MASS TRANSFER IN THE SLURRY PHASE

HYDROGENATION OF ETHYLENE.

by

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MAY, 1955.
The object of the research.
Previous investigations.

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The purpose of this work is the presentation of a quantitative study of the rate of mass transfer occurring in a transport rate controlled exothermic heterogeneous reaction.

The reaction under investigation is the slurry phase hydrogenation of ethylene on a Raney-nickel catalyst. In the slurry phase, gas, liquid and solid phases are in contact with one another. In this system, when the reaction is proceeding steadily, the rate of mass transfer of hydrogen and ethylene into a liquid of constant gas concentration can be evaluated. This can be compared with the corresponding rates for hydrogen and ethylene measured separately.

For the sake of clarity, the work is divided into three units: Part I deals with a study of process variables such as temperature, inlet gas rate, etc., on the reaction rate of the slurry phase hydrogenation of ethylene; Part II presents a study of bubble properties in bubble swarms and an estimation of the area of interfacial contact of bubble swarms; and Part III presents a
a study of the instantaneous absorption rate of both hydrogen and ethylene into toluene under conditions similar to those in the previous sections.

The controlling 'step' for the slurry phase hydrogenation of ethylene is proposed.


PREVIOUS INVESTIGATIONS.

In a preliminary survey of the slurry phase hydrogenation of ethylene, Aikman (3) has evaluated the effect of the process variables on the reaction rate. Because absorption rate data for the reactants, in the liquid in which the catalyst was supported, was not determined, there was doubt as to whether the overall reaction was controlled by the reaction at the catalyst surface or by diffusional processes. Also, the high value of the reaction rate at high temperatures, implying low solubility of both hydrogen and ethylene in the liquid medium, could not be explained alone, by the increase in diffusivity of the reactants in the liquid with increase in temperature of the system. Maximum reaction rate was obtained with an inlet gas rate of \( \text{H}_2 : \text{C}_2\text{H}_4 :: 2 : 1 \) and not as would be expected with \( \text{H}_2 : \text{C}_2\text{H}_4 :: 1 : 1 \) inlet gas ratio.

The results obtained in Part I of this work agree favourably with those of Aikman. It is the aim of this work to clarify and solve these afore-cited problems.
INTRODUCTION.

Most chemical processes can be separated into a number of reactions, each complete in itself and proceeding from reactants to products at a definite reaction rate. The overall rate of the process is thus controlled by the reaction having the slowest reaction rate which is termed the 'controlling step'. The latter, itself, may be conditioned by a number of factors, among which the most important are: diffusion of reactants to the reaction zone; the reaction rate itself; and transfer of products of reaction away from the reaction zone.

Perhaps the most studied diffusion-controlled reaction is the high temperature combustion of carbon. Hottel and co-workers (63), have reported several studies pertaining to this system. However, because of uncertainties in the kinetics of the system, high temperature reaction rates are not yet on a sufficiently quantitative basis from which mass transfer data may be evaluated.

In recent years there has been an active interest in gas-liquid interphase transfer. Although the mechanisms and theories for the absorption of a gas by a liquid show little or no agreement, it can be said that mass transfer data is characteristic only of that system from which it is obtained. The type of dispersion of /
of one phase in another may be selective for one particular absorption process and not for another; for example, if a gas of low solubility is required to be absorbed in a liquid, then dispersion of small amounts of gas in a large quantity of absorbent with large interfacial contact favours high absorption rates as well as the economy of the process, whereas in the case of a very soluble gas, the dispersion of large amounts of gas in a small quantity of liquid favours optimum absorption rates.

The methods of studying a diffusion-controlled reaction and absorption with chemical reaction where the absorption rate is the controlling 'step' are legion. Among the standard types of apparatus applicable may be mentioned those of: the wetted-wall and totem-pole columns (84); the rotating drum method of Danekwerts and Kennedy (26); absorption of gases by liquids from single bubbles and bubble swarms; and variation of the hydrodynamics of these systems as found in centrifugal gas absorbers and Venturi scrubbers.

The transfer data obtained from such laboratory experiments supplies the necessary physico-chemical data required for industrial design and provides information of academic interest about reaction kinetics in solution.

The /
The industrial application of absorption with subsequent reaction is self-evident in the removal of hydrogen sulphide from wash liquors by caustic soda solutions (7, 76); the selective quick-wash process for the removal of hydrogen sulphide in mixtures of hydrogen sulphide and carbon dioxide by diethanolamine solutions (6); the removal of carbon dioxide from coke oven and synthesis gas; the fermentation of bacteria controlled by the rate at which oxygen is absorbed by the bacteria (60, 94); and the decomposition of crude sewage by the activated sludge process (61, 62).

Morris and Jackson (84) effectively present an analysis of the design and equipment used in industrial absorption processes.
PART I.

THE SLURRY PHASE HYDROGENATION OF ETHYLENE.

The Slurry Phase Process.

In the liquid suspended catalyst or slurry phase process the reacting gases are passed through a suspension of finely divided catalyst in a high boiling point oil. The catalyst is maintained in suspension either by the velocity of the gas stream, by mechanical agitation or by circulation of the slurry through an external cooling system. In the vapour phase or 'dry-way' hydrogenation of ethylene, where the control of mass and temperature equilibrium is difficult, the slurry phase technique offers the advantage of simplicity of reactor design; efficient cooling of the catalyst particles; ease of catalyst replacement without interruption of the process and rapid conduction of heat of reaction and absorption of the gases from the reaction zone by the circulating slurry.

An advantage of the use of the slurry phase in the Fischer-Tropsch reaction is that the end-products can be varied by changing the conditions. For example, the use of a nickel-aluminium-kieselguhr catalyst suspended in a heavy sulphur-free oil produces mainly methane whereas /
whereas an iron catalyst suspended in anthracene oil yields paraffin waxes. The apparatus and design problems in liquid phase catalytic synthesis have been discussed by Fischer and Pichler (45). Nevertheless, the two main disadvantages of conducting a reaction in a liquid medium are, firstly; the disposal of reaction products where either the reaction may be slowed down by accumulation of reaction products which themselves may be converted to an unwanted byproduct, and secondly; the larger space requirements of the reacting system.

To overcome these difficulties, the Standard Oil Development Co., (B.P. 496, 159, 1938), have patented a process in which the reaction is performed in a fifty tray bubble cap tower using a catalyst suspension of finely divided nickel and active constituents, in a sulphur-free paraffin wax. The yield from this plant is claimed to be a gallon of liquid hydrocarbon for every $10^3$ cub. ft. of synthesis gas (13).

The slurry phase process is one of the most flexible reaction techniques, the scope of which ranges from the curing of the 'greenness' of whisky by hydrogenation (analogous to the hydrogenation of oils and fats in that the unpleasant odour and taste inherent in the original oils are removed) to that of the Fischer-Tropsch process.
Apart from the slurry phase and fixed bed technique, where the catalyst is in the form of rods or supported on gauze frames, is the fluidised bed reactor. In this process the catalyst is maintained in continual movement by the incoming vapours, the rate of which is sufficient to balance the gravitational force on the catalyst particle. The reaction temperature is controlled by drawing off an adequate proportion of hot catalyst and replenishing the reactor with cold catalyst. A comparison of these three techniques, namely, fixed bed, fluidised bed and slurry phase is described by Hall (55) by a comparison of reaction rates of the hydrogenation of carbon monoxide obtained from each method.

The Reaction Steps Involved in the Slurry Phase Hydrogenation of Ethylene.

In the slurry phase hydrogenation of ethylene, gas, liquid and solid phases are in contact with one another. The reactants, hydrogen and ethylene, are dispersed as a swarm of small bubbles in a liquid supporting the catalyst. Transport of the gases through the liquid to the catalyst surface precedes reaction at the catalyst surface, with consequent desorption of the product, ethane, from the catalyst surface. Here, two processes /
processes predominate, namely, absorption of reactants by the liquid, and reaction at the catalyst surface to form ethane. Further consideration leads to an overall picture of the reaction taking place in a number of steps which are:

(i) Transfer of both hydrogen and ethylene from the bulk gas phase to the gas-liquid interface.

(ii) Penetration of the gas-liquid interface by gas molecules having sufficient energy to surmount the energy barrier existing at the interface, termed the interfacial resistance.

(iii) Gas molecules that have penetrated the interface are absorbed in the liquid.

(iv) The dissolved gases, both hydrogen and ethylene are transported by molecular and eddy diffusion within the liquid to the catalyst surface.

(v) Activated or chemisorption of the reactants then takes place on the catalyst surface.

(vi) Formation of the transient activated complex.

(vii) Decomposition of the complex to form the product ethane.

(viii) Desorption of ethane.

(ix) The ethane produced is transferred as an adsorbed molecule either into an uprising bubble containing reactants, or forms bundles or aggregates in the liquid with the subsequent formation of a separate bubble containing ethane only.

Steps (i) - (iv) characterise the absorption process.
cess whereas (v) - (ix) are related to the reaction rate itself.

Provided conditions such as temperature, inlet gas rate, catalyst amount, etc., are maintained constant the system will approach equilibrium conditions when either the absorption or reaction rate controls the overall reaction rate, i.e., either the reaction rate will be controlled by the rate at which reacting gases are absorbed in the liquid, the concentration of the reactants in the liquid thus reaching an equilibrium value or, the rate of absorption of reactants will be controlled by the rate at which gases react at the catalyst surface.

The Advantages of the Slurry Phase in the Determination of Mass Transfer Data.

In general, satisfactory hydrogenation depends on the choice of temperature, hydrogen pressure, reaction time, and catalyst. Conditions in the slurry phase reactor can be maintained steady while the effect of one process variable on the reaction rate may be studied. The major advantage of this system, namely the hydrogenation of ethylene, is that during reaction there are no byproducts formed. Ethane is the only product of reaction. Also ethylene is readily hydrogenated at low /
low temperatures on an active catalyst such as Raney-nickel. The suspending medium is considered to be inert, and acts only as a transporting agent for the absorbed reactants from the gas phase to the catalyst surface.

The reactants differ markedly in solubility in the suspending liquids used, toluene, decalin, and tetralin. By an evaluation of physical absorption data for both hydrogen and ethylene at different temperatures in the suspending medium (measuring the absorption rate of a gas into a liquid in which the gas concentration is increasing with time), these values can be compared with that obtained under similar conditions for the reacting system (measuring the absorption rate of a gas into a liquid in which, because of the reaction at the catalyst surface, the gas concentration of the reactants is at a fixed equilibrium value). Thus mass transfer rates can be evaluated for two gases differing in diffusivity and solubility in the two systems:

(1) physical absorption of both hydrogen and ethylene from a bubble swarm into a liquid medium of zero gas concentration.

(ii) physical absorption of both hydrogen and ethylene from a bubble swarm into a liquid medium of constant gas concentration.

There is no cause to suspect a different reaction mechanism /
mechanism at the catalyst surface in the slurry phase from that found in the vapour phase hydrogenation of ethylene. At this point it would not be out of place to give a brief preamble of the kinetics of the vapour phase hydrogenation of ethylene on a metal catalyst.
THE VAPOUR-PHASE HYDROGENATION OF ETHYLENE.

Few reactions have received as much attention as the vapour phase catalytic hydrogenation of olefines. Generally the reaction has been studied as a static or fixed bed system so that few investigations have been directed towards the study of the kinetics of the reaction in a tubular reactor where the flow patterns under any given flow rate are understood. For this reason it would be impossible to separate the diffusional steps from the reaction steps and so elucidate the effect of each process variable not only on the reaction rate itself but also on the absorption steps.

Many theories (11, 14) have been proposed in order to explain the kinetics of the hydrogenation of ethylene. Among the most recent reviews are those of Eley (36), Parkas (41) and others (15, 39, 71). Agreement is still in dispute between the associative mechanism for the adsorption of olefine on the catalyst where arguments are based on values of heats of adsorption of reactants, or, the dissociative mechanism or self-hydrogenation of ethylene. The theory supporting the associative mechanism is presented by Eley (36) whereas experimental evidence in favour of the dissociative mechanism is provided by Beeck (8, 9). The intermediate reaction path between that of the associative /
tive and that of the dissociative mechanism proposed by Twigg (115) suggests that the actual mechanism of the hydrogenation may be similar to both processes in that the proton is not fixed but is in a mobile state over the catalyst surface.

It appears that the reaction can be explained by either of two reaction paths, namely:

(i) that gaseous hydrogen attacks the catalyst surface which is covered with strongly adsorbed ethylene molecules

(ii) that only a few active sites on the catalyst surface are available for the adsorption of hydrogen. The adsorption of reactants takes place on the catalyst surface in adjacent sites with subsequent formation of the activated complex.

Eyring (59) gives evidence for (i) and a theoretical picture of the reaction is presented by Laidler (71) in support of (ii) in agreement with the experimental facts of Farkas et al., (42), who have shown that at least 5% of the nickel catalyst surface is available for the adsorption of hydrogen. The reaction path is in favour of the associative mechanism rather than the dissociative mechanism.

Much attention has been directed to the application of exchange reactions between deuterium and ethylene (113) in the hope of revealing the mechanism of hydrogenation /
hydrogenation. No results have been obtained as yet, because the exchange reaction rate is slow and the reaction path is complicated by many side reactions.

The rôle of the catalyst in hydrogenation is described by Beeck (8, 9), who has studied the reaction under conditions where the catalyst surface was preferentially orientated. Beeck found, by comparing hydrogenation rates on specifically orientated nickel surfaces, that the reactants are more readily absorbed on one plane than on another. In the summary of Beeck's work conclusions are drawn regarding the crystalline lattice and geometry of the catalyst surface from which it appears that two-point chemisorption on nickel at the ethylene double bond can occur readily on the (1, 1, 0) planes without interference between adsorbed molecules. Other face centered cubic metals with films preferentially orientated to give (1, 1, 0) planes were also especially active. In passing, it may be mentioned that technical catalysts in general are superior to evaporated metal films in that the latter cannot be completely cleaned by the usual reduction methods. However, it is becoming apparent from recent surveys (115), that despite the different conditions there is no great divergence in activity between technical and metal-film catalysts.

Nickel has been used by many workers as the catalyst for /
for the determination of the kinetics of the hydrogenation of ethylene. Melville (80) has studied the reaction on a nickel wire at temperatures in the range $100^\circ - 300^\circ$ C. and pressures from 1 - 760 m.m., whereas zur Strassen (111) reported similar work using nickel ribbon as a catalyst. The reaction has been investigated in flow systems using a Ni: Cu: 75: 25 alloy as a catalyst (3); platinum wire (43), and palladium wire (46) as catalysts.

The Absolute Reaction Rate of Vapour Phase Ethylene Hydrogenation.

From a study of previous investigations the following statements are considered to be indisputable:

(i) Hydrogen and ethylene are rapidly adsorbed by metallic surfaces even at liquid air temperatures. However, in the case of hydrogen, nearly 20% of the gas can be removed by pumping at room temperature. The product of the reaction, ethane, is weakly adsorbed on nickel surfaces.

(ii) The activation energy is 10.7 K. cals. and represents the amount of work necessary to form gaseous ethane from adsorbed ethylene and gaseous hydrogen, where the rate of reaction is measured independently of ethylene pressure.

(iii) The reaction is best considered from the Langmuir-Hinshelwood mechanism, where the ethylene is assumed to be adsorbed on dual sites and the hydrogen on single sites. Adsorbed ethyl radicals may be formed by reaction between adsorbed hydrogen and ethylene molecules. Ethane is /
is then produced by reaction between an adsorbed ethyl and hydrogen atom.

(iv) The overall heat of reaction is 32 K.cal./mole.

(v) At temperatures below 150°C, the velocity of reaction is first order and varies directly with the hydrogen partial pressure whereas at temperatures above 150°C, the reaction is second order and varies directly with the product of the hydrogen and ethylene pressures. Thus,

at \( T < 150^\circ \text{C} \), \( v \propto p_{\text{H}_2}^1 \cdot p_{\text{C}_2\text{H}_4}^0 \)

and \( T > 150^\circ \text{C} \), \( v \propto p_{\text{H}_2}^1 \cdot p_{\text{C}_2\text{H}_4}^1 \)

(vi) On increasing the temperature and partial pressure of hydrogen, the reaction rate increases showing that the amount of hydrogen adsorbed per unit area of catalyst surface increases with temperature (100).

(vii) The velocity of reaction agrees reasonably well with the equation proposed by Markham, Wall and Laidler (78) expressed as \( v \) in equation 3.

\[
v = s^2 \cdot L \cdot A \cdot E \cdot c_g^* \cdot \frac{KT}{h} \cdot \frac{1}{F_g^*} \cdot e^{-\left(z_0 - z'' - 2z\right)/KT} \quad \text{3}
\]

where \( v \) = the velocity of reaction

\( h \) = Planck's constant

\( K \) = Boltzmann's constant

\( T \) = temperature

\( s \) = the number of active sites on the catalyst surface

\( L \) = /
\[ L = f(\text{cg, ca}) \] where \( \text{cg} \) is the concentration of active sites, where \( \text{ca} \) is the concentration of ethylene on the active sites.

A and B are complex functions of \( x \) where \( x \) is the ethylene pressure.

\[ \text{cg}' = \text{the hydrogen pressure} \]

\[ F_g' = \text{the partition function for the adsorbed species} \]

and \( z, z'' \) = the energy of adsorption per atom of hydrogen, and ethyl radical respectively.

From equation 3 it is seen that the velocity of reaction \( v \) varies directly with \( \text{cg}' \), the hydrogen pressure, and in a complex manner with \( x \), the ethylene pressure. Yet, the possibility of ethane being formed by interaction between two adsorbed ethyl radicals on neighbouring sites, transposes equation 3 as:

\[ v = \frac{4s^3 LAAAAAAAAAA. nB^2. \text{cg}'}{h F_g'} \cdot e^{\frac{KT}{h F_g'} - (z_0 - 2z'' - 2z)/KT} \]

The numerical values in the rate expressions for maximum velocity are,

- from equation 3 at \( s = 4 \), \( v = 0.074s^2 = 1.2 \)
- from equation 4 at \( s = 4 \), \( v = 0.0078s^3 = 0.5 \)

The resulting values for \( v \) are too close to decide whether /
### TABLE 1. ABSOLUTE REACTION RATE OF ETHYLENE HYDROGENATION.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Temp. °C.</th>
<th>Catalyst Type</th>
<th>Area. cms.²</th>
<th>$P_{H_2}$ mm.</th>
<th>$E$; K. cals. (exp.)</th>
<th>R.R. (obs.)</th>
<th>R.R. (calc.)</th>
</tr>
</thead>
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<tr>
<td>(42)</td>
<td>130</td>
<td>Ni</td>
<td>0.47</td>
<td>14</td>
<td>4.7</td>
<td>4.32</td>
<td>23.74</td>
</tr>
<tr>
<td>(114)</td>
<td>117</td>
<td>Ni</td>
<td>1.88</td>
<td>72.5</td>
<td>6.0</td>
<td>3.49</td>
<td>27.10</td>
</tr>
<tr>
<td>(115)</td>
<td>156</td>
<td>Ni</td>
<td>2.51</td>
<td>29.9</td>
<td>3.2</td>
<td>235.80</td>
<td>531.80</td>
</tr>
<tr>
<td>(92)</td>
<td>156</td>
<td>Ni-Si</td>
<td>0.04</td>
<td>760.0</td>
<td>5.5</td>
<td>249.30</td>
<td>415.50</td>
</tr>
</tbody>
</table>

where:

- $E$ = energy of activation K. cals.
- $R.R.$ = reaction rate in gm. moles. sec$^{-1}$ cm$^{-2}$ of catalyst surface $\times 10^8$. 
whether equation 3 or 4 represents the true reaction velocity. As a result, the reaction of adsorbed hydrogen with ethylene for the gas phase is considered by Markham (loc. cit.) to be the fast reaction whereas the rate determining step is the removal of adsorbed ethylene from the catalyst surface by reaction with adsorbed hydrogen.

Table 1 (p. 20) gives values for the reaction rate of the vapour phase hydrogenation of ethylene at various temperatures and partial pressure of hydrogen. The calculated values of the reaction rate, as determined by the means of equations 3 and 4, are in reasonable agreement with the observed experimental data.

In conclusion; gases must reach the catalyst surface where hydrogen and ethylene are adsorbed on adjacent active sites. Reaction then commences by way of an activated complex with formation of ethane, the rates of which are of the order of \(10^{-6}\) gm. moles per unit time per unit area of catalyst surface.
For mass transfer to occur a relative movement of matter must take place in both directions. The coefficient of diffusion, \( D \), of a diffusing substance is a function of \( \lambda \), the component of molecular mean free path and \( u \), the mean velocity of the molecules. The relationship between \( D, \lambda \), and \( u \) is, \( D = \frac{\lambda u}{2} \) and applies only for the diffusion of any two gases. The treatment becomes complex for unsteady state diffusion where the transfer of two substances occurs, each diffusing into the other.

The mixing of two distinct phases occurs by one or both of two processes termed molecular and eddy diffusion. The former may be defined as the spontaneous intermingling of miscible fluids placed in mutual contact and accomplished without the aid of mechanical mixing. If, however, the medium is agitated or mixed, mass transfer takes place by the relatively fast process of eddy diffusion. Conditions favourable for eddy diffusion occur in agitators, mixing devices or by the establishment of turbulent flow. It is a necessary simplification /
plification to consider transfer rates by the use of molecular diffusion and an effective film thickness which represents the resistance to diffusion at an interface. The Nernst theory (87) is a mathematical symbol of little value as the effective film thickness can be deduced from kinetics. Kassel and Schaffer (67) have concluded that at the beginning of a dual controlled reaction, agitation will have a large influence on the reaction rate. As a generalisation, it can only be assumed that agitation will be important until concentration changes of about 10% have taken place. And agitation is far more significant in flow and recycling systems, than in batch reactions.

The study of heterogeneous reactions is mainly concerned with the nature of the processes controlling the observed velocity of the reaction \( V_R \) (obs.). Noyes and Whitney (89) were among the first to suggest that reactions of this type are controlled either by diffusion of reactants to the phase boundary or by diffusion of products of reaction from the phase boundary. However, there remains a third possibility: that is when the rate of reaction is comparable with the rate of diffusion of reactants and products to and from the reaction zone respectively.

Diffusion to and from a phase boundary is important in determining the rate of a heterogeneous reaction.
tion when the rate of diffusion $V_D \ll V_R$ the rate of reaction. In this case the observed reaction velocity approaches that of the rate of diffusion of reactants to the reaction zone (83). General considerations show that the chemical reaction rate is large compared with that of the diffusion rate or alternatively, the free energy of activation is small. Also, if the reaction rate is controlled by the speed of diffusion of reactants the agitation of the system will increase the observed overall reaction rate $V_R$ (obs.). Hence, the reaction rate can be expressed as a function of the stirring rate, and the velocity of reaction obeys first order kinetics. Finally, in a diffusion controlled reaction the temperature coefficient should be approximately equal to the temperature coefficient of diffusion of the reactants, i.e., of the order of 1.4 for each $10^\circ$ rise in temperature.

However if the reaction rate $V_R$ is the controlling factor in determining the overall rate of a heterogeneous reaction, so that the velocity of diffusion of reactants $V_D \gg V_R$ then the overall observed reaction rate approaches that of the reaction rate itself. This type of reaction may be of zero, first, or second order, or of intermediate values. Here, the velocity of reaction is doubled for every $10^\circ$ rise in temperature. Also, the
the observed reaction rate is unaltered by agitation or stirring in the system.

The situation becomes more complex when the rate of reaction is comparable with the rate of diffusion of reactants to the reaction zone, i.e., $V_R = V_D = V_R$ (obs.). Kassel et al. (67) have suggested that when the diffusion and reaction velocities are comparable, the rate of agitation will greatly affect the overall reaction velocity, $V_R$ (obs.), but when the concentration of reactants is large the diffusion effect will be negligible. Hence, the overall rate of reaction will appear to be controlled by the chemical reaction.

Whether a reaction is controlled by diffusion or chemical reaction always depends upon a comparison of the velocity of diffusion of reactants, the velocity of chemical reaction and the overall reaction rate for the process.
HYDROGENATION REACTIONS IN SOLUTION.

A survey of the literature shows that mass transfer studies in slurry phase reactors have received little attention as compared with the industrial development of the Fischer-Tropsch process and in the hydrogenation of oils. Studies in the organic field have naturally tended towards a study of the products of hydrogenation with one reactant already present in solution rather than the mechanism of hydrogenation.

Davies, Thomson and Crandall (20, 30) in 1930, by a study of the hydrogenation of olefines in solution containing a metal catalyst, pictured the hydrogen absorption mechanism as follows:— hydrogen transfer is achieved by diffusion only through a stationary 'unstirred' layer of liquid at the gas-liquid interface, transfer of the absorbed hydrogen through the bulk of the liquid by molecular and eddy diffusion, and penetration to the catalyst surface through a similar stationary unstirred film of liquid with subsequent adsorption of hydrogen on the catalyst surface. The assumed stationary films were stated to be sharply defined, so that the rate of absorption of hydrogen was in agreement with equation 5.

\[ P = \frac{K}{\text{}} \]
\[ P = K_1 \frac{c_1 - c_{\text{cat.}}}{R_1 + \frac{r_2}{W}} \]

where \( P \) = the rate of absorption of hydrogen.

\( K_1 \) = a constant.

\( c_1, c_{\text{cat.}} \) = the concentration of dissolved hydrogen at the gas-liquid and the liquid-solid interfaces respectively.

\( R_1 \) = the total resistance to diffusion in the stationary liquid film at the gas-liquid interface.

\( \frac{r_2}{W} \) = the total resistance to diffusion in the stationary liquid film at the liquid-solid interface.

where \( W \) = the quantity of catalyst (gm.)

and \( r_2 \) = the resistance to diffusion /gm of catalyst.

But from 5 when conditions are such that \( R_1 \) is constant at a fixed rate of agitation; \( r_2 \) is constant; and \( c_{\text{cat.}} \ll c_1 - c_{\text{cat.}} \) then 5 reduces to 6 where

\[ \frac{1}{P} = \frac{1}{K + K_1} \frac{1}{W} \]

Thus a plot of \( \frac{1}{P} \) vs. \( \frac{1}{W} \) is a straight line and \( P \) is equivalent to the initial rate of absorption of hydrogen when an infinite quantity of catalyst is present.

Mass transfer data are given for the hydrogenation of trimethylene, 2-pentene and isopropylethylene over palladium as catalyst.

An /
No values for the rate of hydrogenation of these systems in the vapour phase are given. Also, the rate of absorption of hydrogen is stated to be controlled by the rate of diffusion through the assumed stationary films. The published data show that increase in catalyst amount increases the absorption rate of hydrogen so that all the hydrogen dissolving reacts at the catalyst surface. The equilibrium concentration of hydrogen in the liquid decreases to a very small quantity with a corresponding increase in the concentration gradient of hydrogen between the gas and liquid phase. This concentration gradient represents the potential energy causing mass transfer between phases. It is possible that the rate of diffusion of hydrogen into the liquid is of the same order as the rate of reaction occurring at the catalyst surface. The overall rate of reaction is then controlled both by diffusion and by the chemical reaction at the catalyst surface. Thus, increasing the amount of catalyst in the system will increase the absorption rate of hydrogen in a gas-free liquid containing an infinite quantity of catalyst.

The criticism of Davies, Thomson and Crandall's experiments /
experiments is that although maximum hydrogen absorp-
tion is predicted when an infinite quantity of cata-
lyst is present in the system, the overall reaction is
not only controlled by the rate at which hydrogen can
diffuse to the catalyst surface but also by the rate
of chemical reaction at the catalyst surface.

Morritz et al. (85), have studied the kinetics of
the Raney-nickel catalysed hydrogenation of crotonic
acid. The reaction was discovered to be of zero order
with respect to crotonic acid during the initial stages
of hydrogenation and of first order in the final stages.

Erdey-Crúz (36) has shown that the rate of hydro-
genation of aqueous solutions of sodium cinnamate using
palladium precipitated on finely divided barium sulphate
as catalyst, was proportional to the concentration of
hydrogen per unit area of catalyst surface.

