0.6123	
											21	0.3503	
											28	0.1929	
											33	0.0863	

SERIES 1000

Freshly Distilled Cyclohexene

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
1001	0.9730	1300	6.34	1.01	22.8	0.000298	738.1	740.6	9.4	10.2	0	0.9012	0.000118
											10	0.7602	
											25	0.5486	
											40	0.3334	
											55	0.1247	
											63	0.0220	
1002	0.9731	1300	6.49	1.03	2.14	0.000303	741.5	744.8	9.4	10.2	0	0.9136	0.000118
											15	0.6988	
											30	0.4835	
											45	0.2695	
											60	0.0665	
1003	0.9742	1300	6.77	1.05	24.2	0.000308	737.8	740.1	12.5	13.4	0	0.9166	0.000141
											15	0.6636	
											30	0.4100	
											40	0.2522	
											50	0.0888	
1004	0.9736	1300	6.70	1.00	25.6	0.000293	740.0	742.8	16.3	17.3	0	0.9037	0.000162
											10	0.7037	
											20	0.5082	
											30	0.3165	
											40	0.1215	

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
1005	0.9741	1300	7.08	1.04	25.6	0.000305	741.0	744.3	22.2	22.7	0	0.9000	0.000179
											10	0.6773	
											20	0.4607	
											30	0.2373	
											40	0.0269	
1006	0.8572	1300	7.34	1.01	24.2	0.000299	736.8	738.8	32.0	33.4	0	0.9082	0.000214
											10	0.6443	
											20	0.3957	
											30	0.1576	
											35	0.0467	
1007	0.9744	1300	7.47	1.03	24.4	0.000305	739.5	741.8	39.5	41.1	0	0.9037	0.000248
											5	0.7557	
											10	0.6067	
											15	0.4681	
											20	0.3264	
											25	0.1853	

SERIES 1100

Freshly Distilled Cyclohexene

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
1101	0.9751	2500	7.06	0.99	21.4	0.000290	741.0	743.8	9.3	10.2	0	0.9092	0.000132
											10	0.7577	
											20	0.6042	
											30	0.4409	
											40	0.2893	
											50	0.1358	
1102	0.9761	2500	6.36	1.05	22.8	0.000307	737.5	741.3	9.4	10.2	0	0.9141	0.000135
											10	0.7478	
											20	0.5800	
											30	0.4179	
											40	0.2571	
											50	0.1049	
1103	0.9742	2500	6.94	1.04	26.2	0.000301	737.5	740.3	12.7	14.0	0	0.9037	0.000169
											10	0.6995	
											20	0.4983	
											30	0.3046	
											40	0.1057	
1104	0.9743	2500	6.67	1.13	25.8	0.000326	740.0	742.0	16.4	18.2	0	0.9107	0.000251
											10	0.5864	
											20	0.2819	
											25	0.1354	

(Series 1100 cont.)

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
1105	0.9732	2500	6.66	1.05	25.8	0.000305	740.5	742.8	21.2	23.0	0	0.9062	0.000275
											5	0.7367	
											10	0.5894	
											15	0.4018	
											20	0.2472	
1106	0.9770	2500	7.29	1.03	25.4	0.000306	737.5	739.5	21.2	23.0	0	0.9067	0.000269
											5	0.7458	
											10	0.5820	
											15	0.4137	
											20	0.2620	
1107	0.9752	2500	6.01	1.02	25.4	0.000291	738.0	739.3	29.0	31.6	0	0.8889	0.000374
											5	0.6735	
											10	0.4409	
											15	0.2299	
											20	0.0220	

SERIES 1200

Freshly Distilled Cyclohexene

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
1201	0.9751	700	8.44	2.77	24.6	0.000811	740.5	745.8	25.0	25.8	0	0.9174	0.000151
											15	0.6198	
											30	0.3355	
											40	0.1587	
											45	0.0768	
1202	0.9728	1000	8.49	2.82	27.0	0.000813	739.5	746.6	25.0	26.2	0	0.8995	0.000212
											10	0.6495	
											20	0.3911	
											30	0.1557	
											35	0.0570	
1203	0.9743	1300	10.30	2.68	25.0	0.000819	733.0	744.2	25.0	26.4	0	0.9037	0.000260
											5	0.7329	
											10	0.5616	
											15	0.4056	
											20	0.2398	
											25	0.0933	
1204	0.9745	1600	12.98	2.49	25.8	0.000809	736.5	744.9	25.0	26.6	0	0.8943	0.000306
											5	0.7057	
											10	0.4731	
											15	0.2955	
											20	0.1066	

(Series 1200 cont.)

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
1205	0.9739	1900	10.22	2.71	26.4	0.000822	736.0	744.4	25.0	26.6	0	0.9086	0.000332
											5	0.6839	
											10	0.4545	
											15	0.2571	
											20	0.0567	
1206	0.9747	2200	9.84	2.70	25.8	0.000812	735.2	743.3	25.0	26.6	0	0.8933	0.000346
											5	0.6909	
											10	0.4587	
											15	0.2695	
											20	0.0764	
1207	0.9737	2500	10.41	2.67	24.8	0.000818	733.5	742.6	25.0	26.6	0	0.8988	0.000342
											5	0.6904	
											10	0.4904	
											15	0.2843	
											20	0.1037	

SERIES 1300

Freshly Distilled Cyclohexene

Run No.	Catalyst	RPM	Flowmeter H	Flowmeter H'	Flowmeter T_f	Flowmeter R_f	P_a	Reactor P_r	Reactor T_i	Reactor T_r	Time	Conc.	R_r
1301	0.9782	700	12.03	2.56	26.6	0.000813	739.0	750.7	25.0	26.0	0	0.9186	0.000114
											15	0.6872	
											30	0.4830	
											45	0.3041	
											60	0.1457	
1302	0.9746	1000	11.46	2.61	27.0	0.000819	739.0	749.7	25.0	26.2	0	0.9223	0.000138
											15	0.6409	
											30	0.3848	
											40	0.2279	
											50	0.0888	
1303	0.9743	1300	13.07	2.50	25.8	0.000824	740.0	748.6	25.0	26.4	0	0.9087	0.000180
											10	0.6815	
											20	0.4533	
											30	0.2435	
											38	0.0863	
1304	0.9740	1600	11.65	2.56	25.6	0.000811	739.0	749.2	25.0	26.8	0	0.9062	0.000232
											5	0.7508	
											15	0.4700	
											20	0.3289	
											25	0.1952	
											30	0.0690	

(Series 1300 cont.)

Run No.	Catalyst	RPM	Flowmeter				P_a	Reactor			Time	Conc.	R_r
			H	H'	T_f	R_f		P_r	T_i	T_r			
1305	0.9748	1900	11.74	2.58	26.0	0.000816	740.0	748.9	25.0	27.0	0	0.9186	0.000298
											5	0.7354	
											10	0.5453	
											15	0.3764	
											20	0.2002	
											25	0.0443	
1306	0.9733	2200	11.89	2.52	25.4	0.000813	740.5	748.6	25.0	27.4	0	0.9087	0.000326
											5	0.7057	
											10	0.5052	
											15	0.3133	
											20	0.1185	
1307	0.9755	2500	11.36	2.60	26.4	0.000816	739.5	747.9	25.0	27.4	0	0.8988	0.000323
											5	0.7008	
											10	0.5077	
											15	0.3190	
											20	0.1329	

EXPERIMENTAL PROCEDURE

A description of the apparatus used in the experimental work has been presented in a previous section of the thesis. The fabrication of this equipment to give satisfactory operation was one of the major time consuming portions of the work. Considerable difficulty was experienced in making the flow system leakproof, and it was necessary to re-grind practically all the ball-socket joints.

