MASS TRANSFER FROM BUBBLE SWARMS

DURING THE CATALYTIC OXIDATION OF SULPHUR DIOXIDE

by

JAMES NELSON GIBSON, B.Sc., A.R.I.C.

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UNIVERSITY OF EDINBURGH.
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DISCUSSION

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SUMMARY.

The rate of oxidation of sulphur dioxide in manganese sulphate solutions has been investigated over a range of sulphuric acid concentrations from 0 to 200 gr./l. It is found that in general, the reaction rate increases in a sigmoid manner with acid concentration, either remaining constant or decreasing slowly at high concentrations. The actual form of this sigmoid variation is seen to depend greatly on the sulphur dioxide rate, catalyst concentration, temperature, etc.

Accompanying this variation in rate is an obvious change in interfacial area, which has been measured and found to be due to a reduction in the mean bubble diameter to an apparently constant value; although there is some evidence that at the higher acid concentrations a slight reduction in surface area may occur owing to an increased bubble diameter. The variation in rate is attributed to the resultant effect of this changing surface area and a linearly falling rate/unit area, with increasing acid concentration.

As excess sulphur dioxide is everywhere present in solution except at the lower sulphur dioxide partial pressures, and as the reaction rate/unit area at a constant acid concentration decreases with temperature, it is concluded that the process is controlled by the absorption of oxygen. Consequently,
the overall process is interpreted on the assumption that the rate is limited by the absorption rate of oxygen which is at its maximum value i.e. when no oxygen is present in the bulk liquid. The reduction in rate with increasing acid concentration is postulated as being due to the decreased rate of diffusion of sulphuric acid from the reaction zone into the bulk liquid.

Surface area measurements have also been performed for oxygen bubble swarms in solutions of sulphuric acid of different concentrations and at different temperatures. The surface area is found to increase with acid concentration, this increase being attributed to a reduction in the degree of coalescence of the bubbles. Manganese sulphate is apparently very much more effective in preventing coalescence, so that it is postulated that there is a much greater difference between the static and dynamic surface tensions of manganese sulphate solutions than of sulphuric acid solutions of similar ionic concentrations.

The effect of sulphur dioxide rate, oxygen rate, oxygen partial pressure and catalyst concentration on the overall rate is explained in terms of the surface area effects and the absorption rate of oxygen, the results being expressed in terms of $K_{La}$ values. At low sulphur dioxide partial pressures, there is evidence that the process is limited by diffusion.
diffusion of sulphur dioxide in the gaseous phase.

The absorption rate of oxygen into solutions containing zero concentration of dissolved oxygen has been measured, under conditions similar to those existing during the oxidation measurements, and expressed in terms of $K_L$ values by use of the known surface area figures. These $K_L$ values are found to be everywhere less than those calculated from the reaction measurements, but, as with the latter values, reasonably good agreement is obtained with the values calculated from the equation of Higbie for circulating bubbles, at the lower temperatures. It is therefore concluded that direct comparison of the two series of measurements is prohibited owing to the different hydrodynamic conditions existing in the two systems.
Theoretical Considerations of Physical Absorption.

When studying the rate of solution of benzoic acid in water, Noyes & Whitney\textsuperscript{(1)} found that the results could be expressed by the first-order equation:

\[ \frac{dc}{dt} = k(c_s - c) \] (1)

where \( c \) is the concentration of the solution at time \( t \), and \( c_s \) is the solubility of the solute at the experimental temperature. They suggested that a saturated layer was rapidly formed at the interface and that the measured rate of solution was actually the rate of diffusion of solute from this layer into the bulk of the solution.

Nernst\textsuperscript{(2)} extended this view to heterogeneous reactions, making the following assumptions:

(a) Almost instantaneous establishment of equilibrium at the interface.
(b) Provided the solution is well stirred, the concentration in the bulk of the solution is considered uniform.
(c) The controlling factor is the rate of diffusion through a thin layer of solution, of thickness \( S \), adhering to the solid surface.

By the use of Fick's Law, and equation (1), Nernst derived an expression for the rate of solution of a solid into a liquid.
liquid. Thus,

\[- \frac{dc}{dt} = \frac{D A' (c - c_i)}{V' S}\]  \hspace{1cm} (2)

where \(D\) = diffusion coefficient of the solute,

\(A'\) = surface area of solid in contact with a volume,

\(V'\) of solution

\(c_i\) = concentration of the solute at the surface.

The velocity constant of the reaction is therefore given by:-

\[k = \frac{D A'}{V' S}\]  \hspace{1cm} (3)

The Two-Film Theory.

This theory, postulated by Lewis & Whitman\(^{(3)}\) assumes that, in the transfer of a soluble gas from a gas stream to a liquid stream, equilibrium always exists at the interface so that the rate of absorption is therefore controlled by the rate of transfer of the solute to and from the interface. As in the Nernst theory, it is assumed that complete homogeneity exists in the bulk of the two phases, and that all resistance to transfer across the separate phases is encountered in thin films at the interface. These films are considered to be either stagnant or in laminar flow, so that all transfer through them occurs by molecular diffusion.

Thus the rate of transfer, \(R_1\), through the gas phase is given by:-

\[R_1 / \]
\[ R_1 = k_G (p_o - p_i) \]  
(4)

where \( p_o \) and \( p_i \) are the partial pressures of the gas in the bulk phase and at the interface, respectively, this partial pressure gradient being considered to occur across a thin film of thickness \( \delta \) close to the interface. Similarly, for the liquid phase, the rate of transfer, \( R_2 \), of the dissolved gas from the interface to the bulk of the liquid is given by:

\[ R_2 = k_L (c_i - c_o) \]  
(5)

where \( c_i \) and \( c_o \) are the concentrations of the dissolved gas at the interface and in the bulk of the liquid phase respectively. \( k_G \) and \( k_L \) are the gas and liquid film coefficients, related, as in the Nernst theory to the diffusivity and film thickness.

Thus for steady state diffusion across two resistances in series,

\[ R = R_1 = R_2 = k_G (p_o - p_i) = k_L (c_i - c_o) \]  
(6)

This equation is of little practical value, so it is customary to employ overall mass transfer coefficients defined by:

\[ R = K_G (p_o - p_e) = K_L (c_e - c_o) \]  
(7)

where \( c_e \) is the concentration of the solution in equilibrium with /
with the bulk gas phase, and $p_e$ is the partial pressure of
the gas in equilibrium with the bulk liquid phase. If
Henry's Law is obeyed equations (6) and (7) lead to:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L}$$

(8)

and

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{H.k_G}$$

(9)

where $H$ is the Henry's Law constant, $\frac{1}{K_G}$ is the overall
resistance, $\frac{1}{k_G}$ the gas phase resistance and $\frac{H}{k_L}$ the
liquid phase resistance, expressed in terms of partial
pressure. The corresponding values in concentration units
are $\frac{1}{K_L}$, $\frac{1}{H.k_G}$, and $\frac{1}{k_L}$.

From the above it is obvious that the relative magni-
tudes of the gas and liquid phase resistances will depend on
the solubility of the gas. Thus for gases of very low
solubility, $H$ is large, so that the liquid phase resistance
is significant and is likely to be the controlling factor in
the rate of absorption. For gases of intermediate solubility
both resistances may be significant.

It must be pointed out that the assumption of the
presence of laminar films is not essential for the development
of the foregoing equations. However, by incorporating the
idea.
idea that the total resistance to transfer is encountered in an equivalent thickness of stagnant or laminar film,
theoretical expressions for the film coefficients, \( k_G \) and \( k_L \), may be obtained. On this basis,
\[
\begin{align*}
    k_G &= \frac{D_F}{R'T\delta_{LM}^F} \quad \text{and} \quad k_L = \frac{D}{\delta_L} \quad (10)
\end{align*}
\]
where \( D \) is the diffusion coefficient, \( R' \), the gas constant, \( T \), the absolute temperature, \( P \), the total pressure and \( P_{LM} \), the logarithmic mean of the partial pressures of the inert gas at the interface and in the main gas stream.

The Penetration Theory.

At the instant when the gas and liquid are contacted, it is very unlikely that steady state conditions exist, as a finite time is required for the establishment of a concentration gradient across the hypothetical liquid film. In actual fact, should the time of contact be sufficiently short, it would seem possible that steady state conditions might never be achieved.

Higbie\(^4\), from a survey of the results of various workers on flow conditions in industrial absorption equip-
ment, came to the conclusion that a stagnant or laminar film is always in existence, and suggested, in his Penetration theory,
theory, that each element of liquid surface is continually being renewed according to some systematic mathematical relationship. During its period of existence, the element of liquid surface is assumed to absorb gas in exactly the same manner as a stagnant liquid of infinite depth. As a result of this assumption Higbie derived the following equations:

\[ R = 2 \left( c_i - c_o \right) \sqrt{\frac{D}{\pi \Theta}} \]  \hspace{1cm} (11)

and \[ k_L = 2 \sqrt{\frac{D}{\pi \Theta}} \]  \hspace{1cm} (12)

where \( \Theta \) is the time of exposure.

The results of Higbie on the absorption of carbon dioxide in water showed progressively greater deviation from the theoretical as the contact time was reduced, suggesting the presence, at the interface, of some added resistance to absorption. Consequently the conventional assumption of equilibrium, or constant saturation, at the interface was abandoned. The results were then interpreted in the light of a hypothetical 'first-order process' at the interface, the value of the velocity constant being that which gave the best agreement with the experimental data.

Random Surface Renewal.
Random Surface Renewal.

The existence of laminar liquid films in many types of absorption equipment would appear to be very doubtful. Danckwerts (5) presented a new theory dealing with absorption into turbulent liquids, where the liquid surface is pictured as continually being renewed by fresh liquid brought to the surface by turbulent eddies. As in the Penetration theory, the liquid surface, when exposed is regarded as absorbing gas in the same manner as a stagnant liquid of infinite depth. However, in contrast to the idea of Higbie, no correlation is assumed between the time an element of liquid surface has been exposed, the surface age, and its chance of being remixed. Instead, a statistical distribution is attributed to the surface ages, expressed by the surface-age distribution function,

\[ \phi = s \cdot e^{-s \Theta} \]  

where \( s \) is the mean rate of surface renewal.

The mean rate of absorption per unit area of turbulent surface is then given by:

\[ R = (c_i - c_o) \sqrt{D} \int_0^\infty \frac{se^{-s \Theta}}{\sqrt{\pi s}} d\Theta \]  

which reduces to:

\[ R = (c_i - c_o) \sqrt{D \cdot s} \]  

Hence /
Hence

\[ k_L = \sqrt{D_s} \quad (16) \]

The above theory of Danckwerts has been criticised by Kishinevskii (6) who considered that turbulent and convective diffusion are factors of prime importance, whereas molecular diffusion is thought to be of secondary importance. It is assumed that the layer at the surface becomes instantaneously saturated with gas on exposure, this saturated layer subsequently being carried away into the bulk of the liquid. Danckwerts (36) has likened this to 'surface renewal without penetration'. This theory of Kishinevskii would appear to conflict with evidence on the proportionality of \( k_L \) to a power of \( D \) in the region of 0.5.

**Comparison of the Theories of the Absorption Process.**

Although the foregoing theories have been based on different concepts, they all lead to somewhat similar predictions, and agree on the additivity of resistances. The principal difference between these theories is in the behaviour of the liquid surface layer. The two-film theory postulates that the surface is never renewed, while Higbie and Danckwerts consider that the surface is renewed, but differ in their ideas.
ideas as to its rate of renewal, the former suggesting systematic and the latter, random renewal. There is some evidence\(^{(7)}\) that when a film in laminar flow meets a discontinuity, the surface layer may pass relatively undisturbed, although the underlying liquid may be mixed by eddying. This would result in an increased concentration gradient leading to higher absorption rates than for undisturbed laminar flow, but lower than would be obtained if complete mixing prevailed at the discontinuity. Danckwerts\(^{(36)}\) has described this phenomenon as 'rejuvenation' of the liquid surface.

It is in the definition of \(k_L\) that the different factors involved in the mechanism become apparent, Whitman predicting \(\frac{D}{\delta L}\), Higbie, \(2\sqrt{\frac{D}{\pi \theta}}\), and Danckwerts, \(\sqrt{D.s}\). Owing to the difficulty in obtaining the requisite data with sufficient precision, the value for the exponent of \(D\) still remains in doubt. Lynn, Straatemeier and Kramers\(^{(7)}\), and Groothius and Kramers\(^{(8)}\) have obtained data on the absorption of sulphur dioxide in wetted-wall columns and during the formation of single drops, respectively, which would appear to be consistent with the Penetration theory. From the absorption rates of oxygen and hydrogen in water, Hammerton and Garner\(^{(9)}\) obtained values of 0.41 for 0.3 cm. bubbles and 0.55 for 0.6 cm. bubbles, for the exponent of \(D\).
The Nature of the Interfacial Process.

Miyamoto and Nakata(10), following work on the oxidation velocity of sodium sulphite in water, have developed a theory for the rate of absorption of oxygen in water, the starting point being the kinetic theory of gases. An outline of the theoretical considerations involved will now be given:—

The absorption rate of a gas into a liquid can generally be given by

\[ D' = N'' \cdot S - f(c) \cdot S \]  

(17)

where \( D' \) is the absorption rate (molecules per sec.)

\( N'' \) is the number of molecules which enter the liquid phase through unit area per unit time,

\( f(c) \) is the number of molecules which leave the liquid phase through unit area per unit time,

\( S \) is the surface area.

When the concentration of the surface layer is kept at zero, the absorption rate is given by

\[ D_o = N'' \cdot S \]  

(18)

It is then assumed that only those molecules whose velocity components perpendicular to the surface are greater than a certain threshold value, \( u_o \), are able to enter the liquid phase. Thus,

\[ N'' / \]
\[ N'' = \beta \cdot N' \]  

where \( N' \) is the number of molecules which collide with unit area per unit time,

\( \beta \) is the ratio of the no. of molecules which penetrate into the liquid phase and the no. of molecules which collide with the liquid surface.

Integration of Maxwell's equation for the distribution of gaseous velocities, from 0 to \( \infty \) and from \( u_0 \) to \( \infty \), gives \( N' \) and \( N'' \) respectively.

Thus
\[ N' = \frac{N_0}{\sqrt{2\pi MT}} \quad \text{and} \quad N'' = \frac{N_0}{\sqrt{2\pi MT}} e^{- \frac{Mu_0^2}{2RT}}. \]

Equations (19) and (20) then give
\[ \beta = e^{- \frac{Mu_0^2}{2RT}} \]

where \( R' = \) gas constant; \( M = \) the molecular weight of the solute;

\( T = \) absolute temperature; \( N = \) Avogadro's constant;

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

The above has been further extended by Miyamoto to give a general theory for the rate of solution of a gas in a liquid, the process of solution being considered in two stages:

(a) penetration of gas molecules into the liquid phase, and

(b) escape of gas molecules from the liquid phase.
In addition to the assumption of a threshold velocity, \( u_o \), for molecules entering the liquid, a further threshold velocity, \( u'_o \), is assumed for molecules escaping from the liquid.

The rate of solution is given by,

\[
\frac{N}{S} \frac{dn}{dt} = N'' - N'''
\]  

(22)

where \( N'' \) = the number of molecules escaping from the liquid per unit area per unit time,

and \( n \) = moles of absorbable gas.

By a similar type of procedure as used previously, Miyamoto obtained the following equation for the rate of solution of a gas in a liquid:

\[
\frac{dn}{dt} = \sqrt{\frac{2 \pi M R T}{\nu}} \cdot e^{\frac{-M u_o^2}{2 R T}} \cdot \frac{c_1}{1000} \cdot S \cdot \frac{\sqrt{RT}}{2 \pi M} \cdot e^{\frac{-M u_o^2}{2 R T}}
\]  

(23)

where \( c_1 \) is the mean concentration of gas in the liquid phase.

As a consequence, the initial rate of solution, obtained by putting \( c_1 = 0 \), is given by

\[
\frac{dn}{dt} = \sqrt{\frac{2 \pi M R T}{\nu}} \cdot e^{\frac{-M u_o^2}{2 R T}}
\]  

(24)

Thus the rate of solution at the instant of bringing the gas
and the liquid into contact must have a finite value, given by equation (24), and instantaneous saturation of the surface is impossible.

Equation (23) may be rewritten as:

\[ \frac{dn}{dt} = \frac{P}{2 \pi MRT} \cdot S \cdot \beta - \frac{c_s S}{1000} \sqrt{\frac{RT}{2 \pi M}} \cdot \beta' \tag{25} \]

the coefficients \( \beta \) and \( \beta' \) being known as the accommodation coefficients for molecules entering and leaving the interface, respectively.

The theory of Miyamoto is therefore important in that it introduces the concept of the accommodation coefficient. At very short periods of contact the concentration in the surface layer will be continually changing so that diffusion into the liquid must take place from an unsaturated surface layer, thus offering an explanation for the additional resistance, at the interface, proposed by Higbie. Further work by Danckwerts and Kennedy\(^{(12)}\) on the absorption of carbon dioxide in water would appear to support this idea.

Danckwerts\(^{(5)}\) introduced the idea of the surface mass transfer coefficient, \( k_s \), such that the rate of absorption at any time is given by

\[ R = k_s (c_s - c_l) \tag{26} \]

where /
where $c_S$ is the saturation concentration and $c_1$ is the concentration at, or immediately below the surface, which is a function of the exposure time. Thus the absorption rate is a function of the surface concentration deficiency, which is in keeping with Higbie's suggestion of a first-order process at the interface.

Drickamer and Sinfelt (13) studied the diffusion of molecular sulphur across a saturated liquid-liquid interface for several organic liquids by means of the radioactive tracer technique and found that the free energies involved were higher in the cases with significant interfacial resistance than where the resistance was negligible, from which they concluded that interfacial transfer in systems involving negligible resistance is analogous to van der Waals' adsorption, while for systems involving high resistance the process is comparable to chemisorption. A similar type of hypothesis has been put forward to explain the interfacial resistance occurring during mass transfer from liquid droplets in the presence of surface-active agents. (14, 15)

Emmert and Pigford (16) similarly picture the process of gas absorption as occurring via adsorption at the interface, and derive an alternative and more practical method for the calculation of accommodation coefficients from experimental data.
data. Accommodation coefficients for the absorption of carbon dioxide and oxygen in water containing a wetting agent are given, together with values obtained by Peaceman (17) on the desorption of carbon dioxide from water, and by Danckwerts (18) from Higbie's results.