The amount of hydrogen absorbed as well as adsorbed
in and on a catalyst surface was predicted by Zininova
and Freidlin (123) who, in order to classify systems,
used organic reactants to withdraw from the gas-saturated
nickel surface:

(i) only the adsorbed fraction of hydrogen
(ii) all the adsorbed and part of the absorbed
hydrogen and lastly,
(iii) the total amount of hydrogen available.
MASS TRANSFER BETWEEN PHASES.

The transfer of material between and across phase boundaries implies changes in energies of activation which may differ greatly from those required for the diffusion process in homogeneous phases. Of prime importance in diffusion studies is the evaluation of the distribution of diffusing material in and near the phase boundary.

The fundamental law of diffusion, Fick's Law (44) may be expressed in equation 7 as:

\[
\frac{\Delta Q}{\Delta t} = -D \frac{dc}{dx} \quad 7
\]

where \(\Delta Q\) is the amount of matter diffusing per unit area in the time \(\Delta t\), in steady state flow, i.e. as much solute leaves a given elemental volume per unit time as enters it;

\(c\) = the concentration at a distance \(x\);

\(D\) = a constant termed the diffusion coefficient.

For unsteady state flow where the concentration gradient is a function of time, equation 7 may be expressed in the form of Fick's second Law of Diffusion, equation 8.

\[
\frac{dc}{dt} = \cdot\]
The solutions of equation 8 both for steady and unsteady states are given by Barrer (5) for a variety of diffusion systems. The mathematical solutions of equation 8 for the case of linear diffusion in the x plane may be separated as:

(i) an infinite medium bounded by +∞ and −∞ in the x plane,
(ii) semi-infinite medium bounded by x = 0 and x = +∞,
(iii) finite medium bounded by x = 0 and x = L.

The Infinite Medium.

The solution of equation 8 leads to equation 9

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + D \frac{\partial^2 c}{\partial y^2} + D \frac{\partial^2 c}{\partial z^2} \tag{8}
\]

or \( \frac{\partial c}{\partial t} = D \text{ (div. grad.) } c \) for three dimensional diffusion.

\[
\frac{\partial c}{\partial t} = \int_0^\infty \int_{-\infty}^{\infty} e^{-y^2} \, dy \tag{9}
\]

where \( c(x, t) = \frac{c_0}{2} \left[ 1 - 2 \int_0^{\frac{x}{\sqrt{2Dt}}} e^{-y^2} \, dy \right] \)

where \( c \) = the concentration of solute at time \( t \) and distance \( x > 0 \).

\( c_0 \) = the concentration of solute at time \( t = 0 \) and distance \( x < 0 \).

\( y = / \)
\[ y = \frac{1}{2} \left( x - x' \right) \] where \( D = \) the diffusion coefficient
and \( x' \) is any integer

The conditions when equation 9 is applicable are:

(a) \( D \) is not a function of \( c \),
(b) \( c = c_0 \) at \( t = 0 \) for \( x < 0 \),
(c) \( c = 0 \) at \( t = 0 \) for \( x > 0 \),
(d) Diffusion is normal to a plane boundary of constant area,
(e) The phases are of large enough volume so that the amount diffused does not affect in any way the bulk concentrations,
(f) The molecular state of the diffusing substance is the same in both phases.

Then at \( x > 0 \), equation 9 may be expanded as a function of \( \text{erf}(y) \) such that:

\[ c = \frac{c_0}{2} \left[ 1 - \frac{2}{\sqrt{\pi}} \left( \frac{x}{2\sqrt{D}t} - \frac{x^3}{3!2(2\sqrt{D}t)^3} + \frac{x^5}{5!2(2\sqrt{D}t)^5} - \cdots \right) \right] \]

and similarly at \( x < 0 \),

\[ c = \frac{c_0}{2} \left[ 1 + \frac{2}{\sqrt{\pi}} \left( \frac{x}{2\sqrt{D}t} - \frac{x^3}{3!2(2\sqrt{D}t)^3} + \frac{x^5}{5!2(2\sqrt{D}t)^5} - \cdots \right) \right] \]

Thus for the interdiffusion of two phases, the concentration gradient becomes a function of the partition coefficient in the equilibrium state as well as \( \text{erf}(y) \) where,
the form of a bubble swarm in which each bubble is of approximate spherical shape. Fick's Law, equation 8 may be transformed into equation 13 when diffusion of matter from a sphere is considered. Thus -

$$\frac{\partial c}{\partial t} = D \left[ \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right]$$

where \( r \) is the radius of the sphere.

By substituting \( u = cr \) in 13 equation 14 is obtained, thus -

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial r^2}$$

The general solution of 14 leads to the somewhat complex equation 15.

$$c = c_2 + \frac{2a}{\pi r} \sum_{n=1}^{\infty} \left[ \frac{-1}{n} \right]^n \frac{n \pi r}{a} \cdot \exp \left[ -\frac{Dn^2 \pi^2 t}{a^2} \right] \left( c_3 - c_0 \right)$$

where the boundary conditions are such that:

(a) \( f(r) = c_0 \) at \( t = 0 \),
(b) absorption occurs when \( c_2 > c_0 \),
(c) desorption occurs when \( c_0 > c_2 \),
(d) \( r \) = radius of sphere and \( n \) is any number,
(e) \( u = 0 \) at \( r = 0 \) for all values of \( t \),
(f) \( u = ac_2 \) at \( r = 0 \) for all values of \( t \),
(g) heat of absorption effects are negligible.
where
\[ y = \frac{(x - x')}{2\sqrt{Dt}} \]

(ii) The Semi-infinite Medium.

Equation 9 is again applicable in the form of equation 12 for \( x = 0 \) and \( x = +\infty \).

\[ c(x, t) = c_0 \left[ 1 - \frac{2}{\sqrt{\pi}} \int_0^x \frac{e^{-y^2}}{2\sqrt{Dt}} \, dy \right] \]

where, \( y = \frac{x' - x}{2\sqrt{Dt}} \) and \( x' \) is any integer. Equation 12 represents the concentration of diffusing component at distance \( x \) and time \( t \). And the boundary conditions required by equation 12 are:

(a) \( c = c_0 \) at \( x = 0 \) for all values of \( t \),
(b) \( c = 0 \) at \( x > 0 \) and \( t = 0 \),
(c) \( c = c(x, t) \) at \( x > 0 \) and \( t > 0 \),
(d) The interfacial area remains constant during the time of diffusion of material,
(e) Heat and dilution effects are assumed to be negligible.

(iii) The Finite Medium.

In the slurry phase gas reactants are dispersed in the /
When equation 15 holds for these boundary conditions, 
the quantity of matter absorbed or desorbed per unit area 
of curved surface is given by 15 such that:

\[ Q = \frac{c_2 - c_0}{3} a , \left[ 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( \frac{-Dn^2 \pi^2 t}{a^2} \right) \right] \]

Equation 16 is only applicable to a surface of constant 
area. If, however,

\[ \frac{\partial c}{\partial t} = f(a) \]

the situation becomes complex, e.g., the determination of 
the amount of material transferred from a rising bubble 
into a liquid medium. As the bubble rises, it expands 
because of the decrease in hydrostatic pressure. At the 
same time mass transfer takes place as well as changes in 
bubble shape due to swinging and oscillation of the bubble 
about a mean path. It can only be said that the bubble, 
if small enough, approximates to the form of a rigid 
sphere and changes in the surface area exposed are negli-
gible. From a dimensional analysis of this problem 
Frossling (47) has calculated the rate of mass transfer 
from a rigid sphere to be -

\[ \frac{Q}{t} = 4\pi D \frac{MP}{RT} \left[ 1 + K N_{Sc} \cdot N_{Re} \right] \]

where, /
where,

\[ \frac{Q}{t} = \text{the rate of evaporation gm. sec.}^{-1} \]

\[ D = \text{the diffusivity cma.}^2 \text{sec.}^{-1} \]

\[ M = \text{the molecular weight of the diffusing substance,} \]

\[ P = \text{the difference between the vapour pressure and partial pressure of the solute in the bulk gas,} \]

\[ R = \text{the gas constant,} \]

\[ r = \text{the drop radius cms.} \]

\[ K = 0.275 \text{ by experiment,} \]

\[ \text{NR} = \text{Reynold's number,} \]

\[ \text{Ns} = \text{Schmidt number.} \]

The condition where 17 applies is that the sphere moves in an infinite gaseous medium so that diffusion into or from the sphere does not affect the bulk concentrations of the diffusing component.

Equation 17 has been applied (105) to study the evaporation of liquid drops and the sublimation of napthalene spheres in the range \( \text{NR} < 1000 \). The equation, itself, represents the distribution of the sublimation rate on the surface of solid spheres, and is only applicable to a gas bubble in a liquid when the molecules within the bubble are 'fixed', i.e., when the relative movement of a molecule in the gas approaches that of a molecule in a solid.
FIG. 1.

KEY.

1. ASPIRATOR.
2. GAS HOLDER.
3. COMPRESSOR.
4. REGULATING VALVE.
5. DRYING TOWER.
6. FLOWMETER.
7. MANOMETER.
8. SAFETY VALVE.
9. SATURATOR.
10. TRAP.
11. REACTOR.
12. CONDENSER.
13. GAS SAMPLER.
14. WET GAS METER.
15. ALUMINIUM BOX.
16. FAN.
FIG. 2.

REACTOR

COLUMNS HEATER AND LAGGING.

AIR CONDENSER

THERMOMETER

LAGGING

DOWNCOMER

GLASS SINTER

LIQUID TRAP

GAS OUT

GAS IN

ASBESTOS PAPER

500 W. HEATER

ASBESTOS ROPE

ASBESTOS PAPER
Description of Apparatus.

The method of determining the rate of reaction of the hydrogenation of ethylene was by passing a gas mixture of hydrogen and ethylene, of known composition, at a constant rate into a column of liquid containing a specified quantity of catalyst. The system was maintained at constant temperature during the experiment. The exit gas was metered. From the decrease between the inlet and exit gas rates, the rate of reaction was calculated as gm. moles. of gas reacting to form ethane in unit time.

The flow diagram of the apparatus is shown in Fig. 1, page 37.

An air thermostat made of \( \frac{3}{32} \) " aluminium sheet and asbestos board enclosed the reactor column which was of Pyrex glass with overall dimensions 15" x 1.5" O.D. A down-comer (Figure 2, page 38) was necessary to promote circulation of the slurry within the reactor. A glass sinter of porosity 2 fused to the end of the reactor acted as a gas distributor, beneath which was situated a trap to collect any liquid which seeped through the sinter and so prevented blockage of the gas lines. The reactor was heated by a 500 watt element of Brightray wire.
wire wound on to the column and controlled through a Simmerstat on-off switch. The reactor was lagged with asbestos. The top end of the reactor was fitted with an air condenser both to cool the exit gases and to return any condensed liquid vapour entrained by the gas, to the reactor.

By this set-up, the reactor temperature was maintained at 10.1°C. in the range 30-180°C. The temperature of the slurry was read off a long stem thermometer inserted in the reactor. This arrangement did not affect the bubble properties of the system.

Preparation of Raney-Nickel Catalyst.

The method of preparation used (22) not only produced catalyst of consistent activity but the particle size did not vary to any large extent with each batch of catalyst (2).

The alloy (300 gm. of Ni: Al::1:1 powder) was added to a solution of caustic soda (300 gm.) in water (1.2 litres) in a 3-litre beaker surrounded by a freezing mixture. The alloy was added in small quantities to the caustic solution, meanwhile the temperature of the slurry was maintained below 20°C. by efficient stirring. The alloy additions were complete in two hours, after which the solution was heated to 98°C. on a steam bath and maintained at that temperature for 3 hr. with occasional /
occasional stirring. A further 400 c.c. of 19% caustic soda solution was then added and the solution heated at 95°C. for a period of 4 hr. or until the evolution of hydrogen had ceased.

The slurry was allowed to settle and the supernatant liquid syphoned off. The remaining sponge nickel was washed many times by decantation with distilled water until free from caustic soda, and fine insoluble aluminium salts. The presence of the latter was due to impurities such as carbonate in the caustic soda.

Dehydration of the catalyst was achieved by washing several times with absolute alcohol. 100 c.c. (toluene, decalin, or tetralin as required) was added to the nickel-alcohol slurry and the whole transferred to a 500 cc. Claisen distilling flask. The alcohol was distilled off (40°C. and 20 mms. pressure) when the sponge nickel was observed to be freely dispersed in the liquid. The slurry was transferred to a wide necked litre conical flask and 190 cc. of make-up hydrocarbon added.

Previous work (2) had shown that from 300 gm. of alloy, 140-150 gm. of Raney-nickel were obtained. Thus 10 c.c. of the reacting slurry were equivalent to approximately 5 gm. of catalyst. The catalyst is pyrophoric when dry but was safely preserved in a stoppered bottle.
bottle.

**Sampling of the Nickel Catalyst.**

The flask containing the slurry was rotated by hand and a wide bore pipette (10 c.c. with splash bulb) was inserted into the centre of the circulating slurry. A sample was then drawn off, the volume of which was governed by the amount of catalyst required. This method of sampling was considered to provide a representative sample of catalyst with respect to particle size distribution and reasonable repetitive weights of nickel (± 2%).

**Experimental Technique.**

The gas mixture of desired composition was made up in a 1.2 c.ft. gas holder graduated in 0.008 c. ft. divisions. The heaviest gas, ethylene was introduced first, then hydrogen was added at a fast rate to make up the required mixture which was transferred to a 2 c. ft. aspirator by way of a compressor pump. The graduated gas holder was then refilled with the same gas mixture.

The reactant gases, both hydrogen and ethylene, were used straight run from cylinders supplied by B.C.C.Ltd., and contained impurities not greater than 0.2%. Analysis of gas samples from the cylinders using a G.L.C. gas analysis /
analysis apparatus (51) confirmed the percentage constituents, page 219. The impurities, mainly oxygen, were considered to have little or no poisoning effect on the nickel catalyst surface. Although the diffusion of hydrogen into ethylene was calculated from Gilliland's formula (104) to be $0.163 \text{ ft}^2 \text{ hr}^{-1}$ the gas mixture, after a period of two hours, was considered to be of uniform composition in the gas holders.

The reactor column was filled with hydrocarbon solvent (300 cc.) and 10 cc. of catalyst suspended in the same solvent were added to the reactor liquid by way of the 'Y' glass joint attached to the head of the column. Any catalyst left sticking to the glassware was led into the reactor with small quantities of solvent. The saturator was filled with solvent, and the thermometer placed in position. All Quickfit joints were sealed with Audco grease" to ensure gas-tight joints. The reactor and its contents were brought to the required temperature and together with the aid of a fan which circulated warm air over the reactor the temperature was maintained steady during the experiment.

Gas was passed from the aspirator via the gas train, (Fig. 1, p. 37) at a constant rate and dispersed in the slurry as a swarm of small bubbles. The inlet gas rate found suitable was in the region of $0.5 \text{ gm. moles/hr}^{-1}$. 

A/

"No. 631
A 4 mm. Pyrex stopcock, acting as a regulating valve controlled the inlet gas rate, the value of which was registered on a differential flowmeter. The exit gas from the reactor was passed into a wet gas meter graduated in 0.001 c. ft. divisions. The gases were led off into the atmosphere.

Equilibrium conditions were established after two hours, when temperature, inlet gas rate, and reaction rate attained a constant value. The gas supply was switched from the aspirator to the graduated holder. This switch over of gas supplies was accomplished without any fluctuation in inlet gas rate and did not disturb the equilibrium condition already established.

Readings of both the volume of inlet and outlet gases at ten minute intervals were taken over a period of two hours. The volume of the inlet gas was measured by the distance of fall of the graduated holder and the temperature of the inlet gas read, whereas the volume of the exit gas was measured by the wet gas meter at the temperature of the meter water. Back pressure on the gas holder and water meter were negligible. All gas rates were corrected to S.T.P.

Estimation of Nickel Catalyst.

On completion of a run the reactor was detached from /
from the system and the slurry filtered through a Whatman No. 1 filter paper. The reactor was washed with acetone several times and the washings filtered. The nickel residue was repeatedly washed with acetone until free from hydrocarbon solvent. The residue, nickel, together with the filter paper were placed in a 200 c.c. beaker containing 30 c.c. dilute hydrochloric acid and the beaker covered with a watch glass. When effervescence had ceased, conc. hydrochloric acid (20 c.c.) were added and the solution heated to boiling when all the nickel dissolved. On cooling, the solution was filtered into a litre graduated flask. The pulp residue was washed with distilled water until the filtrate gave no colouration with the dimethylglyoxime reagent. The washings were transferred to the graduated flask and made up to the mark with distilled water.

A Hilger and Watts spectrophotometer was used to estimate absorptiometrically the concentration of nickel in the resulting green solution. The absorptiometer was previously calibrated against solutions of known concentration of nickel determined by gravimetric analysis (118).

This method of analysis, with an error of 0.1% in estimation, was regarded as suitable for the determination of the amount of nickel present in the slurry.
Expression of Results.

(i) The ratio of gases in the inlet gas mixture was expressed as - the ratio of the partial pressure of ethylene to that of hydrogen in the gas mixture.

(ii) The contraction was defined as - the percentage ratio of

\[ \frac{\text{volume in unit time after conversion}}{\text{volume in unit time before conversion}} \]

(iii) The reaction rate was termed as - the amount of either hydrogen or ethylene reacting to form ethane in unit time. Convenient units for reaction rate were gm. moles. of reacting gas at S.T.P. per hour.

Readings of the inlet and outlet gas rates were taken every ten minutes over a period of two hours. The reaction rate was the arithmetic mean of the readings over the two hour period.

Variables under Study.

Experiments were designed to relate the process variables such as temperature, inlet gas rate, catalyst quantity, gas ratio, and catalyst suspending medium with the observed reaction rate.
Variation of reaction rate with catalyst quantity.

**GRAPH 1.**

**H$_2$: C$_2$H$_4$: 1:1 in Decalin**

**Inlet Gas Rate**

0.54 GM. MOLES/HR.
VARIATION OF REACTION RATE WITH CATALYST DISPERSITY.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Catalyst gm.</th>
<th>Reaction Rate gm. moles hr(^{-1}) at N.T.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6479</td>
<td>0.1194</td>
</tr>
<tr>
<td>2</td>
<td>0.9410</td>
<td>0.1347</td>
</tr>
<tr>
<td>3</td>
<td>1.9790</td>
<td>0.1481</td>
</tr>
<tr>
<td>4</td>
<td>2.6210</td>
<td>0.1559</td>
</tr>
<tr>
<td>5</td>
<td>5.0327</td>
<td>0.1573</td>
</tr>
<tr>
<td>6</td>
<td>5.3456</td>
<td>0.1566</td>
</tr>
<tr>
<td>7</td>
<td>5.8990</td>
<td>0.1555</td>
</tr>
<tr>
<td>8</td>
<td>6.8321</td>
<td>0.1570</td>
</tr>
</tbody>
</table>

Gas Ratio

H\(_2\): C\(_2\)H\(_4\) = 1: 1.

Gas Rate = 0.540 g moles. hr\(^{-1}\)

in Decalin at 140\(^\circ\)C.
VARIATION OF REACTION RATE WITH CATALYST DISPERSITY.

**TABLE 3**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Catalyst gm.</th>
<th>Reaction Rate gm. moles. hr⁻¹ at N.T.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9532</td>
<td>0.1121</td>
</tr>
<tr>
<td>2</td>
<td>2.0630</td>
<td>0.1385</td>
</tr>
<tr>
<td>3</td>
<td>4.0037</td>
<td>0.1498</td>
</tr>
<tr>
<td>4</td>
<td>5.3210</td>
<td>0.1521</td>
</tr>
<tr>
<td>5</td>
<td>6.1350</td>
<td>0.1502</td>
</tr>
<tr>
<td>6</td>
<td>7.5670</td>
<td>0.1511</td>
</tr>
</tbody>
</table>

Gas Ratio

\[ \text{H}_2 : \text{C}_2\text{H}_4 : 1 : 1 \]

Gas Rate = 0.540 gm moles. hr⁻¹ in Decalin at 130°C.
DISCUSSION OF EXPERIMENTAL RESULTS.

Variation of Reaction Rate with Catalyst Quantity.

Graph 1 (page 47) shows the effect of variation of catalyst (gm.) on the reaction rate (gm. moles. hr$^{-1}$) at $140^\circ$C. (Table 2, page 48) and $130^\circ$C (Table 3, page 49) with an inlet gas mixture of H$_2$: C$_2$H$_4$: 1: 1 at an inlet gas rate of 0.54 gm. moles. hr$^{-1}$.

It is apparent from Graph 1 that the reaction rate is constant at constant temperature with a finite quantity of catalyst. Thus further addition of catalyst, more than 5 gm. will not alter the observed reaction rate measured at the same temperature. Therefore, the overall reaction rate is independent of the catalyst surface area capable of adsorbing gases, and is then controlled by the rate of transport of reactants, both hydrogen and ethylene, from the gas bubble, through the intervening liquid to the catalyst surface. Also, on the catalyst surface, the reaction rate must needs be greater than the transport rate of the gases through the liquid. This fact disposes any theories of reaction based on direct contact between gas and catalyst. Also, owing to its mode of preparation, the catalyst surface is thoroughly wetted and any partial drying of the surface during reaction would lead to a decrease in the overall reaction rate.
rate because the developing hot spots would destroy the catalyst activity.

The difference in reaction rates measured at $130^\circ$C. and $140^\circ$C. correspond to the temperature coefficient of the reaction itself. Small errors in catalyst sampling have no effect on the reaction rate within the range of Raney-nickel.

Still further increase in catalyst quantity would undoubtedly alter the hydrodynamics of the system such as bubble path and velocity. The results from such experiments would not be comparable with those in Graph 1. The effect of using an 'infinite' quantity of catalyst would change the system from a slurry phase to that of a fluidised bed reactor where no liquid phase would be present. Then, the overall reaction would approximate to the vapour-phase hydrogenation of ethylene where no liquid film resistance to diffusion is present.

Contrary to the experiments of Davies, Thomson and Crandall (20, 30) discussed on p. 28, constant reaction rate is obtained with a finite quantity of catalyst. Absorption of reactants precedes reaction at the catalyst surface and direct contact between gas and solid is not established.

**Variation of Reaction Rate with Inlet Gas Rate.**

Graph 2 (page 52) illustrates the effect of inlet gas /
Variation of reaction rate with inlet gas rate.
TABLE 4

VARIATION OF REACTION RATE WITH INLET GAS RATE.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Catalyst gm.</th>
<th>Inlet Gas Rate gm. moles. hr⁻¹ N.T.P.</th>
<th>Reaction Rate gm. moles. hr⁻¹ N.T.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Ratio</td>
<td>H₂: C₂H₄:: 1: 1 in Decalin at 130°C.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>5.364</td>
<td>0.2730</td>
<td>0.069</td>
</tr>
<tr>
<td>2</td>
<td>4.899</td>
<td>0.3521</td>
<td>0.086</td>
</tr>
<tr>
<td>3</td>
<td>5.007</td>
<td>0.5200</td>
<td>0.152</td>
</tr>
<tr>
<td>4</td>
<td>5.223</td>
<td>0.6069</td>
<td>0.168</td>
</tr>
<tr>
<td>5</td>
<td>4.739</td>
<td>0.7119</td>
<td>0.193</td>
</tr>
</tbody>
</table>
gas rate ($\text{gm. moles. hr}^{-1}$) on reaction rate ($\text{gm. moles. hr}^{-1}$) at 130°C. in decalin with 5 gm of catalyst (Table 4, page 53) and an inlet gas mixture of H₂: C₂H₄ :: 1: 1

Increase of inlet gas rate directly increases the reaction rate over the observed variable range. Thus, doubling the inlet gas rate doubles the reaction rate and hence, the amount of gas transported through the gas-liquid interface available for reaction on the catalyst surface.

The inlet gas rate controls the surface area of gas-liquid contact being dependent on the inlet gas rate and the physical properties of the medium.

Previous work (2) has shown that the value of the reaction rate decreases at higher inlet gas rates of the order $>1\text{ gm. mole. hr}^{-1}$. This phenomenon is attributed to change in bubble properties such as the coalescence of a number of small bubbles to produce one large bubble of the same total volume but of smaller surface area. This fact provides further evidence that the reaction rate in the slurry phase is dependent on bubble surface area, but whether the absorption efficiency is equally distributed over the surface of a bubble is conjecture. Part II deals with the last mentioned problem.
Variation of reaction rate with temperature, inlet gas ratio, and liquid medium.
### Table 5

**Variation of Reaction Rate with Temperature in Toluene.**

**Inlet Gas Rate = 0.550 gm. moles hr\(^{-1}\) at N.T.P.**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Inlet Gas Ratio: H(_2) : C(_2)H(_4) : x : y</th>
<th>Temp. of Reaction °C.</th>
<th>Catalyst gm.</th>
<th>Reaction Rate gm. moles hr(^{-1}) at N.T.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 : 1</td>
<td>70.0</td>
<td>4.972</td>
<td>0.1184</td>
</tr>
<tr>
<td>2</td>
<td>1 : 1</td>
<td>76.0</td>
<td>5.019</td>
<td>0.1213</td>
</tr>
<tr>
<td>3</td>
<td>1 : 1</td>
<td>84.0</td>
<td>4.875</td>
<td>0.0895</td>
</tr>
<tr>
<td>4</td>
<td>1 : 1</td>
<td>90.0</td>
<td>5.274</td>
<td>0.1031</td>
</tr>
<tr>
<td>5</td>
<td>1 : 1</td>
<td>96.0</td>
<td>5.273</td>
<td>0.0977</td>
</tr>
<tr>
<td>6</td>
<td>1 : 1</td>
<td>99.0</td>
<td>4.961</td>
<td>0.0830</td>
</tr>
<tr>
<td>7</td>
<td>1 : 1</td>
<td>105.0</td>
<td>4.996</td>
<td>0.0736</td>
</tr>
<tr>
<td>8</td>
<td>1 : 2</td>
<td>42.0</td>
<td>4.927</td>
<td>0.0826</td>
</tr>
<tr>
<td>9</td>
<td>1 : 2</td>
<td>49.5</td>
<td>5.113</td>
<td>0.1037</td>
</tr>
<tr>
<td>10</td>
<td>1 : 2</td>
<td>61.0</td>
<td>5.055</td>
<td>0.1027</td>
</tr>
<tr>
<td>11</td>
<td>1 : 2</td>
<td>66.0</td>
<td>5.018</td>
<td>0.1141</td>
</tr>
<tr>
<td>12</td>
<td>1 : 2</td>
<td>71.0</td>
<td>4.986</td>
<td>0.1118</td>
</tr>
<tr>
<td>13</td>
<td>1 : 2</td>
<td>76.0</td>
<td>5.188</td>
<td>0.1033</td>
</tr>
<tr>
<td>14</td>
<td>1 : 2</td>
<td>88.0</td>
<td>5.063</td>
<td>0.0958</td>
</tr>
<tr>
<td>15</td>
<td>1 : 2</td>
<td>98.0</td>
<td>4.893</td>
<td>0.0763</td>
</tr>
<tr>
<td>16</td>
<td>1 : 2</td>
<td>41.0</td>
<td>5.076</td>
<td>0.1037</td>
</tr>
<tr>
<td>17</td>
<td>2 : 1</td>
<td>60.0</td>
<td>5.072</td>
<td>0.1240</td>
</tr>
<tr>
<td>18</td>
<td>2 : 1</td>
<td>51.5</td>
<td>5.107</td>
<td>0.1300</td>
</tr>
<tr>
<td>19</td>
<td>2 : 1</td>
<td>48.0</td>
<td>4.813</td>
<td>0.1147</td>
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<tr>
<td>20</td>
<td>2 : 1</td>
<td>55.0</td>
<td>4.813</td>
<td>0.1147</td>
</tr>
</tbody>
</table>
TABLE 6

VARIATION OF REACTION RATE WITH TEMPERATURE IN DECALIN.