The initial work with the equipment was made on the reaction catalyzed with Raney Nickel, and considerable data was taken before it was realized that this material did not lend itself to quantitative studies (see later section). The time spent on this portion of the work was of some value, as considerable experience was gained for operating the apparatus. Many problems were encountered and solved during this period, but since they are of no immediate importance they will not be discussed here.

While a change in catalyst produced more reproducible results, operating difficulties arose occasionally during the course of the work which had to be resolved. The procedure which follows is based upon an accummulation of knowledge of these experimental problems, and represents the best operating conditions and methods for obtaining reliable results.

Preliminary Preparations

To insure the absence of any free moisture in the reaction flask, preliminary to each experimental run the reactor and delivery unit were thoroughly rinsed with c.p. acetone and dried for at least fifteen minutes in an oven at 120°C. When the equipment had cooled, it was placed in the constant temperature bath and the entire flow system purged with nitrogen. It was important that prior to this operation the purifier had reached its operating temperature of 150°C, since the nitrogen contained traces of oxygen.

It was early discovered that the volumetric temperature coefficient of the cyclohexane was too great to measure accurately the quantity of the solvent added to the reactor with a volumetric flask. It was essential, however, that the volume be constant for each run, since any variation might produce a change in the catalyst concentration, and thereby one of the variables effecting the observed rate of reaction.

A constant volume of solvent could be insured by weighing the amount added, since the bath temperature was the same for the majority of runs. Thus, 390 gms. (about 500 ml.) of cyclohexane were weighed out on a large analytical balance to within one gram. A small portion (20 ml.) of this weighed solvent was placed in a small beaker, amd the remainder added directly to the reaction flask.

The appropriate amount of catalyst was weighed out by difference from a covered weighing bottle on an analytical balance. Since the same weight of catalyst was desired for most of the work, this involved several trial weighings to reach the correct amount. To prevent any pickup of moisture by the catalyst during the weighing, it was taken from the weighing bottle on the balance and placed immediately into the beaker containing the small portion of solvent previously mentioned. When the correct amount had been weighed, the catalyst and solvent were transferred quantitatively into the reactor.

The flow system was then completely connected and the reactor purged again with nitrogen to remove all air. At this point, the circulation of ice water through the condenser was started, and stirring begun. The entire system was tested for leaks by closing the exit vent stopcock and nitrogen pressure built up in the system to several hundred millimeters of mercury above atmospheric. If the manometers all showed a steady reading for five minutes, the system was considered tight. The hydrogen flow was then begun.

Initial runs indicated that a definite time period was required for the hydrogen to clear the system of the nitrogen. Thus the observed rate of reaction slowly built up to its steady state value. To eliminate this initial period, hydrogen was passed through the system for a period

of one half hour before the cyclohexene was admitted to the reactor. During this period, the flow rate, stirrer speed, pressure, and temperatures were all adjusted to the desired values for the particular run.

Collection of Data

With the completion of the half hour "saturation" period, the flow rates, temperature, stirrer speed, and other data were recorded and the actual run begun. 25 ml. of cyclohexene were added to the reaction flask through the sample withdrawal tube. The sampling device, such as is shown at the bottom of Figure 17, was attached to the reactor, a minute allowed for thorough mixing to occur, a sample then withdrawn, and the stop watch started.

For runs at atmospheric pressure, the suction bulb was sufficient to draw the sample into the sampling tube. At higher pressures no suction was required, while at below atmospheric pressures a water aspirator, attached by rubber tubing to the sampling tube, permitted the sample to be withdrawn. To insure a representative sample, solution was drawn into the sampling device and returned to the reactor several times before actually taking the sample.

To prevent additional reaction in the sample, due to the dissolved hydrogen, the solution was separated immediately from the catalyst by filtering into a small 2 oz. bottle with a ground stopper. While the solution was filtering, a

record of the flow meter readings, pressure, stirrer speed, and all temperatures was made. All temperatures were measured with I.C. thermocouples connected to a Leeds and Northrup Six-Point Speedomax Recorder.

In some cases it was possible to analyze the samples between samplings; if this was not possible, the sample bottles were capped and the solutions analyzed later. Each time a sample was taken, a record was made of all the operating variables. Data was taken from the exit flow-meter, although this meter was used only as a check to insure an excess flow of hydrogen to the reactor at all times; this data is not presented in this thesis. Room temperature was also recorded, but is of no real value in this work.

Generally all the operating variables remained constant during the run. Any change in any variable was immediately corrected if possible. For runs under vacuum some difficulty was experienced due to fluctuations in the pump action, but this did not affect the reactor pressure due to the control action of the manostat. Adjustment was required primarily to prevent too great a vacuum on the system beyond the exit side of the controller. The time intervals between samplings were determined by the observed rate of reaction. It was intended that at least five samples be taken for any single run. About five minutes was the shortest interval that could be used successfully between samplings.

Upon completion of a run, the system was purged for at least five minutes with nitrogen. The solution remaining in the reactor was filtered to recover both the catalyst and the solvent. The reactor was cleaned with carbon tetrachloride and dried with acetone.

Analytical Procedure

The analytical procedure for determination of the cyclohexene concentration in the samples was adopted from the method of Lucas and Pressman (4). It was based upon bromination of the double bond, and subsequent titration with thiosulfate to measure the excess bromine.

A 10 to 15% excess of 0.1 N bromate-bromide solution (23 ml.) was measured from a burette into a 250 ml. Erlenmeyer flask fitted with a ground joint. Into the upper member of the joint was sealed a tube which extended into the flask. A funnel was sealed to the upper end of this tube, along with a 1 mm. stopcock separating the funnel and flask. A second stopcock was sealed at right angles onto the tube between the first stopcock and the flask.

The funnel stopcock was closed and the flask evacuated through the second stopcock with a water aspirator. The vacuum was then held in the flask by closing both stopcocks. To release free bromine, 5 - 6 mls. of 6 N sulfuric acid were added through the funnel. A 2 ml. sample was then added

to the flask and 10 mls. of carbon tetrachloride used to rinse the sides of the funnel into the flask. Finally, 20 mls. of glacial acetic acid were added to facilitate the bromination in the organic layer.

The flask, continuing under a partial vacuum, was then wrapped in a dark cloth and shaken for at least two minutes (initial tests indicated the bromination was quite rapid and this period of time was sufficient for complete reaction). Upon completion of the shaking period, 20 mls. of a 20% potassium iodide solution was added to the flask, to convert the excess free bromine to iodine. The flask was then unsealed, and the iodine titrated with a 0.05 N thiosulfate solution, using starch solution as an indicator. The concentration of cyclohexene was calculated by the usual methods of quantitative analysis.

This procedure was tested initially with known solutions of cyclohexene in cyclohexane and found to be completely quantitative. Generally one determination only was made for each sample, unless there was some indication of substantial error.

Standard thiosulfate and bromate-bromide solutions were prepared in six-liter quantities. Sodium carbonate was added to the thiosulfate as a preservative. The thiosulfate was restandardized periodically with dichromate, but no appreciable change was ever noted. The bromate-bromide

solution was standardized with the thiosulfate solution.

Calculations

The observed rate of reaction for an experimental run was determined from the slope of the concentration-time curve, such as is plotted in Figure 2. The data for the runs generally fell on such a straight line. Occasionally the last sample taken showed some deviation, as would be expected in the region of very low concentration. In the few cases where irregular deviation was found, the best straight line representing all the points was used to determine the rate.

The hydrogen flow rates were calculated from the data taken with the flowmeters by the method of Whitman (8). The calibration curve for the meter is shown in Figure 10. From the recorded values of the pressure, temperature, and orifice meter manometer (inches of dibutyl phthalate), the flow rate could be calculated from the value of $\frac{W\ T^{1.75}}{P}$ found from this curve.