It must be noted that the interpretation of data apparently confirming the presence of interfacial resistance must be carried out most critically, as the apparent magnitude of the resistance may be due either to some systematic error in the measurements, or to poor reproducibility of experimental results. These points have been noted by Danckwerts (12) and by Sherwood (37).
Fig. 1  REPRESENTATION OF THE CONCENTRATION GRADIENTS INVOLVED IN RAPID SECOND-ORDER IRREVERSIBLE REACTION.
Theory of Chemical Absorption.

As an introduction, fig. 1 shows the concentration gradients involved in a rapid, second-order, irreversible reaction between absorbed gas, A, and a solution of another substance, B, the two-film concept being used as it lends itself most readily to pictorial representation. On first bringing the gas and liquid into contact, the reaction takes place at the interface, PQ, but due to depletion of the liquid reactant at the surface, the reaction zone recedes into the stagnant film, the position of the equilibrium reaction zone, RS, being such that the rates of diffusion of A and B to the zone are equal. The concentration gradients for the reaction product, AB, are also shown.

Sherwood and Pigford\(^{(19)}\), Danckwerts\(^{(5)}\), and Danckwerts and Kennedy\(^{(20)}\), give accounts of the development of the theory, the usual starting point being differential equations for absorption and chemical reaction, derived from a mass balance across a thin element of liquid. By applying the appropriate boundary conditions, a general solution is then obtained, where possible, or alternatively, solutions may be obtained for certain extreme cases. Expressions for the rate of chemical absorption based on the theories of Whitman, Higbie and Danckwerts are given in the above references.
As an illustration of the method of analysis involved, the case of first-order reaction between gas and solvent \((5)\) will be considered briefly, in the light of the Danckwerts theory:

The diffusion of a gas through a liquid is described by Fick's law

\[
\frac{\partial c}{\partial \Theta} = D \frac{\partial^2 c}{\partial x^2} \tag{27}
\]

where \(c\) is the concentration of the dissolved gas in the liquid at \((x, \Theta)\), \(x\) being the distance below the surface. The rate of removal of the gas by the first-order reaction is given by \(r \cdot c\), where \(r\) is the first-order velocity constant; thus,

\[
\frac{\partial c}{\partial \Theta} = D \frac{\partial^2 c}{\partial x^2} - r \cdot c. \tag{28}
\]

This equation is then solved by applying the appropriate boundary conditions, viz.

\[
c = c_0, x > 0, \quad \Theta = 0,
\]

\[
c = c_s, x = 0, \quad \Theta > 0,
\]

\[
c < c_0, x = \infty, \quad \Theta > 0,
\]

where \(c_0\) is the bulk concentration of the gas in the liquid. A special case is now considered in that it is assumed that the concentration of unreacted, absorbed gas in the bulk of the liquid is negligibly small \((c_0 = 0)\), the solution of the equation \((28)\) then being:
being:

\[ \gamma(\theta) = c_s \sqrt{D_r} \left[ e^{\frac{1}{r_r} \theta} + \frac{e^{-r_r \theta}}{r_r} \right] \] (29)

where \( \gamma \) is the rate of absorption per unit area of stagnant liquid surface.

The mean rate of absorption per unit area of non-stagnant liquid is then obtained by applying the surface-age distribution function and integrating. Thus:

\[ R = \int_0^\infty s \cdot e^{-s \theta} \cdot \gamma(\theta) \cdot d\theta \] (30)

\[ = c_s \cdot \sqrt{D_r (r+s)} \] (31)

The solution for the general case leads to:

\[ R = \left[ c_s - c_0 \left( \frac{s}{r+s} \right) \right] \sqrt{k^2_L + D_r} \] (32)

Danckwerts and Kennedy \(^{(20)}\) compared expressions for the rate of chemical absorption on the basis of the three theories, and found that the predictions were somewhat similar. (For the purposes of comparison the mean rate of surface renewal, \( s \), is replaced by \( k^2_L/D \), as in equation (16).)

Hoftyzer /
Hoftyzer and Van Krevelen(21), by the same general method as used above calculated the rate of absorption for certain extreme cases, on the basis of the Two-film and Danckwerts theories. The results of their analysis are expressed in the form of a graph relating absorption rate with the concentration of dissolved gas, concentration of liquid reactant, reaction rate, liquid film coefficient for physical absorption and the diffusion coefficients.

The discrepancies between the theories rest in the factors for which it is difficult to obtain accurate values, e.g. the saturation of a gas in a reacting solution, diffusion coefficients, etc., so that it is extremely difficult to test their validity.
Mass Transfer from Bubbles.

In this section will be discussed the transfer of mass from circulating and non-circulating bubbles; the conditions governing the presence or absence of circulation will be dealt with in the section on the 'Properties of Bubbles'.

Transfer from Solid Spheres.

Garner and Grafton (22) have studied the dissolution of benzoic acid spheres in a water stream and have correlated their results with the flow pattern occurring around the sphere. The situation is depicted by fig. 2, which shows the flow pattern around the sphere at \( N_{Re} \) of 40-50, and also the shape, which gives the requisite mass transfer data.

At very low \( N_{Re} \) (\(< 0.5\)), the flow around the sphere is streamline but at higher \( N_{Re} \) the rear stagnation point, B, moves forward on the side of the sphere to S, S', the points of separation of forward flow, as a result of which, at \( N_{Re} \) of 40-50, a volume of circulating liquid is retained in the wake of the sphere, as evidenced by the use of ink streams. At very much higher \( N_{Re} \) (\( > 480\)), the angle of separation of forward flow reaches a constant value of 103° at which point the wake commences to oscillate.

As /
Fig. 2 - Dissolution of a Benzoic Acid Sphere in a Water Stream.

$\alpha = \text{Angle of separation of forward flow.}$

$N_{Re} = 50.$

Fig. 3 - Circulation and Flow Patterns Associated with Rising Bubbles.
As shown in the figure, Garner and Grafton discovered that the rate of transfer was greater in the region of forward flow than in the wake of the sphere. This is due to the transfer at the rear of the sphere taking place into an 'older' volume of liquid, contained in the vortex rings.

By analogy with heat transfer, the overall transfer was found to be described by:

\[ \frac{Kd}{D} = 4.4 + 0.48 \cdot \frac{N_{Re}^{0.5} \cdot N_{Sc}^{0.33}}{Re} \]  

(33)

where \( K \) is the film coefficient of mass transfer, \( d \), the diameter of the sphere, \( N_{Re} \), the Reynolds No., and \( N_{Sc} \) is the Schmidt No.

**Circulating and Non-circulating Bubbles.**

Figure 3 shows the flow patterns associated with circulating bubbles. The external (liquid) flow pattern is similar to that shown by Garner and Grafton, but the situation is complicated by the distortion of the bubble when the Reynolds No. is still relatively small. The interior vortex rings tend to approach the leading edge of the bubble as \( N_{Re} \), and consequently the distortion increases, fig. 3b.

Hadamard\(^{(23)}\) postulates that internal circulation in a fluid droplet moving in a fluid medium is caused by the viscous drag on the surface, which means that there will be no laminar...
laminar layer on either side of the interface, so that the two-film theory is not applicable. Boussinesq \(^{(24)}\), on the other hand assumes the presence of two surface layers on the droplet, whose surface viscosities cause a resistance to motion of the surface, thus reducing the internal circulation and causing a difference in the velocities on both sides of the interface; this means that diffusion would have to take place through slow-moving layers. It has in fact been demonstrated \(^{(25, 26, 15)}\) that the existence of internal circulation is due to the transfer of momentum from the bulk of the liquid to the bubble surface by viscous shear forces.

Although these viscous forces are present on bubbles of all sizes tending to produce circulation, it would appear that, in the case of very small bubbles and droplets, the effect of surface tension outweighs the viscous shear, so that circulation is prevented. Non-circulating bubbles may thus be pictured as being surrounded by a static layer of liquid, in which case, to employ the nomenclature of the two-film theory, transfer will have to take place from a gas phase, consisting completely of stagnant film, to the liquid phase via a laminar layer of liquid. Thus transfer is due almost entirely to molecular diffusion, and as such, mass transfer coefficients would be expected to be very much lower than for circulating bubbles. This /
This has in fact been observed by Pattle\textsuperscript{(27)}.

Transfer from Non-circulating Bubbles.

Garner and Hammerton\textsuperscript{(9)} compared their results with values calculated from the equation of Frossling\textsuperscript{(28)} derived for transfer from a rigid sphere:

\[
\frac{Q}{T} = 4. \pi . D . \frac{N_\text{P} . \text{r}}{R . T} \left( 1 + 0.276 \cdot \frac{N_\text{Re}^{0.5} \cdot N_\text{Sc}^{0.33}}{N_\text{Sc}} \right)
\]

where \( \frac{Q}{T} \) = the rate of mass transfer (gm./sec.),

\( M \) = the molecular weight of the solute,

\( P \) = the difference between the vapour pressure and the partial pressure of the solute in the bulk of the outer gas phase.

\( T \) = the absolute temperature.

\( r \) = the drop radius (cm.)

This equation has been applied to the evaporation of drops of liquid and to the sublimation of naphthalene spheres in the range of \( N_\text{Re} \) from 2-1000. The effects of flow conditions and diffusion in the phase to which transfer occurs are represented by the exponents of \( N_\text{Re} \) and \( N_\text{Sc} \) respectively.

The results of Garner and Hammerton were, in general, greater than those predicted by Frossling's equation, except for bubbles of very small diameter and those contaminated with grease.
grease, which factors have been shown \(^{(29)}\) to be consistent with absence of circulation.

**Application of Higbie's equation to circulating bubbles.**

In applying this equation to mass transfer from bubbles, the time of contact is normally taken as the time for the bubble to traverse one diameter, which implies that small elemental areas of the bubble surface travelling from the forward to the rear stagnation points along great circles must travel with the same vertical velocity as the bubble itself. As zero velocity is postulated at the stagnation points this would appear unlikely. A further criticism is that in the leading half of the bubble, the surface is expanding thus exposing new elements of liquid, while in the rear half, elements of surface are continually being removed. Thus there will be a variation in the surface ages of these elements, the maximum surface age being the time for a single element of surface to travel from the forward to the rear stagnation point along great circles.

The situation is further complicated by variation in the path length due to oscillation of the rising bubbles, and as with transfer from rigid spheres, the presence of vortex rings in the wake of the bubble will mean that there will be a non-uniform rate of absorption round the bubble surface. In addition, the equation of Higbie is only applicable to bubbles of
of constant area, i.e. where absorption does not affect the interfacial area.

In spite of these complications, the results of Garner and Hammerton show good agreement with values calculated from Higbie's equation in the diameter range 0.3-0.8 cm., in which region there is circumstantial evidence of circulation. (29)
Mass Transfer from Bubble Swarms.

A rigid mathematical treatment of this subject is obviously impossible owing to the variation of bubble diameter within the bubble swarm and consequent lack of knowledge as to the conditions of circulation. The true velocity and path of the individual bubbles within the swarm due to interaction between bubbles, and also the surface area available for mass transfer are also in doubt. As a result of these factors, data on mass transfer has been expressed in a variety of ways, the most important of these being the mass transfer coefficient per unit volume of column, the mass transfer factor of Chilton and Colburn,\(^{(30)}\), which relates the mass transfer coefficient with the properties of the fluid, and by the use of the concept of the transfer unit\(^{(31)}\). By making numerous assumptions, several other methods peculiar to gas absorption from bubbles have been evolved, principally by Pattle\(^{(27)}\), Coppock and Meiklejohn\(^{(32)}\), and Geddes\(^{(33)}\).

The complexities of the problem may be seen by outlining some of the more important assumptions employed by Pattle:-

(1) The concentration of the dissolved gas in the bulk of the liquid is maintained at zero.

(2) The rate of loss of gas from a bubble is proportional to its deficiency in the bulk of the liquid.

(3) The number of molecules in the bubble does not vary.

(4) /
The absorption coefficient, i.e. the proportion of the gas contained in the bubble which is dissolved per unit height of rise in a liquid free from dissolved gas, varies as some power of the bubble volume.

By these and other assumptions, Pattie was able to derive an 'absorption efficiency' to correlate results on the aeration of water.

In this work, the absorption data will be expressed on an area basis, wherever possible, by measurement of the surface area of the bubble swarms.

Mass Transfer from Bubble Swarms in the Slurry Phase Catalytic Hydrogenation of Ethylene.

This process, studied by Aikman(34) and by Macrae(35), involved physical absorption of hydrogen and ethylene from bubble swarms into toluene, followed by transport through the liquid to the catalyst, reaction, and subsequent transport of the product through the liquid to the bubble swarm. It was found that the reaction rate increased with temperature to a maximum at 75°C, and then fell off rapidly, presumably to zero at the boiling point of toluene. In order to elucidate the reason for the high reaction rate at high temperatures, the absorption rates of hydrogen and ethylene into toluene from bubble
bubble swarms, over very short periods of time, were measured, (i.e. the initial absorption rates).

As a result of these measurements, it was concluded that the reaction rate was controlled by the rate of solution of hydrogen into the liquid, the absorption rate curve for hydrogen exhibiting a maximum at about 75°C. This anomalous behaviour is also apparent in the variation of the solubility of hydrogen in toluene with temperature. The results of the absorption measurements enabled the concentration of hydrogen in the liquid medium during the reaction to be calculated, and this was found to be very low. It was concluded that the high reaction rate at the catalyst surface resulted in a very low concentration of hydrogen and ethylene in the liquid, which, due to the very high concentration gradients between the gas and the liquid phases allowed a very high absorption rate from the bubble swarm to be maintained by a gas of low solubility and high diffusivity, namely hydrogen.

The results on the absorption rate of hydrogen and ethylene into toluene were correlated by:

\[ N_{\text{Nu}}(H_2) = 0.14 \cdot N_{\text{Re}}^{0.5} \cdot N_{\text{Sc}}^{0.33} \]  \hspace{1cm} (35)

\[ N_{\text{Nu}}(C_2H_4) = 0.04 \cdot N_{\text{Re}}^{0.5} \cdot N_{\text{Sc}}^{0.33} \]  \hspace{1cm} (36)

These results were also compared with values calculated from the /
the equations of Higbie and Frossling, when it was found that they fell between the two values but were in better agreement with Frossling's equation than with that of Higbie.
Properties of Single Bubbles and Bubble Swarms.

As the information available on the fundamental properties of bubble swarms is very limited, this section will deal principally with the effect of the liquid properties on the characteristics of single bubbles, before proceeding with an outline of the properties of bubble swarms.

Factors affecting Bubbles during Formation.

It is well known\(^{(38, 39, 40)}\) that there must be a fundamental difference in the method of formation of bubbles at single orifices, depending on the gas velocity. Two distinct types of bubbling have been recognised, namely 'separate bubble' and 'chain bubble' types. In the former case, which occurs at low gas velocity, the bubble diameter is considered to be independent of the flow rate and to increase with increasing orifice diameter, whilst above a certain critical gas velocity, the latter type of bubbling exists, the diameter of the bubble being independent of the orifice diameter and increasing with increasing gas velocity.

At low gas velocities, the shape of the bubble is such that the buoyancy forces are balanced by surface tension forces, and as the bubble grows, this balance is maintained by movement of the rim of contact of the bubble with the orifice, until such
such time that it is within the orifice diameter, when no further change can take place. Further increase in the buoyancy forces then causes the neck of the bubble to stretch, leading to detachment of the bubble.

Maier\(^{(38)}\) derived a simple relationship between the orifice diameter and bubble diameter by assuming that the bubble is spherical at the moment of release, and that there is perfect wetting of the orifice by the liquid. Thus:

\[
R = \left(\frac{3}{\pi} \cdot \frac{r \cdot \sigma}{\rho \cdot g}\right)^{1/3}
\]  \hspace{1cm} (37)

where \(R\) is the bubble radius, \(\sigma\), the surface tension of the liquid, \(r\), the orifice radius, and \(\rho\) is the density difference between the liquid and the gas.

For the air-water system at \(20^\circ\text{C}\), this reduces to \(V/D' = 0.231\), where \(V\) is the bubble volume and \(D'\), the orifice diameter. Datta, Napier and Newitt\(^{(39)}\), who obtained an average value of 0.33, give values calculated from the results of other workers.

It can be seen that the only physical properties of the liquid involved in the above equation are surface tension and density. However, when the gas velocity is such that chain bubbling exists, it would be expected that momentum, viscosity and /
and frictional effects would come into play. A detailed mathematical study of this problem was carried out by Maier, who decided that the most important factors are those whose magnitudes are of the same order as the buoyancy forces, namely the liquid momentum, due to the rapidly ascending stream of bubbles, and the viscosity effect. The resulting formula, which is of little practical value, requires that the bubble radius go through either a maximum or a minimum value with increasing rate of formation. The main conclusion was that there is no characteristic bubble diameter for a given orifice.

In general, it may be said that the bubble diameter during formation will be a function of factors tending to increase the bubble diameter and of factors tending to disrupt the bubble. In the former may be included the effects of viscosity, surface tension, and the effect of the kinetic energy of the gas stream \((k.1)\), while the latter will include liquid momentum, buoyancy, gas impact and friction at the liquid-gas-jet junction.

**Mass Transfer from Bubbles during Formation.**

Owing to the factors mentioned above, it is evident that a high degree of turbulence will exist within the bubble during formation, and this turbulence may or may not persist during
the subsequent rise of the bubble, depending on the flow rate and the properties of the liquid. As Dixon and Russell (42) have found that there is a high rate of absorption into liquid drops during formation, it would not be unreasonable to suppose that a similar state of affairs does in fact exist during bubble formation.

**Effect of Liquid Properties on Bubble Size.**

There is a wide variation in the reported results on the effects of liquid properties on the size of bubbles. Schnurmann (43) measured the sizes of bubbles produced from porous diaphragms and concluded that the bubble size was dependent on the viscosity of the liquid, in a number of liquids, e.g. alcohols, sugar solutions, and in solutions of some electrolytes. He failed to take into account the variation of surface tension which was claimed by Halberstadt and Prausnitz (44) to be an important factor, viscosity being regarded as of secondary importance.