Inlet Gas Rate = 0.550 gm. moles hr.\(^{-1}\) at N.T.P.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Inlet Gas Ratio. (\text{H}_2: \text{C}_2\text{H}_4: x:y)</th>
<th>Temp. of Reaction (^{\circ}\text{C})</th>
<th>Catalyst gm.</th>
<th>Reaction Rate gm. moles hr.(^{-1}) at N.T.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1: 1</td>
<td>65.0</td>
<td>4.728</td>
<td>0.0703</td>
</tr>
<tr>
<td>2</td>
<td>1: 1</td>
<td>65.0</td>
<td>5.132</td>
<td>0.0951</td>
</tr>
<tr>
<td>3</td>
<td>1: 1</td>
<td>110.2</td>
<td>4.359</td>
<td>0.1318</td>
</tr>
<tr>
<td>4</td>
<td>1: 1</td>
<td>130.7</td>
<td>4.726</td>
<td>0.1532</td>
</tr>
<tr>
<td>5</td>
<td>1: 1</td>
<td>140.0</td>
<td>5.105</td>
<td>0.1574</td>
</tr>
<tr>
<td>6</td>
<td>1: 1</td>
<td>150.8</td>
<td>4.722</td>
<td>0.1573</td>
</tr>
<tr>
<td>7</td>
<td>1: 1</td>
<td>160.0</td>
<td>5.081</td>
<td>0.1540</td>
</tr>
<tr>
<td>8</td>
<td>1: 1</td>
<td>170.0</td>
<td>4.987</td>
<td>0.1456</td>
</tr>
<tr>
<td>9</td>
<td>1: 2</td>
<td>71.0</td>
<td>5.538</td>
<td>0.0656</td>
</tr>
<tr>
<td>10</td>
<td>1: 2</td>
<td>90.5</td>
<td>4.442</td>
<td>0.0957</td>
</tr>
<tr>
<td>11</td>
<td>1: 2</td>
<td>115.0</td>
<td>5.273</td>
<td>0.1233</td>
</tr>
<tr>
<td>12</td>
<td>1: 2</td>
<td>125.0</td>
<td>5.197</td>
<td>0.1329</td>
</tr>
<tr>
<td>13</td>
<td>1: 2</td>
<td>131.5</td>
<td>5.185</td>
<td>0.1366</td>
</tr>
<tr>
<td>14</td>
<td>1: 2</td>
<td>140.0</td>
<td>5.561</td>
<td>0.1371</td>
</tr>
<tr>
<td>15</td>
<td>1: 2</td>
<td>145.5</td>
<td>5.035</td>
<td>0.1349</td>
</tr>
<tr>
<td>16</td>
<td>1: 2</td>
<td>149.5</td>
<td>5.459</td>
<td>0.1332</td>
</tr>
<tr>
<td>17</td>
<td>1: 2</td>
<td>160.0</td>
<td>4.874</td>
<td>0.1213</td>
</tr>
<tr>
<td>18</td>
<td>1: 2</td>
<td>170.0</td>
<td>4.548</td>
<td>0.1132</td>
</tr>
</tbody>
</table>
### TABLE 7

VARIATION OF REACTION RATE WITH TEMPERATURE IN TETRALIN.

Inlet Gas Rate = 0.543 gm. moles hr.\(^{-1}\) at N.T.P.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Inlet Gas Ratio. (\mathrm{H_2}:\mathrm{C}_{2}H_4: x: y)</th>
<th>Temp. of Reaction °C.</th>
<th>Catalyst gm.</th>
<th>Reaction Rate gm. moles. hr.(^{-1}) N.T.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1: 1</td>
<td>60.5</td>
<td>5.127</td>
<td>0.0864</td>
</tr>
<tr>
<td>2</td>
<td>1: 1</td>
<td>92.0</td>
<td>5.555</td>
<td>0.1295</td>
</tr>
<tr>
<td>3</td>
<td>1: 1</td>
<td>121.0</td>
<td>4.685</td>
<td>0.1640</td>
</tr>
<tr>
<td>4</td>
<td>1: 1</td>
<td>131.5</td>
<td>5.362</td>
<td>0.1884</td>
</tr>
<tr>
<td>5</td>
<td>1: 1</td>
<td>140.0</td>
<td>5.177</td>
<td>0.1493</td>
</tr>
<tr>
<td>6</td>
<td>1: 1</td>
<td>142.0</td>
<td>5.301</td>
<td>0.1580</td>
</tr>
<tr>
<td>7</td>
<td>1: 1</td>
<td>150.0</td>
<td>4.980</td>
<td>0.1545</td>
</tr>
<tr>
<td>8</td>
<td>1: 1</td>
<td>160.0</td>
<td>4.978</td>
<td>0.1452</td>
</tr>
<tr>
<td>9</td>
<td>1: 1</td>
<td>169.0</td>
<td>4.913</td>
<td>0.1422</td>
</tr>
<tr>
<td>10</td>
<td>1: 2</td>
<td>65.0</td>
<td>5.032</td>
<td>0.0559</td>
</tr>
<tr>
<td>11</td>
<td>1: 2</td>
<td>121.0</td>
<td>4.882</td>
<td>0.1321</td>
</tr>
<tr>
<td>12</td>
<td>1: 2</td>
<td>131.5</td>
<td>5.032</td>
<td>0.1597</td>
</tr>
<tr>
<td>13</td>
<td>1: 2</td>
<td>141.0</td>
<td>5.415</td>
<td>0.1422</td>
</tr>
<tr>
<td>14</td>
<td>1: 2</td>
<td>145.5</td>
<td>4.713</td>
<td>0.1428</td>
</tr>
<tr>
<td>15</td>
<td>1: 2</td>
<td>161.0</td>
<td>5.064</td>
<td>0.1405</td>
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<tr>
<td>16</td>
<td>1: 2</td>
<td>160.5</td>
<td>5.247</td>
<td>0.1559</td>
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<tr>
<td>17</td>
<td>1: 2</td>
<td>170.0</td>
<td>5.173</td>
<td>0.1396</td>
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<tr>
<td>18</td>
<td>1: 2</td>
<td>175.0</td>
<td>4.922</td>
<td>0.1342</td>
</tr>
</tbody>
</table>
Gas Analysis of Products of Reaction.

Ethane is the only product of reaction. Several checks were made by analysing gas samples, e.g. Table 2, p.48, run 6 analysis of a sample of exit gases from the reactor gave:-

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>29.3%</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>29.0%</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>42.0%</td>
</tr>
<tr>
<td>Total gases</td>
<td>100.3%</td>
</tr>
</tbody>
</table>

The reaction rate calculated from these values at an inlet gas rate of 0.54 gm. moles hr⁻¹ was 0.1572 gm. moles hr⁻¹, corresponding well with the experimental value of 0.1566 gm. moles hr⁻¹.

Variations of Reaction Rate with Temperature.

The effect of variation of reaction rate (gm. moles. hr⁻¹) with temperature (°C.) in three suspending liquids, toluene, decalin and tetralin in the temperature range 30°C. - b.p.°C. (Tables 5, 6 and 7, pp. 56-58) is illustrated on Graph 3, p.55.

Considering toluene as the catalyst suspending medium: an increase of temperature increases the reaction rate until a maximum value is obtained at approximately 72°C. Thereafter the reaction rate decreases as the temperature approaches that of the boiling point of /
of toluene when the partial pressure of the liquid is one atmosphere and both hydrogen and ethylene are completely insoluble in toluene, i.e. the reaction rate is zero.

Similarly, for decalin and tetralin optimum reaction rate is attained at approximately 150°C.

Alteration of the inlet gas ratio has negligible effect on the optimum reaction rate temperature.

**Variation of Reaction Rate with Inlet Gas Ratios.**

From Graph 3, p. 55, highest reaction rates are obtained with H₂ : C₂H₄:: 2:1 and not as would be expected with H₂ : C₂H₄:: 1:1. Inlet gas ratios with decreasing proportions of hydrogen less than 2:1 and similarly (2) with increasing proportions of hydrogen greater than 2:1 show a decrease in reaction rate.

Assuming absorption of reactants precedes reaction, it is impossible for the reaction rate to be greater than the absorption rate of both pure hydrogen and pure ethylene into the liquid free of gas. Thus the gas ratio H₂ : C₂H₄:: 2:1 is the value necessary for the optimum transfer of both hydrogen and ethylene from a gas bubble into the hydrocarbon solvent during reaction. And under these conditions, since each gas affects the absorption rate of the other, optimum absorption rate occurs /
occurs leading to a maximum value for the reaction rate.

**Variation of Reaction Rate with Catalyst Suspending Liquid.**

Variation of the hydrocarbon liquid alters the physical properties of the system such as surface tension, solubility of reactants and bubble characteristics which in turn affect the rate of absorption of reactants and hence rate of reaction.

Bubble swarms in toluene produced smaller bubbles than in decalin or tetralin. Also higher reaction rates were obtained in toluene than when decalin or tetralin was substituted at the same temperature (Graph 3, p.55). These factors can only be accounted for by the solubility of the reactants being greater in toluene than either in decalin or tetralin, as well as changes in bubble swarm characteristics.

The hydrocarbon liquid remains unchanged after the experiment. It appears that the liquid acts only as a carrier for the reactant gases from the gas bubble through the intervening liquid layer to the catalyst surface.

In every case, toluene, decalin, and tetralin, as the gas bubble rose through the liquid, the catalyst particles were swept to either side of the rising bubble. No particles were observed to adhere on to any one bubble.

*Hydrogen* /
Hydrogen Migration during Catalysis.

In every case, high initial reaction rates were obtained; the value of which decreased to a constant value when equilibrium conditions were established. This fact may be explained in that: during the initial stages of the slurry phase hydrogenation of ethylene, the nickel surface is progressively covered with ethylene, so that surface migration of hydrogen will be increasingly hindered and may eventually become less than the sub-surface migration of absorbed hydrogen within the catalyst. The catalyst, because of its preparation, contains absorbed and adsorbed hydrogen before reaction occurs. It is probable that in the ethylene hydrogenation, the clean-up of adsorbed ethylene is achieved by the hydrogen atoms which emerge at the catalyst surface close to the carbon atoms that are bound to the metal. The absorbed hydrogen may diffuse from one tetrahedral hole to another and eventually reach a tetrahedral hole at the catalyst surface. The hydrogen may then attach itself to the carbon atom rather than diffuse back into the bulk of the catalyst. This means that the effective concentration of hydrogen at the catalyst surface is greater than would be expected from the nickel surface which is covered to a large extent with ethylene molecules. But, as the absorbed hydrogen is depleted by reaction with adsorbed ethylene /
Photomicrograph of a Raney-nickel catalyst particle. X 950.
ethylene in the formation of ethane, the reaction rate decreases as the rate of diffusion of hydrogen from successive layers within the catalyst surface decreases. Finally, all the absorbed hydrogen is reacted to form ethane. Equilibrium is then attained when the reaction rate is controlled by the diffusion of reactants to the catalyst surface.

A photomicrograph taken on a Vicker's projection microscope, (p.63), illustrates the type of surface of a nickel catalyst particle.
SUMMARY.

1. The slurry phase hydrogenation of ethylene has been studied using Raney-nickel as a catalyst supported in either toluene, decalin or tetralin within the temperature range $40^\circ$C. - b.p. of medium. The observed reaction rate has been observed to:

   (i) attain a constant value, with a finite amount of catalyst, at a fixed inlet gas rate,

   (ii) increase directly with inlet gas rate over the range studied (0.1 - 0.8 gm. moles. hr.$^{-1}$).

   (iii) achieve a maximum value in toluene at $72^\circ$C. and both in decalin and tetralin at $150^\circ$C. This maximum is independent of inlet gas ratio.

   (iv) attain a maximum value with an inlet gas ratio of $H_2: C_2H_4:: 2:1$. And is irrespective of the supporting liquid.

   (v) vary markedly with change in physical characteristics of the medium effecting changes in bubble and solubility relationships.

2. Absorption of reactants, both hydrogen and ethylene, must precede reaction at the catalyst surface. Any conception of direct contact between gas and catalyst in the slurry is rejected.

3. The absorption and hence reaction rate is a direct function of the surface area of the bubble swarm.

4. Chemical combination between liquid and reactant gases is unlikely. The liquid medium acts only as a carrier for transporting absorbed gas molecules to the catalyst surface.
PART II

A PRELIMINARY SURVEY OF THE PROPERTIES OF
SINGLE BUBBLES AND BUBBLE SWARMS.

This section of the work deals with effect of
liquid properties on bubble characteristics such as,
velocity of rise, formation effects, rates of absorp-
tion and surface area of bubble swarms.
THE FORMATION AND DETACHMENT OF A BUBBLE
FROM AN ORIFICE.

The shape of an expanding bubble is a function of the pressure difference across the curved surface of the contact angle with the orifice, and the shape of the orifice. If the orifice is assumed to be wetted by the liquid, and the rim of the orifice regarded as a rounded edge, then the mechanism of formation and detachment of the bubble from the orifice may be described as taking place in the following manner:— as the meniscus reaches the mouth of the capillary which is wetted by the liquid, the surface tension at the rim of contact just balances the sum of the upward forces due to excess pressure in the bubble and the bubble upthrust. On increase of bubble size, the pressure within the bubble diminishes so that the bubble rim moves out along the pore surface in order to vary the angle of contact of the rim and equalise the balance of forces. On still further increase in bubble sizes the buoyancy force, which previously was negligible, is now greater than the pressure force. Consequently, the rim of contact moves inwards until it is within the orifice diameter so that no further change in bubble rim angle can take place. The buoyancy forces increase rapidly with further expansion. And the bubble neck is stretched. The result is a rapid acceleration of stretching and thinning of the bubble neck which results /
results in the detachment of the bubble from its neck. The 'tails', left after the walls of the neck contact, contract both into the bubble and the orifice. The bubble neck need not necessarily be attached to the orifice rim, but may be retracted within the capillary neck.

The energy of formation of new surface is given by the equation,

\[ E = 2\pi rTv \]

*E* = the energy in ergs, sec\(^{-1}\)

*r* = the radius of the bubble cms.

*T* = the interfacial surface tension dynes cm\(^{-1}\)

*v* = the tangential velocity at bubble equator cm\(^{-1}\) sec\(^{-1}\)

The disturbance within the bubble immediately after cleavage from the orifice is manifest in a high degree of turbulence within the bubble, oscillation of the bubble about a mean shape, and rippling on the bubble surface.

After cleavage of the bubble from the neck, the residual film at the orifice increases, both by its contraction after bubble formation and by the inlet gas pressure, until the total pressure is sufficient to arrest contraction of the film and again initiate bubble formation.
For increasing gas rates and hence gas pressure, the residual films are prevented from contracting immediately after bubble formation, and a subsequent bubble is formed much sooner than with low gas rates. Because formation or creation of bubble surface is faster than the detachment of a bubble from an orifice, consecutive bubbles at high gas rates will adhere to one another. At large inlet gas rates of the order of 3 gm. moles. hr.\(^{-1}\), the size of bubble formed is independent of pore size (98). This phenomenon is termed 'streaming'.

Coalescence of Bubbles.

For the coalescence of two bubbles, conditions must be such that the bubbles rise in a vertical line, one above the other. Also, the liquid films carried upwards by the bubble must remain in contact for a short time until the liquid film is thin enough for coalescence to occur.

Pattle (94) has established that coalescence of bubbles is more likely to occur in a pure liquid, than in a liquid containing small amounts of surface active agents such as grease, detergents etc. The explanation of this fact is that the contaminants dissolved in the liquid medium are adsorbed on the bubble surface during formation and prevent coalescence by virtue of the repellent /
pellent forces between like groups in the adsorbed molecule.

**Porous Plate Diffusers.**

Porous plate diffusers may be considered as being a bundle of capillaries from which bubbles are formed at one or more capillaries. Various methods, notably those of Harkins and Brown (57) have been designed for the determination of bubble size, pore size, and pore length, by the evaluation of the maximum pressure required to form a bubble for a capillary. Table 8 gives an indication of the mean pore diameter of different grades of glass sinter discs used in the experimental section.

**TABLE 8.**

<table>
<thead>
<tr>
<th>Pore No.</th>
<th>Mean Pore Dia. x 10^4 cms.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>350</td>
</tr>
<tr>
<td>1</td>
<td>120</td>
</tr>
<tr>
<td>2</td>
<td>65</td>
</tr>
<tr>
<td>3</td>
<td>27.5</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
</tr>
</tbody>
</table>
As the gas inlet pressure increases, the pore which gases first is the one with the widest 'narrow cross section'. On further increase of gas pressure successive pores with decreasing 'narrow cross section' values gas. If the radius of the bubble is large compared with the radius of the neck before cleavage, it can be shown that the coalescence of two bubbles will result in the stable form of a bubble having a radius of \( \frac{3\sqrt{2}}{r} \) where \( r \) is the radius cms. of a single bubble.

Similar to the production of single bubbles, bubble swarms formed at porous plates tend to coalesce at high inlet gas rates. It is probable that on increasing the temperature of the system, corresponding to a decrease in viscosity of the liquid medium, coalescence within a bubble swarm will increase. This may be accounted for by the rapid thinning of the liquid layers enveloping the rising bubbles.

At high gas rates, visual observation of the system has shown that a cone formation of bubbles is formed at the sinter face from which the bubbles detach themselves and not, as would be expected, from the capillary ends.

Generally, wider pore openings produce larger bubbles, but the proximity of such pores leads to the coalescence of bubbles during formation and detachment from the pore ends.
THE MOVEMENT OF MATTER INSIDE BUBBLES
DURING FORMATION.

(i) Turbulence within a Bubble during Formation and Detachment from a Capillary.

During formation of a bubble a high degree of turbulence within the bubble is certainly present. Photographs of ammonium chloride aerosols bubbled through water show that, within the bubble, there is no well defined flow pattern. Violent mixing by eddy currents within the bubble occurs.

The degree of turbulence within the bubble is increased when the bubble is 'necked off' from the capillary. This state is created by the rapid vibration of the bubble 'tail' in and out of the mean bubble shape immediately after detachment.

(ii) The Rate of Mass Transfer from a Bubble during Formation.

From a study of liquid drops formed at various rates in a gaseous atmosphere Dixon and Russell (32) have shown that, during short period formation high rates of absorption of gas by the drops are the case. Equation 19 relates the process variables in the form:

\[ K_1 \]
\[ K_L = \frac{2.32 (\Delta + 12.5)}{t^{0.8}} \]  

where \( \Delta \) = the degree of turbulence  
\( t \) = the drop formation time secs.  
\( K_L \) = the overall coefficient of absorption cms. sec\(^{-1}\).

As \( \Delta \) increases, \( K_L \) correspondingly increases. The resistance to diffusion at the drop surface must thus decrease as \( K_L \) increases.

By analogy, there is sufficient evidence for the statement that: 'high mass transfer rates during bubble formation are possible due to the high degree of turbulence within the bubble'.

---
FIG. 6.
STREAMLINE FLOW IN A SLOW RISING BUBBLE.

\[ R < 5 \]

FIG. 7.
CIRCULATION IN A FAST-RISING BUBBLE.

\[ R > 70 \]
CONDIThONS WITHIN A BUBBLE RISING IN A LIQUID.

(i) Flow Patterns inside the Bubble.

The conditions inside a rising bubble have been shown (28) to be dependent on the rate of rise of the bubble and the properties of the liquid in which the bubble is rising. Figure 6, p. 74, illustrates the flow lines in a bubble at $N_{Re} < 5$ where liquid is streaming down the central axis of the sphere and round the bubble surface. Garner (48) has demonstrated that the streamline pattern is due to viscous drag of the outer fluid moving past the drop or bubble. The momentum of the bulk liquid is transferred to the bubble surface by viscous shear forces. The interface, itself, is in motion and, if the oscillation between stretching and contracting of the surface unal ters the surface tension, and the potential energy of the surface is regained, then the energy is transferred to the gas within the bubble. Successive layers within the gas bubble flow with decreasing velocity until a stagnant point is reached where the linear velocity is zero. The position of the stagnant point or ring with respect to the bubble shape changes with alteration of the velocity of the bubble, i.e., with change in the momentum of the outer liquid. Figure 7, p. 74, shows the flow pattern within a bubble at $N_{Re} > 70$ where owing to increased velocity /
velocity, the bubble has flattened and the stagnant point has moved towards the upper or forward surface of the bubble.

The flow pattern inside a bubble in a bubble swarm is difficult to assess owing to many factors, notably those of: rapid changes in shape; coalescence; irregular path of rise; and high $N_{Re}$ in liquids of low viscosity etc. It can only be concluded that in a bubble swarm, bubbles of $<0.5$ mm. radius, conditions approximate to streamline flow within the bubble, whereas for larger bubbles of $>3$ mm. radius conditions approach that of turbulent flow within the bubble.

(ii) Mass Transfer from a Rising Bubble.

The rate of absorption of oxygen into de-aerated water from bubbles of various diameters (94) indicate an average value for $K = 0.8$ for a bubble of 1 mm. diameter where $K$, the absorption coefficient was defined as the percentage of total oxygen dissolving per cm. of bubble rise. The range of bubble diameters studied was $284 \mu - 5$ mm. radius. $K$ values for various bubble diameters given by Pattle (94) indicate that the absorption efficiency of small bubbles is greater than the absorption efficiency of large bubbles of the same total volume.
The results of Pattle's work are comparable with those of Guyer and Pfister (53) who investigated the rate of mass transfer associated with carbon dioxide bubbles formed at the rate of 3 per second. Guyer and Pfister have concluded that the rate of solution of a gas from a rising bubble is independent of the final volume of the bubble.

It is apparent then, that turbulence, of which the mass transfer rate is a function, is damped out within a few centimetres rise, after which the absorption rate attains a constant value.
FIG. 8.

BUBBLE ABOUT TO BURST.

FIG. 9.

BUBBLE BURSTING

FIG. 10.

AREA OF HEAVING SURFACE.
The elucidation of the mechanism by which a bubble bursts at a liquid surface has been revealed by high speed photography (13, 69, 79, 122). Pictures taken at the rate of 3,000 per second have revealed the process to occur in the following manner:-

(a) a polip develops on the hemispherical surface of the bubble. (Fig. 8, p. 78.)

(b) the bubble then collapses. And in doing so, produces a mist or cloud of fine droplets of approximately 60 μ diameter, leaving a large gap in the bubble envelope.

(c) the escaping gas disperses the droplets as a fine spray, Fig. 9, p. 78.

(d) a crater is then formed at the bubble site and the inrushing flow of liquid produces an unstable jet of liquid which

(e) breaks up into a number of large drops of diameter > 1 mm.

Thus the production of a very fine spray of drops, and of a smaller number of large drops, accompanies the bursting of a bubble. The region where bubbles are bursting has been termed (61, 62), the 'area of heaving surface' Fig. 10, p. 78. The terminology is somewhat misleading. An alternative title would be 'area of boiling /
boiling surface' which implies the idea of disruption of the surface. It is of note that at this point the system has altered from a gas bubble in a liquid to that of a liquid drop in a gas. Thus, conditions now favour absorption of a soluble gas whereas during bubble rise conditions favoured absorption of a relatively insoluble gas.

(ii) Mass Transfer at the Region of 'Boiling Surface'.

The efficiency of various surfaces during absorption of a gas by a liquid has been compared by Holroyd (62). The surfaces under study were termed: 'boiling surface'; bubble surface and stagnant film surface; Table 9. groups K values for these respective surfaces.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Area (1) cms.²</th>
<th>Clean water K(1) cms. hr⁻¹</th>
<th>Area (2) cms.²</th>
<th>5pp. 10⁻⁵ T.R.O. K(2) cms. hr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling</td>
<td>50</td>
<td>264</td>
<td>50</td>
<td>264</td>
</tr>
<tr>
<td>Bubble</td>
<td>206</td>
<td>178</td>
<td>300</td>
<td>35</td>
</tr>
<tr>
<td>Stagnant film</td>
<td>400</td>
<td>24</td>
<td>400</td>
<td>0</td>
</tr>
</tbody>
</table>

T.R.O. = Turkey red oil - a sulphonated castor oil.
(a) Stagnant film surface is defined as a surface which
which itself remains undisturbed but below which
velocity currents are flowing.

(b) Bubble surface describes a surface in violent
motion and of irregular shape.

(c) Boiling surface is termed the surface of liquid
where bubbles are bursting.

It is apparent from Table 9 that violent agitation
of the boiling surface is inherent in large values of $K$
the mass transfer coefficient compared with values of $K$
for bubble and stagnant film surfaces.

However in a small diameter tube $\frac{1}{2}$ " the rate of
absorption of gas from a bubble swarm, at the area of
boiling surface, will be less than for on semi-infinite
interface not only in that the area is smaller but that
the mist and fine droplets of absorbent are restricted
by the expanding layers of liquid from the bursting of
neighbouring bubbles.
THE SHAPE AND OSCILLATION OF RISING BUBBLES.

The assumption that all bubbles are spherical can only be made under limiting conditions. Primarily, distortion from the spherical form is caused by an uneven pressure distribution over the bubble surface. It is generally found that only bubbles of small diameters \(< 0.5 \text{ mm}\) moving at low \(N_Re\) values retain their spherical form. At greater diameters and \(N_Re\) the bubble assumes a flattened shape until the bubble shape is that of a 'slug' or capsule. At this point the capsule breaks up into a number of smaller components of nearly spherical dimensions.

The path described by a rising bubble in a liquid is directly related to the velocity and diameter of the bubble. Miyagi (81) has reported that bubbles of diameter \(< 0.1 \text{ cm}\) are spherical and rise in straight vertical lines. Nevertheless, at a diameter of approximately 0.15 cm. the path of rise of a bubble assumes a helix of small pitch and amplitude. With increasing diameter, the pitch and amplitude increase until at a bubble diameter of 0.5 cm. the path of rise alternates between periods of vertical ascent and helical oscillation. Larger bubbles of diameter \(> 0.9 \text{ cm}\) oscillate about the line of ascent and rise in straight lines.

Lamb (72) in a study of the swinging of small rising bubbles has related \(T\), the time of swing of the bubble /
bubble to $r$ the radius of the bubble, $\rho_L$ the liquid density, and $\sigma$ the pressure on the bubble in the equation:

$$T = \pi \sqrt[3]{\frac{\rho_L r^3}{3\sigma}}$$

Values of $T$ derived for an air-water system show that a 1 c.c. (6.2 mm. rad.) bubble rising in water gives an average swinging time of 0.11 sec. whereas a 0.5 c.c. bubble (4.9 mm. rad.) has an average swinging time of 0.073 secs. These values of $T$ obtained from 20 have been shown to be in agreement with experimental values determined from bubble photographs. Equation 20 is applicable to ellipsoidal bubbles provided $r$ is replaced by $\frac{a}{2}$ where $a$ is the major axis diameter.

The properties of a bubble swarm are a mixture of all these modes of ascent. And it is unlikely that straight line vertical ascent is present because of a jostling movement between neighbouring bubbles. A marked feature of bubble swarms produced at small gas rates (0.1 gm. moles. hr$^{-1}$) is that there is always present a cycle of acceleration and deceleration of the production of bubbles at the sinter face (34). This unsteady state condition may be counteracted by reducing the capacity behind the sinter and increasing the pressure of the inlet gas. At higher gas rates of the order of 0.3 gm. moles /
0.3 gm. moles. hr$^{-1}$ the rate of bubble formation is constant.

All the above phenomena hold for gas-liquid systems where the liquid is pure. The effect of contaminants on bubble path is discussed on page 92.
THE VELOCITY OF A RISING BUBBLE.

The factors affecting the velocity of a bubble may be subdivided into the following sections:

(a) The velocity of a bubble in an infinite medium
(b) The variation of velocity with bubble diameter.
(c) Wall and column effects.
(d) Proximity and contact with other bubbles.
(e) Adsorption of materials on the bubble surface.
(f) Changes in temperature of the system which subsequently alter the physical properties of the medium.

(a) The Velocity of a Bubble in an Infinite Liquid Medium.

Siemes (107) has derived a mathematical expression for the velocity of a bubble rising in an infinite medium. The equation is of the form:

\[ \frac{\sigma}{\rho} t(e) + \rho \eta g \cdot j(e) - \rho L \frac{U^2}{2} \cdot f(e)^2 = 0 \]  

where:

\[ t(e) = \sqrt{\frac{1}{e^2 + 1 - 2e}} \]

\[ j(e) = e^{2/3} \]

and

\[ f(e) = \frac{U \theta (b^2 \sin^3 \theta + c^2 \cos^3 \theta)}{U \cdot b \sin \theta} \]  

\[ e = \frac{1}{\sqrt{1 - 2e}} \]
$e$ = the ellipticity of the bubble
$b, c$ = the major and minor axis of the bubble
$U$ = the velocity of the bubble
$V$ = the velocity of the streamlines at the interface.