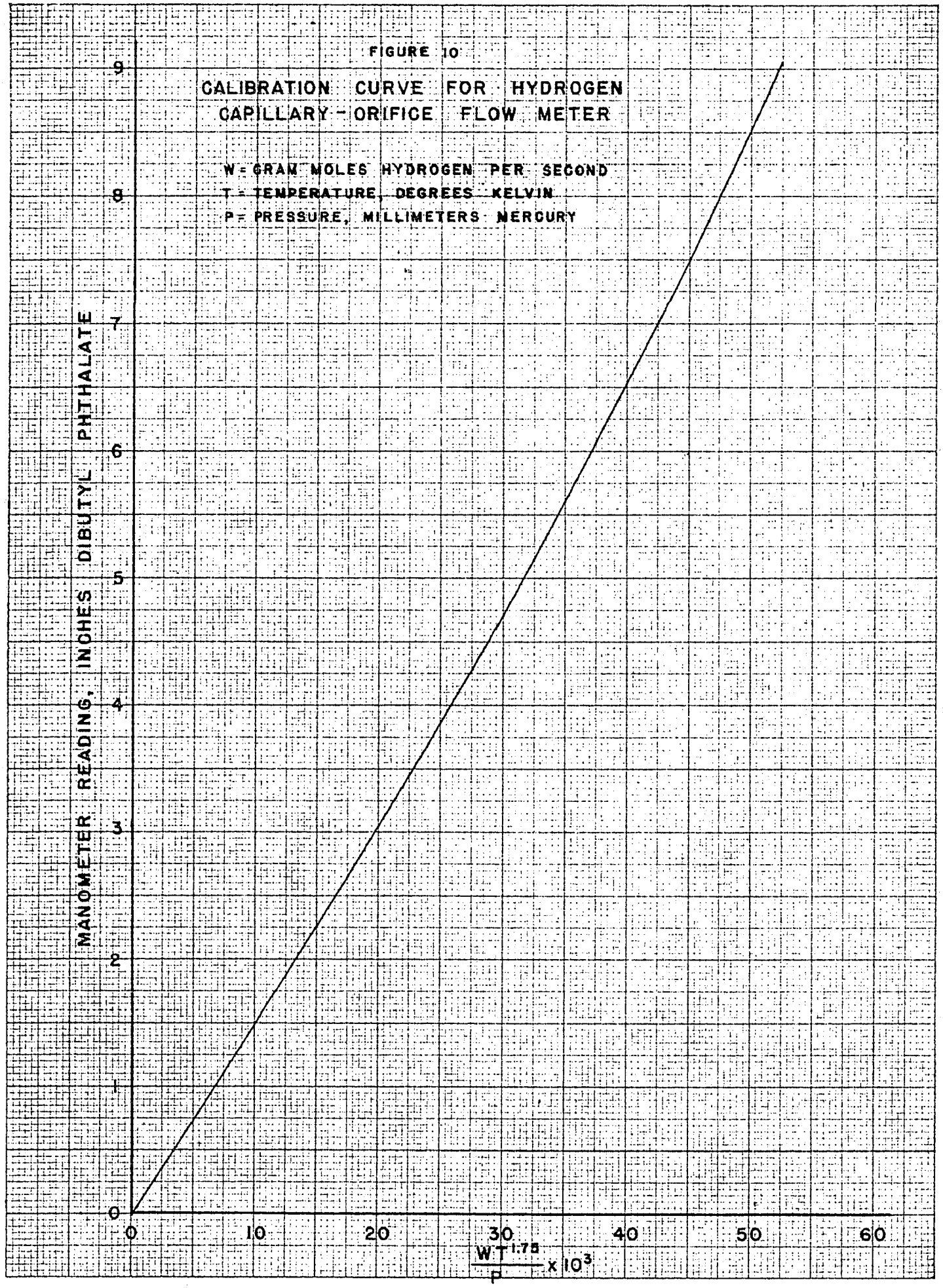
The thermocouple readings recorded by the Speedomax were converted to degrees by the calibration curve of Figure 11. Since the flowmeter thermocouples were sealed into the flow system, and it was not possible to calibrate them directly, the calibration curve is based upon the reaction flask thermocouple. This curve, however, was

also used in preparing the calibration curve for the flow-meters, so no error in its use should be involved.

FIGURE 10

CALIBRATION CURVE FOR HYDROGEN CAPILLARY-ORIFICE FLOW METER

W = GRAM MOLES HYDROGEN PER SECOND
T = TEMPERATURE, DEGREES KELVIN
P = PRESSURE, MILLIMETERS MERCURY



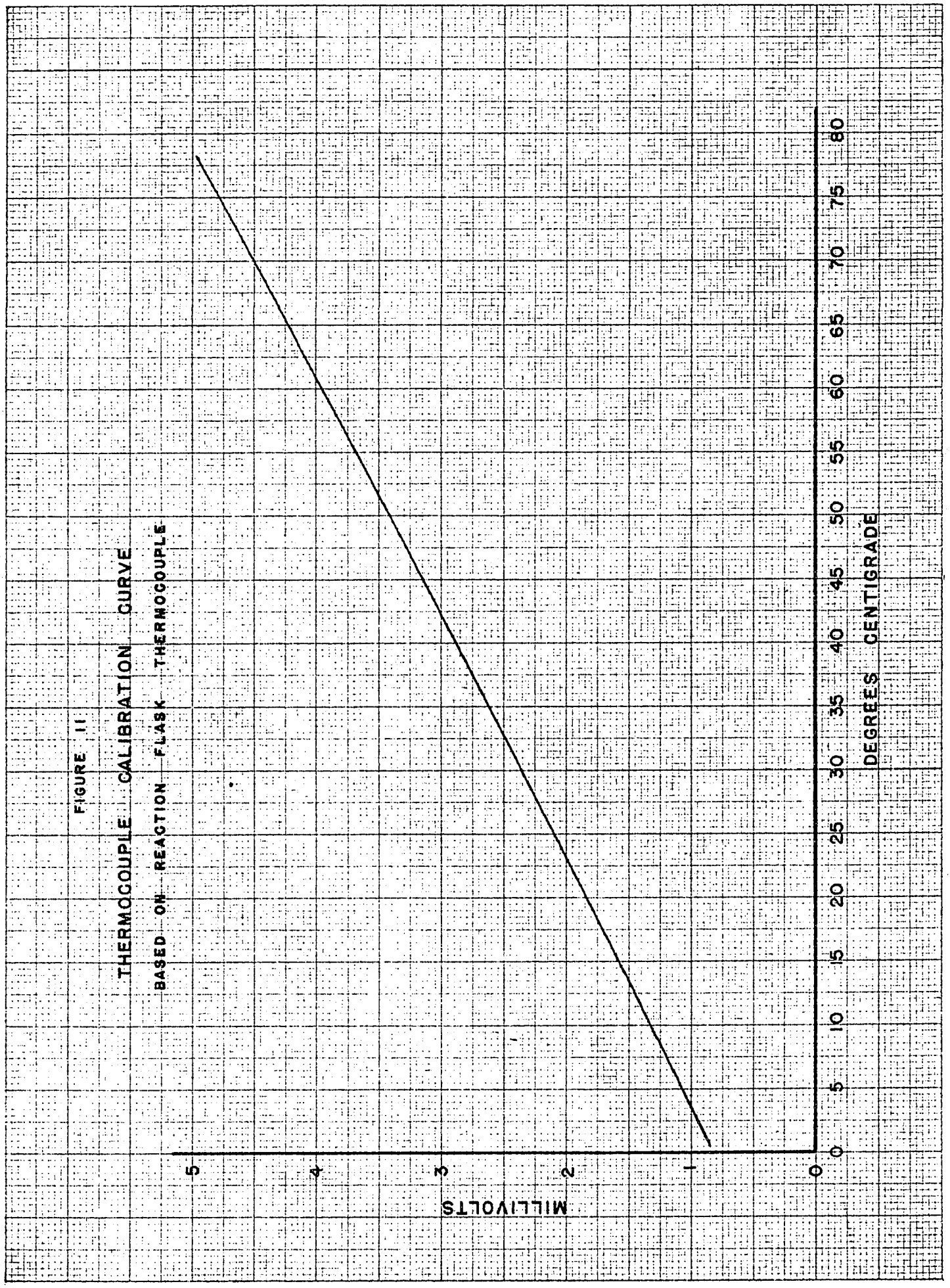


FIGURE II

REPRODUCIBILITY OF DATA

The reproducibility of the data was of major concern throughout the experimental work. In this connection primary reference is made to the observed rates of reaction for a given set of operating conditions. That is, the known variables affecting the rate could be controlled well within the limits of general agreement of the observed rates.