This latter is in agreement with the results of Datta, Napier and Newitt (39), who showed that viscosity played little part in determining the size of bubbles. A linear relationship was found to exist between the bubble volume and the surface tension for water-alcohol mixtures of varying composition. This agreed with the observations of Eversole, Wagner /
Wagner and Stackhouse\(^{(41)}\), that the bubble frequency was higher in alcohol and water mixtures than in pure liquids.
Properties of Spherical Bubbles.

The resistance to movement offered by a rigid sphere in a flowing liquid is given by an integrated form of the Navier-Stokes' equation:

\[ W = \rho_L \left( \frac{U^2}{2} \right) \pi \cdot R^2 \cdot c_w. \tag{38} \]

where \( W \) is the resistance, \( \rho_L \), the liquid density, \( U \), the velocity and \( c_w \) is the drag coefficient which is a function of the Reynold's number.

For very low \( \text{Re} \) \((< 0.4)\), the drag coefficient, \( c_w \), is given by \( 24/\text{Re} \), so that equation (38) reduces to the familiar Stokes' equation:

\[ W = 6 \cdot \pi \cdot \frac{1}{\text{Re}} \cdot \rho_L \cdot R \cdot U. \tag{39} \]

\( \frac{1}{\text{Re}} \) being the viscosity of the liquid.

This equation has been applied by Bond and Newton \(^{(45)}\) and by Allen \(^{(46)}\) to the measurement of the terminal velocities of bubbles, when it was found that on increasing the bubble diameter, at low \( \text{Re} \), the resistance, which at very low diameters had corresponded to that required for a rigid sphere, as calculated from equation (39), became one-third smaller than the predicted value. The reason for this discrepancy would appear to be easily understood.

In
In the derivation of Stokes' equation it is assumed that there is no slip between the liquid and the surface of the sphere, which means that the liquid at the surface of the sphere has zero velocity relative to the sphere. However, in the case of fluid spheres, the existence of motion within the sphere has been predicted \(^{(23)}\), and demonstrated \(^{(25,26,15)}\) to be due to viscous drag acting on the surface of the sphere, which results in reduced drag and an enhanced velocity of ascent. Various factors have been introduced to correct Stokes' equation for this non-static surface, principally by Hadamard \(^{(23)}\), Boussinesq \(^{(24)}\), and Allen \(^{(46)}\). The effects of the correcting factors of Hadamard and Boussinesq have been described in connection with mass transfer from bubbles.

As an illustration of the type of modification to Stokes' equation, the correction postulated by Hadamard is:

\[
W = K \cdot \pi \cdot \frac{3}{3} \cdot R.U. \tag{4.0}
\]

where

\[
K = \frac{3 \cdot 3' + 2 \cdot 3_L}{3 \cdot 3' + 3 \cdot 3_L} \tag{4.1}
\]

\(3'\) being the viscosity of the gas.

Thus neglecting the viscosity of the gas, \(K = 2/3\), which then brings the results of Bond and Newton into agreement with the calculated values at increased bubble diameters. The value of this correcting factor can therefore be employed as /
as an indication of the presence or absence of circulation within the bubble, being equal to $2/3$ for circulating and $1$ for non-circulating bubbles.

As a result of this modification, Stokes' equation may be employed at higher values of $N_{Re}$, the extent of applicability being however limited by the distortion at relatively low $N_{Re}$. 
Properties of Elliptical Bubbles.

An intensive mathematical study of the relationship between the diameter, ellipticity, and velocity of gas bubbles has been carried out by Siemes (17). The shape of the bubble is first described by equating the effects of all the pressure components, including that due to flow along the surface of the bubble. The starting point is:

\[ p_g = p_o + p_\sigma + p_h + p_s \quad (4.2) \]

where \( p_g \) is the pressure inside the bubble, \( p_o \), the pressure on the surface, \( p_\sigma \) that due to surface tension, and \( p_h \) and \( p_s \) are the hydrostatic and hydrodynamic pressures, respectively.

By substituting the appropriate values for these quantities at different points on the bubble surface, (see fig.), the following equations are obtained:

\[ p_\sigma H - p_\sigma N + \rho_L g h_H - \rho_L V_H^2/2 = 0 \quad (4.3) \]
and

\[ p_\sigma N' - p_\sigma N + \rho_L g h_{N'} = 0 \quad (4.4) \]

where /
where \( V \) is the velocity of flow along a streamline.

From this latter equation, it can be seen that the component due to the surface tension at \( N \) is greater than at \( N' \), which means that the radius of curvature at \( N' \) exceeds that at \( N \). Thus the bubble is actually a non-symmetrical ellipsoid. For the purposes of the following, a truly elliptical character is assumed.

Equation (43) can now be used to describe the relationship between the bubble velocity, ellipticity and size. Thus:

\[
P \sigma_H - P \sigma_N = (\sigma/R).e^{1/3}(1/e^2 + 1 - 2e)
= (\sigma/R).t(e)
\]

\( \sigma \) being the surface tension, \( e \), the ellipticity and \( R \), the radius of the bubble of equal volume.

\[
h_H = R.e^{2/3} = R.J(e)
\]

The velocity of the streamline flow at the surface is described by:

\[
V_\theta = U.b \left[ \frac{(1-e^2)^{1/2} - e.\cosh.e}{e^2(1-e^2)^{1/2} - e.\cosh.e} - 1 \right] \sin\theta \frac{\sin\theta}{(b^2\sin^2\theta - c^2\cos^2\theta)^{1/2}}
\]

where \( b \) and \( c \) are the major and minor half-axes, and \( \theta \) is the angular displacement from the direction of the minor axis.
Thus

\[ V_\theta = U \cdot b \cdot f(e) \frac{\sin \theta}{(b^2 \sin^2 \theta - c^2 \cos^2 \theta)^{1/2}} \]  

(4.8)

The flow at H, \( V_H \), where \( \theta = \pi/2 \) is then

\[ V_H = U \cdot f(e) \]  

(4.9)

By substituting equations (45), (46), and (4.9) in (4.3), the expression relating the velocity, ellipticity and size of the bubble is given by:-

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

(50)

Values of the functions \( t(e) \), \( j(e) \) and \( f(e) \) are given in the paper.

Experimental measurements on air bubbles of radius 0.65 - 3.6mm. in water gave velocities in good agreement with equation (50). With bubbles in the larger range of diameters, difficulty was found in measuring the ellipticity of the bubbles owing to the oscillation. The ellipticity of the bubbles may be calculated from a transposed form of equation (50), namely:-

\[ T(e) = \frac{U^2/(R \cdot g)}{\gamma/(\rho L \cdot R^2 \cdot g)} - 0.900 \]  

(51)

\[ - 0.434 \]

The constants (-0.900) and (-0.434) being derived from the relationship /
relationship between the functions $T(e)$, \[ \frac{2t(e)}{f(e)^2} \], and $\frac{2j(e)}{f(e)^2}$.

The Oscillation of Small Bubbles.

It has been reported by many workers \((48,49)\) that increasing bubble diameter and ellipticity are accompanied by oscillation of the bubbles. A similar type of periodic movement has been observed by Schmiedel\((50)\) for rigid spheres falling in a liquid at Reynold's numbers in excess of 500. Thus it would appear that the observed oscillation of bubbles may be due to the vortex rings which appear in the wake of the sphere, or bubble, at increasing $N_{Re}$ \((\text{fig. 2 and 3})\). At $N_{Re} > 480$ it has in fact been shown that oscillation commences in the wake of the sphere\((22)\).

Lamb\((51)\), in a study of the oscillation of small spheres, has related $T'$, the time of oscillation, to the radius $R$, the liquid density and to the surface tension, in the equation:

\[ T' = \pi \sqrt{\frac{\rho_L R^3}{3 \sigma}} \]  \(\text{(52)}\)

Values of $T'$ determined from photographic measurements on an air-water system show that a bubble of 6.2mm. radius rising in water has an average period of oscillation of 0.11 sec., whereas a bubble of 4.9mm. radius has an average period of 0.073sec. These values are in good agreement with equation \((52)\), the major half-axis being employed instead of $R$. 
Properties of Large Bubbles.

It has been seen previously that the factors affecting the bubble properties are the surface tension, hydrostatic and hydrodynamic forces. As the diameter of the bubble increases, the relative importance of the three components changes markedly, so that at large diameters, ($>8\text{mm.}$), the effect of the surface tension may be regarded as negligible. Thus in this region, the major factors are the hydrodynamic forces, and to a lesser extent, the hydrostatic forces. On this basis, and with the assumption that the bubble is spherical, Davies and Taylor (52), have found the velocity to be in accordance with the equation:

$$U = 0.82 \cdot (R \cdot g)^{1/2}$$

(53)

If, however, the bubble is distorted to an extent greater than $10\%$ of the initial distortion, then the coefficient in the equation changes from 0.82 to 0.97. This correction must be applied to account for fluctuations about a mean shape.

The actual shape and path of bubbles $>8\text{mm.}$ diameter has been reported by Bryn (53). It is stated that bubbles in this region nearly always rise along straight paths, the bubbles being hemispherical at the front and flattened at the
the rear, changes of shape being confined to irregular swinging in the rear part.

At exceedingly large diameters, the bubbles are unstable and tend to break up into a number of smaller, approximately spherical bubbles.
GRAPH No. 1

VELOCITY OF AIR BUBBLES IN WATER
The Velocity of Air Bubbles in Water.

Graph 1, which is reproduced from the paper of Datta, Napier, and Newitt (39), shows the variation in the terminal velocity of air bubbles in water with bubble radius at a temperature of about 20°C., the curve being drawn by averaging the results of several workers. It must be noted that there is an error involved in the measurement of the velocities of all but the smallest bubbles owing to the increased path of rise due to the oscillation of the bubble. The velocity-radius curve may be divided into three well defined regions. Thus:–

(1) Bubbles of radius < 1mm., where the bubbles are streamline and ascending along vertical paths, a maximum velocity of about 32 cm./sec. being attained at a radius of approximately 1mm.

(2) Bubbles of radius 1–3mm., the bubbles being ellipsoidal in shape and ascending along a helical path oscillating about the major axis. The diameter of this helix increases till the bubble radius is approximately 2.5mm., at which point periods of vertical rise interrupt the helix. A gradual diminution of the bubble velocity to a value of approximately 24 cm./sec. in the region of a radius of 3mm. is observed.

(3) /
Bubbles of radius 3-12mm, where the bubbles are distorted and the bubble motion is irregular, the velocity gradually increasing from the aforementioned minimum.

In the case of air-glycerine, no sharp maximum has been observed, but only a gradual increase in velocity with increasing diameter. Peebles and Garber have studied the motion of bubbles in numerous liquids in terms of drag coefficients, and have distinguished the following regions:

1. \( \frac{N_{Re}}{Re} < \) approximately 2. The bubbles are spherical, moving along rectilinear paths. In this region, the drag coefficients agree with Stokes' law.

2. \( \frac{N_{Re}}{Re} > \) approximately 2 - some value peculiar to the fluid. Spherical bubbles moving along straight paths, the drag coefficients being slightly less than for a solid sphere of equal volume. This region, as has been explained previously is due to the onset of circulation.

3. At a range of Reynolds' numbers peculiar to the fluid, the bubbles are deformed, being elliptical in shape and move in spiralling zig-zag paths, with drag coefficients increasing sharply with \( N_{Re} \). This increase in drag is due to the increase in frontal area and to the fact that the liquid in the vortex rings is carried...
carried upwards with the bubble.

(4.) The bubbles are greatly deformed, assuming a mushroom shape, and rise along nearly straight paths. The drag coefficient continues to increase in this region, but at a reduced rate.

Regions (1), (2) and (3) may be identified with Graph 1; the discrepancy in the final region may be due to the extreme deformation and to the marked importance of the wall effect, which will now be considered.
Bubble Velocity in a Non-infinite Medium.

In the foregoing, it has been assumed that the frequency of bubble formation was infinitely slow and that the bubble rose in an infinite medium, so that the only factors considered were the physical properties of the liquid medium. The corrections to be applied in the case of several bubbles rising through a column of liquid of restricted diameter will now be considered.

Wall Effect.

There is abundant evidence available that the ratio of the bubble diameter, \( d \), to the tube diameter, \( D \), has a marked effect on the velocity of the bubble. The problem has been outlined by Barr(55), and it was found that the velocity in the region of Stokes' flow could be corrected by using the Ladenburg correction, expressed by:-

\[
U = U' \cdot (1 + 2.1 \cdot d/D)
\]

where \( U' \) is the observed velocity of the bubble in the tube.

This correction applies for \( d/D < 0.1 \) and for \( N_{Re} < 0.2 \). For a given diameter of tube, the correction increases with increasing \( N_{Re} \). The error in the velocity is, however, less than 1% if the tube diameter exceeds the bubble diameter by a factor greater than 100.
Effect of Bubble Proximity.

Stinson and Jeffrey (56) have carried out a mathematical analysis of the resistance to motion of two small spheres moving with equal, low velocity along parallel paths in a viscous fluid. By determining the Stokes' function for the interaction of the flow of liquid round the spheres, the resistance was found to be given by:

\[
W = 6. \pi \frac{r}{R_L} \cdot R.U. \lambda
\]  

\( \lambda \) may be defined as the ratio of the forces necessary to maintain the motion of either sphere in the presence of the other, to the force required to maintain the same motion for a single sphere. As the ratio of the distance between the centres to the sphere diameter increases, \( \lambda \) tends to 1, i.e. equation (55) tends to the normal Stokes' equation.

Thus the effect of the interaction between two rising bubbles will be to increase the velocity of both, as has been reported by O'Brien and Gosline (57). Owens (58) has reported a 12% difference between the velocity derived for a group of bubbles and that for a single bubble. This interaction will thus explain the discrepancies in bubble velocities at different bubble frequencies outlined by Garner and Hammerton (29).
Surface Contamination.

It has been observed\(^{(29)}\) that on addition of contaminants such as grease, the helical mode of rise is changed to a zig-zag path in one plane, thus causing an even greater error in the measurement of bubble velocity, as the bubble must then stall twice in one oscillation. At high \(N_{Re'}\) (200 - 1,200), the drag coefficient of contaminated bubbles is always greater than for clean bubbles, so that the velocity is reduced. This may be due to the reduction in circulation within the bubble brought about by contamination\(^{(9)}\), which will cause some increase in the drag.

If the contaminant is present in an amount sufficient for the formation of a multimolecular layer over the bubble surface, then the adsorptive forces may be sufficiently strong 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, so that a large amount of contaminant will increase the velocity of the bubble.

The Effect of Temperature.

Temperature may be expected to affect the bubble properties by virtue of its effect on the surface tension and the viscosity, and to a very much lesser extent, its effect on the densities of the liquid and gas. In connection with the boiling /
boiling of water, it has been illustrated$^{(59)}$ that increasing the interfacial tension between the liquid and the heating surface causes an increase in the diameter of the bubbles released. Datta, Napier and Newitt$^{(39)}$ have shown that for a given orifice diameter, the bubble volume decreases with decreasing surface tension, over a range of orifice diameters of from $0.036 - 0.63$ cm. As the surface tension decreases with increasing temperature, a reduction in bubble diameter would be expected. Over a temperature range of $20 - 50^\circ$C., the viscosity of water falls off by about 43%. As the viscosity affects the bubble velocity to a greater extent than it affects the diameter, it would appear that, in the region of Stokes' flow, the bubble velocity will be decided by the relative magnitudes of the change in bubble diameter, brought about by the surface tension change, and the direct change in viscosity due to temperature.
Properties of Bubble Swarms.

It has been observed by many workers that the bubble diameters produced from a porous plate diffuser bear little or no relationship to the pore size, except at extremely low gas rates. This may be explained by assuming that at very low gas rates, bubbles are produced only at the widest pores, which are comparatively few in number, so that the conditions are somewhat similar to those previously described for single orifices. On increasing the gas rate, the narrower pores will come into operation, as a result of which the bubbles will be produced from pores in close proximity, so that there will be a marked tendency for coalescence. Aikman(34) and Verschoor(60) have observed that at this stage the porous plate is covered by a thin layer or 'cone' of independent bubbles, rising bubbles becoming detached from this 'cone', rather than from any distinct pores. Thus, as has been observed, no direct relationship between bubble size and pore size can be expected.

A feature of bubble swarms produced at low gas rates (0.1gm.moles/hr.) is that there is always present a cycle of acceleration and deceleration of bubble production at the porous plate(61). This unsteady state condition may be counteracted by reducing the capacity behind the porous plate /
plate and increasing the pressure of the inlet gas. At higher gas rates of the order of 0.3 gm.moles/hr. the rate of bubble formation is constant.

Coalescence of Bubbles.

For coalescence to occur, the bubbles must remain in contact for a period of time long enough for the liquid film between the bubbles to become sufficiently thin. This condition is obviously favoured by the production of bubbles in close proximity, or by bubbles rising along the same vertical path, where one bubble may be drawn in behind the other. Pattle\(^2\), while studying the production of small bubbles from single orifices found that although coalescence occurred most readily in pure water, it was suppressed by the addition of substances which raise the surface tension of water. On the other hand, Seeliger\(^6\) found that while a lower surface tension produced a swarm of minute bubbles, the characteristics of the swarm differed greatly in solutions of similar surface tension, depending on whether the reduced surface tension was due to the addition of ethanol or Teepol (in the former case there was a slight lowering of the kinematic viscosity). The absence of coalescence of air bubbles rising in water containing some acetic acid has also been observed\(^2\). It would thus appear that the reduction in coalescence is not due /
due directly to the change in surface tension, but to some other factor causing an increase in the resistance of the liquid film to disruption\(^{(63)}\), possibly due to a difference in the solute concentration in the liquid film.