Experimental values of $U$ for air bubbles (0.4 - 20 mms. radius) in water have been proved to be in agreement with the value of $U$ predicted by equation 21. From photographs, the ellipticity of 87 bubbles of radius 0.65 - 3.6 mm. and whose velocity varied from 14-26 cm. sec$^{-1}$ were measured (107) to within the accuracy of the photographic grains. The ellipticity values derived experimentally were again in agreement with the theoretical expression 22.

$$T(e) = \frac{\frac{U^2}{rg} - 0.900}{\frac{\sigma_{\phi_L r^2 g}}{\rho_{L r^2 g}} - 0.434}$$

where $e$, the ellipticity, is expressed as a function of $\frac{U^2}{rg}$ and $\frac{\sigma}{\rho_{L r^2 g}}$. Despite good agreement between observed and calculated values of the velocity of rise, the water used was stated to be contaminated with traces of organic impurities. The latter would indeed cause the bubble to assume a more spherical shape and so increase the velocity of the bubble.
For larger bubbles of \( r > 3 \) mm, Davies and Taylor (29) have found the velocity of a bubble to be in accordance with the equation,

\[ U = 0.82 \sqrt{rg} \]  

The theory on which equation 23 is based assumes that the shape of a bubble is spherical of radius \( r \), where \( g \) is the acceleration due to gravity. If, however, the bubble is distorted to an extent greater than 10% of the initial distortion then the coefficient in equation 23 changes from 0.82 to 0.97. This correction must be applied to account for fluctuation of the bubble about a mean shape.

(b) The Variation of Velocity with Bubble Diameter.

From a consideration of experimental data Allen (81) has proposed a linear relation between the velocity and diameter of a rising bubble. The equation is of the form,

\[ U = 103 d \]  

where \( U = \) the velocity in cms. sec\(^{-1}\)

and \( d = \) the diameter of the bubble in cms.

Equation 24 is only valid for bubbles \( < 0.4 \) mms. diameter at \( \text{Re} < 1 \). For increasing values of bubble diameter 0.4 /
The velocity of air bubbles in water at 20°C.
0.4 - 2.4 mm. and $N_{Re} > 1$, the coefficient in equation 24 is altered from 103 to 108.

Graph 8, p. 88, illustrates the variation of terminal velocity of an air bubble in water with bubble radius. The results are taken from the literature (28, 81, 91). The discrepancies in the results are due to experimental technique rather than to actual fluctuation of the bubble velocity. The general sources of error in the experimental measurements were due to failure in the application of wall and column correction factors, impurities in the liquid medium, and the non-saturation of the liquid medium with gas before the velocity was determined. In the last mentioned source of error gas will dissolve in the liquid and the velocity will alter in the manner shown by Graph 8, the value of which will depend on the bubble radius. In Graph 8 the velocity-radius relationship may be divided into three well defined regions:

(i) bubbles of radius < 1 mm., where the bubbles are streamline and rise in vertical lines. The velocity value, $U$, reaches a maximum at $r \sim 1$ mm.

(ii) bubbles of radius 1 - 3 mm., where the bubbles are ellipsoidal in shape and rise in a zig-zag path oscillating about the major axis. In this region the velocity diminishes to a minimum at $r \sim 3$ mm.

(iii) bubbles of radius 3 - 12 mm., where the bubbles are distorted and the bubble path is haphazard. The $U$ value then increases gradually from the minimum /
minimum at \( r \sim 3 \text{ mm} \).

It is important to note that the velocity maximum pertains only to the air-water system. For the air-glycerol system the \( U - r \) relationship depicts no sharp maximum (107) but only a gradual increase of \( U \) with increasing bubble radius.

(c) Column Correction Factor for the Velocity of a Bubble Rising in a Tube.

The effect of tube diameter on the velocity of a rising bubble is accounted for by the Ladenberg correction expressed as:

\[
U = U' \left(1 + 2.1 \frac{d}{D}\right)
\]

where \( U \) = the velocity in an infinite liquid \( \text{cms. sec}^{-1} \)

\( U' \) = the observed velocity in a tube of diameter \( D \) \( \text{cms.} \)

\( d \) = the diameter of the rising bubble \( \text{cms.} \)

Equation 25 is applicable for values of \( \frac{d}{D} < 0.1 \), e.g. Allen's (81) velocity experiments in which the diameter \( d \) of the tube was 3 \( \text{cms.} \) and \( d \) was studied in the range \( D \) 0.005 - 0.04.
(d) Variation of Bubble Velocity with Bubble Proximity.

By a theoretical analysis, Stimson and Jeffrey (110) have proved the proximity of two spheres to affect the value of the bubble velocity in a way such that

\[ U = f \left( P \cdot \frac{d}{L} \right) \]

where

- \( U \) = the bubble velocity \( \text{cms. sec}^{-1} \)
- \( P \) = the bubble velocity in \( \text{cms. sec}^{-1} \) derived from Stoke's Law.
- \( d \) = the bubble diameter \( \text{cms.} \)
- \( L \) = the distance between centres of two adjacent bubbles \( \text{cms.} \)

It is then possible that several bubbles rising in a liquid will have a velocity greater than two bubbles under the same conditions (91). The circulating liquid in a tube through which bubbles are rising is then due to the upward stream of bubbles which induces a rising stream of liquid in the centre of a liquid column.

Correspondingly there is present a down-current of liquid near the column wall. Owens (93) has reported a 13% difference between the velocity derived for a group of bubbles and that for a single bubble.

When the bubbles differ markedly in size the larger bubble having the greater velocity will jostle and push aside the small bubble which may either be decelerated for /
for a short period or be sucked into the slipstream of the larger bubble and consequently be accelerated in movement.

(a) The Velocity of Bubbles Rising in Liquids Containing Surface Active Agents.

It has been said (page 82) that clean bubbles (that is to say, bubbles rising in pure liquids) rise in a spiral path. But, on the addition of contaminants such as grease, Pattle (94) has noted that the spiral mode of rise is changed to that of a zig-zag path. If the surface active agents are present in small amount in the liquid phase, then adsorbed molecules on the bubble will be swept to the rear of the bubble surface, thus leaving the frontal bubble surface clean during bubble rise. The effect on the bubble velocity will then be small or negligible. But, if sufficient contaminant is present in an amount required for the formation of a multimolecular layer over the bubble surface, then the adsorptive forces may be strong enough to alter the shape of the bubble from that of an ellipsoid to that of a sphere. A spherical form offers least resistance to flow in a liquid, so that, by addition of contaminant in sufficient quantity to mould the bubble as a sphere, the velocity of such a bubble will increase.

Hixon /
Hixon and Gaden (50) have ascertained that the addition of foam control agents causes marked changes in the physical properties of liquid fermentation media. The fermentation broth is aerated by bubbling oxygen through the system. This process is accompanied by the formation of an undesirable froth at the liquid surface. The addition of an anti-foam agent not only alters the average bubble size and hence the area of transfer, but controls the bubble froth and reduces the number of bubble coalescences in unit time.

The addition of surface active agents apart from increasing the velocity of a bubble, by changing the bubble shape to that of a sphere, does have the disadvantage of decreasing the mass transfer rate of solute into solvent. On referring to Table 9, page 80, it is seen that on the addition of 5 pp. $10^5$ of Turkey red oil to a bubble swarm in clean water the value of $K$ is reduced by 12% of the original value. The additives have then the effect of hindering transfer at the bubble interface, because of the close packed adsorbed layers together with the reduction of the mixing velocity gradient on the liquid side of the interface.

(f) The Variation of Bubble Velocity with Temperature.

Increase in temperature of the system alters the physical/
physical properties of the liquid. A decrease in surface tension appears to increase the volume of a bubble found at an orifice. The results of Datta (28) confirm this statement within the range of orifice diameter 0.036 - 0.63 cms.

Proof as to whether viscosity or surface tension is the major factor controlling bubble size is inconclusive. It is an experimental fact that a hundred-fold increase in viscosity decreases the bubble volume by nearly 10%. It can be concluded that viscosity has little effect on bubble velocity, and it is surface tension that characterises bubble volume and so determines the velocity value.
THE VELOCITY OF BUBBLE SWARMS.

It must be appreciated that the determination of the velocity of a bubble swarm presents many problems of which the greatest is the unpredictable movement of bubbles within the swarm.

To regard a bubble swarm as composed of bubbles each of radius $r$ and moving in straight vertical lines, is too great a simplification. Also at various gas rates different pores at the sinter interface will characterise different bubble sizes and shapes. Again, the average distance between bubble centres will vary considerably over the length of the liquid column; and to consider the bubble swarm as a close packed spherical pattern positioned stationary in a flowing liquid leads only to a figure for bubble swarm velocity having an error of as much as 30% (107).

As a generalisation; at small gas rates when only a few of the sinter pores are in action, the mean velocity of a bubble swarm approaches that of the velocity of a single bubble under similar conditions, but when the inlet gas rate has increased to such an extent that all the pores at the sinter interface are gassing and the bubble size distribution has greatly altered, then the mean bubble velocity is a complex function of the number of pores, pore /
pore size, distance between bubble centres and bubble size distribution. In the latter case, only an approximate value can be assigned for the mean velocity of a bubble in a bubble swarm, so that experimental determination of the bubble velocity is the best solution. In the former case, when only few pores are in action, the predicted values should agree with experimental observations.
Preliminary determinations using the apparatus described by Verschoor (117) which related the total bubble volume to the liquid hold up gave varying results. The liquid hold up corresponding to a change in hydrostatic head pressure was measured by a water manometer sensitive to changes of 0.01 mms. pressure. The variations in measuring the liquid hold up were attributed to the small diameter tube (32 mms.) and the fluctuating liquid surface within the tube. This method after several trials was rejected and replaced by a photographic technique.

The essence of the method was to photograph a swarm of bubbles rising at a known gas rate in a column of liquid. From the photograph thus obtained; the total number of bubbles was counted; a random sample from the bubble population was taken and the dimensions of each bubble in the sample measured; and the liquid hold up measured. From these measurements the surface area of gas-liquid contact was calculated for a fixed inlet gas rate.

The dimensions of the column containing the liquid (toluene, decalin or tetralin) were similar to those of the reactor used in the hydrogenation experiments, Part I, namely /
nearly of 32 x 35 mm. Pyrex tubing which had a glass sinter of porosity 2 fused at the end. The 15" tube was placed inside a 4 x 4 x 17" Perspex box and the intervening space filled with water. A vertical scale graduated in millimetres was attached to the outside face of the box. The box prevented distortion of the bubbles when photographed - the water acting as a planar-concave lens to the convex lens produced by the column when filled with liquid.

A quarter plate camera was positioned so that the paper scale and column were in focus. Behind the box and facing the camera was placed a black screen. A lamp flash was positioned 1\(\frac{1}{2}\)" distant from the Perspex box in a line perpendicular to that made by the camera and paper scale. A white screen was placed behind the box in a line with the lamp flash. The whole apparatus was excluded from daylight.

Experimental Technique.

The required gas or gas mixture was made up in the 1.2 c.ft. gas holder. Two hours were allowed for the system to attain room temperature. The column was filled with liquid (200 cc.) and photographed by simultaneously triggering the flash and exposing the photographic plate /
plate at f. 32. This photograph was referred to as the 'master' copy, which gave the height of liquid column when no gas was passing. Gas was then passed into the liquid at a known constant rate via the gas train shown in Fig. 1, p. 37. Two minutes were allowed for the liquid to become saturated with the gas before the bubble swarm was photographed. The gas rate was checked by leading the exit gases through a soap film meter.

The amount of liquid entrained by the gas during the experiment was found to be negligible, i.e. there was no observable difference between the liquid heights before and after the experiment.

Photographs of bubble swarms of both ethylene and mixtures of hydrogen and ethylene were taken in the liquids toluene, decalin and tetrailin. The systems were studied for a series of gas rates in the range 0.4 - 0.6 gm. moles. hr\(^{-1}\).

**Photographic Materials.**

Special Rapid Panchromatic 1/4 Plates were suitable for photographing a bubble swarm without loss in sharpness of silhouette. Exposed plates were developed in I.D.11 and fixed in an acid wash. The plates were enlarged to 10" x 8" on normal glossy bromide paper using I.D. 163 as developer.
Method of Measurement of Bubble Size and Calculation of Bubble Swarm Surface Area.

The following measurements were taken from each photograph.

(i) The number of bubbles in the liquid column was counted. An estimate of the number of bubbles forming at the sinterface together with those bursting or floating at the liquid surface, was made, and added to the total. The arithmetic mean of four counts was taken as the value representing the total number of bubbles in the column at that particular gas rate.

(ii) The liquid hold up was measured by the difference in height of liquid in the column while gas was passing and no gas passing. The cross section of the tube was calculated to be 8.03 cm$^2$ and the tube assumed to be of uniform internal diameter.

(iii) A random sample of approximately 300 bubbles was taken from each photograph; and the vertical and horizontal diameter of each bubble was measured by a cathetometer. Measurements were accurate to 0.1 mms, and the sample considered sufficiently large to approximate closely to the actual swarm.

(iv) From the measurements obtained in (iii) a grouped frequency /
frequency table was formed from which was calculated, for both horizontal and vertical diameters, a statistical mean for each diameter respectively.

(v) The surface areas of bubble swarms at their respective inlet gas rates were calculated where the bubbles were assumed to be:

(a) spheres,
(b) prolate spheroid,
(c) oblate spheroid.

(a) The surface area of a sphere was taken as

\[ A \text{ cm}^2 = 4\pi r^2 \]

where \( r \) is the bubble radius cm.

(b) The surface area of a prolate spheroid or the surface area of an ellipse rotating about the \( x \) axis was expressed as:

\[ A \text{ cm}^2 = 2\pi b^2 + \frac{2\pi ab}{e} \cdot \sin^{-1} e \]

where \( a, b \) = the horizontal and vertical bubble diameters cm, respectively.

and \( e \) = the eccentricity defined as

\[ e = \sqrt{1 - \frac{b^2}{a^2}} \]

(c) The surface area of an oblate spheroid or the surface area /
### TABLE 10.

**THE SURFACE AREA OF BUBBLE SWARMS AT VARYING GAS RATES**

---

**BUBBLE ASSUMED TO BE A SPHERE.**

<table>
<thead>
<tr>
<th>Plate No.</th>
<th>Liquid</th>
<th>Gas $\text{C}_9\text{H}_8$: $\text{H}_2$: $\text{X}$: $\text{Y}$</th>
<th>Inlet Gas Rate, gm. moles, hr$^{-1}$, N.T.P.</th>
<th>Bubble No.</th>
<th>(L - Lo) cems.</th>
<th>Volume $\Lambda$(L - Lo)cems.$^3$</th>
<th>Mean Radius cems.</th>
<th>Surface Area cems.$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>1: 0</td>
<td>0.42054</td>
<td>1339</td>
<td>0.27</td>
<td>2.1712</td>
<td>0.0729</td>
<td>89.3</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>1: 0</td>
<td>0.47472</td>
<td>1429</td>
<td>0.31</td>
<td>2.4923</td>
<td>0.0747</td>
<td>100.1</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>1: 0</td>
<td>0.51870</td>
<td>1520</td>
<td>0.45</td>
<td>3.167</td>
<td>0.0828</td>
<td>131.1</td>
</tr>
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<td>4</td>
<td>Toluene</td>
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<td>1630</td>
<td>0.66</td>
<td>5.3072</td>
<td>0.0933</td>
<td>201.9</td>
</tr>
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<td>5</td>
<td>Toluene</td>
<td>1: 1</td>
<td>0.46720</td>
<td>1137</td>
<td>0.43</td>
<td>3.4577</td>
<td>0.0891</td>
<td>116.4</td>
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<td>0.52914</td>
<td>1346</td>
<td>0.57</td>
<td>4.5836</td>
<td>0.0933</td>
<td>147.3</td>
</tr>
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<td>0.86</td>
<td>6.9157</td>
<td>0.1010</td>
<td>206.5</td>
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<tr>
<td>8</td>
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<td>1687</td>
<td>0.97</td>
<td>7.8000</td>
<td>0.1033</td>
<td>225.4</td>
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<tr>
<td>9</td>
<td>Decalin</td>
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<td>0.49664</td>
<td>935</td>
<td>0.51</td>
<td>4.1010</td>
<td>0.1020</td>
<td>120.7</td>
</tr>
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<td>10</td>
<td>Decalin</td>
<td>1: 1</td>
<td>0.55215</td>
<td>1257</td>
<td>0.61</td>
<td>4.9052</td>
<td>0.0977</td>
<td>150.7</td>
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<td>11</td>
<td>Decalin</td>
<td>1: 1</td>
<td>0.62007</td>
<td>1619</td>
<td>0.74</td>
<td>5.9506</td>
<td>0.0957</td>
<td>186.4</td>
</tr>
<tr>
<td>12</td>
<td>Decalin</td>
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<td>0.65258</td>
<td>1743</td>
<td>0.86</td>
<td>6.9154</td>
<td>0.0932</td>
<td>211.2</td>
</tr>
<tr>
<td>13</td>
<td>Tetrinal</td>
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<td>0.49664</td>
<td>932</td>
<td>0.52</td>
<td>4.1814</td>
<td>0.1025</td>
<td>122.4</td>
</tr>
<tr>
<td>14</td>
<td>Tetrinal</td>
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<td>0.55215</td>
<td>1333</td>
<td>0.64</td>
<td>5.1463</td>
<td>0.0973</td>
<td>199.6</td>
</tr>
<tr>
<td>15</td>
<td>Tetrinal</td>
<td>1: 1</td>
<td>0.62007</td>
<td>1625</td>
<td>0.77</td>
<td>6.1918</td>
<td>0.0959</td>
<td>191.7</td>
</tr>
<tr>
<td>16</td>
<td>Tetrinal</td>
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<td>0.65258</td>
<td>1735</td>
<td>0.81</td>
<td>6.5134</td>
<td>0.0955</td>
<td>204.6</td>
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<td>17</td>
<td>Toluene</td>
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<td>0.49564</td>
<td>1171</td>
<td>0.29</td>
<td>2.3320</td>
<td>0.0723</td>
<td>96.9</td>
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<td>Toluene</td>
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<td>1450</td>
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<td>3.6887</td>
<td>0.0752</td>
<td>105.3</td>
</tr>
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<td>Toluene</td>
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<td>0.53</td>
<td>4.2817</td>
<td>0.0849</td>
<td>147.0</td>
</tr>
<tr>
<td>20</td>
<td>Toluene</td>
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<td>0.57385</td>
<td>1657</td>
<td>0.70</td>
<td>5.6290</td>
<td>0.0933</td>
<td>181.0</td>
</tr>
<tr>
<td>21</td>
<td>Toluene</td>
<td>1: 0</td>
<td>0.59741</td>
<td>1758</td>
<td>0.82</td>
<td>6.5920</td>
<td>0.0971</td>
<td>208.4</td>
</tr>
<tr>
<td>Plate No.</td>
<td>Bubble Vel. cms. sec^{-1}</td>
<td>Mean a. cms.</td>
<td>Mean b. cms.</td>
<td>Volume cms^3 about Ox.</td>
<td>Volume cms^3 about Oy.</td>
<td>Inlet Gas Rate gm. moles hr^{-1}</td>
<td>Ellipticity e.</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------------</td>
<td>--------------</td>
<td>--------------</td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>33.8</td>
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area of an ellipse rotating about the y axis was defined as:

$$A_{cm}^2 = 2\pi a^2 + \frac{\pi b^2}{e} \cdot \ln \frac{1 + e}{1 - e}$$

where a, b, and e were the same as in (b).

The experimental results were tabulated: Tables 10 and 11, pp. 102 and 103. The results were of the order predicted by Halberstadt and Prausnitz (54) i.e., bubbles formed at a sinter of mean pore diameter 90 \( \mu \) at an inlet gas rate of 0.5 gm. moles hr\(^{-1}\) have a diameter of 1.8 mm in water.
DISCUSSION OF RESULTS.

Specimen photographs are shown on pp. 106-7 from which bubble dimensions were taken. Photograph A illustrates the method of detachment of bubbles emerging from a single orifice at high gas rates. The gas phase is an ammonium chloride aerosol passing through a capillary tube (0.224 cms. diam.) at a gas rate of 2 gm. moles hr$^{-1}$. The gas rate is large enough in order that an emerging bubble is in contact with a bubble that has been previously formed. Bubble detachment is rather from the bubble contact area than from the capillary because the time of contact is so short that coalescence does not occur.

Photograph B shows A a short time later when the bubbles are now parted. The rising bubble is in violent oscillation. And the 'beehive' shape will subsequently flatten out into an ellipsoidal shape. Necking off of the bubble appears to take place within the capillary bore and not necessarily at the pore end.

The random distorted shape of two bubbles about to coalesce at a gas rate of 4 gm. moles hr$^{-1}$ is exemplified in Photograph E.

At lower gas rates, in the range 0.5 gm. moles hr$^{-1}$ a more symmetrical bubble, D, is the general rule. The tail-like protruberance present immediately after formation /
Graph 4.

- ○ Ethylene in Toluene
- ● Mixture in Toluene
- △ Mixture in Decalin
- × Mixture in Tetralin

Bubble Count: $10^2$

Inlet Gas Rate: GM. Moles/HR.

Bubble number.
tion oscillates in and out of the mean bubble shape until, after a few centimetres rise, the movement is damped out and the bubble assumes a symmetrical form. The phenomenon of rippling at the interface in D is absent.

A typical swarm, from a sinter of porosity 3, at a gas rate of 0.7 gm. moles. hr.\(^{-1}\) is shown in C where the area of boiling surface is clearly seen.

The movement of matter inside a bubble is illustrated in F and G by analogy with liquid drops. F and G show drops of chloroform plus small quantities of aluminium powder, falling in a viscous solution of cellofas. The circular whirls at either end of the drop are similar to the type of motion found inside a rising bubble.

**Variation of Bubble Number with Inlet Gas Rate.**

The relationship is depicted on Graph 4, p. 108 where it is seen that the number of bubbles in toluene is considerably greater than either of those obtained in decalin or tetralin at the same inlet gas rate. The effect of inlet gas mixture on bubble number is difficult to predict.

**The Ellipticity Distribution in a Bubble Swarm.**

Graph 5, page 110, represents the distribution curve of the percentage bubbles having any diameter \(< 3.0 \text{ mm}\).
Graph 5.

A. Major Axis.
B. Minor Axis.

Plate 14, inlet gas rate 0.55 gm.moles/hr. in tetralin.

Bubble size distribution in tetralin.
The distortion of air bubbles in water.
The measurements are taken from Plate 14, Table II. Two curves, A and B, are found. The former is a normal Gaussian curve for the diameter of the major axis, whereas the latter is a skew distribution for the diameter of the minor axis. The variation in bubble shape lies mainly in the value of the major axis diameter so that the bubble shape approximates not to a sphere but to an ellipsoid.

Values taken from the literature (97, 107, 112), for the mean ellipticity of bubbles are shown in Graph 8A, p.111. For air bubbles in water Stuke (loc. cit.) found that at

\[ e = 0.80, \ r = 0.065 \text{ cms.} \]

compared with the present work Table 11, p.103, of

\[ e = 0.82, \ r = 0.070 \text{ cms.} \]

Graph 8A shows that as the bubble diameter decreases values of \( e \rightarrow 1 \), i.e. the bubble assumes a spherical form at diameters \(< 0.07 \text{ cms.}\).

Variation of Surface Area with Bubble Shape.

The surface area of a bubble swarm naturally depends on the mean bubble shape whether it be spherical or a flat plate. Graph 6, p. 115, shows this relationship for the surface area of bubble swarms in toluene, decalin and tetralin where the mean bubble shape is considered to /
Variation of bubble swarm surface area with bubble shape.
The surface area of a bubble swarm in toluene.

GRAPH. 7.

ETHYLENE IN TOLUENE.
AREA CALC. ASSUMING BUBBLE TO BE AN OBLATE SPHEROID.
to be either a sphere, or a prolate ellipsoid, or an oblate spheroid. The surface area of the bubble swarms is greatest for a mean shape of an oblate spheroid and least for that of a sphere.

The surface area of a bubble swarm in toluene at various inlet gas rates is shown in greater detail in Graph 7, p. 114. At higher gas rates the surface area will be expected to increase as shown until a point is reached where coalescence becomes appreciable, so that the surface area decreases in value. This region was not investigated as it was outside the range of inlet gas rates used for determining reaction rates in the slurry phase.

A statistical analysis (64) and 't' tests where

\[
t = \frac{\bar{x} - \bar{x}'}{\sigma} \sqrt{\frac{n_1n_2}{n_1 + n_2}}
\]

where \( \sigma^2 = \left[ \sum (x'^2) - \frac{(\sum x')^2}{n_2} + \sum (x'^2) - \frac{(\sum x)^2}{n_1} \right] \frac{n_1 + n_2 - 2}{n_1 + n_2 - 2} \)

and \( \bar{x} = \frac{\sum x}{n_1} \), \( \bar{x}' = \frac{\sum x'}{n_2} \)

\( x \times x' = \text{determination} \)

\( n_1n_2 = \text{number of determinations} \)
shows that $t = 2.17$ for Plates 13 and 18 where $t$ must not be less than 1.96 for infinite degrees of freedom to be significant at the 5% level. There is then evidence to believe that the bubble swarm formed in toluene is different from that in either tetralin or decalin.
SUMMARY.

(i) The surface area of bubble swarms in toluene, decalin and tetralin has been determined at gas rates comparable with those used in hydrogenation experiments, Part I.

(ii) Bubbles $> 0.07$ cms. diameter at $N_{Re} > 100$ approximate to the shape of an oblate spheroid whose surface area is given by equation 30.

(iii) Bubble swarms in toluene are significantly different from those in either decalin or tetralin at the same inlet gas rate and temperature.

(iv) The ellipticity of bubbles within the inlet gas rate range $0.4 - 0.6$ gm. moles. hr$^{-1}$ are of the order $e = 0.80$. 
PART III

THE INSTANTANEOUS ABSORPTION RATES OF ETHYLENE AND HYDROGEN IN TOLUENE.

Theories of the Absorption Process.

The efficiency of transfer of solute to a solvent medium depends to a large extent on how the solute is dispersed or contacted with the solvent, and on the conditions of turbulence in the solvent and solute adjacent to the interface. The physical absorption of a gas by a liquid is a function only of the design, operating characteristics of the equipment, and the physical properties of the media.

Although the efficiency of absorption differs in various equipment the manner in which the transfer of matter occurs remains the same. The theories of absorption, namely those of Lewis and Whitman (77), Higbie (58), and Danckwerts (27) although differing in concept, all arrive at the same final conclusion by use of a coefficient $K$ which, in combining the liquid characteristics of the system, leads to an overall equation for the rate of absorption of a gas in a liquid. $K$, the mass transfer coefficient, is of more practical use than the mathematical equations described in Part I, page 34.

(1) The
The Two-Film Theory of Lewis and Whitman.

This theory of absorption assumes that the exchange of solute between gas and liquid is so rapid that equilibrium is maintained at the interface between gas and liquid. The rate at which absorption occurs is controlled by the rate of transfer of solute to and from the interface. Mixing in the main bulk of the phases by convection is rapid. Within the bulk phases no concentration gradient exists until conditions approach close to the interface where each phase is regarded as made up of a thin stagnant film in which no convection occurs. Mass transfer of solute occurs through these films by molecular diffusion only. And it is the thickness of these films that controls the rate of absorption.

The subsequent effect of these films is represented by a coefficient $k_g$ for the gas film and $k_L$ for the liquid film. The rate of diffusion or the amount of solute transferred is also proportional to the difference in concentration of solute between the two phases, i.e. to the concentration gradient of solute, which represents the potential causing transfer to take place.

The two-film theory is applicable only for steady state conditions where the amount of gas transferred through the film is greater than the amount of gas within the film.