The calculation of the reaction rate from the concentration-time plots has been previously discussed. The accuracy of the analysis of the samples, and probably more properly, the success in obtaining representative samples, could be judged on the basis of how well the individual points fell on a straight line. Since generally it was found that the data determined a straight line surprisingly well, it is felt that such data is reasonably precise. Of course, some deviations were found, but these were never more than 2%, never indicated a regular pattern, and it was never necessary to use least squares or a similar method to determine the rate from the concentration plots.

For a given series of runs in which only one variable was being studied, the other known variables could be held constant to any degree desired. Thus inspection of the tabulated data shows that the reactor pressure and catalyst weight generally varied as little as $\pm$ 0.5%, and the flow

rate ± 1-2%, for a given series of runs. The flow rate was not controlled more closely simply because it was felt that it was not warranted. The accuracy of the stirrer speed measurement has to be taken as that claimed for the instrument used.

A run for which the observed rate was not in general agreement with the trend of other runs in the series was usually easily detected at the time. Such runs were repeated, and generally an explanation found for the deviation. No data was discarded without a sound reason for doing so. About 40-50 runs in addition to the data presented in this thesis were made in the course of the work. A good portion of these runs were faulty due to equipment failure, inadequate hydrogen purification or drying, improper preparation of catalyst, or similar reasons. To insure reproducible data, check runs at given conditions were made at regular intervals during the work.

The rise in temperature of the contents in the reactor flask to a constant value somewhat dependent on the observed reaction rate has been mentioned previously. It is highly probable that this factor influences the results to some degree and that the effect was most likely not the same for different operating conditions. This effect no doubt accounts for some of the observed deviations. However, the magnitude of this factor for the observed rise of 1 to 2°C can be seen from Figure 7 to generally be of a relatively

minor import.

It is felt that the variations in observed reaction rate were in part determined by uncontrollable and perhaps unknown factors simply inherent in the system and procedures used. For example, indications are that mixing efficiencies were somewhat unstable at higher stirrer speeds. The possibilities of such factors in experimental work such as this are very real, and also very complex. Their overall effect is negligible in a series of runs, but for any single run may have a marked influence. Indicative of this is the general agreement of the data in this work, although some individual data shows random deviations, i.e. the plotted data is not extremely "smooth".

The data is reproducible within reasonable limits. With the same apparatus and materials, the data could be reproduced to give the same plots as presented in this work, and would indicate the same conclusions, although comparison of individual points of data might show slight variations. But this variation would be completely random, and would in no way indicate previous data was faulty. Considering the kinetic data presented in the literature, and the complexities involved in this work, it is felt that the data taken and presented indicates surprisingly good accuracy and reproducibility.

THE PURITY OF CYCLOHEXENE

Previous reference has been made to the autoxidation of stored cyclohexene and its effect upon the observed rate of reaction. Kinetic studies reported in the literature which employed cyclohexene as a reactant have made no reference to this factor, although Figure 12 indicates that the impurity can appreciably alter the experimental results. The data used for the plot were from Series 100, which employed cyclohexene stored approximately two and a half to three months. The apparently greater effect of the impurity at higher stirring speeds may be due to the gradual increase in impurity concentration, or to a difference in effect with a change in control of the observed rate. That is, the impurity may depress the observed rate more in the duo control region than that where mass transfer prevails. The effect of an increase in concentration may be seen by comparing the data of Series 600, which show lower observed rates at the higher speeds than that of Series 100, although the flow rate was higher.

General agreement is found in the literature that the initial product of the autoxidation is the hydroperoxide. The point of attack of molecular oxygen is at the carbon atom adjacent to the double bond, and not the double bond itself. Royals (7) has suggested that the autoxidation is

a free radical chain reaction, wherein a free radical must be produced by some process to initiate the reaction.

The steps of such a chain reaction are pictured in Figure 13. It is likely that the reaction of oxygen on the double bond of the cyclohexene produces the initial free radical (I). This free radical then initiates the reaction proper by reacting with cyclohexene to produce a second free radical (II). The process propagates itself by reaction of the second free radical with oxygen to form the third free radical (III), which in turn reacts with cyclohexene to give the hydroperoxide, and regenerate the free radical II. The chain reaction continues as the hydroperoxide decomposes to give various products.

This effect was observed in this work, as the hydroperoxide concentration in the cyclohexene could be determined by addition of potassium iodide and subsequent titration of the liberated iodine with thiosulfate. The rate of autoxidation of freshly distilled cyclohexene could be increased by bubbling oxygen through it. By analyzing such test samples, it was observed that the hydroperoxide concentration increased to a certain limiting value, which corresponded closely to its concentration in material which had been stored for a number of months. It was concluded that other compounds were being formed by the hydroperoxide,