**Modes of Ascent in a Bubble Swarm.**

The modes of ascent in a bubble swarm are likely to be a mixture of the previously described modes for single bubbles, namely vertical, helical and zig-zag, but it is unlikely that straight line ascent will exist to any great extent owing to the jostling movement between neighbouring bubbles. In addition, with bubbles of diameter \(> 2\text{mm.}\), there will be a marked circulation of liquid up the centre of the tube and down the walls, owing to liquid being carried in the wake of the bubbles. As a result of the existence of these currents and the jostling movement, there will be a tendency for smaller bubbles to move downwards when near the walls, and for the establishment of eddies, in which the smaller bubbles will travel, within the column.

**The Velocity of Bubble Swarms.**

The determination of the bubble velocity within a bubble swarm presents many problems owing to the variation of the movement of bubbles within the swarm. In general, it may be said /
said that at low gas rates, the mean velocity of a bubble swarm will be close to the velocity of a single bubble under similar conditions, but at high gas rates, the mean bubble velocity within a swarm will be a complex function of the number of pores, pore size, distance between the bubble centres, bubble size distribution, liquid properties and the diameter of the tube. It is thus obvious that prediction of the mean velocity of a bubble swarm, except at very low gas rates, will be exceedingly difficult, so that experimental determination of the mean velocity is the best solution.

A survey of the dimensionless groups describing the problem was carried out by Klinkenburg and Mooij (64), by comparing the forces of inertia, gravity, viscous and surface tension forces. This was developed by Kaiszling (65), giving the following relationship:

\[
\frac{U}{\sqrt{g}} \frac{\gamma}{\sigma} = f \left[ \frac{(1 - l_0)}{l} , \frac{(\gamma L)}{(\rho L \cdot \sigma^3)} \right] \]

(56)

where \(l_0\) is the initial height of the liquid column and \(l\) is the height when gas is passing.

Kaiszling concluded that the principal factors influencing the bubble swarm velocity were the first two factors in the above, namely the gas content of the column, and the properties /
properties of the liquid. The third factor increases in importance with decreasing tube diameter.

Verschoor (60) has carried out measurements of the gas content of air bubble swarms in various liquids and has found that in water, methanol and glycerine, the gas content increases rapidly with gas rate to a maximum, after which it falls sharply to a minimum, followed by a gradual increase. The mean bubble velocity was then calculated from:--

\[ U = \left( \frac{V_g}{A} \right) \cdot \frac{1}{(1 - 1_o)} \]  \( (57) \)

where \( V_g \) is the gas flow rate (volume/unit time), and \( A \) is the cross-section area of the column. On plotting the bubble velocity against the gas content, three regions were noted:--

1. A region where the gas content increased while the bubble rate remained approximately constant. On the appearance of large bubbles in the column, in addition to the small bubbles,

2. a region where the bubble rate increased at an approximately constant gas content was observed. In this region, circulation of the liquid in the column was evidenced by the downward movement of the small bubbles near the walls of the tube.

3. Simultaneous increase of the bubble rate and gas content was observed, accompanied by a thickening of the layer of bubbles on the porous plate, together with an increase in the diameter of the bubbles released.
The Mechanism of the Catalytic Oxidation of Sulphur Dioxide in Aqueous Solutions.

The earliest reference to the use of salts of manganese and iron for the catalytic oxidation of sulphur dioxide by air in aqueous solutions was in a patent obtained by Clark in 1888. Since then, the reaction has been studied with two aims in view, firstly, for the regeneration of spent pickle acid, and for the leaching of low grade ores of iron and manganese, and secondly, for the removal of sulphur dioxide from flue gases.

In the former process, bubbles of air and sulphur dioxide were passed through a solution of ferrous sulphate; the resultant overall reaction was found to depend on the initial concentration of ferrous ion. If very low concentrations were employed, dilute solutions of sulphuric acid were obtained, whereas, with high initial concentrations, the ferrous sulphate was almost completely oxidised to ferric sulphate, sulphuric acid then being almost completely absent. Ralston has represented the reaction as:

\[
2 \text{FeSO}_4 + \text{SO}_2 + \text{O}_2 = \text{Fe}_2(\text{SO}_4)_3 \tag{1}
\]

\[
\text{Fe}_2(\text{SO}_4)_3 + \text{SO}_2 + 2 \text{H}_2\text{O} = 2 \text{FeSO}_4 + 2 \text{H}_2\text{SO}_4 \tag{2}
\]

In addition, some sulphuric acid is produced by the direct oxidation of dissolved sulphur dioxide. It may be seen that
a 'steady state' limit for the concentration of ferric sulphate will exist, depending on the relative rates of the above reactions. The concentration of ferric ion in this 'steady state' has been shown to decrease with increasing proportions of sulphur dioxide in the inlet gas. With low initial concentrations of ferrous ion, the limiting ferric concentration is achieved quite rapidly, thus explaining the overwhelming formation of sulphuric acid.

A similar type of hypothesis involving alternation between Mn$^{++}$ and Mn$^{+++}$ has been proposed by Grodzovskii\textsuperscript{(83)}, and by Kashtanov and Oleshchuk\textsuperscript{(87)}, to explain the oxidation of sulphur dioxide in dilute manganese sulphate solutions. The formation of Mn$^{+++}$ has been investigated\textsuperscript{(87)}, and it has been found that its formation is favoured by increased sulphuric acid concentration. There is however complete agreement in the literature that the oxidation rate of sulphur dioxide in the manganese solution decreases at high acid concentrations. Various attempts have been made to speed the reaction at high acid concentrations by the use of ozone\textsuperscript{(80, 82, 86, 87)}, and, while an increased rate has been observed, it has been found that the rate continues to fall with increasing acid concentration\textsuperscript{(86)}. If, in fact, the catalytic activity is due to trivalent manganese, the above would appear to suggest that the reaction might be controlled by some other /
other factor.

When the rate of oxidation of sulphur dioxide is very slow, as when catalysed by a suspension of manganese dioxide (69, 70), or when oxidation is due to pure oxygen, in the absence of catalyst (71), there is some evidence that manganese dithionate or dithionic acid is formed during the reaction.

Johnstone (73) and Keyes (76), who studied the use of iron and manganese for the removal of sulphur dioxide from the flue gases found that manganese is approximately 50 times as effective as iron for the conversion of sulphur dioxide to sulphuric acid, the optimum concentrations being respectively 0.025 and 1.2%. This optimum concentration of manganese has also been observed by Copson and Payne (75).

The above workers have also shown that the absorption rate of sulphur dioxide increases very rapidly with manganese concentration to the optimum value, but that further increase, up to about 1% causes very little increase in rate. At the optimum catalyst concentration, Copson and Payne found that, in solutions of sulphuric acid of concentration greater than 20%, the absorption rate is proportional to the partial pressure of oxygen and decreases with increasing acid concentration as observed previously. The absorption rate was also shown to increase with temperature in the range 30 - 70°C, which is in agreement /
agreement with the results obtained by Kashtanov and Ruizhov (79). Previously, Johnstone had found that, at the optimum catalyst concentration, the efficiency of the process was more susceptible to acid concentration with decreasing oxygen partial pressure, but less so with decreasing sulphur dioxide partial pressure. Increasing temperature was also observed to decrease the acid concentration at which the efficiency falls.

As the process consists of three separate processes, namely, absorption of sulphur dioxide, absorption of oxygen, and the reaction of the dissolved gases, it will be controlled by the slowest of these reactions. On the basis of the above evidence, Copson and Payne have assumed that, below the optimum catalyst concentration, the overall absorption rate of sulphur dioxide is limited by the rate of the oxidation reaction, whereas with concentrations in excess of the optimum, it is assumed that the concentration of oxygen in the solution becomes vanishingly small, so that the overall absorption rate of sulphur dioxide tends to become limited by the initial absorption rate of oxygen in the solution. This conclusion was also arrived at by Chi-Kwang Chen (83), and by Grodzovskii (83), and is supported by the observed dependence on the number and size of the bubbles (67, 69, 75, 81, 88).
At very low sulphur dioxide partial pressures, the evidence of Johnstone that the efficiency is less susceptible to acid concentration would appear to indicate that the absorption rate of sulphur dioxide from gas mixtures containing very little sulphur dioxide may be less than that required for reaction with the oxygen dissolving at its maximum rate. The oxygen concentration in the solution will therefore increase to a constant value, such that the amount of oxygen dissolving will be just sufficient to react with the sulphur dioxide dissolving at its maximum rate.

While this reaction would appear to be a very promising method for the removal of sulphur dioxide from flue gases, it has been found that its usefulness is restricted owing to the inhibition of the reaction by phenolic and other substances present in flue gases\(^{(7)}\). Attempts have been made to overcome this difficulty by oxidising these substances, either by the use of ozone\(^{(86)}\), or by employing simultaneous d.c. electrolysis and aeration\(^{(89)}\).
EXPERIMENTAL - PART I

Rate of Oxidation of Sulphur Dioxide in Manganese Sulphate Solution.
APPARATUS FOR OXIDATION OF SULPHUR DIOXIDE

1. Manometer
2. Wet Gas Meter
3. Smoothing Bottle
4. Compressor
5. Drying Tower
6. Flowmeter
7. Safety Valve
8. Preheater
9. Saturator
10. Reaction Vessel
11. Condenser
12. Continuous Scrubber
13. Reservoir
14. Gas Wash Bottle
Description of Apparatus.

Oxygen and sulphur dioxide were passed at known rates into the reaction vessel and the resulting conversion of sulphur dioxide to sulphuric acid measured by metering the excess of oxygen, after removal of sulphur dioxide from the exit gases from the reaction vessel.

Metering of Sulphur Dioxide.

The sulphur dioxide flow rate was measured by using an oil-filled differential flow meter, the flow rate being controlled by means of a stopcock and a mercury filled safety valve.

Metering of Oxygen.

This was achieved by the use of accurate, stainless steel, wet gas meters (0.02c.ft./rev.), obtained from Scientific and Projections, Ltd. After metering, the pressure of the oxygen was boosted by means of a diaphragm compressor, control of the flow rate being maintained by altering the recycle on the compressor. To prevent contamination of the oil-filled flow meter, which gave a visual indication of the oxygen rate, the gas was then passed through a drying tower.

Sulphur /
Fig. 5 REACTION VESSEL AND PREHEATER

Reactor Heater and Insulation

Preheater
Sulphur Dioxide Removal.

The obvious method for the removal of sulphur dioxide is by the use of caustic soda. However, the sodium sulphite so produced is easily oxidised, so that the reaction rate indicated from the volume of oxygen absorbed would be in excess of the actual figure. Haller (90) has reported that the use of a 5% solution of glycerine inhibits this oxidation. Tests were carried out which indicated that a solution of caustic soda and 5% glycerine could safely be employed. The bulk of the sulphur dioxide was therefore removed by a continuous scrubber packed with glass beads employing a solution containing 2% sodium hydroxide and 5% glycerine, any sulphur dioxide remaining being removed by wash bottles containing a solution of 10% sodium hydroxide and 5% glycerine.

Reaction Vessel.

The oxygen and sulphur dioxide streams were combined and passed through a preheater, consisting of an electrically heated copper coil wound round a copper tube, the temperature being controlled by a Simmerstat on-off control. Further mixing of the gases took place in a compartment below the sinter of the reaction vessel, this compartment being designed to act as a saturator, but owing to the reaction between oxygen and sulphur dioxide in water solution, it could not be employed. /
employed. The use of glycerol as an inhibitor during saturation was also prohibited owing to possible contamination of the solution in the reaction vessel by glycerine vapour.

Subdivision of the gas stream was effected by means of a Pyrex glass sinter of porosity No. 2, sealed into the base of the reaction vessel, which was of approximately 500 ml. capacity, being of 1.5in. bore Pyrex tube of approximately 15in. in length, fitted with a side arm to improve circulation.

The reaction vessel was heated by means of a 250 watt element wound round the tube, the lagging consisting of a single layer of asbestos paper, owing to the highly exothermic nature of the reaction. Temperature control to within ± 0.3°C. was maintained by a Variac transformer. In order to exclude draughts, the preheater and reaction vessel were enclosed in a hardboard box.
Experimental Technique.

Before commencement, the water levels in the wet gas meters were checked, after which the meters were separately compared with the outflow from a standard 1.2 c.ft. gas holder, graduated in 0.002 c.ft. divisions. The meters were then connected into the apparatus, which was made gas-tight, and oxygen passed for 60 minutes at the rate required during the run. It was found that, in general, complete agreement between the meters existed over this period, despite comparatively minor fluctuations of the order of 0.5% in the intervening period.

The required volume (400 ml.) of catalyst solution was then made up and heated in a beaker to approximately the temperature at which the run was to be carried out. In order to allow the preheater to attain the partial pressures required for the particular run, the oxygen-sulphur dioxide mixture, at the desired partial pressures, was then passed through the pre-heater and reaction vessel at a fairly slow rate while the reactor was being filled with the solution. After stoppering the reaction vessel, using Audco grease (No. 631) in order to provide a leak-free seal at elevated temperatures, the gas rates were immediately boosted to the required values. Readings were taken as soon as the exit gas meters commenced motion.
At this stage the flow of inhibited caustic solution to the scrubber was started, at approximately 750 mls. per hour. The actual time consumed between filling the reactor and taking the initial readings was never in excess of one minute, so that very little error in the measurements was incurred.

It has been noted previously that the reaction is highly exothermic, which meant that strict attention had to be paid to the control of temperature. As a result of this, the majority of the runs were carried out at a temperature of 60°C, when, despite the increased reaction rate, better temperature control was obtained. In one case, however, the evolution of heat was such that it was found necessary to switch off the heating completely for a short period when the reaction rate had attained its maximum value.

As a complete study of the reaction in the light of maximum efficiencies and concentrations of sulphuric acid attainable was not the object of this research, the runs were only continued until the reaction rate had definitely commenced to decrease, in the majority of cases. Readings were taken at half- or quarter-hourly intervals. All readings of the wet gas meters were corrected for the vapour pressure of water, and all gas volumes reduced to standard temperature and pressure. On completion of a run, the reaction vessel was drained as quickly /
**TABLE No. 1.**  
Specimen of Observed Results for a Single Run. (No. 17)

<table>
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<th>Time (min)</th>
<th>Reactor Temp. °C</th>
<th>Inlet Oxygen Meter Press. cm. Hg</th>
<th>Temp. °F</th>
<th>Reading</th>
<th>Inlet O₂ Press. cm. Hg</th>
<th>Reading</th>
<th>Inlet SO₂ Meter Press. cm. Hg</th>
<th>Reading</th>
<th>Outlet Oxygen Meter Press. cm. Hg</th>
<th>Reading</th>
<th>Outlet O₂ Press. cm. Hg</th>
<th>Reading</th>
<th>O₂ Absorbed l. at N.T.P.</th>
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Concn. of Catalyst = 0.230 gm./m³.  
Inlet O₂ Rate = 0.218 gm. moles/hr.  
Inlet SO₂ Rate = 0.241 gm. moles/hr.  
Atmospheric Press. = 753 mm.  
Volume of Solution = 400 ml.  
Atmospheric Temp. = 64.2 °F.
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<th>$O_2$ Absorbed (l. at N.T.P.)</th>
<th>Gas Reacted (gm. mole)</th>
<th>Reaction Rate over Interval (SO$_2$/hr.)</th>
<th>Total SO$_2$ Reacted (gm. mole)</th>
<th>Mean Reacted SO$_2$ over Interval (gm. mole)</th>
<th>Total H$_2$SO$_4$ o. (gm.)</th>
<th>Mean H$_2$SO$_4$, Conc. over Interval (gm./1.)</th>
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Note: All acid concentrations based on a constant volume of 400ml.
GRAPH No.2 (TABLE No.1)

TOTAL SO₂ REACTED v. TIME

O₂ Rate = 0.218 gm.moles/hr.
SO₂ Rate = 0.241 gm.moles/hr.
Catalyst Concentration = 0.230 gm.Mn/l.
Temperature = 60°C.
quickly as possible into a bottle which was then sealed and cooled. Analyses were then carried out to determine the sulphur dioxide and sulphuric acid contents, (Appendix 1). The volume and specific gravity of the reactor solution at room temperature were also measured.

Calculation of Results.

Tables 1 and 2 show the complete series of experimental observations and derived results for a single run.

The amount of sulphur dioxide reacted over any interval of time is equivalent to twice the difference between the inlet and outlet volumes of oxygen over the interval. From the amounts of sulphur dioxide reacted, the total weight, and hence the concentration of sulphuric acid was then calculated. Graph 2 shows the variation in the total amount of sulphur dioxide reacted with time. Owing to the introduction of this additional variable, namely the concentration of sulphuric acid in the reaction vessel, it was decided to plot the reaction rate against the amount of sulphur dioxide reacted, which is equivalent to the amount of sulphuric acid in the reaction vessel. By this means, comparison of the results on the same basis was allowed. As the measurement of gradients from Graph 2 is extremely inaccurate, the method employed /
GRAPH No. 3 (TABLE No. 2)

REACTION RATE vs. SO₂ REACTED (H₂SO₄ CONCN.)

O₂ Rate = 0.218 gm.moles/hr.
SO₂ Rate = 0.241 gm.moles/hr.
Catalyst Concentration = 0.230 gm/Mn/l.
Temperature = 60°C.
employed was that of plotting the mean reaction rate over
an interval of time against the mean quantity of reacted
sulphur dioxide in the reactor over that time. This pro-
cedure is illustrated in Graph 3 (table 2).

It was found that, in general, agreement between values
for the weight of sulphuric acid produced, determined
analytically, and the values calculated from the rate
measurements was within 1.5%. The possibility of the dis-
crepancy between the analytical results and the calculated
results being due to the formation of dithionate during the
process was investigated, in one instance, using the method
of Bassett and Henry[71], (Appendix 1), but no indication as
to the presence of dithionate was obtained.

During reaction, the volume of solution in the reaction
vessel was found to increase, the maximum volume increase over
a period of 11 hours being 20 ml., i.e. a 5% increase in
volume. Knowing the specific gravity of the reactor solution,
it was possible to carry out a mass balance over the reactor,
whence it was found that this volume increase corresponded
very closely to that calculated from the reaction measurements,
so that there was very little vapour loss. The comparison
of the results on the basis of concentrations of sulphuric
acid based on a constant volume (400 ml.) was therefore
considered to be quite permissible.
**Graph No. 4**

**Reaction Rate vs. $SO_2$ Reacted For Different Inlet Gas Ratios $[SO_2/(InletSO_2 + O_2)]$**

Inlet Gas Rate = 0.676 gmmoles/hr.
Catalyst Conc. = 1.724 gm Mn/ll.
Temperature = 60°C.