Nevertheless /
Nevertheless, it appears doubtful whether the conventional picture of a stagnant film of gas or liquid bears any relation to the absorption conditions. In practice, it is unlikely that such films exist so that turbulence extends from the bulk liquid to the interface itself. $x_L$, the stagnant film thickness may be regarded only as a mathematical expression for the resistance to transfer of material through an interface. The term, $x_L$, should then represent an indefinite thickness of liquid very close to the surface where all turbulent movement is damped out, i.e., where the size of eddy currents and their capacity for mass transfer have decreased until conditions are such that transfer of solute occurs only by molecular diffusion. Theory relates $k_L$ to $D$, the diffusion coefficient of solute in solvent $\text{cms}^2 \text{sec}^{-1}$, and $x_L$, the effective film thickness $\text{cms}$, as:

$$k_L = \frac{D}{x_L} \quad 32$$

This equation is only an approximation as $x_L$ is indeterminate, but because of its small value ($4.10^{-2}$ cms. for the air-water system), $x_L$ can be assigned a definite value without incurring any appreciable error.
Expression of Results.

The rate of mass transfer is defined by equation 33 such that

\[ \frac{Q}{t} = kA \Delta c \]

where

- \( Q \) = the quantity of material in gm. moles. transferred in the time \( t \) secs.
- \( A \) = the area of interfacial contact cms\(^2\).
- \( \Delta c \) = the driving force represented by the concentration gradient of solute between solute and solvent in gm. moles. cms\(^{-3}\) of solvent.
- \( K \) = the coefficient of mass transfer.

The units of \( K \), expressed by equation 33 are in cms. sec\(^{-1}\) or more conveniently cms. hr\(^{-1}\). \( K \) is defined as the weight of solute gas passing through unit area in unit time under unit concentration difference.

The two-film theory indicates a transfer coefficient \( k_G \) which is of importance in the absorption of a very soluble gas such as ammonia and sulphur dioxide, but is negligible when the solution of a relatively insoluble gas is considered. In the latter case, the resistance to absorption may be regarded as due totally to diffusion in the liquid film. It is known that for gases less soluble than carbon dioxide, the gas film is zero so that \( k_L \) becomes \( K \) where \( k_L \) is the liquid film coefficient of mass transfer.
(ii) The Penetration Theory of Absorption.

If conditions arise such that the amount of gas transferred is comparable with the amount of gas contained within the stagnant film, then for unsteady state conditions Higbie (58) has shown, for a carbon dioxide bubble in water, that the rate of mass transfer is dependent on the time of exposure of the phases. The relation found was:

$$ K = 2 \frac{D}{\sqrt{\pi t}} \quad \quad 34 $$

where $K$ has the same dimensions as before cm$s^{-1}$ sec$^{-1}$ and varies directly and inversely with the square root of $D$, the diffusion coefficient and $t$ the time of exposure respectively. Thus the shorter the exposure time, the greater the rate of transfer of solute to solvent. The creation of fresh liquid surface by increased agitation decreases $t$ and so increases $K$.

(a) The equation suggests that small elemental areas travelling in great circles from the forward to the rear face of the bubble have the same tangential velocity as that of the bubble. Also, the closer the elements of area are to the front and rear of the bubble, the greater will be the tangential velocity. Consideration of the system shows that zero velocity will be the case at these forward and rear bubble regions compared with that predicted by Higbie's equation.

(b) /
(b) Higbie's equation is applicable to a bubble of fixed area, but it is a condition of a rising bubble dissolving in a liquid, that the area is a function of time.

(c) The time of contact between phases is difficult to establish as the time of contact of small elemental areas will be different as the distance travelled by these areas may vary from 0 - \( \pi \) radians.

(d) Again, the surface renewal is not necessarily complete in the time taken for the bubble to rise a distance equivalent to one bubble diameter.

From these criticisms equation 34 is only an approximation to the conditions met with in practice.

(iii) The Surface Renewal Theory of Absorption.

The recently reported picture of absorption, presented by Danckwerts (27) appears to be more reasonable than the two theories previously discussed. The essential assumption of the theory is that the movement of liquid continually replaces 'old' elements of surface by 'fresh' elements of surface. 'Old' surface is the term for an element of surface which has been resident at the interface for a finite time; and in so doing absorbs gas. The term 'fresh' surface denotes an element of liquid free from gas. The rate of production of new surface is assumed to be constant at a value \( s \), so that the probability of surface refreshment is independent of surface age where the average absorption rate per unit /
unit area is given by

\[ Q = a \int_{t=0}^{\infty} e^{-st} \, dq(t) \]  

where \( s \) = the rate of surface renewal

and \( dq(t) \) = the amount of gas absorbed per unit area in \( t \) secs.

The only limitation of this concept lies in the fact that \( s \), the rate of surface renewal cannot be directly measured. In the case of physical absorption, \( s \) is related to the coefficient of mass transfer \( K \) and to \( D \) the difference coefficient as

\[ K = \sqrt{D \cdot s} \]

Danckwerts (27), in a detailed mathematical study of the three models of the absorption process described above, has shown that similar predictions are arrived at concerning the effect of chemical reaction rate in solution on the absorption rate of the reacting gas.

Thus, whatever the mechanism for the absorption process any of the three theories will lead to a favourable approximation, for the prediction of physico-chemical data, provided that the hydrodynamics of the system remain the same. If momentum is transferred through gas-liquid interfaces by successive layers then the true picture /
picture of absorption must be considered by taking into account not only molecular but also eddy diffusion of the solute in the solvent.
THE RATE OF ABSORPTION OF GAS FROM BUBBLES.

The first comprehensive experiments on the rate of solution of gases into liquids were those of Adeney and Becker (1) who studied the rate of absorption of oxygen into water by passing gas bubbles of varying volume (5 - 16 c.c.) up a tube of cross section 1 cm² containing pure water. The whole of the liquid was made to pass between the bubble and the wall of the tube; and the oxygen dissolved was found by chemical analysis of the resulting liquor. The results of Adeney and Becker's experiments were expressed as:

\[
\frac{dw}{dt} = f \left( \frac{A}{V} \right) \left( V \cdot s \cdot p - w \right)
\]

where \( \frac{dw}{dt} \) = the amount of gas dissolved at any time \( t \).

\( A = \) the area of interface between phases.

\( p = \) the partial pressure of the gas

\( f = \) the rate of escape of gas molecules back into the atmosphere, from unit area of surface as the amount of gas in solution increases.

\( s = \) the solubility of the gas in the liquid.

Equation 37 can be reduced to

\[
\frac{dc}{dt} = K (c_s - c)
\]

where /
The overall conclusion of these experiments shows that the rate of solution from air bubbles is $3 - 4$ times greater than that for an exposed gas-liquid surface; directly proportional to the surface area exposed; and inversely proportional to the diameter of the bubble. This conclusion is in agreement with the findings of Miyamoto and Nakata (82), who found that the rate of oxidation of sodium sulphite by bubbling air through a solution was constant when bubbles of similar size were used.

Their experiments also illustrated the fact that when the bubble size was increased, using the same volume of air as for the smaller bubbles, the rate of oxidation of the sodium sulphite solution decreased proportionally. Schwab and Berninger (101), and Scouller et al., (102) have extended these investigations using various gases in the temperature range $20 - 80^\circ C$. The rate of solution of the gas was measured by a manometric method.

In all the above studies, the effect of velocity on the bubble shape was not accounted for and, consequently, the rates per surface area of the gas-liquid interface are dubious. Also the experiments of Scouller et al., (102) lack data on contact times between phases.

The rate at which a gas dissolves in a liquid is closely /
closely related to the economy of the process. Short
contact times ensure high absorption rates. It is, then,
a natural trend for measurements of absorption rates to
be studied in laboratory apparatus which brings the solute
and solvent together for a short period of time ($10^{-3}$ secs.).

In 1923, Ledig and Weaver (75) reported a method
whereby the rate of solution of carbon dioxide in caustic
solutions could be measured. The essentials of the
system lay in the fact that a bubble of gas was absorbed
in a column of liquid open only to the atmosphere through
a capillary tube. The gas which was absorbed from the
bubble causes a contraction of volume in the system,
which was ascertained by photographing the movement of the
capillary meniscus. High initial rates of absorption
were obtained but soon decreased to a value which was
controlled by the rate at which the reagent diffused to
the liquid interface as well as the rate at which the
absorbed product could diffuse from the reaction zone.
This method of measuring instantaneous absorption rates
may be considered inaccurate because of the inertia of
the capillary meniscus in the initial stages of absorption
from the gas bubble.

Higbie (58) has designed an apparatus to test the
accuracy of equation 34. The method was restricted to
the absorption of carbon dioxide in pure water where a
capsule shaped bubble of gas was forced downwards through
a /
a glass tube filled with water. During the downward movement of the gas bubble, a film of liquid remained stationary between the bubble and the tube wall. The time of contact between gas and liquid was then a function of the bubble size and velocity. The liquid phase was analysed after each bubble passage for the total amount of gas absorbed. Contact times of \(< 0.01\) secs. were achieved. However, the experimental results were \(20\%\) below those predicted by equation 34. And for contact times of the order of \(10^{-2}\) sec., the experimental values were as much as \(50\%\) below the theoretical amount. This discrepancy was ascribed to the replacement of equilibrium conditions at the interface by a first order process.

Values for the absorption rate of carbon dioxide in water were of the order of

\[
5.3 \cdot 10^{-7} \text{ gm. moles. cm}^{-2} \text{ sec}^{-1} \quad \text{from equation 34.}
\]

and \(4.1 \cdot 10^{-7} \text{ gm. moles. cm}^{-2} \text{ sec}^{-1}\) from the assumption of first order process at the gas-liquid interface.

In a search for greater accuracy in the measurement of mass transfer rates Goodridge (52), in 1953, described an apparatus which measured the rate of solution in a liquid drop falling through a static gas layer, by recording the change in total pressure of the system. Pressure changes activated a sensitive diaphragm, the movement of which was electrically recorded on an oscillograph screen.
screen. Photographic records of the electron trace were taken enabling the rate of absorption of gas into liquid to be measured in $10^{-3}$ sec. In absorption experiments the solvent drop was formed in an atmosphere of hydrogen then allowed to fall through a layer of solute gas.

The objection to this method, delicate in the extreme, is that during drop formation the liquid layers nearest the surface are saturated with hydrogen so that on entering the solute gas, the rate of absorption of the gas in the liquid will depend on -

(i) penetration of the hydrogen layer within the surface layers;

(ii) the manner in which hydrogen diffuses from the interface into the bulk of the liquid. This fact is of importance since the contact time between phases is comparable with the speed of diffusion of hydrogen in the liquid;

(iii) the introduction of the liquid drop into the solute gas is by way of a wide bore tap. A more elegant alternative is the barrier film of aqueous alkyl sulphonates (31) which permits smooth passage of the drop without rupture of the film.

A similar apparatus has been used by Winfield (121) in order to investigate the rate of gas uptake by oxide catalysts, and by Prime Chi (96) and Willey (120) who have investigated sensitive methods for the electrical measurement of small changes in pressure.

An interesting method of studying absorption rates, apart from the well known totem-pole and wetted wall columns /
columns (109) is that of Danckwerts and Kennedy (26) whose apparatus consisted of a cylindrical drum which was rotated at high speeds. The drum was designed to carry a film of liquid through the gas so that the time of contact between phases was a function of the speed of rotation and the fraction of drum circumference exposed. Contact times were in the region of 0.0075 secs.

The only criticism of this method is the possibility of gas entrainment by the liquid film when contacted with the bulk liquid phase and distortion of the liquid film at high speeds with increase of surface area exposed. The apparatus although suitable for physical absorption studies is not adaptable to the study of absorption with chemical reaction in the liquid film where temperature effects due to heat of solution are appreciable as in the case of absorption of carbon dioxide by alkaline solutions.
EXPERIMENTAL.

The object of the experiments was to obtain values for the instantaneous absorption rate of both hydrogen and ethylene in toluene in the temperature range 20 - 100°C.

An experimental preamble met with little success. In the first apparatus gas was bubbled through a column of gas free liquid. The non-absorbed gas then entered a small gas bell floating in water. The bell was counterpoised by weights so that any movement of the bell did not incur a back pressure; and the inlet gas rate remained constant. The rate of movement of the bell as it filled with non-absorbed gas was measured by noting the rise of a pointer attached to the bell top. The pointer followed a paper scale. Readings of the pointer position were taken every 0.5 secs. The rate of absorption of the gas in the liquid was related to the difference in rates of rise of the pointer for gas in gas saturated liquid and gas in gas free liquid respectively. No values for the instantaneous absorption rate of hydrogen in toluene, decalin or tetralin were obtained.

The second apparatus was a modification of the first in that the gas bell was replaced by a soap film meter of cross section 3.463 cms. The movement of the soap film was followed by hand operation of a cathetometer mounted on slides and operated by a winding pulley mechanism.
The telescope was suitably counterpoised to provide easy movement of the assembly. The soap film could be followed over a vertical distance of 2\(\frac{1}{2}\) ft. An ink pen operated by an electromagnet attached to the telescope marked a trace on a strip of paper attached vertically to the cathetometer. An impulse time clock connected to an 8v. supply, actuated the magnet every 0.5 secs. thus producing a time mark on the ink trace. On passing gas through the liquid column the soap film was followed by winding the pulley mechanism so that the cross-wires of the telescope coincided with the soap film. The rate of rise of the soap film was measured off the ink trace and the rate of absorption of the gas in the liquid obtained as before. This method did not supply data on the instantaneous absorption rates but only gave a measure of the amount of gas required to saturate the liquid i.e., \(\alpha\), the solubility coefficient where:

\[
\alpha = \frac{V_o}{pV}
\]

where \(V_o\) = the volume of gas at N.T.P. dissolving in \(V\) cc. of liquid whose partial pressure is \(p\).

From the experiments, \(\alpha\) \(\text{H}_2\) in toluene (18\(^0\text{C.}\)) = 0.067 which is of the same order as the value reported by Lannung (74) \(\alpha = 0.066\) for \(\text{H}_2\) in benzene.

The ineffectiveness of this method was apparent so that /
**FIG. 3.**

**KEY**

1. FLOWMETER.
2. MANOMETER.
3. LUTE.
4. ABSORBER.
5. FIXED VOLUME.
6. BOURDON GAUGE.
7. DRUM RECORDER.
8. SOAPFILM METER.
9. LIQUID AIR TRAP.
10. VACUUM GAUGE.
11. VACUUM PUMP.
12. THERMOSTAT.
that it was considered necessary to revert from a constant pressure system to that of a constant volume system which required a sensitive pressure recording device.

Description of Apparatus.

The basic idea of the apparatus, Fig. 3, p.134, was that gas was passed as a swarm of bubbles at a known constant rate and temperature into a volume of liquid. The gas that was not absorbed by the liquid entered a closed system whose volume depended on the desired rate of pressure increase. The latter was automatically recorded on a revolving drum mechanism. The apparatus operated over the same conditions as those met with in Parts I and II; and was thermostatted in the range 20 - 180°C, ± 0.2°C. Calculations expressed the pressure time curve as instantaneous absorption rate values for the gas in the liquid.

The Air Thermostat.

The lagging comprising the sides of the thermostat, \(2\frac{1}{3} \times 1\frac{1}{2} \times 2 \text{ ft} \) wide consisted of sheets of aluminium foil, asbestos sheet, \(\frac{1}{2}\)-inch layer of glass wool matting, and cardboard, sewn together with wire in that order. The lagged sides were fitted on to a \(\frac{1}{2}\)-inch angle iron framework with the Al foil facing inwards. Heating was provided /
FIG. 4.

DRUM RECORDER.

MOTOR.

GEAR TRAIN

DRUM.

COLLIMATOR.

MOTOR.

LIGHT-TIGHT BOX.

THERMOSTAT.

BOURDON GAUGE.

FOOT SWITCH.

MIRROR ASSEMBLY.

SILVERED COVERSLEEPI.

ALUMINIUM FOIL.

GLASS ROD STIRRUP.

SILK THREAD.

BRASS WASHER.
provided by two 250 w. fire bar heaters in series with one another and operated by a Sunvic expanding copper-brass regulator through a Sunvic relay. A fan, driven by a constant speed motor placed outside the thermostat provided sufficient air currents around the apparatus to maintain the temperature inside the box at \( \pm 0.1^\circ\text{C} \) at 60\(^\circ\text{C} \) and \( \pm 0.2^\circ\text{C} \) at 150\(^\circ\text{C} \). The temperature was recorded by taking the mean reading of two thermometers placed at opposite corners of the thermostat.

The Pressure Recording System.

The pressure measuring system was a Bourdon gauge (40) which had the following characteristics:

(i) sufficient sensitivity to record pressure changes of \( 10^{-2} \) mms. mercury.

(ii) a delay in response of \( < 10^{-2} \) secs.

(iii) a linear response over small deflections.

In the recorder, Fig. 4, p. 136, a small pencil of light from a 6v. 6w. collimator was made to fall on the mirror assembly which was of Al foil and a silvered microscope coverslip (73). The light beam was operated by an on-off foot switch. The mirror assembly was attached by means of a silk thread and washer to the spindle of the Bourdon gauge. A glass stirrup ground flat on the top /
FIG. 5.

KEY

1. LUTE.
2. PREHEATER.
3. SATURATER.
4. ABSORBER.
5. BOURDON GAUGE.
6. COMPENSATOR.
7. REGULATOR.
8. FAN.
9. HEATERS.
10. THERMOSTAT.
11. WINDOW.
12. GLASS SINTER.
13. CAPILLARY.

PLAN

SCALE IN INCHES:

0 1 2 4 8
top surface provided a pivot for the mirror assembly.

Increase of pressure in the apparatus caused the light spot to be deflected on to a revolving drum 12.5 inches in circumference and 4 inches high. The drum driven by an 18,000 r.p.m. shaded pole motor through a gear train revolved at a speed of 9.7 secs. per revolution.

Oscillograph light sensitive paper, C.P.5, proved to be a suitable photographic paper for obtaining a clear trace of the light spot. By means of this optical lever system any small movement of the Bourdon gauge was amplified by the light spot deflection.

The complete recording device was enclosed in a light-tight 21 x 7 x 13 inches high box so constructed that the drum was able to be removed and loaded with photographic paper without disconnecting the mirror from the Bourdon gauge.

The Absorption System.

The apparatus, Fig. 5, page 138, consisted of; a preheater through which the gas was passed and so attained the temperature of the thermostat; a saturator containing hydrocarbon solvent through which the gas passed and so became saturated with hydrocarbon vapour at the working temperature; a compensator column containing gas saturated solvent from which the exit gases, after passing through a /
a soap film meter to check the inlet gas rate, were led off to the atmosphere; and an absorber column containing gas free solvent. The non-absorbed gases from the absorber column were passed into a system of fixed volume whose capacity could be varied from 2 - 9 litres by any combination of the 2, 3 and 4 litre glass bulbs. Attached to the closed system was a Bourdon gauge, whose spindle deflection measured changes in pressure of the system. The gauge was enclosed in a glass jacket to protect it from dust and fluctuations caused by draughts.

The absorber and compensator columns were of the same dimensions, (Pyrex 32 x 35 mms. tubing) and had the same porosity sinter (por.2) attached to the base, as the columns used in Parts I and II. The bubble size and height of rise in the liquid remained the same as that found in the hydrogenation experiments.

It was essential that the inlet gas rate should remain constant during the experiment. To ensure this a water lute, having one leg connected to the main gas supply line and the other leg connected to a water column open to the apparatus, compensated for the drop in the inlet gas rate caused by back pressure in the closed system.

Experimental Technique.

The required gas mixture was made up in the graduated gas holder. With tap E closed both the compensating /
ing and absorber columns were filled with freshly distilled toluene (300 c.c.); the former through tap F and the latter through the capillary filter 13 which provided minimum contact between gas free solvent and the atmosphere in the apparatus, during filling. Hence only very small amounts of gases were absorbed during filling of the absorber column. The saturator was half-filled with toluene and the apparatus brought to the temperature of the thermostat. The temperature of the liquid in the absorber column was taken, as that of 300 c.c. toluene in a tube of similar dimensions placed near the absorber column.

After 1½ hrs. were allowed for the establishment of equilibrium conditions, gas was passed at a constant rate via the preheater, and by opening E, the saturator and compensating column. When the liquid within the compensator column was saturated with gas, the inlet gas rate was checked by a soap film meter attached to the compensator outlet. An arbitrary gas rate of 0.463 gm. moles. hr.⁻¹ at N.T.P. was suitable in that the leg of the water lute attached to the main gas supply emitted gas bubbles at the rate of 2 per sec.

The drum was loaded with photosensitive paper, G.P.5, as supplied by Ilford Ltd., positioned inside the box, and /
and set revolving. A base line was marked on the bromide paper by switching the collimator light on and off several times at short intervals.

The absorption system was closed from the atmosphere by turning tap D. The gas stream still passing through the compensator column at a steady rate was diverted into the absorber column by turning tap E. Simultaneously with this operation the light spot was switched on. Diversion of the gas stream incurred negligible pressure fluctuation as each column had the same pressure drop, i.e. the gas rate remained unchanged after diversion to the absorber column. The non-absorbed gases from the bubble swarm were passed into the closed system whose volume was dependent on the gas solubility in toluene. Experiments had shown that suitable capacities were

(i) for hydrogen - 2 litre capacity and 8 secs. run duration.

(ii) for ethylene - 7 litre capacity and 18 secs. run duration.

Increase in pressure of the closed system actuated the Bourdon gauge and so caused the light spot on the revolving drum to be deflected. Throughout this time the inlet gas rate remained constant.

On completion of the run the light beam was switched off and the pressure in the system released by opening tap D. Passage of the gas through the liquid in the absorber /
absorber column was continued for 4 mins. or until the liquid was saturated with gas when the gas stream was diverted back into the compensator column by turning tap E. Tap D was closed and the complete operation repeated with gas-saturated liquid in the absorber column.

The drum was removed from its mounting, the paper developed in I.D.33, fixed, washed and glazed. Temperatures of the thermostat, liquid in the absorber, and inlet gas were noted.

On completion of a run, the gas supply was switched off and tap E closed. The toluene in the absorber column was drained off through the sinter by opening the tap at the foot of the column. Tap D was closed and the Bourdon gauge isolated by closing tap G. By connecting the capillary filler 15, to a pumping system, Fig. 3, p. 134, the absorption system was evacuated to 15 mns. for 10 mins. After this period the pumping and absorption systems were disconnected, and taps D and G opened to equalise the pressures. Pumping out of the apparatus reasonably ensured that little or no solute gas was present at the start of another experiment.

Maintenance of Apparatus.

All taps and joints were sealed with Silicone grease marketed by W. Edwards and Co. Ltd., with the exception of the taps at the foot of the absorber and compensator.
column which were lubricated with a paste of glycerine and kaolin. This lubricant was insoluble in the small amounts of solvent which seeped through the sinters and so preserved gas-tight joints.

The inside of both the absorber and compensator columns was cleaned by:

(i) wetting the sides with detergent,
(ii) filling with hot alcoholic potash solution and allowing to stand for three hours before
(iii) flushing with weak chromic acid solution,
(iv) washing free from acid with water, then with acetone,
(v) acetone vapour was removed by pumping.

By this method the glass sinters were freed from grease so producing uncontaminated bubbles.

The hydrocarbon solvent, toluene, was freshly distilled b.p. 110.5 - 111°C. before use. The gases, both ethylene and hydrogen, were run straight from the cylinders.

Calculation of Results.

On completion of a run 4 traces were obtained on the photographic paper; firstly, a pressure time curve for gas passed at a constant rate into gas free liquid; and secondly, 3 pressure time curves for gas passed at a constant rate into gas saturated liquid. The former was referred to as the absorption curve whereas the latter were
An example calculation showing how the instantaneous absorption rate is obtained from the pressure-time trace.

\[ \text{INST. ABSORPTION RATE} = \frac{\text{SLOPE CD.} - \text{SLOPE AB.}}{\text{SLOPE CD.}} \times \text{INLET GAS RATE.} \]

\[ = \frac{0.7280 - 0.4625}{0.8360} \text{ GM. MOLES./HR.} \]

\[ = 0.403 \text{ GM. MOLES./HR.} \]
were termed calibration curves. Lines perpendicular to the base line were ruled on the trace at distances apart equivalent to a time interval of 0.5 sec. (the length of the trace was equivalent to the time taken for 1 drum rev. = 9.7 sec.) The slopes of the calibration curves were plotted against time and the mean slope determined (this value corresponds to the absorption rate of a gas into gas saturated liquid at the working inlet gas rate). Similarly the slope of the absorption curve was plotted against time (this value corresponds to the rate at which gas is not absorbed by the system at any instant). Since the slope of the calibration curve was equivalent to the inlet gas rate, the absorption rate of a gas in a liquid was expressed as the ratio of

\[
\frac{(\text{Cal. Curve Slope} - \text{Absorb. Curve Slope}) \times \text{Inlet gas rate}}{\text{Cal. Curve slope}}
\]

Values for the instantaneous absorption rate, i.e. for gas dissolving in gas free liquid were obtained by determining the slopes of both the calibration and absorption curves at zero time by extrapolation. A worked example is shown on p. 145.

Experiments were designed to evaluate the instantaneous absorption rate of both ethylene and hydrogen in toluene in the temperature range 20 - 100°C. and at an inlet gas rate of 0.4625 gm. moles hr⁻¹ at N.T.P.
The rate of absorption of ethylene in toluene at 18°C.
The instantaneous absorption rate of ethylene in toluene.
The instantaneous absorption rate of hydrogen in toluene.
The instantaneous absorption rates of both ethylene and hydrogen in toluene.
TABLE 12.

VARIATION OF INSTANTANEOUS ABSORPTION RATE, A.R. (corrected to an inlet gas rate $I = 0.4825$ g. moles. hr$^{-1}$ N.T.P.) of Ethylene in Toluene with Temperature.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. °C</th>
<th>Inlet Gas Rate I. gm. moles. hr$^{-1}$</th>
<th>Slope Diff.</th>
<th>Inst. Absorb. Rate (A.R.) gm. moles. hr$^{-1}$</th>
<th>Absorb. Efficiency $E = \frac{(A.R.)}{I}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.0</td>
<td>0.4625</td>
<td>1.0850</td>
<td>0.4014</td>
<td>0.86</td>
</tr>
<tr>
<td>2</td>
<td>18.0</td>
<td>0.4625</td>
<td>1.0270</td>
<td>0.3903</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>18.0</td>
<td>0.4625</td>
<td>1.0860</td>
<td>0.3998</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>31.0</td>
<td>0.4582</td>
<td>0.9240</td>
<td>0.3511</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>31.0</td>
<td>0.4575</td>
<td>0.9450</td>
<td>0.3526</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>31.0</td>
<td>0.4575</td>
<td>0.8750</td>
<td>0.3452</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>39.5</td>
<td>0.4786</td>
<td>0.8657</td>
<td>0.3405</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>39.5</td>
<td>0.4786</td>
<td>0.9515</td>
<td>0.3363</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>39.5</td>
<td>0.4786</td>
<td>0.9516</td>
<td>0.3363</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>39.5</td>
<td>0.4786</td>
<td>0.8916</td>
<td>0.3476</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>54.2</td>
<td>0.4755</td>
<td>0.9268</td>
<td>0.2790</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>54.2</td>
<td>0.4755</td>
<td>0.5271</td>
<td>0.2302</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>54.2</td>
<td>0.4755</td>
<td>0.4938</td>
<td>0.2028</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>54.2</td>
<td>0.4755</td>
<td>0.5080</td>
<td>0.2728</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>54.2</td>
<td>0.4755</td>
<td>0.5523</td>
<td>0.2597</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>54.2</td>
<td>0.4755</td>
<td>0.6304</td>
<td>0.3136</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>73.6</td>
<td>0.4613</td>
<td>0.5584</td>
<td>0.2930</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>73.6</td>
<td>0.4617</td>
<td>0.6708</td>
<td>0.3014</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>73.6</td>
<td>0.4634</td>
<td>0.4791</td>
<td>0.2225</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>73.6</td>
<td>0.4634</td>
<td>0.4800</td>
<td>0.2351</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>73.6</td>
<td>0.4634</td>
<td>0.5532</td>
<td>0.2633</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>73.6</td>
<td>0.4634</td>
<td>0.5967</td>
<td>0.2599</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>73.6</td>
<td>0.4634</td>
<td>0.2058</td>
<td>0.1094</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>95.0</td>
<td>0.4750</td>
<td>0.2817</td>
<td>0.1433</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>95.0</td>
<td>0.4778</td>
<td>0.2926</td>
<td>0.1510</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>95.0</td>
<td>0.4786</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 15.