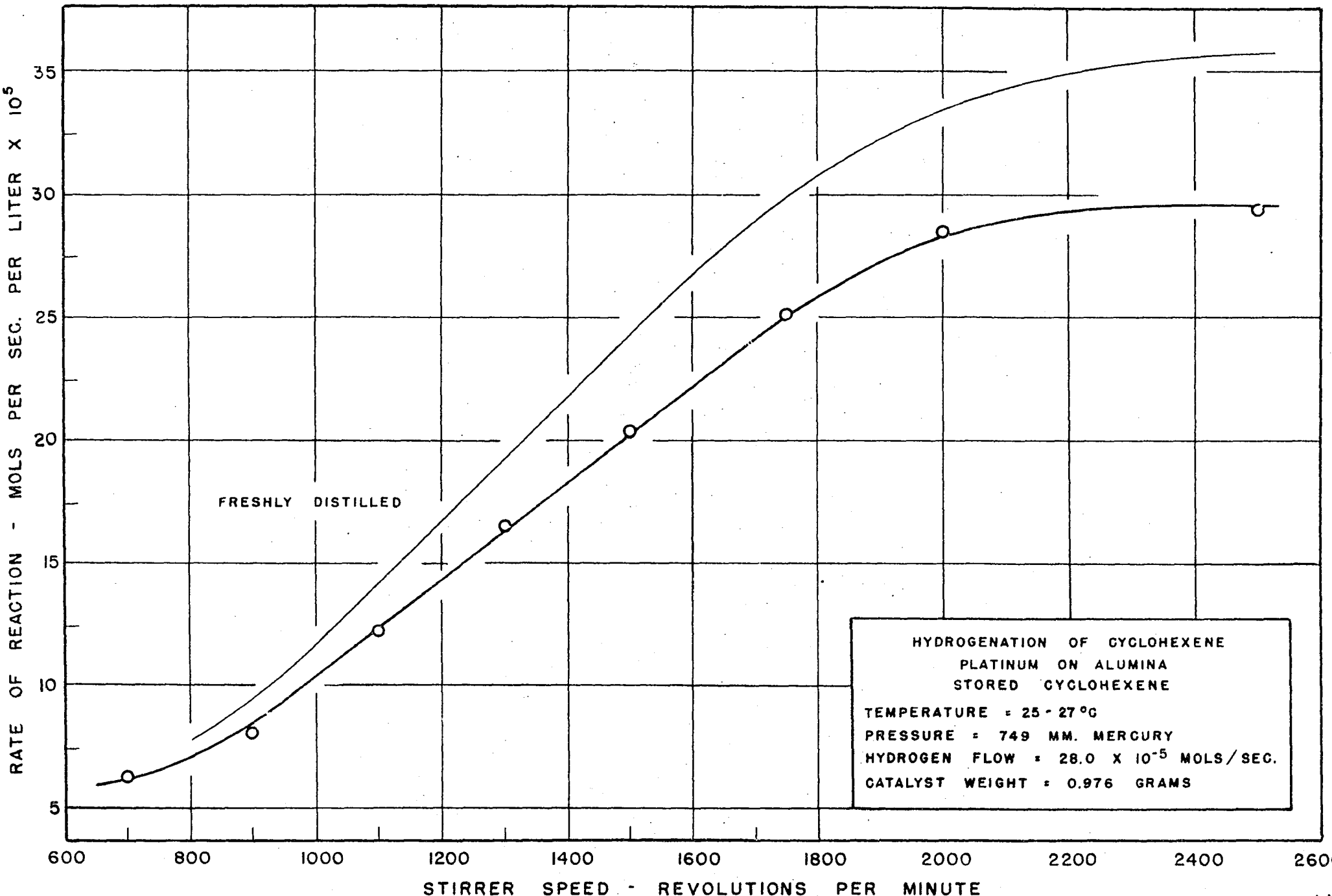


FIGURE 12 EFFECT OF AUTOXIDATION PRODUCTS OF CYCLOHEXENE ON RATE OF REACTION

its concentration reaching some "equilibrium" value while the other material continued to build up in the cyclohexene.

Royal has pointed out some seven different compounds that have been isolated from the autoxidation of cyclohexene, such as cyclohexen-3-ol, cyclohexanone, adipic acid, hydroxycyclohexane, and others. He comments, "There can be little doubt that the initial product of autoxidation of an alkene is an allylic hydroperoxide; far too little is known, however, about the subsequent transformations of such hydroperoxides and the dependence of these transformations on experimental conditions".

A good many of the decomposition products found had been formed under acid or alkaline conditions, and could be removed from consideration for the cyclohexene. The most plausible final product, and that which has been most frequently observed, is cyclohexen-3-ol. This is formed by a bimolecular reaction of the hydroperoxide with cyclohexene, pictured in Figure 13, wherein the hydroperoxide behaves like a peracid in affecting epoxidation of the alkene linkage. An infrared analysis of a sample of cyclohexene stored for three months definitely indicated the presence of an alcohol. Although absorption data was somewhat limited for this type of compound, it appeared that this was the principal impurity.

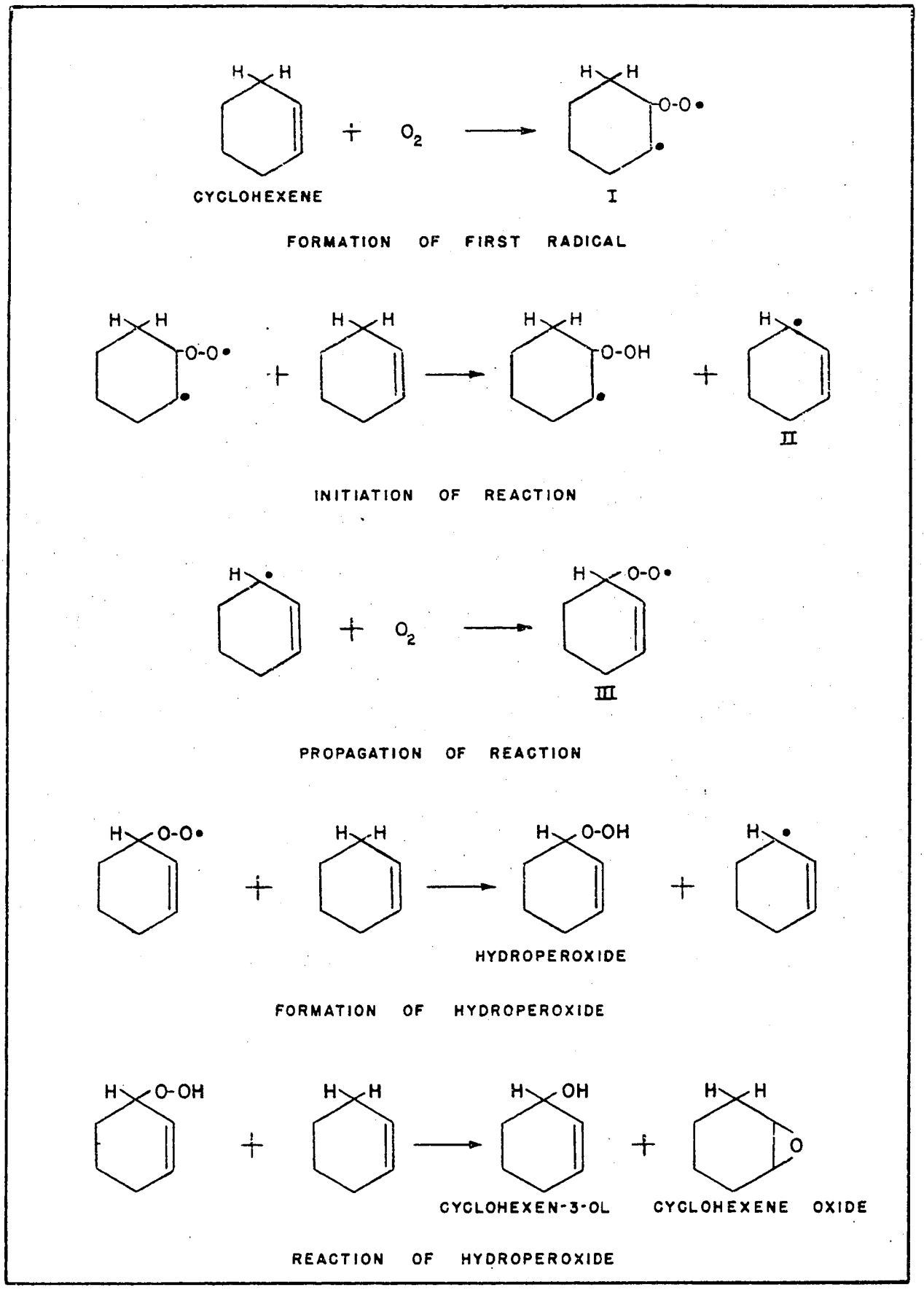


FIGURE 13 AUTOXIDATION OF CYCLOHEXENE

It is interesting to speculate upon the reason for the effect of the alcohol impurity in the cyclohexene upon the observed rate of reaction. Since catalyst used with the impure material could be reactivated to its initial activity simply by washing and drying, it is evident that the alcohol was not a permanent "poison" such as is found with sulfur and metallic catalysts.

It also does not seem plausible that the alcohol even temporarily "poisoned" the catalyst surface. No values could be found for the molecular cross-sectional area of the cyclohexen-3-ol in an adsorbed monomolecular layer, although values of 23.3 sq. Å and 23.8 sq. Å have been reported for benzene and phenol, respectively (1). The total surface area of the platinum catalyst has been measured as 80 sq. meters/gram (2). Using an estimated value for the cross-sectional area of cyclohexen-3-ol as 23.5 sq. Å, and the given value for the catalyst surface, calculation shows that only 0.054 grams of the alcohol would be required to completely cover the surface of one gram of catalyst in a monomolecular layer. This corresponds to about .06 ml. of the impurity in 25 ml. of cyclohexene, or about 0.2%. Although no quantitative measurements were made, it would seem reasonable that the cyclohexene contained at least this amount of the alcohol. If the impurity temporarily "poisoned" the surface, it would seem that no reaction

should have been observed at all.