**TABLE No. 3**

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<thead>
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<th>$SO_2$ Reacted (gmmoles)</th>
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<td>0.36</td>
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<tr>
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<td>0.40</td>
<td>0.40</td>
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<tr>
<td>0.32</td>
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<tr>
<td>0.34</td>
<td>0.48</td>
<td>0.48</td>
</tr>
</tbody>
</table>

**H$_2$SO$_4$ Concentration (gmmoles/l.)**

**TOTAL SO$_2$ Reacted (gmmoles)**

0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.20
0.24
0.28
0.32
0.36
0.40
0.44
0.48
0.52

0.8906
0.5345
0.3670
0.6068
0.6780
0.7520
0.0932
0.04
0.028
0.020
0.012
0.008
0.004
0.000
0.000
Variation of Inlet Gas Ratio.

The variation of reaction rate with inlet gas ratio, in a solution containing 1.724 gm.Mn/l., at 60°C., was studied at an inlet gas rate of 0.676 gm.moles/hr. Graph 4 (table 3) shows the results plotted as reaction rate against the amount of sulphur dioxide reacted, which, as has been indicated previously is equivalent to the nominal concentration of sulphuric acid in the reaction vessel, based on a constant (400 ml.) volume of solution.

All the curves are of somewhat similar form in that they exhibit an initial region of comparatively rapid increase in reaction rate, followed by a region where the rate is either constant or slowly decreasing. These two regions will now be described separately.

With increasing percentage of sulphur dioxide in the inlet gas, up to about 60%, the maximum rate is achieved at progressively greater sulphuric acid concentrations. When the percentage of sulphur dioxide is less than approximately 20% /
20\%, the reaction rate remains constant on reaching its maximum value, and substantially 100\% oxidation is obtained. The analysis of the resulting solutions obtained in this region showed complete absence from sulphur dioxide (table 3). On increasing the proportion of sulphur dioxide to about 37\%, the reaction rate no longer remains constant, at the maximum, but falls slowly, and complete oxidation is not obtained, despite the fact that analysis revealed the solution to be free from sulphur dioxide.

When approximately 50\% sulphur dioxide is present in the gas stream, the highest reaction rate is obtained (0.23 gm. moles S0₂/hr.), the decrease in reaction rate with increasing acid concentration then becoming somewhat accelerated. In this, as in all runs with higher ratios of sulphur dioxide, the final solution was found to contain unreacted sulphur dioxide, the concentration of which increased with increasing sulphur dioxide ratios.

On still further increasing the amount of sulphur dioxide, the maximum rate achieved commences to fall, the decrease in rate at higher acid concentrations gradually lessening, until, when 90\% sulphur dioxide is present, the rate becomes approximately constant. When the proportion of sulphur dioxide exceeds 60\%, the acid concentration at which the
**Graph No. 5**

*Table No. 13*

**Reaction Rate vs. SO₂ Reacted**

- SO₂: Rate = 0.458 gm.moles/hr.
- O₂: Rate = 0.218 gm.moles/hr.

Catalyst Conc. = 1.724 gm.Mn/l.

Temperature = 60°C.

Volume = 425 ml.

**SO₂ Concentration (gm./l.)**

**Total SO₂ Reacted (gm.moles)**
the maximum rate is achieved becomes progressively less with increasing sulphur dioxide ratio.

In the region where the rate is increasing rapidly, a marked change in the character of the bubble swarm is evident, the bubbles becoming much smaller and greater in number. The manner in which the rate increases with acid concentration in the early stages of the reaction is shown in Graph 4 to depend greatly on the proportion of sulphur dioxide present in the gas stream. When less than 37% is present, the initial region is always convex upwards, the rate in solutions of constant acid concentration being seen to increase with increasing sulphur dioxide percentage. At higher sulphur dioxide ratios, however, the form of this initial region becomes concave upwards, exhibiting a point of inflection, and the rate at any given acid concentration decreases with increasing proportion of sulphur dioxide.

An interesting feature of the above is that the change in form of the initial region occurs when unreacted sulphur dioxide becomes present in the resulting solution. Consequently, a run was carried out to study the variation of the concentration of unreacted sulphur dioxide during reaction. The results are shown in Graph 5 (table 13). The sulphur dioxide concentration is seen to rise very sharply, reach a maximum, and then fall slightly, after which it rises at an exceedingly /
**GRAPH No. 6**

(TABLE No. 4)

**REACTION RATE v. INLET GAS RATIO**

**AT CONSTANT ACID CONCN.**

Inlet Gas Rate = 0.676 gmmoles/hr.
Catalyst Conc. = 1.724 gmMn/l.
Temperature = 60°C.
exceedingly low rate. It would seem, therefore, that after the initial rapid absorption, the concentration attains a dynamic equilibrium with the gas phase, the position of this equilibrium being controlled by the rate of reaction. An analysis of the solution obtained before the maximum was achieved, in a run carried out at a low sulphur dioxide content (19%), revealed no unreacted sulphur dioxide in solution. It would appear that the change in the character of the initial region is due to the presence of free sulphur dioxide in solution.

Graph 6 (table 4), which employs values taken from Graph 4, shows the variation of reaction rate with inlet gas ratio for two different acid concentrations (20 and 60 gm./l.), together with the corresponding inlet sulphur dioxide and oxygen flow rates. It is obvious that a complete 'family' of such curves could be drawn, illustrating the gradual change in the gas ratio at which the maximum occurs, from 37% to 50% sulphur dioxide. The region where 100% oxidation is obtained is directly evident. In contrast, with decreasing oxygen content, complete utilisation of the oxygen does not occur, the potential rate being far in excess of the actual rate.

**Variation of Catalyst Concentration.**

Graph 7 (table 5) shows the reaction rate plotted against /
GRAPH NO. 7 (TABLE NO. 5)

REACTION RATE vs. \( \text{SO}_2 \) REACTED (H\(_2\)SO\(_4\) CONCN.)

FOR DIFFERENT CATALYST CONCENTRATIONS

\[
\text{SO}_2 \text{ Rate} = 0.301 \text{ gm.moles/hr.}
\]

\[
\text{O}_2 \text{ Rate} = 0.218 \text{ gm.moles/hr.}
\]

Temperature = 60°C.
against acid concentration for various catalyst concentrations. All runs were carried out at 60°C., and at an inlet gas rate of 0.519 gm.moles/hr., the proportion of sulphur dioxide in the gas being 58%. In graph 8 (table 6) is shown the variation of reaction rate with catalyst concentration in solutions of different acid concentration (20, 80 and 140 gm./l.).

From Graph 7 (table 5) it may be seen that, when catalyst is present up to a concentration of 6 gm.Mn/l. all the curves are of similar form, the reaction rate increasing with catalyst concentration, except at high acid concentrations. At low catalyst concentration (< 0.23 gm.Mn/l.) there is, however, a slight change in the form of the initial region, two distinct periods of rapid increase in reaction rate being evident. When no catalyst is present in the solution the reaction rate is at its greatest at the beginning of the run, thereafter decreasing steadily.

The rate becomes more susceptible to acid concentration with increasing catalyst concentration so that the acid concentration at which the maximum rate occurs becomes progressively less, tending to a constant value of approximately 40 gm./l. In the region beyond the maximum, the fall in rate with increasing acid concentration is approximately constant. At catalyst concentrations greater than 6 gm./l., after the maximum is reached, a gradual decline in the change of reaction rate with acid concentration is /
is observed. In addition, when the catalyst concentration exceeds 4 gm./l., the maximum rate remains constant at about 0.21 gm. moles SO₂/hr.

In all the above runs unreacted sulphur dioxide was found to be present in the final solution, the concentration falling slightly with increasing catalyst concentration (table 5).

The effect of catalyst concentration on the reaction rate, and its dependence on the concentration of sulphuric acid is more clearly evident in Graph 8 (table 6.) When the acid concentration is 20 gm./l., the manner in which the rate varies with catalyst concentration, up to 1 gm./l., is similar to that observed by Copson and Payne (75). The reaction rate increases more rapidly with catalyst concentration, up to 3 gm.Mn/l., after which it remains constant.

Increasing the acid concentration to 80 gm./l. leads to an increase in the rate at low catalyst concentrations and to a decrease in the rate at high concentrations, this decrease in rate increasing with increasing catalyst concentration. On still further increasing the acid concentration to 140 gm./l., the rate at low concentrations of manganese ( < 1 gm./l.) continues to increase, while at all manganese concentrations in excess of this figure, the rate is reduced.
It is interesting to note that the susceptibility of the reaction rate to catalyst concentration is most marked when the rate is changing rapidly with acid concentration. As has been remarked previously, it is in this region that a change in the character of the bubble swarm is seen. A further feature of interest is that at the beginning of the runs, the bubble swarm was also observed to be influenced by the amount of catalyst in the solution. This effect is illustrated in figure 6, which shows photographs taken at an oxygen rate of 0.218 gm.moles/hr., in solutions containing various amounts of catalyst at 60°C.

Variation of Sulphur Dioxide Rate.

In this, as in the following series of runs, it is appreciated that two factors were varied, namely the gas ratio and the total inlet gas rate. However, in view of the fact that the rate has been observed to depend to a great extent on the number and size of the bubbles, which will in turn be influenced by the uncontrollable changes in the acid concentration and the amount of unreacted sulphur dioxide present in the solution, it was felt that the addition of a further variable would not unduly complicate the interpretation of the results.

Graph 9 (table 7) represents the variation of reaction /
GRAPH No. 9 (TABLE No. 7)

REACTION RATE v. SO₂ REACTED (H₂SO₄ CONCN.)
FOR DIFFERENT SULPHUR DIOXIDE RATES.

O₂ Rate = 0.218 gm.moles / hr.
Catalyst Conc. = 0.230 gm.Mn/l.
Temperature = 60°C.
reaction rate at 60°C. with acid concentration, for different sulphur dioxide flow rates, at an oxygen rate of 0.218 gm. moles/hr. and at a catalyst concentration of 0.230 gm.ln/l.

When the sulphur dioxide rate exceeds 0.153 gm.moles/hr., all the curves are of similar form, the maximum rate becoming more susceptible to acid concentration with increasing sulphur dioxide rate. With increasing sulphur dioxide rate the two regions where the rate increases rapidly with acid concentration, occurring as has been noted previously only at low catalyst concentration, become more pronounced. At inlet sulphur dioxide rates greater than 0.181 gm.moles/hr., the maximum reaction rate achieved remains constant with increasing sulphur dioxide rate.

In order to reduce the period of time elapsing before the maximum rate was attained, at low sulphur dioxide rates, the runs were commenced with a dilute solution of sulphuric acid in the reaction vessel. The result of this is evident in Graph 9, at a sulphur dioxide rate of 0.153 gm.moles/hr., where it is seen that the presence of sulphuric acid in the reactor at the start leads to a more direct increase in the rate to the maximum value, after which the rate curve coincides with that obtained when no acid is present at the beginning.

At still lower sulphur dioxide rates, the reaction rate
No.

(TABLE No. 8)

REACTION RATE v. SO₂ RATE AT CONSTANT
ACID CONCENTRATION

O₂ Rate = 0.218 gm.moles/hr.
Catalyst Conc. = 0.230 gm.Mn/l.
Temperature = 60°C.

SULPHUR DIOXIDE RATE (gm.moles/hr.)

GRAPH No. 10

TABLE No. 8

REACTION RATE (gm.moles SO₂/hr.)
rate rises rapidly, until, in the region of the maximum it increases at a very slow rate, before decreasing with increasing acid concentration. In none of the above runs was complete oxidation achieved, unreacted sulphur dioxide always being present in the final solution, except at the lowest sulphur dioxide rate (table 7).

The variation of reaction rate with sulphur dioxide rate in solutions of sulphuric acid of concentrations 20, 80, 120 and 200 gm./l. is shown in Graph 10 (table 8).

At low acid concentrations (20 gm./l.), the rate decreases slowly with increasing sulphur dioxide rate. However, on increasing the acid concentration above approximately 40 gm./l., the reaction rate is seen to increase at all sulphur dioxide rates studied, as shown at 80 gm./l. If the acid concentration is still further increased to about 120 gm./l., the reaction rate increases rapidly with sulphur dioxide rate until, at a sulphur dioxide rate in the region of 0.20 gm.moles/hr., it increases very slowly. When the sulphuric acid concentration is increased to 200 gm./l., this slow increase is replaced by a slowly falling rate. The spread of the points on the curve for 80 gm./l. is due to the rapidly increasing rate over that concentration range.
Graph No. 11 (Table No. 9)

Reaction Rate v. SO₂ Reacted (H₂SO₄ Conc.)

For different oxygen rates

SO₂ Rate = 0.458 gm.moles/hr.
Catalyst Conc. = 1.724 gm.Mn/l.
Temperature = 60°C.
Reaction Rate $v. O_2 Rate$ at Constant Acid Concentration

SO$_2$ Rate $= 0.458$ gm.moles/hr.
Catalyst Concn. $= 1.724$ gm.Mn/l.
Temperature $= 60^\circ$C.
Variation of Oxygen Rate.

The manner in which the reaction rate varies with acid concentration at different oxygen rates is shown in Graph 11 (table 9). The overall effect of increasing the oxygen rate is an increase in the reaction rate at all acid concentrations, the maximum rate being attained at increasing acid concentrations, except at the highest oxygen rate. In the region beyond the maximum, the decrease in rate becomes somewhat accelerated with increasing oxygen rate. As expected, the concentration of unreacted sulphur dioxide decreases with increasing oxygen rate (table 9).

In Graph 12 (table 10) the effect of increasing oxygen rate on the reaction rate is shown to be greatly influenced by the acid concentration. At an acid concentration of 10 gm./l., the rate increases almost linearly with oxygen rate. When the acid concentration is increased, the rise in reaction rate becomes greater with increasing oxygen rate, until at an inlet gas ratio of approximately 50% oxygen, further increase in the oxygen rate leads only to a slow increase in reaction rate. This stage is shown at 60 gm./l. At acid concentrations greater than 75 gm./l. the rate becomes slightly reduced at all oxygen rates, except at the highest oxygen rate employed (66%) when a substantial reduction is observed.
Graph No. 13 (Table No. 11)

Reaction rate vs. SO₂ reacted (H₂SO₄ concn.) for different temperatures

SO₂ Rate = 0.458 gm. moles/hr.
O₂ Rate = 0.218 gm. moles/hr.
Catalyst Conc. = 1.724 gm. Mn/l.

Reaction rate (gm. moles SO₂/hr)

H₂SO₄ concentration (gm./l.)

0.50

0.40

0.30

0.20

0.10

0.0

0.04

0.08

0.12

0.16

0.20

0.24

0.28

0.32

0.36

0.40

0.44

0.48

0.52

50°

40°

30°

20°

10°

0°
observed.

Variation of Temperature.

In all the foregoing results it was obvious that the surface area was a factor of prime importance. It was therefore decided to carry out measurements of the surface area in conjunction with the study of this variable. As the vapour pressure of the solutions changes appreciably with temperature, the gases were presaturated before reaction. Owing to the reaction in solutions even in the absence of catalyst, the method employed was that of separately presaturating the oxygen and sulphur dioxide streams at the reactor temperature, before combining them and passing them into the reaction vessel. The modified apparatus is depicted in figure 7, showing that the gases were preheated and saturated by passing them in the form of bubble swarms through columns of water saturated with the gases and maintained at the reactor temperature.

Graph 13 (table 11) shows the variation of reaction rate with sulphur dioxide reacted (acid concentration) at temperatures from 20 - 90°C. at a catalyst concentration of 1.724 gm.Mn/l. when the inlet oxygen rate is 0.210 and the sulphur dioxide rate 0.458 gm.moles/hr. In this series of runs the volume of solution employed was 425 ml. With increasing temperature it is obvious that the maximum rate is attained /
GRAPH No. 14

(TABLE No. 12)

REACTION RATE v. TEMPERATURE
AT CONSTANT ACID CONCENTRATION

SO$_2$ Rate = 0.458 gm.moles/hr.
O$_2$ Rate = 0.218 gm.moles/hr.
Catalyst Conc. = 1.724 gm./Mn/l.

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<tr>
<th>Temperature (°C.)</th>
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<tbody>
<tr>
<td>20</td>
</tr>
<tr>
<td>80</td>
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</table>

Reaction Rate (gm.moles SO$_2$/hr)
attained at lower acid concentrations, and that the reaction rate tends to decrease more rapidly after the maximum at the higher temperatures. The concentration of unreacted sulphur dioxide, as shown in table 11, decreases with rising temperature.

The variation of the reaction rate with temperature at 20 and 80 gm./l. sulphuric acid is shown in Graph 14 (table 12), where it would appear that the reaction rate falls to a minimum at 30°C. and then rises, reaching a maximum at 80°C. when the concentration is 20 gm./l. and at 70°C. when the concentration is 80 gm./l., after which the rate would appear to fall to zero at 100°C.

In order to examine the effect of presaturation, the run at 60°C. was repeated without presaturating the gases, when the surprising result was obtained that no significant change in the reaction rate could be detected.
Table No. 3

Reaction Rate at Different Inlet Gas Ratios.

Inlet Gas Rate = 0.676 gm.moles/hr.; Catalyst Concentration = 1.724 gm Mn/l.
Temperature = 60°C.
Volume of Solution = 400 ml.

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<th>65</th>
<th>67</th>
<th>68</th>
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<td>Rate (gm.moles SO₂/hr.)</td>
<td>Mean SO₂ Reacted (gm.moles)</td>
<td>Rate (gm.moles SO₂/hr.)</td>
<td>Mean SO₂ Reacted (gm.moles)</td>
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Reacted SO₂ gm.mole: 0.3645, 0.3708, 0.6482, 0.9320
Free SO₂ Conc, gm/m³: nil, nil, nil, 5.56
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<td>Rate</td>
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<td>reacted gm.moles</td>
<td>SO$_2$/hr.</td>
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Table No. 4:

Reaction Rate in Solutions of Constant Acid Concentration at Different Inlet Gas Ratios.