INSTANTANEOUS ABSORPTION RATE A.R. (corrected to an inlet gas rate \( I = 0.4825 \text{ gm. moles hr}^{-1} \text{ N.T.P.} \)) of Hydrogen in Toluene at Room Temperature.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. °C.</th>
<th>Inlet Gas Rate, I, gm. moles hr(^{-1}) N.T.P.</th>
<th>Slope Diff.</th>
<th>Inst. Absorb. Rate, A.R. gm. moles hr(^{-1})</th>
<th>A.R. gm. moles sec(^{-1}) cms.(^{-2}) ( \times 10^8 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.9</td>
<td>0.4330</td>
<td>0.120</td>
<td>0.0537</td>
<td>7.28</td>
</tr>
<tr>
<td>2</td>
<td>16.9</td>
<td>0.4330</td>
<td>0.118</td>
<td>0.0613</td>
<td>7.60</td>
</tr>
<tr>
<td>3</td>
<td>16.9</td>
<td>0.4330</td>
<td>0.111</td>
<td>0.0462</td>
<td>5.75</td>
</tr>
<tr>
<td>4</td>
<td>18.0</td>
<td>0.4530</td>
<td>0.134</td>
<td>0.0623</td>
<td>7.73</td>
</tr>
<tr>
<td>5</td>
<td>18.0</td>
<td>0.4330</td>
<td>0.131</td>
<td>0.0651</td>
<td>8.08</td>
</tr>
<tr>
<td>6</td>
<td>18.0</td>
<td>0.4330</td>
<td>0.130</td>
<td>0.0610</td>
<td>7.57</td>
</tr>
<tr>
<td>7</td>
<td>18.0</td>
<td>0.4330</td>
<td>0.118</td>
<td>0.0698</td>
<td>11.15</td>
</tr>
<tr>
<td>8</td>
<td>18.0</td>
<td>0.4330</td>
<td>0.122</td>
<td>0.0553</td>
<td>6.86</td>
</tr>
<tr>
<td>9</td>
<td>19.3</td>
<td>0.4330</td>
<td>0.111</td>
<td>0.0486</td>
<td>6.02</td>
</tr>
<tr>
<td>10</td>
<td>19.3</td>
<td>0.4330</td>
<td>0.140</td>
<td>0.0688</td>
<td>5.54</td>
</tr>
<tr>
<td>11</td>
<td>19.3</td>
<td>0.4330</td>
<td>0.134</td>
<td>0.0603</td>
<td>7.48</td>
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<td>12</td>
<td>19.3</td>
<td>0.4330</td>
<td>0.136</td>
<td>0.0665</td>
<td>8.26</td>
</tr>
<tr>
<td>13</td>
<td>19.3</td>
<td>0.4330</td>
<td>0.136</td>
<td>0.0665</td>
<td>8.26</td>
</tr>
<tr>
<td>14</td>
<td>19.4</td>
<td>0.4330</td>
<td>0.117</td>
<td>0.0552</td>
<td>6.85</td>
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<td>0.4330</td>
<td>0.127</td>
<td>0.0521</td>
<td>7.71</td>
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<tr>
<td>16</td>
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<td>0.4330</td>
<td>0.131</td>
<td>0.0642</td>
<td>6.72</td>
</tr>
<tr>
<td>17</td>
<td>19.4</td>
<td>0.4330</td>
<td>0.119</td>
<td>0.0572</td>
<td>7.09</td>
</tr>
</tbody>
</table>

Area = 224 cms.\(^2\)
TABLE 14

VARIATION OF INSTANTANEOUS ABSORPTION RATE, A.R. (corrected to an inlet gas rate \( I = 0.4625 \text{ gm. moles. hr}^{-1} \text{ N.T.P.} \)) of Hydrogen in Toluene, with Temperature.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. °C.</th>
<th>Inlet Gas Rate, ( I ) ( \text{gm. moles. hr}^{-1} ) N.T.P.</th>
<th>Slope Diff.</th>
<th>Inst. Absorb. Rate A.R. ( \text{gm. moles. hr}^{-1} )</th>
<th>A.R. ( \text{gm. moles. sec}^{-1} \text{ cms.}^{-2} \times 10^{8} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>50.0</td>
<td>0.4770</td>
<td>0.305</td>
<td>0.1543</td>
<td>15.64</td>
</tr>
<tr>
<td>19</td>
<td>50.5</td>
<td>0.4770</td>
<td>0.340</td>
<td>0.1523</td>
<td>15.44</td>
</tr>
<tr>
<td>20</td>
<td>51.1</td>
<td>0.4770</td>
<td>0.320</td>
<td>0.1504</td>
<td>15.35</td>
</tr>
<tr>
<td>21</td>
<td>51.5</td>
<td>0.4770</td>
<td>0.320</td>
<td>0.1481</td>
<td>14.83</td>
</tr>
<tr>
<td>22</td>
<td>51.8</td>
<td>0.4770</td>
<td>0.330</td>
<td>0.1461</td>
<td>14.35</td>
</tr>
<tr>
<td>23</td>
<td>50.7</td>
<td>0.4770</td>
<td>0.325</td>
<td>0.1415</td>
<td>14.35</td>
</tr>
<tr>
<td>24</td>
<td>50.7</td>
<td>0.4770</td>
<td>0.300</td>
<td>0.1374</td>
<td>14.35</td>
</tr>
<tr>
<td>25</td>
<td>51.0</td>
<td>0.4770</td>
<td>0.280</td>
<td>0.1332</td>
<td>14.35</td>
</tr>
<tr>
<td>26</td>
<td>51.0</td>
<td>0.4770</td>
<td>0.265</td>
<td>0.1295</td>
<td>14.35</td>
</tr>
<tr>
<td>27</td>
<td>69.6</td>
<td>0.4770</td>
<td>0.450</td>
<td>0.1169</td>
<td>14.35</td>
</tr>
<tr>
<td>28</td>
<td>70.2</td>
<td>0.4770</td>
<td>0.479</td>
<td>0.1320</td>
<td>14.35</td>
</tr>
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<td>29</td>
<td>70.1</td>
<td>0.4770</td>
<td>0.455</td>
<td>0.1285</td>
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</tr>
<tr>
<td>30</td>
<td>69.5</td>
<td>0.4770</td>
<td>0.450</td>
<td>0.1253</td>
<td>14.35</td>
</tr>
<tr>
<td>31</td>
<td>73.5</td>
<td>0.4770</td>
<td>0.450</td>
<td>0.1299</td>
<td>14.35</td>
</tr>
<tr>
<td>32</td>
<td>74.2</td>
<td>0.4770</td>
<td>0.450</td>
<td>0.1298</td>
<td>14.35</td>
</tr>
<tr>
<td>33</td>
<td>84.2</td>
<td>0.4770</td>
<td>0.450</td>
<td>0.1277</td>
<td>14.35</td>
</tr>
<tr>
<td>34</td>
<td>88.7</td>
<td>0.4770</td>
<td>0.410</td>
<td>0.1300</td>
<td>14.35</td>
</tr>
<tr>
<td>35</td>
<td>88.2</td>
<td>0.4770</td>
<td>0.280</td>
<td>0.1399</td>
<td>14.35</td>
</tr>
<tr>
<td>36</td>
<td>88.5</td>
<td>0.4770</td>
<td>0.280</td>
<td>0.1297</td>
<td>14.35</td>
</tr>
<tr>
<td>37</td>
<td>88.7</td>
<td>0.4770</td>
<td>0.285</td>
<td>0.1238</td>
<td>14.35</td>
</tr>
</tbody>
</table>
### Table 15

**Instantaneous Absorption Rates of H<sub>2</sub>: C<sub>2</sub>H<sub>4</sub> in Toluene Saturated with C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> Respectively.**

Inlet gas: H<sub>2</sub>: C<sub>2</sub>H<sub>4</sub> :: 1:1

<table>
<thead>
<tr>
<th>Run No.</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;: C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</th>
<th>Temp. °C</th>
<th>Inlet Gas Rate, gm. moles. hr&lt;sup&gt;-1&lt;/sup&gt; N.T.P</th>
<th>Slope Diff.</th>
<th>Inst Absorb. Rate, A.R. gm. moles. hr&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>A.R. gm. moles. sec&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-2&lt;/sup&gt; 10&lt;sup&gt;8&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>18.3</td>
<td>0.4340</td>
<td>0.520</td>
<td>0.1534</td>
<td>16.96</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>18.3</td>
<td>0.4340</td>
<td>0.731</td>
<td>0.1529</td>
<td>16.85</td>
</tr>
<tr>
<td>3</td>
<td>sat. C, H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>18.3</td>
<td>0.4340</td>
<td>0.563</td>
<td>0.1383</td>
<td>17.10</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>18.3</td>
<td>0.4340</td>
<td>0.452</td>
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</tr>
<tr>
<td>5</td>
<td></td>
<td>18.3</td>
<td>0.4340</td>
<td>0.501</td>
<td>0.1389</td>
<td>17.14</td>
</tr>
<tr>
<td>6</td>
<td>Toluene</td>
<td>22.5</td>
<td>0.4340</td>
<td>0.132</td>
<td>0.0396</td>
<td>4.88</td>
</tr>
<tr>
<td>7</td>
<td>sat. C, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>22.6</td>
<td>0.4340</td>
<td>0.142</td>
<td>0.0439</td>
<td>5.42</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>22.8</td>
<td>0.4340</td>
<td>0.138</td>
<td>0.0410</td>
<td>5.06</td>
</tr>
<tr>
<td>9</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;: C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt; :: 2:1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Tolu. sat. H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>16.2</td>
<td>0.4340</td>
<td>0.441</td>
<td>0.1153</td>
<td>14.22</td>
</tr>
<tr>
<td></td>
<td>Tolu. sat. C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>20.1</td>
<td>0.4340</td>
<td>0.207</td>
<td>0.0623</td>
<td>7.70</td>
</tr>
</tbody>
</table>
DISCUSSION OF RESULTS.

The Possibility of a Mixing Gradient in the Absorption Column.

In the absorption column, where toluene is absorbing gas, it is possible that local gas concentrations may occur in random areas within the liquid. These areas may be distributed to the more remote parts of the medium until the latter attains a uniform concentration distribution. In this event, these concentration areas would affect the value of K, the liquid transfer coefficient, by offering an additional resistance to transfer.

Consideration of the dimensions of the apparatus and visual observations with colouring matter show that the inrushing gas thoroughly mixes the liquid bulk. The bubble swarm in rising through the liquid acts as an efficient stirrer so that the gas concentration in the liquid at any instant is the same throughout the bulk of the liquid.

The Instantaneous Absorption Rate of Ethylene in Toluene.

Graph 9, p. 147, expresses the rate at which ethylene is absorbed in toluene. In the first half second the rate of absorption is approximately constant but, as time increases the rate of absorption will decrease because of the /
the decrease in concentration gradient.

The parabolic curve shown in Graph 10, p. 148, illustrates the variation of instantaneous absorption rate of ethylene in toluene in the temperature range 20 - 111°C. The curve has an absorption rate at 18°C, equivalent to an absorption efficiency of \( E = 0.86 \), Table 12, p. 151, and zero absorption rate at the boiling point of toluene. All absorption rates are expressed as gm. moles. sec\(^{-1}\) cm\(^2\) 10\(^8\) where the values for the bubble swarm surface areas are taken from Graph 7, p. 114.

The Instantaneous Absorption Rate of Hydrogen in Toluene.

Graph 11, p. 149, depicts the variation of instantaneous absorption rate with temperature. The results shown on Tables 13 and 14, pp. 152-3, are somewhat scattered because of the small slope difference between the calibration and absorption curves. The curve is parabolic with a maximum absorption rate at 71°C, occurring approximately at the temperature for which the solubility of hydrogen in toluene is greatest (0.0763 cc./cc. at 52°C. by extrapolation). Graph 11A, p. 150, compares the instantaneous absorption rate of ethylene in toluene with that of hydrogen in toluene.
From Plate 4. The total number of bubbles = 1630 = 5.3072 c.c. volume.

Therefore the volume of a single bubble = \( \frac{5.3072}{1630} \) = \( 3.26 \times 10^{-3} \) c.m. There are approximately 20 jet sources on the sinter. Thus considering one jet source the rate of production of bubbles = 52 bubbles/sec. giving a time of formation of one bubble to be = 0.019 sec.

<table>
<thead>
<tr>
<th>Time sec. 10^1</th>
<th>Volume c.m. 10^4</th>
<th>Area A. c.m. 10^2</th>
<th>Conc. grad. gm. c.m. 10^4</th>
<th>( \frac{dc}{dx} \cdot 10^5 ) (T = 20°C.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.26</td>
<td>2.29</td>
<td>26.6</td>
<td>6.14</td>
</tr>
<tr>
<td>2</td>
<td>6.52</td>
<td>3.55</td>
<td>21.3</td>
<td>7.78</td>
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<td>3</td>
<td>9.78</td>
<td>4.76</td>
<td>16.8</td>
<td>8.00</td>
</tr>
<tr>
<td>4</td>
<td>13.04</td>
<td>5.77</td>
<td>14.4</td>
<td>8.31</td>
</tr>
<tr>
<td>5</td>
<td>16.30</td>
<td>6.69</td>
<td>12.6</td>
<td>8.42</td>
</tr>
<tr>
<td>6</td>
<td>19.56</td>
<td>7.56</td>
<td>11.2</td>
<td>8.42</td>
</tr>
<tr>
<td>7</td>
<td>22.82</td>
<td>8.38</td>
<td>10.2</td>
<td>8.54</td>
</tr>
<tr>
<td>8</td>
<td>26.08</td>
<td>9.16</td>
<td>9.4</td>
<td>8.60</td>
</tr>
<tr>
<td>9</td>
<td>29.34</td>
<td>9.88</td>
<td>9.0</td>
<td>8.88</td>
</tr>
<tr>
<td>10</td>
<td>32.60</td>
<td>10.63</td>
<td>8.6</td>
<td>9.14</td>
</tr>
</tbody>
</table>

\[ \sum \frac{dc}{dx} = 82.23 \]

Q, the amount absorbed = \( D \sum \frac{dc}{dx} \cdot dt \)

\[ = 2.53 \times 10^{-5} \cdot 82.23 \cdot 10^{-5} \cdot 1.9 \cdot 10^{-2} \]

\[ = 3.96 \cdot 10^{-10} \text{ gm./bubble} \]

\[ = 1.5 \cdot 10^{-5} \text{ gm./hr.}^{-1} \]

\[ = 15.2 \cdot 10^{-8} \text{ gm. moles sec.}^{-1} \text{ c.m.}^{-2} \]

at Area = 274 c.m.²
Absorption Rates of Gas Mixtures into Toluene.

Determination of absorption rates was made using an inlet gas mixture of \( \text{H}_2 : \text{C}_2\text{H}_4 : 1 : 1 \) with toluene previously saturated with either hydrogen or ethylene. The results are expressed in Table 15, p. 154, where the area of gas-liquid contact at an inlet gas rate of 0.4340 gm. moles. hr\(^{-1} \) is \( A = 225 \text{ cm}^2 \).

The instantaneous absorption rate depends on the partial pressure of the solute. Thus by halving the partial pressure the absorption rate is decreased by half.

Calculation of the Rate of Absorption during Bubble Formation.

Assuming that bubbles are spherical during formation at the sinter face the rate of absorption of ethylene into tetralin during bubble formation was estimated as in Table 16, p. 157. From the photographs of Plate 4, Table 10, p.102, the time of formation of a single bubble was calculated to be 0.019 secs. The area of that bubble every \( \frac{1}{10} \) sec. was calculated over a period of 1 second. An estimation of the concentration gradient during this period was obtained from Guyer and Pfister's results (53) and the rate of absorption summed as shown. The quantity of ethylene absorbed into toluene was calculated to be \( 15.2 \text{ gm. moles. sec}^{-1} \text{ cm}^2 \times 2 \times 10^8 \).

If /
If a comparison may be drawn between the instantaneous absorption rate of ethylene into toluene as $39.0 \text{ gm. moles. sec}^{-1} \text{ cms}^{-2} \cdot 10^8$ compared with the absorption rate value of ethylene into toluene during bubble formation only, it can be said that formation effects contribute more than 40% of the total absorption rate.
SUMMARY.

(1) The instantaneous absorption rates of both hydrogen and ethylene in gas free toluene have been measured in the temperature range 20 - 111°C.

(2) The instantaneous absorption rate of ethylene in toluene decreases from a maximum at 18°C to zero at 111°C, whereas that of hydrogen increases to a maximum at 71°C, then decreases to zero at 111°C, over the temperature range 18 - 111°C.

(3) The instantaneous absorption rate into a liquid of a gas component in a gas mixture increases proportionately to an increase of the mole fraction of the component in the gas phase.

(4) High absorption rates are estimated during bubble formation at the sinter face.
In the hydrogenation experiments reactants are absorbed by the liquid from the bubble swarm. Simultaneously with this process, reactants are removed from the liquid by reaction at the catalyst surface. Since the process is diffusion controlled there is an equilibrium concentration of both hydrogen and ethylene in the liquid, the value of which establishes a concentration gradient between gas and liquid phases. The magnitude of the concentration gradient also controls the rate at which reactants are absorbed by the liquid.

The experimental section of Part I illustrates the variation of reaction rate of the slurry phase hydrogenation of ethylene with temperature, inlet gas ratio, liquid properties, etc. Absorption rate data for both hydrogen and ethylene under similar experimental conditions have been determined in Part III. Then, from the determined data in Parts I and III it is possible to evaluate the equilibrium concentrations of the reactants in the liquid medium during hydrogenation at various temperatures. Hence the concentration gradients of the dissolving reactants may be calculated. Also, from the collected results the rate controlling step which controls the overall reaction rate in the slurry phase hydrogenation of ethylene is proposed.

The /
The experimental data, herein described, for the absorption rates of both hydrogen and ethylene into toluene of zero gas concentration is compared with both the theoretical values and those reported in the literature.
TABLE 17.

CALCULATION OF \( K \text{cms. hr}^{-1} \) for the dissolving gas when its partial pressure in gas phase is \(< 1\). The conditions are such that the Toluene is saturated with the diluent gas.

Inlet Gas \( \text{Hg: C}_2\text{H}_4:: 1: 1 \)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Gas.</th>
<th>Temp. (^\circ\text{C.})</th>
<th>( q \times 10^8 \text{ gm. moles. sec}^{-1} \text{ cms}^{-2} )</th>
<th>( c \times 10^6 \text{ gm. moles. cms}^{-3} )</th>
<th>( x )</th>
<th>( K \text{ cms. hr}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>( \text{C}_2\text{H}_4 )</td>
<td>18.3</td>
<td>18.96</td>
<td>142</td>
<td>0.50</td>
<td>9.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.3</td>
<td>18.25</td>
<td>142</td>
<td>0.50</td>
<td>9.56</td>
</tr>
<tr>
<td>SAT. C</td>
<td>( \text{Hg} )</td>
<td>18.3</td>
<td>17.10</td>
<td>142</td>
<td>0.50</td>
<td>9.37</td>
</tr>
<tr>
<td></td>
<td>( \text{C}_2\text{H}_4 )</td>
<td>18.3</td>
<td>16.40</td>
<td>142</td>
<td>0.50</td>
<td>9.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.3</td>
<td>17.14</td>
<td>142</td>
<td>0.50</td>
<td>8.69</td>
</tr>
<tr>
<td>Toluene</td>
<td>( \text{Hg} )</td>
<td>21.0</td>
<td>4.88</td>
<td>3.12</td>
<td>0.50</td>
<td>112.60</td>
</tr>
<tr>
<td>SAT. C</td>
<td>( \text{Hg} )</td>
<td>21.0</td>
<td>5.42</td>
<td>3.12</td>
<td>0.50</td>
<td>125.11</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td></td>
<td>21.0</td>
<td>5.06</td>
<td>3.12</td>
<td>0.50</td>
<td>116.82</td>
</tr>
</tbody>
</table>

where the concentration gradient \( c = c(100 - x) \). \( x \) is expressed as the \% of 'insoluble' or diluent gas in the inlet gas mixture.
The Effect of Partial Pressure on the Instantaneous Absorption Rate of a Gas in a Liquid.

The experimental results on Table 15, p. 154, verify that the rate at which a gas in a gas mixture can be absorbed by a liquid of zero gas concentration, depends on the partial pressure of the gas in the gas mixture. Thus, if the absorption rate of pure hydrogen into gas free toluene is \( a \) gm. moles/sec., then the rate of absorption of hydrogen from a gas mixture of \( H_2 : C_2H_4 : \frac{y}{y+z} \) into gas free toluene will be \( a \cdot \frac{y}{y+z} \) gm. moles/sec. Similarly, if the absorption rate of pure ethylene into gas free toluene is \( b \) gm. moles/sec., then the rate of absorption of ethylene from a similar gas mixture into gas free toluene will be \( b \cdot \frac{z}{y+z} \) gm. moles/sec. Alternatively, the absorption rate of a gas from a gas mixture into a liquid of zero concentration with respect to that gas is the product of the absorption rate of the pure gas into the gas free liquid and the mole fraction of the gas in the gas mixture.

From Tables 12, 14, 15, and 17, the rate of absorption of pure ethylene into toluene of zero gas concentration (the instantaneous absorption rate) is of the order of \( 39.0 \cdot 10^{-3} \) gm. moles sec\(^{-1}\) cm\(^2\) at 18.3°C. Thus, following the above argument, the rate of absorption of ethylene from a gas mixture of \( H_2 : C_2H_4 : 1:1 \) into gas free /
free toluene will be $39.0 \cdot 10^{-8} \cdot \frac{1}{2} = 19.5 \cdot 10^{-8}$ gm. moles sec.$^{-1}$ cms.$^{-2}$ at 18.3°C. This value agrees well with the average experimental value of $18.1 \cdot 10^{-8}$ gm. moles sec.$^{-1}$ cms.$^{-2}$ at 18.3°C.

Similarly the rate of absorption of pure hydrogen into toluene of zero gas concentration at 22°C. is $8.4 \cdot 10^{-8}$ gm. moles sec.$^{-1}$ cms.$^{-2}$ at 22°C. Then the rate of absorption of hydrogen from a gas mixture of $H_2: C_2H_4: 1: 1$ will be $8.4 \cdot 10^{-8} \cdot \frac{1}{2} = 4.2 \cdot 10^{-8}$ gm. moles sec.$^{-1}$ cms.$^{-2}$ which agrees with the average experimental value of $5.1 \cdot 10^{-8}$ gm. moles sec.$^{-1}$ cms.$^{-2}$ at 22°C. Further verification for this concept is given in Table 15 for evaluating the absorption rate of both hydrogen and ethylene into toluene from gas mixtures of $H_2: C_2H_4: 2:1$.

Thus by halving the partial pressure of the dissolving hydrogen by mixing with an equal proportion of ethylene, the instantaneous absorption rate of hydrogen from this mixture into toluene is of the order of half the instantaneous absorption rate of pure hydrogen into toluene.

The Absorption Rate of Reactants during Hydrogenation.

In the slurry phase hydrogenation of ethylene reactants are absorbed from the bubble swarm by the liquid medium, transported to the catalyst surface as gas molecules
in solution, and there react to form ethane. Part I shows that absorption of the reactants must precede reaction at the catalyst surface. There are thus two major rate processes,

(i) the absorption of reactants into the slurry and

(ii) reaction of the absorbed reagents at the catalyst surface.

All gases that are absorbed then react at the catalyst surface. Thus the rate of absorption of the reactants may control the rate of reaction at the catalyst surface.

Part I shows that maximum reaction rate during the slurry phase hydrogenation of ethylene in toluene with an inlet gas ratio of $H_2: C_2H_4: 1:1$ occurs at 72°C. The experimental value found for the reaction rate under these conditions can be expressed as an absorption rate of either hydrogen or ethylene in toluene. This is so because one mole of hydrogen reacts with one mole of ethylene at the catalyst surface to form one mole of ethane. This value under the conditions described above is of the order of $8.8 \times 10^{-8}$ gm. moles sec$^{-1}$ cm$^{-2}$ and represents the amount of ethylene or the amount of hydrogen that is absorbed by the toluene reacting to form ethane in unit time per unit surface area of gas-liquid interface.

The value for the instantaneous absorption rate of pure hydrogen into toluene under the same experimental conditions /

conditions is $14.3 \times 10^{-8}$ gm. moles sec$^{-1}$ cms$^{-2}$ i.e. the maximum rate at which pure hydrogen can be absorbed into toluene of zero gas concentration is $14.3 \times 10^{-8}$ gm. moles sec$^{-1}$ cms$^{-2}$. Similarly the maximum possible rate at which pure ethylene can be absorbed into toluene of zero gas concentration is $28.5 \times 10^{-8}$ gm. moles sec$^{-1}$ cms$^{-2}$.

The respective values at $72^\circ$C are then:

(i) the absorption rate of either hydrogen or ethylene required to maintain the observed reaction rate during hydrogenation in toluene = 

$$8.8 \times 10^{-8} \text{ gm. moles sec}^{-1} \text{ cms}^{-2}.$$ 

(ii) the maximum possible absorption rate of pure hydrogen in toluene under similar working conditions as (i) = 

$$14.3 \times 10^{-8} \text{ gm. moles sec}^{-1} \text{ cms}^{-2}.$$ 

(iii) the maximum possible absorption rate of pure ethylene in toluene under similar working conditions as (i) = 

$$28.5 \times 10^{-8} \text{ gm. moles sec}^{-1} \text{ cms}^{-2}.$$ 

But in (i) the inlet gas is a mixture of $H_2: C_2H_4: 1:1$ whereas in (ii) and (iii) pure hydrogen and pure ethylene are used respectively, i.e. in (i) both hydrogen and ethylene are at a partial pressure of 0.5 atm. in the gas phase compared with a partial pressure of 1.0 atm. for hydrogen in (ii) and a partial pressure of 1.0 atm. for ethylene in (iii). Then following the previous argument, that halving the partial pressure of the solute gas halves the maximum absorption rate of the solute gas into a liquid, comparable values for (i), (ii) and (iii) would be respectively:

(i) /
Comparison of the instantaneous absorption rates of $\text{H}_2$ & $\text{C}_2\text{H}_4$ in toluene with the absorption rate required for reaction rate in the slurry phase under similar conditions.
(i) the absorption rate for an inlet gas mixture of $\text{H}_2: \text{C}_2\text{H}_4:: 1:1$ of either hydrogen or ethylene into toluene required to maintain the observed reaction rate in the formation of ethane at $72^\circ\text{C}$. = 
\[8.8 \times 10^{-8}\text{ gm. moles sec}^{-1}\text{ cm}^{-2}\].

(ii) the maximum possible absorption rate of hydrogen from a gas mixture of $\text{H}_2: \text{C}_2\text{H}_4:: 1:1$ into toluene without reaction and under similar conditions to (i) = 
\[7.2 \times 10^{-8}\text{ gm. moles sec}^{-1}\text{ cm}^{-2}\].

(iii) the maximum possible absorption rate of ethylene from a gas mixture of $\text{H}_2: \text{C}_2\text{H}_4:: 1:1$ into toluene and without reaction and under similar conditions to (i) = 
\[14.3\text{ gm. moles sec}^{-1}\text{ cm}^{-2}\].

The experimental data in Part I expresses values from which (i) may be calculated at various temperatures with an inlet gas ratio of $\text{H}_2: \text{C}_2\text{H}_4:: 1:1$ and corrected to an inlet gas rate of $0.4525\text{ gm. moles hr}^{-1}$ (for it has been shown that the observed reaction rate varies in proportion to the inlet gas rate. The surface area of the bubble swarm under these conditions is of the order of $274\text{ cm}^2$. Also, the experimental data in Part III expresses values from which (ii) and (iii) may be calculated for the same temperature range and under the same experimental working conditions of (i).