It is proposed that the effect of the alcohol in the cyclohexene on the observed reaction rate was due to the competitive adsorption of the two materials. It has already been mentioned that the cyclohexene appeared to be strongly adsorbed, i.e. its concentration on the surface was constant even to very dilute solution. If the cyclohexe-3-ol were similarly strongly adsorbed, the two solutes would have to share the available surface. Assuming monomolecular adsorption as described by the Langmuir equation, for each material alone may be written:

$$\theta_C = \frac{b\ a\ C_C}{1 + a\ C_C} \qquad \theta_{alc.} = \frac{b'\ a'\ C_{alc.}}{1 + a'\ C_{alc.}}$$

On the linear portion of the isotherm where the surface concentration is unaffected by the concentration in solution:

$$\theta_C \simeq b$$
$$\theta_{alc.} \simeq b'$$

When both solutes are present in the solution, the factors determining the division of the surface between the two are unknown. As an approximation, it may be that:

$$\frac{\theta_C}{\theta_{alc.}} \simeq \frac{b}{b'} \simeq \text{Constant}$$

Thus for a limited range of concentrations such as employed in this study, the "equilibrium" ratio of the two materials on the catalyst surface may remain approximately constant, being almost independent of the concentrations of the materials in solution.

In this work, no specific data were taken to confirm such a postulate. Since the concentration of the impurity was very much lower than that of the cyclohexene, it would seem that the alcohol would have to be more strongly adsorbed by the catalyst for its surface concentration to remain independent of its concentration in solution. The "equilibrium" ratio would then favor the alcohol, and the surface occupied by it would not be in proportion to its concentration in solution. That is, even though the impurity was present in very small amounts, it occupied a relatively large portion of the surface.

There is no reason to believe that the alcohol impurity itself was not hydrogenated under the experimental conditions employed, i.e. cyclohexen-3-ol to cyclohexanol. It is possible however, that due to the substituted OH group the rate of reaction for this material would be slower than for cyclohexene. The rates of reaction for both materials would be constant for most of a run, since their concentration on the catalyst surface remained essentially constant as just discussed. As the method of analysis could

not distinguish between cyclohexene and cyclohexen-3-ol, the overall effect would be that the observed rate of reaction based on the cyclohexene concentration (of which the alcohol would be part) would be lower than that for cyclohexene alone. It would seem that the rate of hydrogenation of the alcohol would have to be considerably slower than that of the cyclohexene for its presence to have the magnitude of effect found in this work.

This proposed mechanism reasonably explains why the effect of the impurity was not indicated during a single run. If the two materials were not strongly adsorbed, their concentration on the surface would be continually changing as determined by the ratio of their concentrations in the bulk of solution. Thus more and more of the alcohol would be adsorbed since its bulk concentration would be increasing relative to cyclohexene due to its slower hydrogenation rate, and the overall observed rate would have been continuously decreasing. While the suggested effect of the impurity is speculative, it does seem to correspond to the observed facts.

THE AGING OF RANEY NICKEL CATALYST

In the initial selection of a catalyst for the reaction to be studied, Raney nickel was chosen because of its demonstrated utility for hydrogenation at atmospheric conditions. The literature abounds with studies which employed this catalyst, and several were found which reported some data for the hydrogenation of cyclohexene in batch systems.

Thus considerable time was spent in investigating the various methods for preparation of this catalyst from the powdered aluminum-nickel alloy, and in developing suitable handling procedures for this work. Preliminary tests were made in a Parr apparatus for hydrogenation to determine the proper operating quantities, and the catalyst activity. Although no appreciable difference in the initial activity of the catalyst prepared at different times by different methods was found, a large quantity of the catalyst, sufficient for all future work, was prepared to eliminate any such variations. This catalyst was stored under cyclohexane.

A considerable number of early runs in the flow apparatus using the Raney nickel were made. Because of initial difficulties with the equipment, a goodly number of runs were made before any desired operating conditions

could be achieved. When initial conditions were finally duplicated, the observed rate of reaction was found to be somewhat lower than previously.

The collection of data was continued, however, as there was some doubt as to the accuracy of the control of some of the operating variables. As the experimental procedure became refined, check runs showed a continual decrease in the observed rates of reaction under given conditions, and it became apparent that the activity of the catalyst was declining.

A report in the literature (3) of this effect indicated that the decline in activity is rapid at first but then decreases until fairly constant catalyst activity is reached. It was also reported that the specific surface of the catalyst decreased paralleling the activity. Theorizing that the decline in activity might be caused by a gradual change of the amorphous structure of Raney nickel to a more stable crystalline structure, attempts were made to "age" the catalyst to a constant activity. The aging method employed was essentially that of heating the catalyst for a period of time to increase the velocity of the change. Several different conditions were used, but without success.

The data presented in Series 000 represents a small portion of that taken using Raney nickel catalyst. The

particular data shown illustrate the aging effect and are all at the same operating conditions; the data is plotted in Figure 14. The scattering of the data on the plot is indictative of the uncertain control of operating conditions at that time. The data seems to indicate a fairly linear decrease in catalyst activity with "natural" aging, rather than the initial rapid decline reported in the literature.

Since the properties of Raney nickel catalyst were not pertinent to this work, once it was determined that the catalyst could not be used quantitatively, a new catalyst was selected. The aging effect of Raney nickel is presently being studied by another investigator (6).