Inlet Gas Rate = 0.676 gm.moles/hr., Temperature = 60°C.
Volume of Solution = 400 ml.

<table>
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<th>SO₂/Inlet Gas</th>
<th>SO₂ Rate gm.mole/hr.</th>
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<th>20</th>
<th>60</th>
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<td>0.361</td>
<td>0.143</td>
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<td>0.228</td>
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<td>0.040</td>
<td>0.040</td>
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### Table No. 5

Reaction Rate at Different Catalyst Concentrations.

O₂ Rate = 0.301 gm.moles/hr.  
SO₂ Rate = 0.218 gm.moles/hr.  
Temperature = 60°C  
Volume of Solution = 400 ml.

<table>
<thead>
<tr>
<th>Min No.</th>
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<th>71</th>
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<td>Time min.</td>
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<td>Mean SO₂ gm.moles</td>
<td>Rate gm.moles SO₂/hr.</td>
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<td>---------</td>
<td>----</td>
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<tr>
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<td>8.620</td>
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<td>Rate gm. moles SO₂/hr.</td>
<td>Rate gm. moles SO₂/hr.</td>
<td>Rate gm. moles SO₂/hr.</td>
</tr>
<tr>
<td>Mean SO₂ reacted gm. moles</td>
<td>Mean SO₂ reacted gm. moles</td>
<td>Mean SO₂ reacted gm. moles</td>
<td>Mean SO₂ reacted gm. moles</td>
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<td>0.6949</td>
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</table>

| Reacted SO₂ gm. mole | 0.5944 | 0.5771 | 0.7338 | 0.5637 |
| Free SO₂ Conc. gm. /l | 5.65 | 5.77 | 6.70 | 7.01 |
Table No. 6.

Reaction Rates in Solutions of Constant Acid Concentration at Different Catalyst Concentrations.

\( \text{O}_2 \) Rate = 0.218 gn.moles/hr.  
Temperature = 60° C.  
\( \text{SO}_2 \) Rate = 0.301 gn.moles/hr.  
Volume of Solution = 400 ml.

<table>
<thead>
<tr>
<th>Catalyst Conc. (gm.Mn/l.)</th>
<th>H\textsubscript{2}SO\textsubscript{4} Conc. (gm./l.)</th>
</tr>
</thead>
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<tr>
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<td>0.006</td>
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<td>0.042</td>
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Table 7: Reaction Rate at Different Inlet Sulphur Dioxide Flow Rates.

Oxygen Rate = 0.218 gm-moles/hr.; Catalyst Concentration = 0.230 gm.i'n/l.
Volume of Solution = 400 ml.
Temperature = 60°C.

<table>
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<tr>
<th>Time (min.)</th>
<th>Rate</th>
<th>Mean SO₂ Rate (gm-moles/hr.)</th>
<th>Mean SO₂ Reacted (gm-moles)</th>
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Free SO₂ Concentration (gm/l): 0.7061 to 1.1043.
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<th>18</th>
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<td>0.301</td>
<td>0.418</td>
<td>0.458</td>
</tr>
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<td>Rate (gm.moles/hr.)</td>
<td>Mean (SO_2) Rate (gm.moles)</td>
<td>Mean (SO_2) Rate (gm.moles)</td>
<td>Mean (SO_2) Rate (gm.moles)</td>
<td>Mean (SO_2) Rate (gm.moles)</td>
<td>Mean (SO_2) Rate (gm.moles)</td>
</tr>
<tr>
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<td>0.0177</td>
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<td>0.0525</td>
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<td>0.0580</td>
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<td>0.0768</td>
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**Reacted \(SO_2\) gm.mole**

| 1.0490 | 1.0714 | 1.0753 | 0.8451 | 0.7610 |

**Free \(SO_2\) Conc. gm/lt.**

| 3.93 | 6.54 | 8.47 | 9.46 | 10.29 |
Table No. 8.

Reaction Rates in Solutions of Constant Acid Concentration at Different Sulphur Dioxide Rates.

Oxygen Rate = 0.213 gm. moles/hr., Catalyst Concentration = 0.230 gm. Mn/l. Temperature = 60°C. Volume = 400 ml.

<table>
<thead>
<tr>
<th>SO₂ Rate (gm. mole/hr.)</th>
<th>H₂SO₄ Conc. (gm./l.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td>0.090</td>
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</tr>
<tr>
<td>0.125</td>
<td>-</td>
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<tr>
<td>0.153</td>
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</tr>
<tr>
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<tr>
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<tr>
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<tr>
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<td>0.053</td>
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<tr>
<td>0.458</td>
<td>-</td>
</tr>
<tr>
<td>Time (min.)</td>
<td>SO₂ Reacted (gm. moles)</td>
</tr>
<tr>
<td>------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>0</td>
<td>0.0367</td>
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</tr>
<tr>
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<td>0.1295</td>
</tr>
<tr>
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<td>465</td>
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</table>

**Reactor No.** 4

**Temperature** 60°C

**Catalyst Concentration** 1.724 rm.Mn/l

**Volume of Solution** 400 ml

---

**Reaction Rate at Different Oxygen Flow Rates:**

- SO₂ Rate = 0.158 gm. moles/hr.; Catalyst Concentration = 1.724 gm.Mn/l.
- Temperature = 60°C.

Table No. 9, Continued...
### Table No. 9. (contd.)

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<th>63</th>
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<td>0.434</td>
<td>0.621</td>
<td>0.890</td>
</tr>
<tr>
<td>Time min.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate of SO₂ (gm. moles/hr)</td>
<td>Mean SO₂ Reacted (gm. moles)</td>
<td>Rate of SO₂ (gm. moles/hr)</td>
<td>Mean SO₂ Reacted (gm. moles)</td>
<td>Rate of SO₂ (gm. moles/hr)</td>
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<tr>
<td>300</td>
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<td>-</td>
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<tr>
<td>Reacted SO₂ (gm. mole)</td>
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Table No. 10.

Reaction Rates in Solutions of Constant Acid Concentration at Different Oxygen Rates.

SO₂ Rate = 0.458 gm.moles/hr.; Catalyst Concentration = 1.724 gm. Mn/l.
Temperature = 60°C.
Volume of Solution = 400 ml.

<table>
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<th>H₂SO₄ Conc. (gm./l.)</th>
</tr>
</thead>
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<tr>
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<tr>
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Table No. 11.

Reaction Rate at Different Temperatures.

SO₂ Rate = 0.458 gm. moles/hr. Catalyst Concentration = 1.724 gm Mn/l.
O₂ Rate = 0.218 gm. moles/hr. Volume of Solution = 425 ml.

<table>
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<th>P. 13</th>
<th>P. 14</th>
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<td>Mean SO₂ reacted gm. moles</td>
<td>Rate gm. moles SO₂/hr.</td>
<td>Mean SO₂ reacted gm. moles</td>
</tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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</tbody>
</table>

| Reacted SO₂ gm. mole | 0.3734 | 0.4445 | 0.3817 | 0.4368 |
| Free SO₂ gm. mole/l. | 44.18  | 30.27  | 20.66  | 15.73  |

| Concn. SO₂ gm./l. | 44.18  | 30.27  | 20.66  | 15.73  |
Table No. 11. (contd.)

<table>
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<th>Run No.</th>
<th>P.15</th>
<th>P.16</th>
<th>P.17</th>
<th>P.18</th>
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<td>Rate SO(_2)/hr.</td>
<td>Mean (\text{SO}_2) Reacted gm.mole</td>
<td>Rate (\text{SO}_2)/hr.</td>
<td>Mean (\text{SO}_2) Reacted gm.mole</td>
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<td>P.16</td>
<td>P.17</td>
<td>P.18</td>
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<td>420</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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</table>

| Reacted \(\text{SO}_2\) gm.mole | 0.5412 | 0.7420 | 0.6040 | 0.1817 |
| Free \(\text{SO}_2\) Conc., gm./l. | 11.76 | 7.15 | 5.41 | 2.20 |
Table No. 12.

Reaction Rates in Solutions of Constant Acid Concentration at Different Temperatures.

$O_2$ Rate = 0.218 gm.moles/hr. Catalyst Concentration = 1.724 gm.Mn/l.

$SO_2$ Rate = 0.458 gm.moles/hr. Volume of Solution = 425 ml.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$H_2SO_4$ Conc. (gm./l.) 20</th>
<th>$H_2SO_4$ Conc. (gm./l.) 80</th>
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<tr>
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<td>0.051</td>
<td>0.079</td>
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<td>0.074</td>
</tr>
<tr>
<td>40</td>
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<td>0.084</td>
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<tr>
<td>50</td>
<td>0.073</td>
<td>0.106</td>
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<tr>
<td>60</td>
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<td>0.127</td>
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<tr>
<td>70</td>
<td>0.128</td>
<td>0.136</td>
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<tr>
<td>80</td>
<td>0.135</td>
<td>0.123</td>
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<tr>
<td>90</td>
<td>0.095</td>
<td>-</td>
</tr>
</tbody>
</table>
EXPERIMENTAL - PART II

Surface Area Measurements.
Measurement of Surface Area

The method employed for the determination of the surface areas of the bubble swarms required the measurement of two separate quantities, namely the gas content of the liquid column (the gas hold-up) and the mean bubble surface and volume in the bubble swarm. Figure 7 shows the apparatus employed. Subdivision of the gas stream was effected by means of a Pyrex sinter, of porosity No. 2, sealed into the lower end of a Pyrex tube of length 15 in. and of diameter approximately 1.5 in., which was fitted with a side-arm as employed in the oxidation measurements.

In order to eliminate distortion of the bubbles due to the refractive effect of the curved glass tube, the reaction vessel was immersed in a water-filled rectangular perspex box, of dimensions 3.5 in. X 3.5 in. X 17 in. The temperature of the liquid in the reaction vessel was maintained by controlling the rate of supply of heat to the water in the outer perspex box by means of a Variac transformer. It was found possible to control the temperature within the limits $\pm 0.1^\circ C$, in the temperature range 30 - 90$^\circ C$, at which latter temperature, however, prolonged heating caused some distortion of the perspex box.
Fig. 7 APPARATUS FOR GAS HOLD-UP AND PHOTOGRAPHIC MEASUREMENTS

Fig. 8 ILLUSTRATION OF CAMERA ARRANGEMENT

1 1/4 plate camera
2 Perspex box
3 White cloth
4 Black cloth
5 Electronic flashes
Measurement of the Gas Hold-up.

As measurements of this quantity were carried out while the reaction was proceeding, the method of Verschoor (60) could not be employed. It was found that the apparatus shown, consisting essentially of a differential manometer, gave consistent results provided the manometer tube was absolutely free from grease, which gave rise to an irregular meniscus. After setting the gas rates to the desired values, readings were taken of the level of the liquid in the manometer tube when the gas stream was passing, and after cessation of the gas flow, thus giving the increase in the height of the liquid column while gas was flowing. The total height of the undisturbed liquid column was also measured by means of the travelling microscope.

Where possible, the manometer tube was filled with liquid of the same composition as in the reaction vessel, but in the case of measurements taken during reaction, the manometer tube was filled with a saturated solution of sulfur dioxide. In all cases, corrections were applied for the increase in the volume of the thermometer and measuring tube immersed in the liquid while gas was passing, and for the density difference between the manometer liquid and the solution in the reaction vessel.

Photography /
Photography of Bubble Swarms.

The arrangement of the camera, flashes, etc. is shown in figure 8. Illumination was provided by means of two electronic flashes situated as shown, and were such that the exposure time corresponded to $1/5000$ sec. at $f.16$ on Ilford Ordinary N.30 quarter plates. The flashes were manually synchronised with the camera. After development using D.163, full-scale enlargements were made on Ilford Normal and Ultra-hard Bromide papers.

Measurement of the Bubble Photographs.

As the bubble swarms were so densely packed that it was obviously impossible to carry out a 'bubble count', it was decided to determine the distribution of bubble diameters by means of a travelling microscope and thence to calculate the mean diameter, area and volume of the bubbles present in the swarm. Owing to the obvious variation in diameter with increasing distance from the sinter, in many of the photographs, measurement of the diameter distribution were carried out at three equally spaced levels in the column, viz. two centimetre bands at distances of 8, 16 and 24 cm. from the sinter, as shown in figure 9. Measurement of the diameters in the neighbourhood of the sinter and at the surface were found to be /
Mean Diameter \( = 0.09 \text{ cm.} \)

Mean Volume \( = 0.910 \times 10^{-3} \text{ cm}^3 \)

Mean Surface \( = 35.97 \times 10^3 \text{ cm}^2 \)

Mean Diameter \( = 0.0795 \text{ cm.} \)

Mean Volume \( = 0.549 \times 10^{-3} \text{ cm}^3 \)

Mean Surface \( = 26.13 \times 10^3 \text{ cm}^2 \)

Mean Diameter \( = 0.0737 \text{ cm.} \)

Mean Volume \( = 0.449 \times 10^{-3} \text{ cm}^3 \)

Mean Surface \( = 22.35 \times 10^3 \text{ cm}^2 \)
be impossible. After calculating the mean diameter in each band, an overall arithmetic mean diameter was obtained.

The procedure employed was therefore measurement of the diameters against the calibrated graticule of the microscope, at a magnification of X 10, during traverses across the photographs, at 2 mm. intervals within these 2 cm. bands. As every bubble crossing the graticule was measured, the selection of bubbles measured should be completely random. In cases where the bubbles were ellipsoidal, the diameter was taken as the mean of the major and minor axes.

Calculation of the Surface Area.

It must be emphasised that the mean bubble surface and volume do not correspond to the mean diameter, so that it was necessary to recalculate the diameter distributions in terms of mean surfaces and volumes within the measured ranges of bubble diameters. The method employed for the change of axis is shown in the table below, and is illustrated by the results of a typical series of measurements as shown in Graphs 15a, b, and c which apply to oxygen passing at 0.218 gm.moles/hr. through a 20 gm./l. solution of sulphuric acid at 70°C.
GRAPH No.16

H₂SO₄ Concentration:
- 5.75 g/m³ (5.75 gm./l)
- 13.38 g/m³ (13.38 gm./l)
- 24.06 g/m³ (24.06 gm./l)
- 95.02 g/m³ (95.02 gm./l)

DISTRIBUTION OF BUBBLE DIAMETERS DURING REACTION AT 60°C
(at a distance of 16 cm. from sinter)
Experimental Results.

Part II A Surface Area During Reaction.

Bubble Measurements during Reaction at 60°C.

The bubble swarms were photographed and gas hold-up measurements carried out on completion of runs of duration 30, 60, 90, 120, 150, 180, 240 and 300 minutes, during reaction at 60°C. in 425 ml. of solution containing 1.724 gm. Mn/l., at an oxygen rate of 0.218 and at a sulphur dioxide rate of 0.458 gm. moles/hr. A selection of the photographs is shown in figure 10, where the striking change in the character of the bubble swarm is immediately evident, the bubbles obviously becoming smaller and the swarm more densely packed. Owing to this extreme bubble density, the measurement of the diameters will be limited in their accuracy.

Graph 17a (table 13) shows the variation in diameter as the reaction proceeds. After the maximum reaction rate was achieved no further decrease in the mean bubble diameter could be detected owing to the density of the swarm, but, as the gas hold-up increases and then remains constant in this region (Graph 17b), it is reasonable to suppose that this constancy of diameter is correct.

The
TABLE No.13

SURFACE AREA MEASUREMENTS DURING REACTION AT 60°C.

SO₂ Rate = 0.458 gm.moles/hr.
O₂ Rate = 0.218 gm.moles/hr.
Catalyst Conc. = 1.724 gm.Mn/l.
Initial Volume = 425 mls.

(a) BUBBLE DIAMETER v. H₂SO₄ CONCN.

(b) GAS HOLD-UP v. H₂SO₄ CONCN.

(c) TOTAL SURFACE v. H₂SO₄ CONCN.
The manner in which the diameter distribution changes, at a distance of 16 cm. from the sinter, as reaction proceeds is shown in Graph 16. In the early stages of the reaction the distribution is very wide and unsymmetrical, but as reaction proceeds, this distribution tends to a natural form. A slight increase in diameter with increasing distance from the sinter, similar to that shown in Graph 15 was also observed.

**Reaction Rate/Unit Area at 60°C.**

In Graph 17c, the surface area is seen to increase and then attain a constant value with increasing acid concentration. These surface area measurements were combined with the reaction rate figures from Graph 13, the acid concentration however being based on the true volumes of solution, to give the reaction rate/unit area shown in Graph 19 (table 13), where a slow linear decrease in the rate (expressed in gm.moles oxygen/sec./cm² × 10^3) with acid concentration is evident.

**Variation of Reaction Rate/Unit Area with Temperature.**

As before, the gas hold-up was found to increase and then reach a constant value at acid concentrations in excess of that at /
**Graph No. 18 (Tables No. 13 & 14)**

Surface area measurements after maximum reaction rate

- $\text{SO}_2$ Rate = 0.458 gm.moles/hr.
- $\text{O}_2$ Rate = 0.218 gm.moles/hr.
- Catalyst Conc. = 1.724 gm Mn/l.

**(a) Diameter v. Temperature**

**(b) Gas Hold-up v. Temperature**

**(c) Total Surface Area v. Temperature**

Temperature (°C.)
GRAPH No. 19  (TABLES No. 13 & 14)

REACTION RATE / UNIT AREA v. ACID CONCN.
AT DIFFERENT TEMPERATURES

SO₂ Rate = 0.458 gm.moles/hr.
O₂ Rate = 0.218 gm.moles/hr.
Catalyst Conc. = 1.724 gm Mn/l.
GRAPH No. 20 (TABLE No.15)

REACTION RATE / UNIT AREA v TEMPERATURE

AT 20 gm. $H_2SO_4$ /l.

$SO_2$ Rate = 0.458 gm.moles /hr.
$O_2$ Rate = 0.218 gm.moles /hr.

Catalyst Conc. = 1.724 gm.Mn/l.
GRAPH No. 21
DISTRIBUTION OF BUBBLE DIAMETERS IN H₂SO₄ SOLUTIONS AT 60°C.
(at a distance of 16 cm. from sinter)

H₂SO₄ Concn. = 0 gm/l.