Graph 12 expresses values of (i), (ii) and (iii) in the temperature range $20 - 111^\circ\text{C}$. The dotted curve (the absorption rate of either reactant required to maintain reaction in the slurry) is parabolic with a maximum absorption rate temperature of approximately $72^\circ\text{C}$. And this curve is closely related to the maximum absorption rate /
rate of hydrogen into toluene in that the optimum absorption rate temperature is approximately 75°C.

In the slurry hydrogenation of ethylene solution of reactants, both hydrogen and ethylene, must precede reaction at the catalyst surface. Hence, the reaction rate at the catalyst surface cannot exceed either the maximum possible absorption rate of either hydrogen or ethylene into the slurry. Graph 12 shows that ethylene can be absorbed into the liquid medium at a greater rate than hydrogen under similar working conditions. As one molecule of hydrogen can only react with one molecule of ethylene at the catalyst surface to form ethane, together with the fact that ethylene can be absorbed into the slurry at a greater rate than that of hydrogen, then the rate controlling step that governs the overall reaction rate must be the rate of absorption of hydrogen into the liquid medium. Graph 12 illustrates this fact in that, within experimental error, the absorption rate of hydrogen required to maintain reaction rate in toluene is the same as the maximum absorption rate of hydrogen into toluene without reaction.

Maximum absorption rate occurs when a gas is dissolving in a liquid of zero gas concentration. It is apparent then that during the slurry phase hydrogenation, hydrogen is being absorbed from the inlet gas mixture into liquid of very low hydrogen concentration, i.e. the concentration /
concentration gradient causing mass transfer to occur is very large. However, in the case of ethylene there is excess ethylene in the liquid available for reaction at the catalyst surface and consequently the concentration gradient between gas and liquid phases of ethylene is smaller in proportion to that of hydrogen.

In conclusion, with a 1:1 inlet gas mixture there is excess ethylene available for reaction at the catalyst surface to form ethane, the rate of formation of which is controlled by the rate at which hydrogen can be absorbed by the liquid medium and diffuse to the catalyst surface.

Variation of Reaction Rate with Inlet Gas Ratio.

It has been shown in Part I, that on increasing the hydrogen to ethylene inlet gas ratio the reaction rate increases until a maximum reaction rate is achieved with an inlet gas ratio of \( \text{H}_2: \text{C}_2\text{H}_4 = 2:1 \).

As was stated in Part III the instantaneous absorption rate into a liquid of a gas in a gas mixture increases in proportion to its mole fraction in the gas phase. Thus by increasing the hydrogen to ethylene gas ratio in the inlet gas, the absorption rate of hydrogen into the slurry will tend to approach the maximum possible absorption rate of hydrogen into the slurry.
Simultaneously with this process, the absorption rate of ethylene into the slurry will decrease until with increasing hydrogen to ethylene ratio the rate of absorption of ethylene into the slurry is equivalent to the rate of hydrogen absorption of hydrogen under similar conditions. At this point reactants are present in equimolar proportions in the slurry and maximum reaction rate will be observed. On further increase of the hydrogen to ethylene gas ratio, the rate of absorption of hydrogen will exceed that of ethylene into the slurry where the rate of reaction is now dependent on the amount of ethylene that can be absorbed by the slurry in unit time. The reaction rate will then tend to zero as the mole fraction of ethylene in the gas mixture decreases.

By experiment, the instantaneous absorption rates of pure hydrogen and pure ethylene into toluene at 72°C. are $14.3 \times 10^{-8}$ and $28.5 \times 10^{-8}$ gm. moles sec$^{-1}$ cms$^{-2}$ respectively. Thus the maximum possible absorption rates of hydrogen and ethylene from a gas mixture of $\text{H}_2 : \text{C}_2\text{H}_4 = 2:1$ under the same experimental conditions is the same for both gases—namely $9.2 \times 10^{-8}$ gm. moles sec$^{-1}$ cms$^{-2}$ which is the value required by the reaction rate under the working conditions. This value agrees reasonably well with the experimentally determined value of $11.3 \times 10^{-8}$ gm. moles sec$^{-1}$ cms$^{-2}$.

Thus maximum reaction rate in the slurry phase hydrogenation /
Comparison of the instantaneous absorption rates of $\text{H}_2$ & $\text{C}_2\text{H}_4$ in toluene with the absorption rate required for reaction rate in the slurry phase under similar conditions.
hydrogenation of ethylene with toluene as the catalyst supporting liquid occurs with an inlet gas ratio of \( H_2 : C_2H_4 : 2 : 1 \). Under these conditions the rates of mass transfer of hydrogen and ethylene from the gas phase to the catalyst surface are equivalent. Graph 13 compares the absorption rate required for reaction rate for a 2:1 inlet gas ratio with the instantaneous absorption rates of hydrogen and ethylene into toluene under the same working conditions. As with a \( H_2 : C_2H_4 : 1 : 1 \) inlet gas ratio maximum reaction rate is obtained at a temperature of 72°C.

The Absolute Reaction Rate of the Slurry Phase Hydrogenation of Ethylene.

Values for the absolute reaction rate of the vapour phase hydrogenation of ethylene, Table 1, p. 20, are expressed in \( \mu \text{mol sec}^{-1} \text{cm}^{-2} \) of catalyst, moles of gas reacting to form ethane per second per cm² of catalyst surface area. Values reported in the literature for the surface area of Raney nickel are diverse (108, 85) but 30 m²/gm. is a reasonable estimate of the surface area.

A comparison between the absolute reaction rates of both the vapour and the slurry phase systems is such that

\[ \text{Temp./} \]
where 3 gm. of nickel is taken as the quantity of catalyst in the slurry phase, i.e. where the reaction rate is still dependent on the quantity of catalyst present in the reactor.

The difference in reaction rates between the vapour phase and slurry phase hydrogenation of ethylene is then of a factor of $10^5$. In the vapour phase the reactants are present in excess at the catalyst surface and the reaction rate controls the overall reaction rate whereas in the slurry phase the overall reaction is controlled by the rate of transport of reactants to the catalyst surface.

A speculation, as to the concentration of reactants present in the liquid during reaction, shows that the concentration of hydrogen in the slurry (assuming that every molecule reacts to form ethane on reaching the catalyst surface) is 1 molecule of gas for every $(10^5 - 1)$ molecules of liquid (See Table 24, p. 207.). The concentration value of ethylene will be larger because of its greater solubility in toluene compared with hydrogen in toluene.
toluene.

The relation between the rate of mass transfer of reactants, the observed reaction rate and the actual reaction rate is deduced in Appendix III, p. 209.

The Optimum Reaction Rate Temperature.

Experiments show that in toluene the critical temperature is approximately 72°C, and in tetralin and decalin the critical temperature is approximately 150°C. Above these respective temperatures the reaction rate presumably decreases to zero at the boiling point of the liquid in which the solubility of the reactants is zero. Graphs 12 and 13 show that the maximum reaction rate temperature is controlled by transfer processes and not by the kinetics of the reaction at the catalyst surface.

It is coincidence that the optimum reaction rate temperature in both decalin and tetralin in 150°C where the kinetics of the reaction at the catalyst surface change from being proportional to the concentration of hydrogen at the catalyst surface below 150°C., to being proportional to both the concentration of hydrogen and ethylene at the catalyst surface above 150°C. This optimum reaction rate temperature is again governed by mass transfer of reactants and not by the reaction kinetics because the reaction rate at the catalyst surface is /
is considerably faster ($10^5$) than the observed reaction rate in the slurry phase.

**Variation of Reaction Rate with Gas-Liquid Interfacial Area.**

In the hydrogenation experiments it is found that the reaction rate varies directly with the inlet gas rate which is itself a measure of the bubble swarm surface area. This is true for bubbles of diam. < 1 cms. (16) but above this limit mass transfer subsequently decreases owing to a decrease in surface area due to an increase in the coalescence of adjacent bubbles.

The Rate Controlling Step in the Slurry Phase Hydrogenation of Ethylene.

It has been shown, p. 175, that the rate of reaction of hydrogenation of ethylene in the vapour phase is greater than that in the slurry phase. The reaction rate of the latter is controlled by the rate of mass transfer of hydrogen to the catalyst surface. Thus, providing that the rate of transport of hydrogen to the catalyst surface is greater than that required by the reaction rate at the catalyst surface, an increase in temperature of the system will increase the reaction rate at the catalyst surface. This reaction rate increases in proportion /
proportion to the temperature coefficient of reaction.

But when toluene is the catalyst supporting medium in the temperature range 72°C. - b.p., experiments show that the observed reaction rate is controlled by the mass transfer rate of hydrogen to the catalyst surface.

Thus, at low temperatures, the observed reaction rate may be controlled either by the rate of mass transfer of hydrogen to the catalyst surface or the reaction rate at the catalyst surface. But at high temperatures the observed reaction rate is controlled only by the rate of transport of hydrogen to the catalyst surface.
AN EVALUATION OF THE EQUILIBRIUM CONCENTRATION OF HYDROGEN IN THE SLURRY DURING THE SLURRY PHASE HYDROGENATION OF ETHYLENE.

From previous arguments, the slurry phase hydrogenation of ethylene, at least at the higher temperatures, is considered to be controlled by the rate of mass transfer of $H_2$ from the bubble swarm to the catalyst surface. Also, the equilibrium concentration of hydrogen present in the slurry during hydrogenation must be very small in order to maintain the high absorption rate of hydrogen into the slurry which is a requisite of the reaction rate at the catalyst surface.

It is of interest to estimate the equilibrium concentration of hydrogen in the slurry for the following reasons:

(i) it will enable the concentration gradient of hydrogen between gas and liquid phases to be established.

(ii) the mass transfer rate of hydrogen calculated from the data in (i) can be compared with the experimental values of the mass transfer rate of hydrogen required by the reaction under similar experimental conditions.

From the experimental work in Part III, it is possible to determine the manner in which the absorption rate of a gas into a liquid varies with time, i.e. the manner in which the absorption rate decreases as the gas concentration in the liquid increases from zero to the saturation value. Clearly, the absorption rate will
The determination of the conc. of H₂ in toluene during the S.P. hydrog. of C₂H₄ at different temperatures.
will be a maximum value when the liquid is of zero gas concentration and decreases to zero when the liquid is saturated with gas.

Graph 14, p.180, illustrates the manner in which the rate of absorption of pure hydrogen into toluene varies with time at four different temperatures. These curves represent the value of the absorption rate of hydrogen in the toluene. The absorption rate of hydrogen into toluene at zero time is the absorption rate of hydrogen into toluene of zero hydrogen concentration. The area under the curves represents the saturation value of hydrogen in toluene at the operating temperature.

On the same graph is superimposed the absorption rate of hydrogen in toluene required to maintain reaction rate in the slurry phase at similar temperatures. These values are shown for reaction rates occurring with inlet gas mixtures of $\text{H}_2: \text{C}_2\text{H}_4:: 1:1, 1:2$, and $2:1$.

From Graph 14, the equilibrium concentration of hydrogen in the slurry during reaction at various temperatures can be calculated. For example, the absorption rate of hydrogen into toluene required by the reaction rate at $88.5^\circ\text{C}$, with an inlet gas ratio of $\text{H}_2: \text{C}_2\text{H}_4:: 1:1$ is $0.58$ c.c./sec. Hence the absorption rate of hydrogen required by the reaction rate is then equivalent to the absorption rate of hydrogen into toluene $1.02$ sec. after absorption begins. Thus the concentration of hydrogen in the slurry in c.c. per volume /
Variation of the equilibrium conc. of H₂ in the slurry during reaction at different temperatures and inlet gas ratios.
volume of toluene in the reactor (300 c.c.) during reaction at 88.5°C is 0.58 x 1.02 c.c. = 0.59 c.c. By similar means the equilibrium concentration of hydrogen in the slurry can be calculated at other temperatures and inlet gas ratios.

Graph 15, p.182, illustrates the manner in which the equilibrium concentration of hydrogen in the slurry with different inlet gas ratios varies with the operating temperature.

Following the same procedure as described above, values for the equilibrium concentration of ethylene in the slurry during reaction were unobtainable because the absorption rate of ethylene into toluene decreased slowly with increasing gas concentration in the liquid. As a result of this, the absorption rate experiments were unable to be continued for a long enough time, until the absorption rate of ethylene in toluene was equivalent to the absorption rate of ethylene in the slurry required by the reaction rate. In order to achieve this aim, the absorption apparatus would require to be modified. This would be accomplished at the sacrifice of sensitivity, by increasing the volume into which the non-absorbed gases enter. By this method the rate of increase in pressure in the system would be decreased so that the duration of the experiment could be increased.
An Evaluation of the Concentration Gradient Causing Mass Transfer of Hydrogen to the Catalyst Surface during Hydrogenation.

The rate of mass transfer of a gas dissolving in a liquid is directly proportional to the concentration gradient of the gas between phases. By classical theory, the resistance to diffusion of a solute from a gas bubble into a liquid occurs within a thin layer of liquid surrounding the gas bubble. The layer of liquid is in laminar flow and transport of gas can only occur by molecular diffusion through this layer. The gas-liquid interface is presumed to be saturated with gas and the potential energy causing transfer is the concentration gradient of gas between the gas-liquid interface and the main bulk of the liquid. Similarly in a solid-liquid system, there is a layer of liquid in laminar flow surrounding the solid phase. And it is only through this layer of liquid that gas can penetrate to the solid interface by molecular diffusion. Again, the rate of mass transfer is governed by the concentration gradient of gas between the main bulk of liquid and the catalyst surface.

In the slurry phase hydrogenation reactants must dissolve from the bubble into the liquid and be transported to the catalyst surface. In so doing the total resistance /
The variation of the equilibrium conc. of H₂ during the S.P. hydrogenation of C₂H₄ in toluene with temperature.

Graph 16.

CH₃—toluene saturated with hydrogen.

CEH₂ — equilibrium H₂ conc. during slurry phase hydrogenation of ethylene.

CEH₂ — calc. from Miyamoto's theory.

AC — variation of the equilibrium conc. of H₂ during the S.P. hydrogenation of C₂H₄ in toluene with temperature.
Solubility of hydrogen in various non-polar liquids.
resistance to transport is the sum of the resistance present in the laminar flowing layers of liquid surrounding both the gas bubble and the catalyst particle (the mathematical relationship for the resistance to mass transfer through liquid films in series is given in Appendix III, p. 209). The overall concentration gradient is then the sum of resistances of the two liquid films in series with one another the value of which controls the rate of transport of reactants to the catalyst surface. High transport rates of matter then require large concentration gradients between phases.

Graph 16, p. 185, compares the hydrogen concentration in the slurry with a $H_2: C_2H_4: 1: 1$ ratio during the hydrogenation of ethylene in the temperature range $20 - 110^\circ C$. when:

(i) the toluene is completely saturated with hydrogen

(ii) the hydrogen concentration has reached an equilibrium value in the slurry. The value is controlled by the operating conditions of the reactor and determines the overall reaction rate.

(iii) the value of the equilibrium hydrogen concentration calculated from theory, Appendix III, p. 205.

The data for curve (i) was obtained from Cook's data (21) for the solubility of hydrogen in non-polar solvents, Graph 17, p. 186. The equilibrium concentration of hydrogen in the slurry determined by experiment shown /
Estimated diffusion coefficients of hydrogen and ethylene in toluene.

**Graph 18.**

- **H₂ in Toluene.**
- **C₂H₄ in Toluene.**

**Estimated diffusion coefficients of Hydrogen and Ethylene in Toluene.**
$\Delta C$, HYDROGEN CONC. GRADIENT — GM. MOLES/C.C. TOLUENE. $10^6$

Graph 19. Comparison of $Q$ expt. with that of $Q$ calc. from Higbie's equation.
shown in curve (ii) agrees well with the theoretical values calculated from theory, Appendix II. The overall concentration gradient $\Delta c$, which controls the rate of transport of hydrogen from the gas bubble to the catalyst surface is the difference between curves (i) and (ii) at the same temperature.

The overall concentration gradient of hydrogen causing mass transfer to occur and hence reaction to take place at the catalyst surface during the slurry phase hydrogenation of ethylene is plotted on Graph 19, p. 189, for different temperatures ranging from $20^\circ\text{C.}$ to b.p. of toluene, an inlet gas ratio of $\text{H}_2 : \text{C}_2\text{H}_4 = 1 : 1$. It is seen that the concentration gradient of hydrogen during reaction has a maximum value of $3.22 \times 10^{-5}$ gm. moles/cc. of toluene at $50^\circ\text{C.}$ which decreases presumably to zero at the boiling point of toluene where the solubility of hydrogen in toluene is zero.

However the rate of transport of hydrogen from the gas bubble through the liquid to the catalyst surface is not only proportional to the concentration between phases but also to the diffusion coefficient of hydrogen in toluene. Graph 18, p. 188, illustrates the manner in which the diffusion coefficient of both hydrogen and ethylene in toluene varies with temperature. By using the estimated values for the diffusivity of hydrogen in /
in toluene and the overall concentration gradient of hydrogen at the same temperature during reaction in the slurry phase, the rate of mass transfer of hydrogen calculated from Higbie's equation (58) compares favourably with the mass transfer rate of hydrogen required by the reaction. The resulting values shown on Graph 19, for the observed and calculated absorption rates of hydrogen into toluene are of the same order together with the fact that the optimum absorption rate temperature is approximately 70°C. in both cases.

The experimental work agrees with theoretical considerations in that, although the equilibrium concentration of hydrogen in the slurry during the hydrogenation of ethylene is low, the concentration gradient of hydrogen between gas and liquid phases is large. In addition to this fact and together with the high diffusivity of hydrogen in toluene, it is apparent that high mass transfer rates of hydrogen into toluene and hence high reaction rates are possible even when the reactants are of low concentration in the slurry. On increasing the temperature of the system both the concentration gradient and diffusivity of hydrogen in toluene increase until maximum transfer rate of hydrogen and hence reaction rate occurs at approximately 72°C. Further increase of temperature of the system decreases the mass transfer rate of hydrogen until at the boiling point of the slurry
the transfer of hydrogen is presumably zero and hence the reaction rate is zero.

By increasing the hydrogen to ethylene gas ratio the rate of mass transfer of hydrogen between gas and liquid phases is increased until a maximum value is reached at 71°C. with an inlet gas ratio of H₂: C₂H₄:: 3:1. Under these conditions the absorption rates of reactants into the slurry are equal and maximum reaction rate is achieved. Further increase of the hydrogen to ethylene ratio in the inlet gas decreases the reaction rate where the rate is now controlled by the rate of absorption of ethylene into the slurry.
Comparison of $K_{expt.}$ with values of $K$ derived from Higbie's and Frossling's equations.
A COMPARISON BETWEEN THE OBSERVED AND CALCULATED VALUES OF $K$, THE MASS TRANSFER COEFFICIENT FOR THE SYSTEMS $H_2$ - TOLUENE AND $C_2H_4$ - TOLUENE.

The values of $K$, the mass transfer coefficient found by experiment for pure hydrogen and ethylene in toluene (Table 18) are compared in Graph 20, p. 193, with the values of $K$ predicted by Higbie's (58) and Frossling's (47) equations (Table 19).

It is apparent from Graph 20 that the experimental values are in better agreement with the values of $K$ calculated from Frossling's equation than from Higbie's equation. The former is applicable only to a rigid sphere of solute at $N_Re \geq 1,000$ whereas the latter is applicable to a bubble of fixed area, i.e. where solute transfer from the bubble does not effect change in interfacial area.

Also, $K_{H_2} > K_{C_2H_4}$ in toluene at the same temperature which implies high mass transfer rates of hydrogen in the liquid. $K$ increases with temperature. This fact is contrary to the results of Cryder and Maloney (25) who found no appreciable change of $K$ in the temperature range 25 - 55°C, for the system $CO_2$ - diethanomaline. This discrepancy may be explained by the fact that the solubility decrease of $CO_2$ in diethanomaline with increasing temperature is much greater than that
### Table 18.

**Calculation of \( K \), the Liquid Film Absorption Coefficient**

**CMS** HR\(^{-1} \), from experimental data \( N \).

<table>
<thead>
<tr>
<th>Gas</th>
<th>T. °C.</th>
<th>( c_1 \cdot 10^6 ) g.moles.cms(^{-3} )</th>
<th>( N \cdot 10^8 ) g.moles.sec(^{-1} ) ( \times ) cms(^{-2} )</th>
<th>( \frac{N}{c_1} = K ) cms.hr(^{-1} )</th>
</tr>
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<tbody>
<tr>
<td>Hydrogen</td>
<td>18.0</td>
<td>3.068</td>
<td>7.8</td>
<td>91.2</td>
</tr>
<tr>
<td></td>
<td>31.0</td>
<td>3.305</td>
<td>10.04</td>
<td>113.3</td>
</tr>
<tr>
<td></td>
<td>39.5</td>
<td>3.372</td>
<td>11.80</td>
<td>126.0</td>
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<td></td>
<td>54.2</td>
<td>3.380</td>
<td>13.70</td>
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<td>64.2</td>
<td>3.306</td>
<td>13.90</td>
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<td></td>
<td>73.6</td>
<td>3.104</td>
<td>14.25</td>
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<td></td>
<td>83.4</td>
<td>2.827</td>
<td>13.20</td>
<td>168.0</td>
</tr>
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<td></td>
<td>95.0</td>
<td>2.188</td>
<td>10.50</td>
<td>172.8</td>
</tr>
<tr>
<td>Ethylene</td>
<td>18.0</td>
<td>148.9</td>
<td>41.80</td>
<td>10.54</td>
</tr>
<tr>
<td></td>
<td>31.0</td>
<td>107.2</td>
<td>40.35</td>
<td>13.54</td>
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<td>64.2</td>
<td>41.5</td>
<td>29.97</td>
<td>26.00</td>
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<td></td>
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<td></td>
<td>83.4</td>
<td>17.8</td>
<td>25.36</td>
<td>51.30</td>
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<td></td>
<td>95.0</td>
<td>8.1</td>
<td>17.11</td>
<td>76.00</td>
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### Table 19.

**Calculation of $K_r$, the Liquid Film Absorption Coefficient, **

**CMS. HR$^{-1}$ from Frossling's and Higbie's Equations.**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temp. $^\circ$C</th>
<th>$D \cdot 10^5$ cm$^2$ sec$^{-1}$</th>
<th>0.5</th>
<th>0.33</th>
<th>$\frac{4\pi D M}{R_T} \cdot 10^5$</th>
<th>$P$ atm</th>
<th>$Q \cdot 10^6$ g.moles/sec</th>
<th>$c_1 \cdot 10^6$ g.moles/cm$^3$</th>
<th>$A$ cm$^2$</th>
<th>$R$ kms</th>
<th>Fross. K. cms. hr$^{-1}$</th>
<th>Hig. K. cms. hr$^{-1}$</th>
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<td><strong>HYDROGEN</strong></td>
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<td></td>
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<tr>
<td>20.0</td>
<td>5.08</td>
<td>98.04</td>
<td>5.04</td>
<td>2.194</td>
<td>0.975</td>
<td>13.35</td>
<td>5.122</td>
<td>250</td>
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<td>61.60</td>
<td>211.0</td>
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<td>111.40</td>
<td>3.61</td>
<td>3.425</td>
<td>0.875</td>
<td>15.94</td>
<td>3.394</td>
<td>250</td>
<td>0.91</td>
<td>67.70</td>
<td>278.0</td>
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<td>70.0</td>
<td>11.20</td>
<td>123.60</td>
<td>3.30</td>
<td>4.150</td>
<td>0.730</td>
<td>15.53</td>
<td>3.213</td>
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<td>69.60</td>
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<td>11.26</td>
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<td>9.76</td>
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<td>Press. Atm.</td>
<td>Temp. °C.</td>
<td>Gas</td>
<td>K. cms.hr⁻¹</td>
<td>Q. g.moles.sec⁻¹</td>
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<tr>
<td>(101)</td>
<td>10 cms. through a water column.</td>
<td>1</td>
<td>25</td>
<td>H₂</td>
<td>26</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(18,19)</td>
<td>Shaking 400 times min⁻¹ with 15 cms³ of water.</td>
<td>1</td>
<td>25</td>
<td>H₂</td>
<td>130</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(18,19)</td>
<td>Shaking with 15 cms.³ oleic acid solution.</td>
<td>1</td>
<td>25</td>
<td>H₂</td>
<td>27</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(18,19)</td>
<td>Shaking with 5 cms.³ tetrachloroethane.</td>
<td>1</td>
<td>25</td>
<td>H₂</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This Work.</td>
<td>Bubble swarms (mean diam. 0.16 cms.) in toluene.</td>
<td>1</td>
<td>25</td>
<td>C₂H₄</td>
<td>11.5</td>
<td>38.5</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(20)</td>
<td>Rate of solution of ethylene in 95.8% sulphuric acid.</td>
<td>1</td>
<td>25</td>
<td>C₂H₄</td>
<td>-</td>
<td>60</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(20)</td>
<td>Rate of solution of hydrogen in alcohol.</td>
<td>2.4</td>
<td>25</td>
<td>H₂</td>
<td>-</td>
<td>23</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(20)</td>
<td>Rate of solution of hydrogen in tetrachloroethane.</td>
<td>2.4</td>
<td>25</td>
<td>H₂</td>
<td>-</td>
<td>21</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 31.

**CORRELATION OF \( N_{Nu} \) AS A FUNCTION OF \( (N_{Re} \cdot N_{Sc}) \).**

<table>
<thead>
<tr>
<th>GAS</th>
<th>Temp. (^\circ)C.</th>
<th>D. (\text{cm}^2) sec(^{-1}) (10^5)</th>
<th>K. (\text{cm}) hr(^{-1})</th>
<th>(N_{Re}0.5)</th>
<th>(N_{Sc}0.33)</th>
<th>(N_{Re}0.5 \cdot N_{Sc}0.33)</th>
<th>(N_{Nu} = \frac{Kd'}{D})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_2\text{H}_4)</td>
<td>20</td>
<td>2.52</td>
<td>11.00</td>
<td>96.04</td>
<td>6.35</td>
<td>623</td>
<td>17.00</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.31</td>
<td>17.50</td>
<td>111.40</td>
<td>4.82</td>
<td>537</td>
<td>15.80</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>5.53</td>
<td>33.50</td>
<td>123.60</td>
<td>4.20</td>
<td>520</td>
<td>23.60</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>6.73</td>
<td>65.00</td>
<td>134.60</td>
<td>5.72</td>
<td>501</td>
<td>36.40</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>20</td>
<td>5.08</td>
<td>101.0</td>
<td>96.04</td>
<td>5.04</td>
<td>494</td>
<td>77.30</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>9.75</td>
<td>134.0</td>
<td>111.40</td>
<td>3.61</td>
<td>425</td>
<td>59.60</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>11.20</td>
<td>155.0</td>
<td>123.60</td>
<td>3.50</td>
<td>408</td>
<td>53.90</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>13.54</td>
<td>177.0</td>
<td>134.60</td>
<td>2.95</td>
<td>397</td>
<td>50.80</td>
</tr>
</tbody>
</table>

where: Reynolds number \( N_{Re} = \frac{vf}{\mu} \)

Schmitt number \( N_{Sc} = \frac{V}{\mu} \)

Nusselt number \( N_{Nu} = \frac{Kd'}{D} \)
that of hydrogen in toluene over the same temperature range.

The experimental values of $K$ found in this work are compared in Table 20 with those reported in the literature.