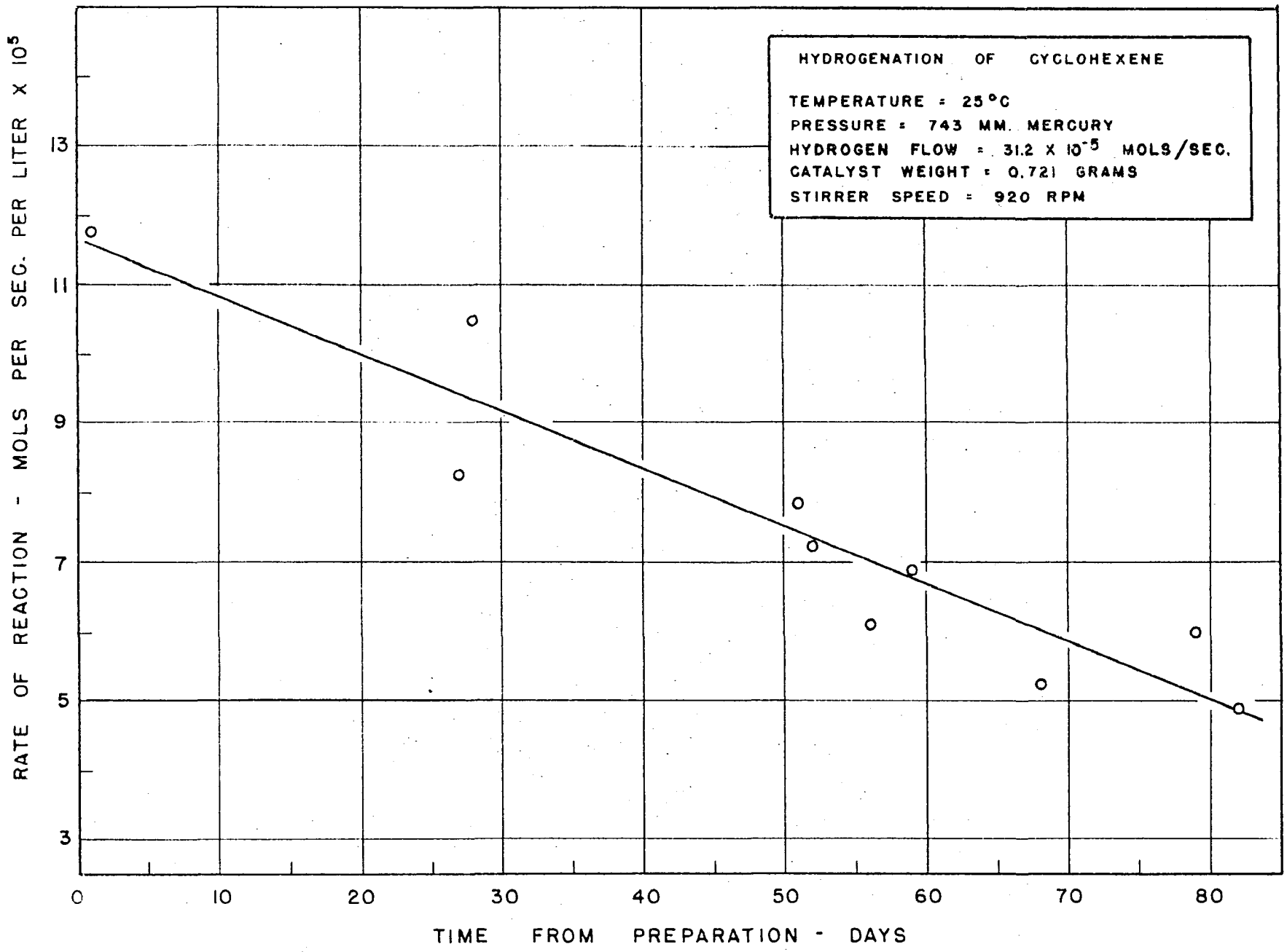


FIGURE 14 DECREASE IN ACTIVITY OF RANEY NICKEL CATALYST WITH TIME

OVERALL EQUILIBRIUM CONSTANT

Before initiating the experimental work, the following thermodynamic calculation was made to determine the reversibility of the chosen reaction, to insure that it would be of no importance under the conditions employed.

Standard Free Energy of Formation (5):

Cyclohexene (1): $\Delta F^\circ_{298^\circ} = 18{,}200$ cal./mol

Cyclohexane (1): $\Delta F^\circ_{298^\circ} = 6{,}800$ cal./mol

Hydrogen (soln., 1 atm.): $\Delta F^\circ_{298^\circ} = 0$

For the reaction:

Cyclohexene (1) + Hydrogen (1 atm.) = Cyclohexane (1)

$$\Delta F^\circ_{298^\circ} = 6{,}800 - 18{,}200 = -11{,}400 \text{ cal./mol}$$

By thermodynamic considerations:

$$\Delta F^\circ = - R\,T \ln K_a$$

where K_a = equilibrium constant based on activities

Therefore:

$$\log K_a = \frac{-\Delta F^\circ}{2.3\,RT} = \frac{-(-11{,}400)}{2.3(1.987)(298)} = 8.337$$

And:

$$K_a = 2.17 \times 10^8$$

The largest part of the data was taken at the temperature of the above calculation. It is seen that K_a is so large that the reverse reaction is negligible.