H₂SO₄ Concn. = 41.4 gm/l.

H₂SO₄ Concn. = 101.2 gm/l.

H₂SO₄ Concn. = 172.1 gm/l.
GRAPH No. 22 (TABLE No.18)

SURFACE AREA MEASUREMENTS FOR OXYGEN IN SULPHURIC ACID SOLUTIONS AT 60°C.

\[ O_2 \text{ Rate} = 0.218 \text{ gm.moles/hr} \]
\[ \text{Volume} = 425 \text{ mls.} \]

(a) DIAMETER vs \( \text{H}_2\text{SO}_4 \) CONCN.

(b) GAS HOLD-UP vs \( \text{H}_2\text{SO}_4 \) CONCN.

(c) TOTAL SURFACE vs \( \text{H}_2\text{SO}_4 \) CONCN.
Part IIE  
Surface Areas of Oxygen Bubble Swarms.

Variation of Surface Area with Acid Concentration.

In figure 12, which shows photographs of bubble swarms of oxygen in sulphuric acid at 60°C., the oxygen rate being 0.218 gm.moles/hr., there would at first sight appear to be a marked reduction in the bubble diameter. However, as shown in Graph 21, the actual effect is a marked change in the distribution of diameters with increasing concentration.

When no acid is present, the distribution exhibits a most probable diameter at approximately 0.07 cm., being symmetrical about this value to a diameter of approximately 0.12 cm., together with varying small numbers of bubbles in all ranges of diameters to 0.30 cm. On increasing the acid concentration the distribution changes, the bubbles in the largest ranges of diameters disappearing, so that the distribution tends to become natural in character. The effect on the mean diameter, as shown in Graph 22a (table 18) is that, apart from pure water, the mean diameter remains approximately constant with increasing acid concentration. Owing to the changes in the distribution, the mean bubble volumes and surfaces continue to decrease with acid concentration (table 18).

The results on the gas hold-up are given in table 16, which /
GRAPH No. 23

DISTRIBUTION OF BUBBLE DIAMETERS AT DIFFERENT TEMPERATURES IN 20gm/l. ACID.
(at a distance of 16 cm from sinter)

TEMP. = 30°C.

TEMP. = 50°C.

TEMP. = 70°C.

TEMP. = 90°C.

NUMBER OF BUBBLES

BUBBLE DIAMETER (cm.)
which shows the complete series of measurements and the method of calculation employed. When plotted against acid concentration (Graph 22b), the hold-up is seen to increase in a sigmoid manner with concentration. From the diameter and hold-up measurements the surface area variation with acid concentration was then calculated and is shown in Graph 22c (table 16), where it is seen to increase almost linearly with concentration.

Variation of Surface Area with Temperature.

The effect of increasing temperature on oxygen bubble swarms in a 20.4 gm./l. solution of sulphuric acid at an oxygen rate of 0.218 gm.moles/hr. is illustrated in figure 13. With increasing temperature, there is obviously an increase in bubble diameter and a decrease in the number of bubbles, the 'background' of small bubbles gradually disappearing, especially at the highest temperatures as shown in Graph 23. As always, a slight increase in diameter with distance from the sinter was evident.

The above increase in diameter with temperature (Graph 24a) is in direct contrast to the effect observed during reaction, after the maximum rate was achieved (Graph 18a). Measurements of the gas hold-up and the combined results, namely the surface area, as shown in Graph 24b,c (tables

17
GRAPH No. 24 (TABLE No.19)

SURFACE AREA MEASUREMENTS FOR OXYGEN IN 20gm/l. $\text{H}_2\text{SO}_4$ AT DIFFERENT TEMPERATURES

$\text{O}_2$ Rate = 0.218 gm.moles/hr.
Volume = 425 mls.

(a) DIAMETER v. TEMPERATURE

(b) GAS HOLD-UP v. TEMPERATURE

(c) TOTAL SURFACE v. TEMPERATURE
17 and 19) on the other hand bear a close resemblance in form to those during reaction after the maximum rate (Graphs 18b,c), the hold-up and area increasing at an accelerating rate with increasing temperature.

The surface area measurements obtained in this section are employed in the third part of the experimental work.
### Table No. 13
Complete Study of Run P.15, including Rate, SO₂, and Area Measurements.

Temperature = 60°C.  
SO₂ Rate = 0.458 gm.moles/hr.  
Catalyst Conc. = 1.724 g.Mn/l.  
O₂ Rate = 0.218 gm.moles/hr.  
Atmospheric Press. = 758mm.Hg.

<table>
<thead>
<tr>
<th>Total SO₂ Reacted</th>
<th>Volume of Solution</th>
<th>Conc. of H₂SO₄ ml.</th>
<th>Conc. of SO₂ gm/l.</th>
<th>Reaction Rate gm.mole SO₂/hr.</th>
<th>Density of Solution gm.cm³</th>
<th>Ht. of Liquid Column cm.</th>
<th>Gas Hold-up (cm)</th>
<th>Mean Bubble</th>
<th>Number of Bubbles</th>
<th>Total Surface Area cm²</th>
<th>Reaction Rate gm.mole O₂/sec. cm² × 10⁸</th>
<th>gm.mole SO₂/sec. cm² × 10⁸</th>
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</thead>
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<td>33.76</td>
<td>0.567</td>
<td>6.668</td>
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<td>6.668</td>
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<td>14.57</td>
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</table>
Table No. 14.

Surface Area and Reaction Measurements during Temperature Variation.

\[
\text{SO}_2 \text{ Rate } = 0.458 \text{ gm.moles/hr.}, \quad \text{Initial Volume of Solution } = 4.25 \text{ ml.}
\]

\[
\text{O}_2 \text{ Rate } = 0.218 \text{ gm.moles/hr.}, \quad \text{Catalyst Concentration } = 1.724 \text{ gm.Mn/l.}
\]

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>SO₂ Reacted (gm.mole)</th>
<th>Vol. of Soln. (gm/l)</th>
<th>H₂SO₄ Conc. (gm/l)</th>
<th>Reaction Rate (gm.moles SO₂/hr.)</th>
<th>Gas Hold-up (cm³)</th>
<th>Mean Bubble Diam. (cm)</th>
<th>Surface Area (cm²)</th>
<th>Volume (cm³) X 10³</th>
<th>Reaction Rate (gm.moles/sec. cm² X 10⁶)</th>
</tr>
</thead>
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</tr>
<tr>
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<td>0.2741</td>
<td>4.30</td>
<td>62.47</td>
<td>0.0862</td>
<td>4.999</td>
<td>0.0678</td>
<td>16.46</td>
<td>0.233</td>
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</tr>
<tr>
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<td>0.3854</td>
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<td>0.0844</td>
<td>4.708</td>
<td>0.0678</td>
<td>16.46</td>
<td>0.233</td>
<td>332.4</td>
</tr>
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<td>50.0</td>
<td>0.0610</td>
<td>4.26</td>
<td>14.03</td>
<td>0.0614</td>
<td>4.476</td>
<td>0.0961</td>
<td>12.85</td>
<td>0.644</td>
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<tr>
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<td>0.3108</td>
<td>4.30</td>
<td>70.87</td>
<td>0.1067</td>
<td>5.835</td>
<td>0.0658</td>
<td>15.46</td>
<td>0.212</td>
<td>425.8</td>
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<td>4.33</td>
<td>98.92</td>
<td>0.1034</td>
<td>5.835</td>
<td>0.0658</td>
<td>15.46</td>
<td>0.212</td>
<td>425.8</td>
</tr>
<tr>
<td>60.0</td>
<td>0.0431</td>
<td>4.26</td>
<td>9.92</td>
<td>0.1117</td>
<td>6.778</td>
<td>0.0739</td>
<td>19.34</td>
<td>0.292</td>
<td>448.6</td>
</tr>
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<td>60.0</td>
<td>0.2281</td>
<td>4.30</td>
<td>52.00</td>
<td>0.1393</td>
<td>7.072</td>
<td>0.0596</td>
<td>12.32</td>
<td>0.146</td>
<td>596.9</td>
</tr>
<tr>
<td>60.0</td>
<td>0.5028</td>
<td>4.35</td>
<td>113.22</td>
<td>0.1270</td>
<td>7.072</td>
<td>0.0596</td>
<td>12.32</td>
<td>0.146</td>
<td>596.9</td>
</tr>
<tr>
<td>70.0</td>
<td>0.0626</td>
<td>4.27</td>
<td>18.96</td>
<td>0.1352</td>
<td>9.070</td>
<td>0.0511</td>
<td>9.19</td>
<td>0.095</td>
<td>878.1</td>
</tr>
<tr>
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<td>0.4963</td>
<td>4.35</td>
<td>111.83</td>
<td>0.1102</td>
<td>9.070</td>
<td>0.0511</td>
<td>9.19</td>
<td>0.095</td>
<td>878.1</td>
</tr>
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<td>0.0613</td>
<td>4.27</td>
<td>18.67</td>
<td>0.0947</td>
<td>12.40</td>
<td>0.0508</td>
<td>9.43</td>
<td>0.102</td>
<td>1146.0</td>
</tr>
<tr>
<td>90.0</td>
<td>0.1821</td>
<td>4.29</td>
<td>14.63</td>
<td>0.0900</td>
<td>12.40</td>
<td>0.0508</td>
<td>9.43</td>
<td>0.102</td>
<td>1146.0</td>
</tr>
</tbody>
</table>
Table No. 15.

Variation of Reaction Rate/Unit Area with Temperature in a 20 gm./l. Solution of Sulphuric Acid.

\[ \text{SO}_2 \text{ Rate} = 0.458 \text{ gm.moles/hr.}, \quad \text{Catalyst Concentration} = 1.724 \text{ gm.Hn/l.} \]
\[ \text{O}_2 \text{ Rate} = 0.218 \text{ gm.moles/hr.} \quad \text{Volume of Solution} = 425 \text{ ml.} \]

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Reaction Rate ( \text{gm.moles } \text{O}_2/\text{sec. } /\text{cm}^2 \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3.99</td>
</tr>
<tr>
<td>40</td>
<td>5.89</td>
</tr>
<tr>
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<td>3.73</td>
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<td>3.41</td>
</tr>
<tr>
<td>80</td>
<td>2.14</td>
</tr>
<tr>
<td>90</td>
<td>1.14</td>
</tr>
</tbody>
</table>
Table No. 16.

Gas Hold-up Measurements in Sulphuric Acid Solutions at 60°C.

<table>
<thead>
<tr>
<th>H₂SO₄ Conc.</th>
<th>Ht. of Liquid Column (1°)</th>
<th>Increase in Ht. (1°)</th>
<th>Density at Room Temp.</th>
<th>Density at 60°C.</th>
<th>Corrected (1°)</th>
<th>Ht. of Liquid Column (1)</th>
<th>Gas Hold-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>gm./l</td>
<td>cm.</td>
<td>cm.</td>
<td>gm./cc.</td>
<td>gm./cc.</td>
<td>cm.</td>
<td>cm.</td>
<td>cm³</td>
</tr>
<tr>
<td>0.0</td>
<td>32.72</td>
<td>0.228</td>
<td>0.996</td>
<td>0.983</td>
<td>0.223</td>
<td>32.94</td>
<td>2.72</td>
</tr>
<tr>
<td>20.4</td>
<td>32.72</td>
<td>0.228</td>
<td>1.015</td>
<td>0.999</td>
<td>0.223</td>
<td>32.94</td>
<td>2.72</td>
</tr>
<tr>
<td>41.4</td>
<td>32.72</td>
<td>0.232</td>
<td>1.027</td>
<td>1.010</td>
<td>0.226</td>
<td>32.95</td>
<td>2.76</td>
</tr>
<tr>
<td>59.7</td>
<td>32.72</td>
<td>0.235</td>
<td>1.038</td>
<td>1.020</td>
<td>0.229</td>
<td>32.95</td>
<td>2.80</td>
</tr>
<tr>
<td>88.2</td>
<td>32.72</td>
<td>0.240</td>
<td>1.056</td>
<td>1.037</td>
<td>0.234</td>
<td>32.95</td>
<td>2.86</td>
</tr>
<tr>
<td>104.2</td>
<td>32.72</td>
<td>0.248</td>
<td>1.065</td>
<td>1.045</td>
<td>0.242</td>
<td>32.96</td>
<td>2.96</td>
</tr>
<tr>
<td>124.8</td>
<td>32.72</td>
<td>0.275</td>
<td>1.080</td>
<td>1.059</td>
<td>0.269</td>
<td>32.99</td>
<td>3.28</td>
</tr>
<tr>
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<td>0.284</td>
<td>1.094</td>
<td>1.072</td>
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<td>33.00</td>
<td>3.40</td>
</tr>
<tr>
<td>172.1</td>
<td>32.72</td>
<td>0.288</td>
<td>1.109</td>
<td>1.087</td>
<td>0.282</td>
<td>33.00</td>
<td>3.44</td>
</tr>
</tbody>
</table>

Table No. 17.

Gas Hold-up Measurements at Different Temperatures in Sulphuric Acid (20.4gm./l)

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Ht. of Liquid Column (1°)</th>
<th>Increase in Ht. (1°)</th>
<th>Density at Temp.</th>
<th>Corrected (1°)</th>
<th>Ht. of Liquid Column</th>
<th>Gas Hold-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>ºC.</td>
<td>cm.</td>
<td>cm.</td>
<td>gm./cc.</td>
<td>cm.</td>
<td>cm.</td>
<td>cm³</td>
</tr>
<tr>
<td>30.0</td>
<td>32.35</td>
<td>0.176</td>
<td>1.012</td>
<td>0.170</td>
<td>32.52</td>
<td>2.08</td>
</tr>
<tr>
<td>40.0</td>
<td>32.46</td>
<td>0.192</td>
<td>1.008</td>
<td>0.185</td>
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<td>2.26</td>
</tr>
<tr>
<td>50.0</td>
<td>32.57</td>
<td>0.210</td>
<td>1.004</td>
<td>0.203</td>
<td>32.77</td>
<td>2.48</td>
</tr>
<tr>
<td>60.0</td>
<td>32.72</td>
<td>0.228</td>
<td>0.999</td>
<td>0.223</td>
<td>32.84</td>
<td>2.76</td>
</tr>
<tr>
<td>70.0</td>
<td>32.83</td>
<td>0.262</td>
<td>0.993</td>
<td>0.257</td>
<td>33.09</td>
<td>3.14</td>
</tr>
<tr>
<td>80.0</td>
<td>33.13</td>
<td>0.319</td>
<td>0.987</td>
<td>0.314</td>
<td>33.44</td>
<td>3.84</td>
</tr>
<tr>
<td>90.0</td>
<td>33.24</td>
<td>0.394</td>
<td>0.980</td>
<td>0.491</td>
<td>33.73</td>
<td>6.00</td>
</tr>
</tbody>
</table>

Oxygen Flow Rate = 0.218gm.moles/hr.; Volume of Solution = 425 ml.

Note: All values corrected for the density of the solution in the measuring limb of the manometer, which was at room temperature, and for the reduced cross section due to the thermometer and measuring tube.

X-section area of tube = 12.22 cm².

Reduced X-section area of tube = 11.72 cm².
Table No. 18.
Summary of Surface Area Measurements in Sulphuric Acid Solutions at 60°C.

<table>
<thead>
<tr>
<th>Photo. No.</th>
<th>H₂SO₄ Conc. (gm./l)</th>
<th>Gas Hold-up (cm³)</th>
<th>Ht. of Liquid Column (cm)</th>
<th>Mean Bubble Diam. (cm)</th>
<th>Surface Area (cm² × 10³)</th>
<th>Volume (cm³ × 10³)</th>
<th>No. of Bubbles</th>
<th>Total Surface Area (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.0</td>
<td>2.72</td>
<td>32.94</td>
<td>0.0907</td>
<td>34.53</td>
<td>0.902</td>
<td>3,017</td>
<td>104.1</td>
</tr>
<tr>
<td>3</td>
<td>20.4</td>
<td>2.72</td>
<td>32.94</td>
<td>0.0813</td>
<td>27.16</td>
<td>0.587</td>
<td>4,633</td>
<td>125.8</td>
</tr>
<tr>
<td>4</td>
<td>41.4</td>
<td>2.76</td>
<td>32.95</td>
<td>0.0795</td>
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<td>0.475</td>
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<tr>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table No. 19.
Summary of Surface Area Measurements at Different Temperatures in Sulphuric Acid (20.4gm./l)

<table>
<thead>
<tr>
<th>Photo. No.</th>
<th>Temp. (°C)</th>
<th>Gas Hold-up (cm³)</th>
<th>Ht. of Liquid Column (cm)</th>
<th>Mean Bubble Diam. (cm)</th>
<th>Surface Area (cm² × 10³)</th>
<th>Volume (cm³ × 10³)</th>
<th>No. of Bubbles</th>
<th>Total Surface Area (cm²)</th>
</tr>
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<tbody>
<tr>
<td>29</td>
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<td>32.52</td>
<td>0.0708</td>
<td>20.19</td>
<td>0.388</td>
<td>5,365</td>
<td>108.3</td>
</tr>
<tr>
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<td>40.0</td>
<td>2.26</td>
<td>32.65</td>
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<td>0.481</td>
<td>4,705</td>
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</tr>
<tr>
<td>31</td>
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<td>2.48</td>
<td>32.77</td>
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<td>5,890</td>
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<td>0.0813</td>
<td>27.16</td>
<td>0.587</td>
<td>4,635</td>
<td>125.8</td>
</tr>
<tr>
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<td>70.0</td>
<td>3.14</td>
<td>33.19</td>
<td>0.0820</td>
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<td>0.636</td>
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</tr>
<tr>
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<td>6.00</td>
<td>33.73</td>
<td>0.1289</td>
<td>56.35</td>
<td>1.378</td>
<td>4,355</td>
<td>245.5</td>
</tr>
</tbody>
</table>

Oxygen Flow Rate = 0.218 gm.moles/hr.; Volume of Solution = 425 ml.
EXPERIMENTAL PART III

The Initial Absorption Rate of Oxygen.
Previous Work on the Measurement of the Initial Absorption Rate.