In recent years, attention has been directed to the evaluation of mass transfer data as a function of dimensionless groups (33) in the form

$$N_{Nu} = f(N_{Re}, N_{Sc}, N_0)$$

The experiments of Frossling (47) are summarised by Sherwood and Williams (105) in that

(i) at $N_{Re} < 4.0$, $N_{Nu} = \frac{RT \cdot D \cdot \rho}{D} = 2.0$

(ii) at $4 < N_{Re} < 400$, $N_{Nu} = 1.5 N_{Sc}^{0.33} N_{Re}^{0.5}$

(iii) at $N_{Re} > 400$, $N_{Nu} = 0.45 N_{Sc}^{0.33} N_{Re}^{0.5}$

Table 21 shows the relationship of $N_{Nu}$, $N_{Sc}$ and $N_{Re}$ calculated for the system hydrogen-toluene where,

$$N_{Nu} = 0.14 N_{Sc}^{0.33} N_{Re}^{0.5}$$

and for the system ethylene-toluene where

$$N_{Nu}$$
\[ N_{\text{Nu}} = 0.04 \, N_{\text{Sc}}^{0.33} \, N_{\text{Re}}^{0.5} \]

In both cases the Nusselt number was defined as \( \frac{Kd'}{D} \)
where the mean bubble diameter was taken as \( d' = 0.14 \) cms.
APPENDIX I

The Mathematical Relationship between the Instantaneous Absorption Rate and Reaction Rate of Both Ethylene and Hydrogen in Toluene.

The absorption rate \( Q \) is proportional to the mass transfer coefficient \( K \) so that \( K \) may be regarded as the resistance offered to mass transfer or more simply the conductivity of the interface with respect to the solute. \( 1/Q \) is then the resistance of the interface to solute transfer. An empirical relationship in reasonable agreement with the experimental values (Table 22 and Graph 21).

\[
\frac{1}{Q_R} = \frac{1}{Q_{H_2}} + \frac{R_2}{R_1} \frac{1}{Q_{C_2H_4}}
\]

where \( Q_{H_2} \) and \( Q_{C_2H_4} \) is the instantaneous absorption rate of hydrogen and ethylene in toluene respectively, \( Q_R \) is the absorption rate of either hydrogen or ethylene required to maintain the reaction rate, and \( R_2: R_1: H_2: C_2H_4 \) in the inlet gas.

From equation 41 when \( R_2/R_1 = 1/0 \) then \( Q_R = 0 \) and maximum reaction rate is obtained when the conductance of the hydrogen film is lowered sufficiently so that all the available ethylene is converted into ethane.

It /
Comparison of $Q$ expt. and $Q$ derived from equation 41.
### TABLE 22.

**COMPARISON BETWEEN \( q_R(\text{expt.}) \) AND \( q_R(\text{calc.}) \) DERIVED FROM EQUATION 42.**

<table>
<thead>
<tr>
<th>Temp. ( ^\circ \text{C} )</th>
<th>( q_{\text{H}_2} )</th>
<th>( q_{\text{C}_2\text{H}_4} )</th>
<th>( \frac{\text{H}_2: \text{C}_2\text{H}_4}{1:1} )</th>
<th>( 1:2 )</th>
<th>( 2:1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_R \text{ calc.} )</td>
<td>( q_R \text{ obs.} )</td>
<td>( q_R \text{ calc.} )</td>
<td>( q_R \text{ obs.} )</td>
<td>( q_R \text{ calc.} )</td>
</tr>
<tr>
<td>20</td>
<td>8.0</td>
<td>39.4</td>
<td>6.6</td>
<td>5.8</td>
<td>7.3</td>
</tr>
<tr>
<td>40</td>
<td>12.0</td>
<td>35.1</td>
<td>8.9</td>
<td>7.5</td>
<td>7.1</td>
</tr>
<tr>
<td>60</td>
<td>14.0</td>
<td>30.5</td>
<td>9.6</td>
<td>9.8</td>
<td>7.3</td>
</tr>
<tr>
<td>80</td>
<td>13.5</td>
<td>25.3</td>
<td>8.8</td>
<td>10.4</td>
<td>6.5</td>
</tr>
<tr>
<td>100</td>
<td>8.5</td>
<td>11.3</td>
<td>5.0</td>
<td>7.3</td>
<td>3.4</td>
</tr>
</tbody>
</table>

where \( \frac{1}{q_R \text{ calc.}} = \frac{1}{q_{\text{H}_2}} + \frac{R_2}{R_1} \frac{1}{q_{\text{C}_2\text{H}_4}} \)

and \( q_R \) is the absorption rate required to maintain reaction rate in toluene at \( T^\circ \text{C.} \) in gm. moles. sec\(^{-1}\) cms\(^{-2}\) \( \times 10^8 \).

\( q_{\text{H}_2}, q_{\text{C}_2\text{H}_4} \) are the instantaneous absorption rates for \( \text{H}_2 \) and \( \text{C}_2\text{H}_4 \) in toluene respectively, gm. moles. sec\(^{-1}\) cms\(^{-2}\) \( \times 10^8 \).

\( R_2/R_1 = \frac{\text{H}_2}{\text{C}_2\text{H}_4} \) fraction in the inlet gas mixture.
It is concluded that the reaction rate is not only proportional to the hydrogen absorption rate but is also a function of both hydrogen and ethylene absorption rates.
APPENDIX II.

Calculation of the Equilibrium Concentration of the Reactants in the Slurry Phase Hydrogenation of Ethylene at Different Temperatures.

Consideration of the solubility of hydrogen in toluene indicates that the equilibrium concentration of hydrogen in the slurry during reaction must be very small in order to support the high rate of absorption required by the reaction rate at the catalyst surface.

Evaluation of the equilibrium concentration (\(< 10^{-5}\ c.c.\ gas/c.c.\ liquid\) presents many difficulties. However, Miyamoto (63), in an investigation of the rate of oxidation of sodium sulphite has proposed that the rate of solution of oxygen into the liquid was in agreement with equation 42.

\[
\frac{dn}{dt} = \frac{u_0^2}{2RT} \cdot p \cdot \frac{c_1^3}{10^3} \cdot \frac{RT}{2\pi M} \cdot \sqrt{\frac{RT}{2\pi}} \cdot e^{-\frac{-Mu_0^2}{2RT}}
\]

where \(\frac{dn}{dt}\) = the rate of absorption of oxygen in sodium sulphite/unit area of interface

\(u_0\) = the velocity required for a gas molecule to penetrate from the gas to the liquid phase

\(u_0^*\) = the velocity required for a gas molecule to penetrate from the liquid to the gas phase

\(p\) = the partial pressure of the gas in the liquid
TABLE 23. Calculation of \( u_0 \) and \( u'_0 \), the minimum velocity required for absorption and desorption of a molecule of \( \text{H}_2 \) or \( \text{C}_2\text{H}_4 \) into toluene, in the temperature range 18° - 950°C.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temp. oC</th>
<th>Press. atms.</th>
<th>( k \times 10^3 ) ems/sec</th>
<th>( Z \times 10^2 )</th>
<th>( \beta \times 10^3 )</th>
<th>( \frac{\alpha_c \times 10^3}{\text{moles/lit.}} )</th>
<th>( \sqrt{-u_0^2 x 10^4} ) cms/sec</th>
<th>( u_0 \times 10^5 ) cms/sec</th>
<th>( u'_0 \times 10^5 ) cms/sec</th>
<th>( \frac{u'_0}{u_0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>18.0</td>
<td>0.978</td>
<td>0.464</td>
<td>0.835</td>
<td>0.364</td>
<td>3.068</td>
<td>19.10</td>
<td>4.37</td>
<td>4.96</td>
<td>0.88</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>31.0</td>
<td>0.950</td>
<td>0.813</td>
<td>0.833</td>
<td>0.669</td>
<td>3.305</td>
<td>19.48</td>
<td>4.30</td>
<td>4.88</td>
<td>0.88</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>39.5</td>
<td>0.925</td>
<td>1.004</td>
<td>0.818</td>
<td>0.846</td>
<td>3.372</td>
<td>19.74</td>
<td>4.28</td>
<td>4.86</td>
<td>0.88</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>54.2</td>
<td>0.854</td>
<td>1.247</td>
<td>0.817</td>
<td>1.163</td>
<td>3.380</td>
<td>20.22</td>
<td>4.28</td>
<td>4.85</td>
<td>0.88</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>64.2</td>
<td>0.786</td>
<td>1.273</td>
<td>0.826</td>
<td>1.326</td>
<td>3.306</td>
<td>20.53</td>
<td>4.31</td>
<td>4.86</td>
<td>0.89</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>73.6</td>
<td>0.698</td>
<td>1.263</td>
<td>0.828</td>
<td>1.483</td>
<td>3.104</td>
<td>20.80</td>
<td>4.33</td>
<td>4.87</td>
<td>0.89</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>83.4</td>
<td>0.575</td>
<td>1.173</td>
<td>0.436</td>
<td>0.904</td>
<td>2.827</td>
<td>21.08</td>
<td>4.56</td>
<td>5.27</td>
<td>0.87</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>95.0</td>
<td>0.375</td>
<td>0.762</td>
<td>0.434</td>
<td>0.934</td>
<td>2.188</td>
<td>21.44</td>
<td>4.62</td>
<td>5.11</td>
<td>0.91</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>18.0</td>
<td>0.978</td>
<td>4.160</td>
<td>0.601</td>
<td>2.766</td>
<td>142.9</td>
<td>5.09</td>
<td>1.01</td>
<td>1.80</td>
<td>0.56</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>31.0</td>
<td>0.950</td>
<td>3.662</td>
<td>0.656</td>
<td>2.793</td>
<td>107.2</td>
<td>5.20</td>
<td>1.03</td>
<td>1.81</td>
<td>0.57</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>39.5</td>
<td>0.925</td>
<td>3.220</td>
<td>0.628</td>
<td>3.096</td>
<td>86.4</td>
<td>5.28</td>
<td>1.04</td>
<td>1.69</td>
<td>0.62</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>54.2</td>
<td>0.854</td>
<td>1.874</td>
<td>0.984</td>
<td>2.466</td>
<td>57.5</td>
<td>5.40</td>
<td>1.08</td>
<td>1.94</td>
<td>0.56</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>64.2</td>
<td>0.786</td>
<td>2.060</td>
<td>0.874</td>
<td>2.660</td>
<td>41.6</td>
<td>5.48</td>
<td>1.09</td>
<td>1.66</td>
<td>0.67</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>73.6</td>
<td>0.698</td>
<td>2.591</td>
<td>0.668</td>
<td>3.474</td>
<td>29.0</td>
<td>5.56</td>
<td>1.08</td>
<td>1.33</td>
<td>0.81</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>83.4</td>
<td>0.575</td>
<td>2.090</td>
<td>0.727</td>
<td>3.146</td>
<td>17.8</td>
<td>5.63</td>
<td>1.10</td>
<td>1.20</td>
<td>0.92</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>95.0</td>
<td>0.375</td>
<td>0.950</td>
<td>1.045</td>
<td>3.077</td>
<td>8.1</td>
<td>5.73</td>
<td>1.12</td>
<td>1.25</td>
<td>0.90</td>
</tr>
</tbody>
</table>

where $\beta = \sqrt{\frac{2KRTkz}{p6.10^3s}}$, $u_0 = \sqrt{-\frac{2RTln\beta}{M}}$, $\sqrt{-u_0^2} = \sqrt{\frac{3RT}{M}}$, $u_0^2 - u'_0^2 = -\ln\left(\frac{\alpha_cRTz}{6.10^6p}\right)$, $k = \text{velocity constant}$, $z = \text{Q}$ where Q is the instantaneous velocity constant of the gas.
**TABLE 24.**

**CALCULATION OF $c_{e1}$, THE EQUILIBRIUM CONCENTRATION OF REACTANTS IN TOLUENE DURING SLURRY PHASE HYDROGENATION.**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temp. °C.</th>
<th>$(A.R. - R.R.) \times 10^8$ gm.moles/sec$^{-1}$cm$^{-2}$</th>
<th>$u_0 \times 10^{-5}$ cm$^2$/sec$^{-1}$</th>
<th>$c_{e1}$ moles/litre</th>
<th>Molecules of toluene per molecule of gas.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>31.0</td>
<td>5.5</td>
<td>4.88</td>
<td>$3.934 \times 10^{-5}$</td>
<td>2.2 $\times 10^5$</td>
</tr>
<tr>
<td></td>
<td>54.2</td>
<td>4.8</td>
<td>4.65</td>
<td>$2.310 \times 10^{-5}$</td>
<td>3.7 $\times 10^5$</td>
</tr>
<tr>
<td></td>
<td>73.6</td>
<td>4.7</td>
<td>4.87</td>
<td>$1.437 \times 10^{-5}$</td>
<td>5.9 $\times 10^5$</td>
</tr>
<tr>
<td></td>
<td>95.0</td>
<td>3.5</td>
<td>5.11</td>
<td>$1.411 \times 10^{-5}$</td>
<td>6.8 $\times 10^5$</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>31.0</td>
<td>32.5</td>
<td>1.81</td>
<td>$3.25$</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>54.2</td>
<td>22.8</td>
<td>1.94</td>
<td>$1.730 \times 10^{-1}$</td>
<td>4.9 $\times 10^1$</td>
</tr>
<tr>
<td></td>
<td>73.6</td>
<td>16.5</td>
<td>1.35</td>
<td>$2.55 \times 10^{-3}$</td>
<td>3.3 $\times 10^3$</td>
</tr>
<tr>
<td></td>
<td>95.0</td>
<td>3.0</td>
<td>1.25</td>
<td>$2.302 \times 10^{-5}$</td>
<td>3.0 $\times 10^5$</td>
</tr>
</tbody>
</table>

where $\frac{dn}{dt} = \frac{-Mv_0^3}{\sqrt{2\pi MRT}} - \frac{c_{e1}^3 S}{1000 \sqrt{\frac{RT}{2\pi M}}} - \frac{-Mv_0^2}{\sqrt{\frac{RT}{2\pi M}}}$

(R.R. Absorption Rate required by Reaction Rate in the slurry phase,)

$= (A.R. Instantaneous Absorption Rate) - \alpha c_{e1}$
Equation (42) may be applied to determine $c_{e1}$, the equilibrium concentration of both hydrogen and ethylene in toluene during slurry phase hydrogenation of ethylene. The calculated values are shown in Tables 23 and 24 where $c_{e1}(H_2) \ll c_{e1}(C_2H_4)$. It is probable that the surface of the catalyst is covered with adsorbed ethylene molecules and the overall reaction rate is controlled by the diffusion of hydrogen to the surface of the catalyst.
APPENDIX III.

Relation between the Rate of Mass Transfer of Reactants \( k_R \), the Observed Rate of Reaction \( k \), and the Actual Rate of Reaction \( k_C \).

The rate of hydrogenation of ethylene in the vapour phase may be expressed by the equation

\[
- \frac{dc_1}{dt} = k_C A_1 c_L^n / V
\]

where \( A_1 \) = catalyst surface area

\( c_L \) = concentration of hydrogen at the catalyst surface

\( V \) = volume of solution

\( n \) = order of reaction

\( k_C \) = the chemical velocity constant per unit area at unit volume.

Similarly for mass transfer, the rate of reaction may be expressed by

\[
- \frac{dc}{dt} = k_R A_2 (c - c_L) / V
\]

where \( c \) = concentration of hydrogen in the bulk liquid phase

\( c_L \) = concentration of hydrogen at the catalyst surface

\( A_2 \) = bubble swarm surface area.

Then /
Then for steady state conditions assuming a bimolecular reaction of the second order, and an excess of catalyst surface available for reaction —

\[ k_c \frac{A_1 c_L^2}{V} = k_R \frac{A_2 (c - c_L)}{V} \]  

\[ \therefore A_1 k_c c_L^2 + A_2 k_R c_L - A_2 k_R c = 0 \]

from which \( c_L = -\frac{c}{2} \pm \frac{c}{2} \left(\alpha^2 + 4\alpha\right)^{0.5} \)

where \( \alpha = \frac{k_R \cdot A_2}{k_c \cdot c \cdot A_1} \) and on substitution in 44 gives

\[ \frac{dc}{dt} = \frac{k_R A_2 c}{V} \left[ 1 + \frac{\alpha}{2} - \left(\alpha + \frac{\alpha^2}{4}\right)^{0.5} \right] \]

Thus the observed velocity constant per unit area per unit time, \( k \), for the slurry phase hydrogenation of ethylene is of the form

\[ k = k_R \left[ 1 + \frac{\alpha}{2} - \left(\alpha + \frac{\alpha^2}{4}\right)^{0.5} \right] \]

where \( k_R \ll k_c \), i.e. the reaction is transport rate controlled both by diffusion and convection of hydrogen to the catalyst surface.
The Resistance to Mass Transfer through Liquid Films in Series.

Following the procedure of Watt and Walling (119) the net rate of diffusion of solute may be expressed by Fick's Law as

\[ Q = -D \frac{dc}{dx} \]

Thus for steady state diffusion \( \frac{dc}{dx} \) is constant and the rate equation becomes

\[ Q = \frac{D(c_1 - c_2)}{x_2 \int \frac{dx}{A}} \]

The rate of diffusion of hydrogen through the liquid film at the gas-liquid interface may be expressed from 49 as

\[ q^1 = D(c_{H_2}^1 - c_{H_2}^2)/M \]

or \[ q^1 = D(c_{H_2}^1 - c_{H_2}^2)/M \]

where \( c_{H_2}^1 \) is the conc. of hydrogen in the gas phase.
\[ c_{H_2}^2 = \text{the conc. of hydrogen in the bulk liquid phase} \]
\[ c_{H_2}^1 = \text{Henry's constant, and} \]
\[ P_{H_2} = \text{pressure of hydrogen in the gas phase} \]

\[ \int_{x_1}^{x_2} \frac{dx}{A} = M \text{ constant for equilibrium conditions.} \]

The diffusional area of the liquid film at the catalyst surface is proportional to the total surface area of the catalyst which is itself proportional to the total weight of catalyst present. The rate of diffusion of hydrogen through the liquid film at the catalyst surface may be expressed from 49 as

\[ Q^2 = D \left( c_{H_2}^3 - c_{H_2}^2 \right) \frac{N}{W} \]

where \( c_{H_2}^3 = \text{the conc. of hydrogen at the catalyst surface} \)
\( W = \text{weight of catalyst} \)
\( N = \text{constant for catalyst surface} \).

For steady state conditions \( q^1 = q^2 \) and

\[ c_{H_2}^2 = \frac{M \cdot W \cdot c_{H_2}^3 + N \cdot P_{H_2}}{(M \cdot W + N)} \]

Substituting
Substituting $c^2_{\text{H}_2}$ in 51 leads to 54

$$Q_i = \frac{D(HP_{\text{H}_2} - c^3_{\text{H}_2})}{M + \frac{N}{W}}$$

The reaction rate of the slurry phase hydrogenation of ethylene has been shown (Graph I, p. 47), to be dependent on the concentration of hydrogen at the catalyst surface, $c^3_{\text{H}_2}$, and also proportional to the weight of catalyst $W$ in the slurry. Thus the rate of reaction $R$ is

$$R = Kc^3_{\text{H}_2}W$$

and substituting in 54 for $c^3_{\text{H}_2}$ gives 55

$$D(HP_{\text{H}_2} - \frac{R}{KW}) = R(M + \frac{N}{W})$$

which on rearrangement gives

$$\frac{WP_{\text{H}_2}}{R} = \frac{D}{W} + \frac{M}{D.H.} + \frac{N + K}{D.H.}$$

For the conditions satisfied by equation 57 a plot of $\frac{WP_{\text{H}_2}}{R}$ vs. $W$ should be linear.

When the reaction rate is dependent only on the concentration of hydrogen at the catalyst surface $c^3_{\text{H}_2}$ i.e. further increase in weight of catalyst $W$ in the slurry /
• R = REACTION RATE IN DECALIN AT 130°C.
〇 R = REACTION RATE IN DECALIN AT 140°C.

Test of equation Linear plot of $\frac{WP_{H_2}}{R}$ vs. W.
slurry does not affect the rate of reaction, the rate of reaction \( R \) is

\[
R = K_1 c_3 \text{H}_2
\]

And by substitution in 54 for \( c_3 \text{H}_2 \) leads to 59

\[
\frac{W_{\text{PH}_2}}{R} = \frac{W (M + \frac{K_1}{D})}{DH} + \frac{N}{DH}.
\]

For the conditions satisfied by equation 57 a plot of \( \frac{W_{\text{PH}_2}}{R} \) vs. \( W \) should be linear. The general form of equation 57 and 59 is

\[
R = \frac{W_{\text{PH}_2}}{1 + \beta W}
\]

where \( \alpha \) and \( \beta \) are constants whose values are dependent on the reaction equations 55 and 58.

Graph 22 is a linear plot of \( \frac{W_{\text{PH}_2}}{R} \) vs \( W \) predicted by equation 60 for the conditions where the reaction rate is dependent on the quantity of catalyst < 3 g. and independent on the quantity of catalyst > 3 g. (see Graph 1, p. 47).
(1) The reaction rate of the slurry phase hydrogenation of ethylene on a Raney-nickel catalyst suspended in non-polar, non-associated hydrocarbon solvents, has been evaluated under a variety of conditions. The reaction rate is such that:

(a) an increase in temperature of the system increases the observed reaction rate which reaches a maximum at 72°C, when toluene is the catalyst supporting liquid and 150°C. when decalin and tetralin are the supporting liquids. Thereafter the reaction rate is presumed to decrease to zero at the boiling point of the liquid.

(b) reaction rate reaches a limiting value with a finite quantity of catalyst (3 gm.) illustrating that the reaction is transport rate controlled.

(c) reaction rate increases in proportion to the inlet gas rate over the range 0.1 - 0.7 gm. moles/hr., thus showing that the reaction rate is controlled by the surface area of bubble swarm.

(d) maximum reaction rate occurs with an inlet gas ratio of H₂: C₂H₄:: 2: 1

(e) the nature of the supporting liquid is unchanged after reaction and it acts only as a transport carrier for the reactants and products to and from the catalyst surface respectively.

(2) An estimate of the surface area of bubble swarms at inlet gas rates comparable with conditions in the slurry reactor has been made on the generalisation that the mean bubble shape is a prolate ellipsoid.

(3) Absorption rate data have been determined for the systems hydrogen and ethylene in toluene of zero gas concentration in the temperature range 20 - 100°C. under working conditions similar to those of the hydrogenation experiments. The data are expressed as
(4) The absorption rate of a gas component in a gas mixture into a liquid of zero gas concentration increases in proportion to the mole fraction of the component in the mixture.

(5) The slurry phase hydrogenation of ethylene is transport rate controlled by the rate at which hydrogen dissolves from the gas bubble into the catalyst supporting liquid—a process governed by physical absorption.

(6) The mass transfer rate of hydrogen and hence reaction rate in the slurry phase hydrogenation of ethylene is controlled by the ratio of H₂: C₂H₄ in the inlet gas mixture. Maximum reaction rate is achieved with an inlet gas ratio of H₂: C₂H₄: 2: 1. At higher hydrogen to ethylene ratios in the gas mixture, the rate of reaction is controlled by the rate of mass transfer of ethylene from the gas bubble to the catalyst surface.

(7) High reaction rates at high temperatures implying high mass transfer rates of both hydrogen and ethylene are possible because the concentration gradient of reactants between gas and liquid phases is large. And gases of low solubility and of high diffusivity can maintain high absorption rates into liquids of low gas concentration.
### PHYSICAL DATA AND MATERIALS.

#### TABLE 25.

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>10</td>
<td>3.78</td>
<td>1.96</td>
<td>6.42</td>
<td>3.75</td>
</tr>
<tr>
<td>20</td>
<td>5.02</td>
<td>2.55</td>
<td>7.00</td>
<td>3.07</td>
</tr>
<tr>
<td>30</td>
<td>6.23</td>
<td>3.14</td>
<td>7.35</td>
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<td>40</td>
<td>7.44</td>
<td>3.72</td>
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<td>50</td>
<td>8.68</td>
<td>4.32</td>
<td>7.60</td>
<td>1.47</td>
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<tr>
<td>60</td>
<td>9.91</td>
<td>4.92</td>
<td>7.50</td>
<td>1.06</td>
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<td>70</td>
<td>11.14</td>
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<td>7.20</td>
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<td>80</td>
<td>12.37</td>
<td>6.13</td>
<td>6.60</td>
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<td>90</td>
<td>13.52</td>
<td>6.73</td>
<td>5.67</td>
<td>0.27</td>
</tr>
<tr>
<td>100</td>
<td>14.83</td>
<td>7.40</td>
<td>3.85</td>
<td>0.10</td>
</tr>
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</table>

Values for D the diffusion coefficient of both hydrogen and ethylene in toluene were calculated from Othmer's Nomogram (92), Graph 18. Solubility data were extrapolated from Seidall (103) and Cook's (21, 59, 74) data, Graph 17.

Vapour pressure data (65) and viscosity values of toluene (66) were taken from 'International Critical Tables'.

#### TABLE 26

**Molecular Volumes. M.V.**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Hydrogen cc/gm.mole</th>
<th>Ethylene cc/gm.mole</th>
<th>Toluene cc/gm.mole</th>
<th>Decalin cc/gm.mole</th>
<th>Tetralin cc/gm.mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.V.</td>
<td>14.30</td>
<td>44.40</td>
<td>118.2</td>
<td>184.6</td>
<td>163.4</td>
</tr>
</tbody>
</table>

The molecular volumes of the respective substances were calculated from the atomic volumes given in Perry (95).
Composition of Cylinder Cases.

Gas samples were taken straight run from the hydrogen and ethylene cylinders marketed by B.O.C., Ltd. The samples were analysed in a G.L.L.C. apparatus (51). The sample composition was:

**Ethylene**

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Percentage ±0.02%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>99.88</td>
</tr>
<tr>
<td>Methane</td>
<td>0.01</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.03</td>
</tr>
<tr>
<td>Higher Homologues</td>
<td>0.08</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td><strong>100.00</strong></td>
</tr>
</tbody>
</table>

**Hydrogen**

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Percentage ±0.02%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>99.85</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.06</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.09</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td><strong>100.00</strong></td>
</tr>
</tbody>
</table>

**Hydrocarbon Solvents Used.**

- **Toluene**
  - b.p. 110.5° - 111°C.
- **Decalin**
  - b.p. 184° - 185°C.
- **Tetralin**
  - b.p. 206° - 207°C.

All liquids were distilled before use in a 3 litre still fitted with a fractionating column 3 ft. high packed with 1/16 inch Dixon rings.
NOTATION.

\[ A, S \] Area of interfacial contact \( \text{cm}^2 \)

\( a \) Major bubble axis m.m.

\( b \) Minor bubble axis m.m.

\( c \) Gas conc. per vol. of liquid c.c./c.c.

\( \Delta c \) Equilibrium gas conc. per vol. of liquid c.c./c.c.

\( \Delta \) Conc. gradient per vol. of liquid gm./mole.

\( D \) Diffusion coefficient c.c./c.c.

\( d \) Bubble diameter \( \text{cm} \) or \( \text{m} \)

\( d \) Tube diameter \( \text{cm} \) or \( \text{m} \)

\( e \) Bubble eccentricity

\( e \) Activation energy K. cal./mole

\( E \) Absorption efficiency cms. /sec.

\( E \) Acceleration due to gravity cms./sec²

\( k \) Mass transfer coefficient cms./hr.

\( K \) Constant

\( M \) Molecular weight

\( M.V. \) Molecular volume c./m³

\( N \) Avogadro's number molecules per mole.

\( N_{Re} \) Reynolds number \( \frac{v d \varphi}{\mu} \)

\( N_{Sc} \) Schmitt number \( \frac{V}{\mu} \)

\( N_{Nu} \) Nussult number \( \frac{K d}{D} \)

\( p \) Partial pressure atm.

\( P \) Atmospheric pressure atm.

\( Q \) Rate of absorption gm. moles./sec./cm²

\( R \) Gas constant erg./deg./mole.

\( R \) Bubble radius cm.

\( R_s \) Rate of surface renewal cms.²/hr.

\( T \) Temperature °C.

\( t \) Time sec.

\( U, v \) Bubble velocity cm./sec.

\( U_o \) Velocity of absorbing molecule gm. moles./hr.

\( U_0 \) Velocity of desorbing molecule gm. moles./hr.

\( \sqrt{\frac{v}{g}} \) Root mean square velocity gm./cm. sec.

\( v \) Velocity of reaction gm. moles./hr.

\( \nu \) Kinematic viscosity cm²/sec.

\( x \) Film thickness cm.

\( \xi \) Constant.

\( \alpha, \theta \) Constant.

\( \Delta \) Degree of turbulence

\( \mu \) Viscosity gm./cm. sec.

\( \varphi_L \) Liquid density gm./c.c.
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