PICTURES OF EXPERIMENTAL APPARATUS

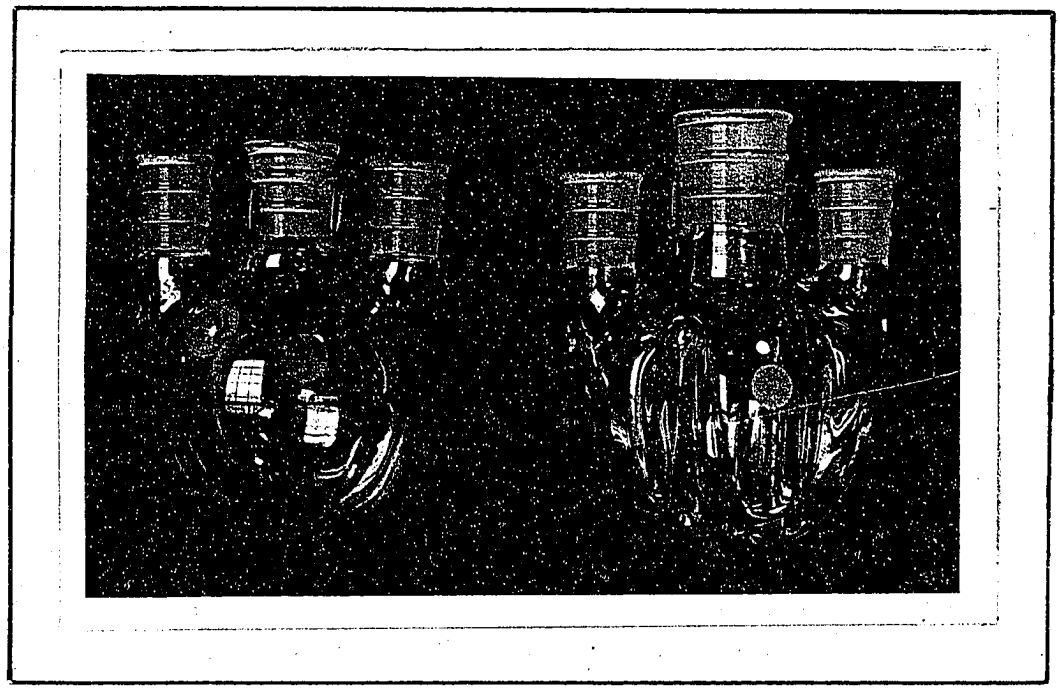


FIGURE 15 REACTION FLASKS

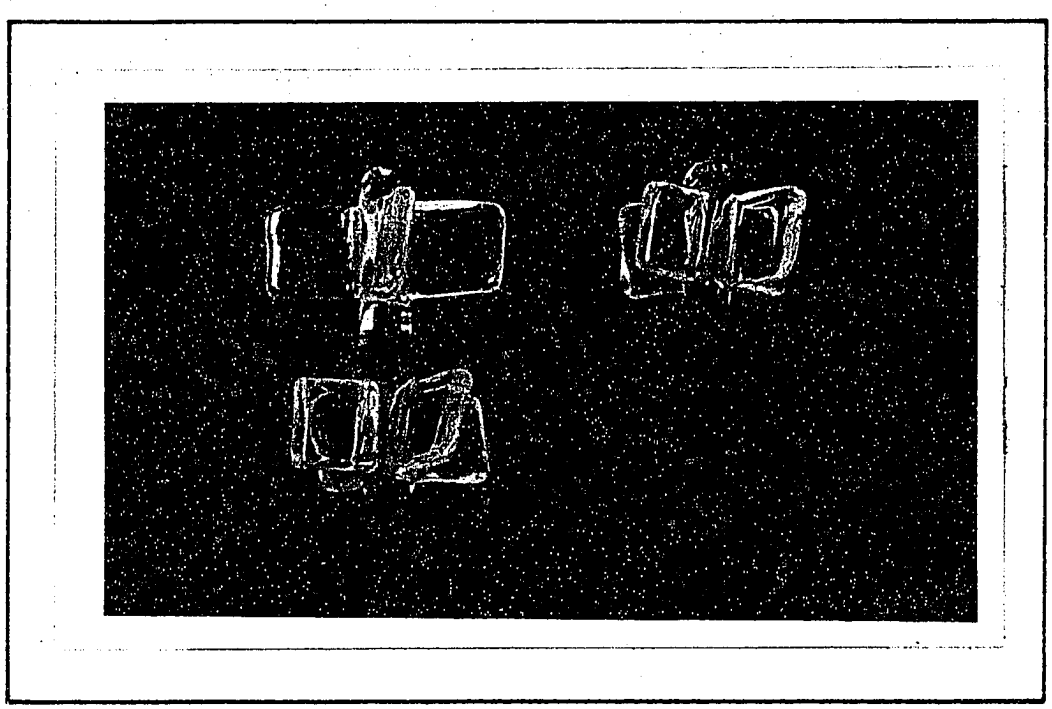


FIGURE 16 STIRRER PADDLES

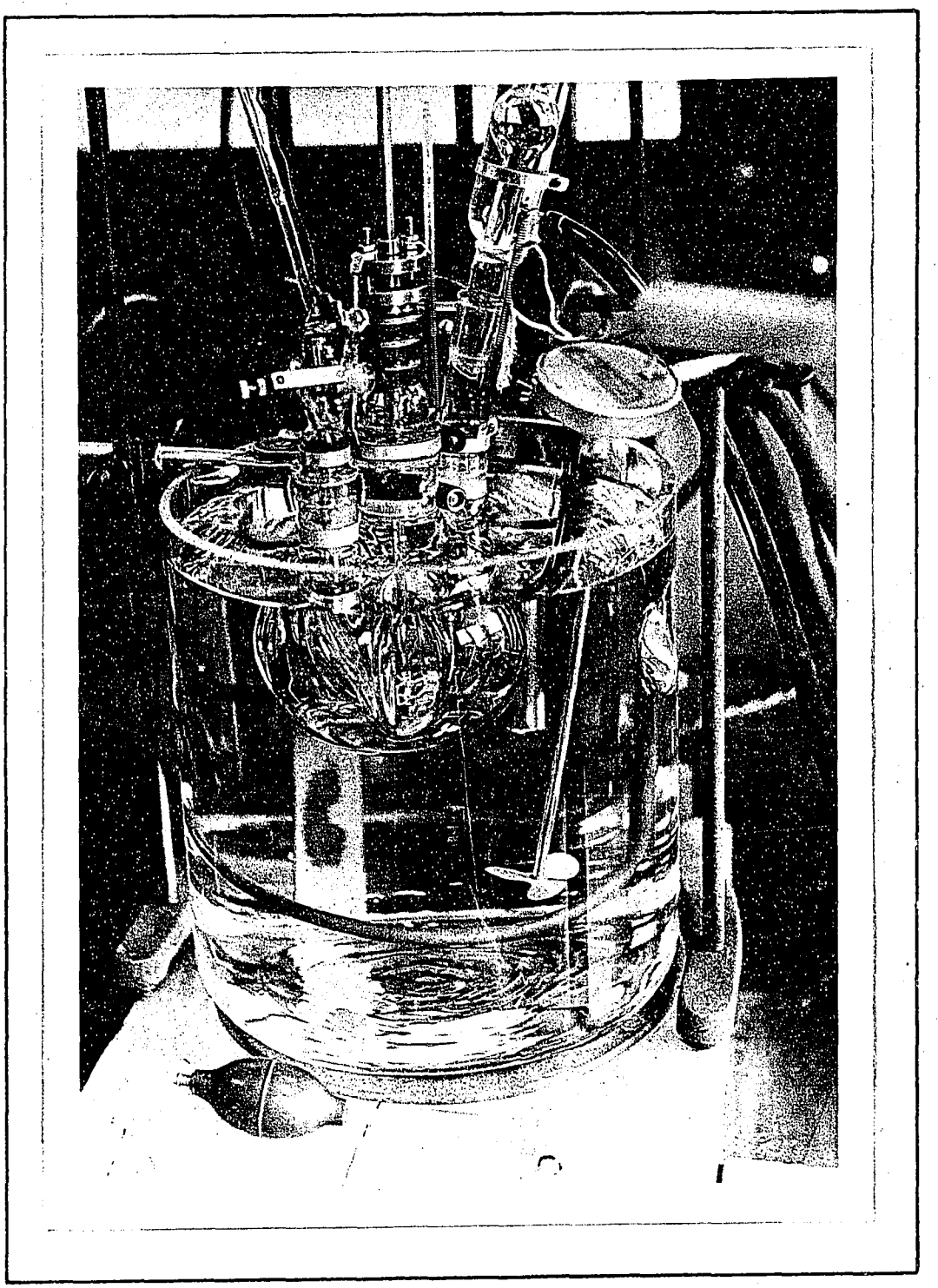


FIGURE 17 REACTION FLASK AND CONSTANT TEMPERATURE BATH

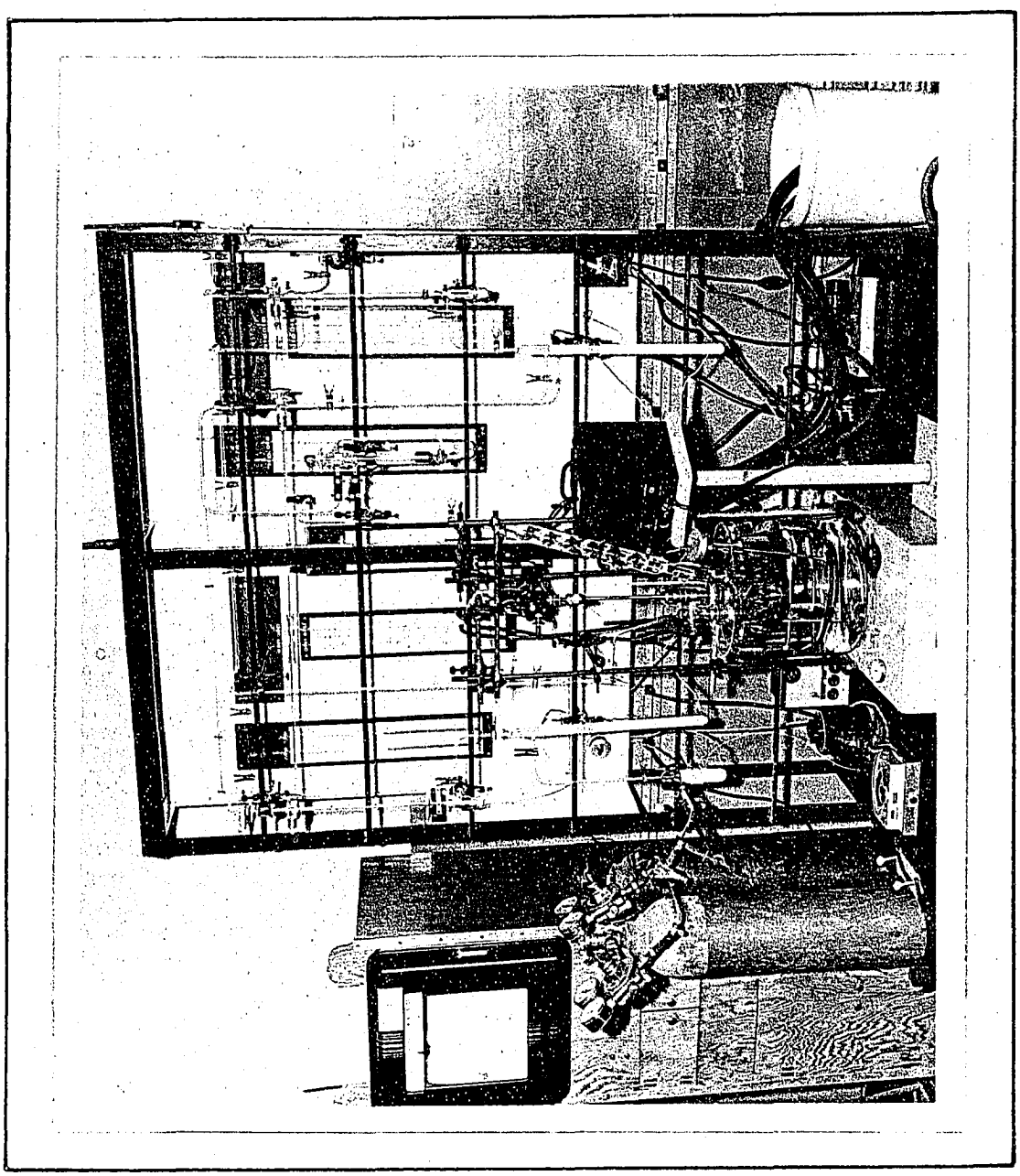


FIGURE 18 EXPERIMENTAL APPARATUS

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