Equation (23), which defines the rate of solution of a gas in a liquid may be written in the form:

\[
\frac{dw}{dt} = R_i - bw
\]

(58)

where \( w \) is the weight of gas dissolved at any instant, \( R_i \) is the initial absorption rate and \( b \) may be termed the 'escape factor'. This equation was deduced by Adeney and Becker (91) prior to the development of the theory of Miyamoto (10,11), to explain their results on the absorption rate of oxygen into water, from gas bubbles of varying volume (5-16 cm.\(^3\)) in a tube of cross section, 1 cm.\(^2\), all the water being passed between the bubble and the tube. The gas absorbed was determined by chemical analysis of the resulting solution.

From the above equation, it can be seen that the initial rate of absorption may be determined in two ways, namely, by maintaining the concentration of the gas in the liquid at zero, possibly by some fast irreversible reaction between the dissolving gas and an excess of reagent in the surface of the liquid, as has been previously described (10). The reliability of this method is doubtful owing to the possibility of an alteration of the accommodation coefficient for molecules entering the surface from the gas phase. The alternative, and fundamentally more correct method is the determination of transient
transient absorption rates at exceedingly short times of contact, and extrapolating to zero time of contact. Methods based on the latter procedure will now be described.

Ledig and Weaver (92) have described a method for measuring the rate of absorption of carbon dioxide in sodium hydroxide solutions at very short time intervals. In this method, the bubble of gas was formed under mercury, and then passed into a column of downflowing liquid which was open to the atmosphere only through a capillary tube. The absorption of gas caused a contraction in the volume of the system which was followed by recording the movement of the capillary meniscus on a photographic drum, a time scale being supplied by an electrically operated tuning fork. By forming the bubble under mercury, absorption during formation was avoided, and the slight delay before the bubble broke the surface of the mercury was sufficient to allow the recording system to be set in operation, so that very short time intervals were achieved. A criticism of the method is the delay in the movement of the capillary meniscus when very rapid absorption is taking place. This effect was to a certain extent eliminated during the absorption of carbon dioxide in potassium hydroxide solutions (93) by employing a liquid of low viscosity and density in the manometer.
The absorption of carbon dioxide from capsule shaped bubbles in pure water was studied by Higbie (4), the bubble being forced downwards through a tube filled with water. During the downward movement, a film of liquid remained almost stationary between the bubble and the tube. Each element of the bubble surface was therefore regarded as being formed at the bottom of the bubble, passing up the sides and being destroyed in the rear. The time of contact was assumed to be the time for the bubble to pass through a distance equal to its length. By varying the length of the bubble, contact times of the order of 0.01 seconds were achieved. Absorption during the introduction of the bubble was reduced to a minimum by coating the top of the tube with a water-repellant material, so that no film was formed between the bubble and the tube. The discharged liquid was analysed after the passage of a known number of bubbles.

A method for the measurement of very small pressure changes has been developed by Goodridge (94) and employed for the measurement of the absorption rate of carbon dioxide in 2-aminoethyl alcohol droplets. During drop formation in an atmosphere of hydrogen, the two gaseous phases were separated by a wide bore stopcock, through which the droplet was subsequently allowed to fall. The changes in pressure were measured by means of a sensitive diaphragm, the movement of which /
which altered the capacity in a tuned circuit, the resulting effect being amplified and applied to the plates of a cathode ray tube. The time scale was imposed on the time base by a standard oscillator and triggered by the falling droplet which actuated a photocell. A photographic record of the electron trace thus gave a record of the pressure-time variation in the system from which the absorption rate was calculated. The process of absorption may be complicated by the fact that hydrogen is absorbed during the formation of the droplet, so that, when the droplet is falling, in addition to the absorption of carbon dioxide, there will be diffusion of hydrogen from the surface layers into the droplet and passage of hydrogen from the surface into the gaseous phase.

The methods described by Ledig and Weaver, and by Goodridge measure the history of the instantaneous absorption rate over a continually varying short period of time, and as such, extremely sensitive methods are required for the detection and measurement of the volume or pressure changes. This is avoided in the method of Higbie, by employing a system where the measured absorption rate is actually an average rate over a discrete interval of time, this interval being independently variable. All the above methods may be subjected to changes in surface area due to distortion, or, in the methods employing bubbles, to reduction in the bubble volume. A further /
further criticism of Higbie's method is the systematic error which may be introduced owing to the somewhat idealised contact time (p. 24).

Danckwerts and Kennedy (12) have measured absorption rates at very short times of contact by employing a rotating drum designed to carry a film of liquid through the gas, so that the time of contact depended on the speed of rotation and on the fraction of the surface of the drum which was exposed. In this way, the time of contact between the liquid and the gas was varied from 0.0075 to 0.25 seconds. The method thus allowed extended measurements to be carried out on the absorption rate of the gas into a stagnant liquid film, of known area, which was exposed to the gas for a very short time. A criticism of the method is the possibility of entrainment of gas by the liquid film when contacted with the bulk liquid phase, and also the possible distortion of the liquid film at high speeds.
Fig. 14: SCHEMATIC REPRESENTATION OF ABSORPTION APPARATUS.

1. Compressor
2. Drying Tower
3. Smoothing Volume
4. Manometer
5. Flowmeter
6. Deoxygenation Apparatus
7. Preheater
8. Saturator
9. Absorption Column
10. Fixed Volume
11. Bourdon Gauge
12. Recording System
13. Thermostat
Description of Apparatus.

The principle of the apparatus (fig. 14), was that gas, in the form of a swarm of bubbles was passed at a known constant rate through a column of liquid and thence to a closed volume, the rate of increase of pressure being measured, and recorded on a revolving drum. By measuring the rate of pressure increase in the system at the same inlet gas rate during the presence and in the absence of absorption, the initial rate of absorption of the gas in the liquid was obtained. The apparatus employed here is a modification of that devised by Macrae (35).

The Metering System.

Oxygen from a 1.2c.f.t. gas holder was compressed, passed through a calcium chloride drying tower, and metered by means of an inclined oil-filled differential flowmeter. A 3 litre bulb was fitted in order to damp out any pulsations in the gas flow.

The Air Thermostat.

The thermostat, which was built on a framework of \( \frac{1}{2} \)" angle iron, was of dimensions 2'4" X 1'6" X 2', the walls consisting of sheets of cardboard, fibre-glass insulation, asbestos /
Fig. 15 ABSORPTION SYSTEM

KEY

1 Preheater
2 Saturator
3 Compensating column
4 Absorption column
5 2-litre volume
6 3-litre volume
7 Bourdon gauge
8 Double surface condenser
9 Capillary nitrogen bleed
10 Regulator
11 Fan
12 Heaters
13 Window
14 Thermostat
15 Deoxygenation apparatus
16 Recording system
asbestos, and an inner layer of aluminium foil. The removable front of the thermostat was fitted with two small double-glazed windows, which were placed to coincide with the sinter and the liquid surface in the absorption column. Heating was provided by two 250W. fire bar heaters in series, and controlled by a Sunvic bimetallic regulator through a Sunvic relay. Air circulation within the thermostat was effected by a fan, and was such that the temperature drop across the thermostat was reduced to 0.2°C. at the maximum operating temperature of 90°C. ± 0.2°C.

The Deoxygenation of Solutions.

This was achieved by boiling the solutions for 30 min. under vacuum, a slow capillary bleed of nitrogen being employed only during the initiation of boiling. The solution was then transferred to the absorption column along a line containing no stopcocks, as it was essential that no grease should come into contact with the solutions. Transfer of solutions was carried out by evacuating the absorption column and admitting a small amount of nitrogen to the deoxygenation system.

The Absorption System.

The apparatus, (fig. 15) consisted of a preheater followed /
Fig. 16  PRESSURE RECORDING SYSTEM

- clip
- drum
- collimator
- thermostat
- Bourdon gauge
- ball bearing
- mirror assembly
- reduction gear
- foot switch
- thread to gauge
- needle bearings (from ammeter coil)
- counterbalance
- silvered coverslip

Mirror Assembly
followed by a saturator at the temperature of the thermostat, and containing the same solution as the absorption column, a compensator column containing gas saturated solution, and the absorption column containing gas-free solution. After passing through the absorption column, non-absorbed gases were passed into a system of fixed volume (2, 3 or 5 litres) to which was attached a Bourdon Gauge, whose deflection measured the changes of pressure in the system. The gauge was enclosed in a glass jacket to shield it from draughts.

The absorption and compensation columns were of the same dimensions as those employed during the reaction and photographic measurements, namely, 1.5" diameter and approximately 15" in length, and fitted with side arms. As before, the sinters were of porosity no. 2. It was assumed that the bubble dimensions and gas hold-up values were of the same magnitude as those previously measured.

The Pressure Recording System.

The Bourdon gauge employed was such that it gave a rapid response to pressure changes in excess of $10^{-2}$ mm. mercury, the response being linear over small deflections. In the recorder, (fig. 16), a small pencil of light was directed from a 6V. 6W. collimator, controlled by a foot switch, on to a small mirror, consisting /
consisting of a silvered fragment of microscope coverslip, mounted on pivots. The mirror was so balanced that the moment about the pivot had negligible effect on the movement of the Bourdon gauge, to which it was attached by means of a short length of silk thread and a small wire ring looped over the spindle of the gauge.

As the pressure in the system increased, the movement of the gauge was magnified by the optical lever causing a vertical deflection of the light spot on the revolving drum, which carried a length of light-sensitive paper (Ilford G.P.5). The drum was of 13cm. height and 37cm. circumference, when fitted with the paper, and was driven by a 11,25 r.p.m. constant speed motor geared down to give the drum a speed of 9.25 sec. per revolution.

The complete recording device was enclosed in a light-tight box 21 X 7 X 13 inches, so constructed that the drum could be removed and loaded without disconnecting the mirror from the gauge.

Experimental Technique.

With taps C, L, and H closed, the compensation and absorption tubes were filled with 4.25ml. of gas-saturated solution, the compensation tube being filled through the funnel.
funnel on tap D, and the absorption column by means of a funnel attached to a B.7 drip cone which replaced tap F, so that no grease was permitted to enter the absorption column. While the liquid in the columns was attaining the temperature of the thermostat, 2 litres of solution were placed in the deoxygenation apparatus, the screw-clip K closed, and vacuum applied through tap C at the upper end of the reflux condenser. A gentle bleed of oxygen-free nitrogen entered through the capillary. When the solution was boiling the nitrogen supply was shut off. After boiling for 30 minutes, tap G was closed and the solution allowed to cool under its own vapour pressure.

When the liquid in the columns had attained the temperature of the thermostat, as indicated by the temperature of the solution in a tube of the same bore as the columns, the gas supply was started and diverted through the compensating column by tap C, tap D being open. In order to duplicate the conditions existing during the actual absorption measurements, after noting the level in the absorption column, 5 ml. of solution at the thermostat temperature were added to the absorption column and 5 ml. removed by tap H, so that the pores of the sinter were flooded. Tap F was now fitted to the column.

It was found that, while there was no noticeable variation of the gas flow with time over a period of 30 seconds, as measured /
measured on a soap-film meter attached to tap F, from the pre-
flooded sinter, there was a small stepwise variation in flow
through the absorption column on repeatedly alternating the
flow between the compensation and the absorption columns, if
the sinter was not flooded before each alternation. This
stepwise increase is probably due to the slight pressure built
up in the gas line while tap C was being turned, which would
tend to cause a slight reduction in the pressure drop across
the sinter due to the clearance of liquid from an increasing
number of pores. In adjusting the gas rate through the
compensating column to give the required gas rate in the
absorption column, on diverting the gas stream by tap C, the
sinter in the absorber was always flooded before passing gas
through the absorption column.

Having now obtained the desired flow rate through the
compensator, the absorption tube was drained through tap H and
washed out with distilled water. With taps C, H and F closed,
the absorption tube was now evacuated and filled with nitrogen
several times, through tap E, before being finally evacuated.
A small amount of nitrogen was now admitted to the deoxygena-
tion apparatus through tap G, so that, on opening clip K, the
oxygen-free solution entered the absorption column, flooding
the sinter and the gas supply line, the flow being stopped when
the level in the absorption column rose about 1.5 inches above
the /
the required level.

When the temperature of the solution in the absorption column had reached the desired value, gas was passed through the compensation column at the predetermined rate. The drum was loaded with the photographic paper and positioned in the box. A small amount of nitrogen was fed in through tap E to break the vacuum. With a continuous slow flow of nitrogen entering by tap E, and leaving by tap F, tap H was opened so that the liquid drained slowly from the absorption column. Simultaneously, tap G was partially opened to the absorber so that the solution in the gas supply line was ejected together with that from the absorption column through tap H, the level in the absorber being brought to the required value. At this point, the gas stream was diverted back to the compensator, and tap H was closed. During this period, no bubbles rose up the column, and, as there was a continuous slow downflow of liquid from the sinter, it is unlikely that any oxygen was absorbed in the liquid above the sinter. A small amount of nitrogen would however be dissolved at the surface of the liquid.

The nitrogen flow was now stopped and tap E diverted to the constant volume system. Taps F and I were then closed and a base line marked on the photographic paper by switching on the collimator light after setting the drum in motion. The gas stream, still passing through the compensator at the required rate /
rate was diverted to the absorption column by tap C, and simultaneously, the light spot was switched on. After the required time, the pressure in the system was released by opening tap F and the light spot was switched off. Passage of gas through the absorber was now continued for 10 minutes, in order to saturate the liquid, whereupon the gas was diverted back to the compensator.

The sinter of the absorber was re-flooded, as described previously, by the addition of oxygen-saturated solution, and the procedure repeated in order to obtain the rate of pressure increase when no absorption was taking place. This was carried out three times, after which the drum was removed from the box, and the paper developed in I.D.33, fixed, and glazed after washing.

The volume of the closed system employed was 2 litres, the corresponding duration of run required being 5 seconds. At the higher temperatures, the magnification of the optical lever system was reduced, so that runs of the same duration could be employed, despite the increased rate of pressure change caused by the high vapour pressure of the solution.

Maintenance of the Apparatus.

All taps and joints which were situated outside the thermostat /
Fig. 17 SPECIMEN PRESSURE-TIME TRACE TOGETHER WITH METHOD OF CALCULATION

Calculation:

Initial absorption rate = \frac{\text{Slope CD} - \text{Slope AB}}{\text{Slope CD}} \cdot \text{Inlet gas rate.}

\begin{align*}
\text{Slope CD} &= 0.315, \quad \text{Slope AB} = 0.218, \\
\text{Inlet gas rate} &= \frac{1.734}{0.0396}, \\
\text{Initial absorption rate} &= \frac{0.315 - 0.218}{0.315} \cdot 1.734 = 0.0396 \text{ gm.moles/hr.}
\end{align*}
thermostat were lubricated with Silicone grease, while those inside the thermostat, which were never moved during a run, were sealed using Audco No. 631 grease.

The interiors of the absorption and compensation columns were cleaned by filling with a hot solution of alcoholic potash, followed after three hours by a rinse with a weak solution of chromic acid. The columns were then thoroughly washed with distilled water.

**Calculation of Results.**

The photographic record thus obtained contained four pressure-time relationships, at a constant inlet gas rate, three of which corresponded to the rate of pressure increase in the system in the absence of absorption, and the fourth, which had a smaller gradient than the others, and corresponded to the rate of pressure increase in the system while gas was being absorbed. Fig. 17 shows a typical record obtained during a run, the former curves being termed the calibration curves and the latter, the absorption curve. Knowing the speed of rotation of the drum, the time scale was inserted by drawing lines perpendicular to the base line at intervals equivalent to 0.25 seconds. The pressure-time relationships for the straight-line calibration curves were now plotted so that the mean slope of the calibration curves was obtained.
A similar plot of the absorption curve was then made.

If \( y \) and \( x \) are the saturated gas rates (cm\(^3\)/hr.) entering the constant volume \( V \), in the presence and in the absence of absorption, respectively, then the absorption rate of saturated gas is given by \( (x - y) \). The corresponding rates of pressure increase are \( y P/V \) and \( x P/V \) gm./cm\(^2\)/hr., \( P \) being the initial pressure in the system (gm./cm\(^2\)).

Thus \( (x - y) = \frac{x P/V - y P/V}{x P/V} \cdot x \) cm\(^3\) of saturated gas/hr.

On now reducing the gas volumes to gm. moles of dry gas, the absorption rate \( R \), at any instant is given by:

\[
R = \frac{\text{Calibn. Curve Slope} - \text{Absn. Curve Slope}}{\text{Inlet dry gas rate}}
\]

Values for the initial absorption rate were obtained by determining the slopes of both the calibration and the absorption curves at zero time by extrapolation. A specimen calculation is shown in the figure.

Owing to the very small slope difference, the accuracy of the results will be somewhat limited. Any attempt to increase the sensitivity of the system resulted in a greater uncertainty in the initial region, so that no great advantage was obtained.
GRAPH No.25  (RUN No.1)

ABSORPTION OF OXYGEN IN 20 gm./l. H₂SO₄ AT 30.5°C.

O₂ Rate = 0.218 gm.moles/hr.
Volume = 425 mls.
INITIAL ABSORPTION RATE OF OXYGEN
IN 20.4 gm/l. H₂SO₄ v TEMPERATURE

A - Pure Oxygen
B - Nitrogen / Oxygen = 2 / 1
Experimental Results.

Variation of Initial Absorption Rate with Temperature.

Graph 25 represents the manner in which the amount of oxygen absorbed varies with time, at a temperature of 30.5°C., in 4.25 ml. of a solution containing 20.4 gm./l. sulphuric acid, the oxygen rate being 0.218 gm.moles/hr.

The absorption rate is approximately constant in the early stages, to about 0.8 sec., but subsequently decreases owing to the gradual reduction in the concentration gradient.

With increasing temperature an almost linear decrease in the initial absorption rate is evident (Graph 26, table 20), the rate, expressed as gm.moles/sec. \(\times 10^{-2}\), apparently tending to zero at the boiling point of the solution. All surface area values employed are taken from Graph 24c.

Variation of Initial Absorption Rate with Partial Pressure.

Several runs were carried out at temperatures of 30 and 60°C. with a gas mixture containing nitrogen and oxygen in the ratio 2 : 1. (Graph 26, table 21). The results obtained are somewhat scattered, but would appear to indicate that the initial absorption rate is reduced to one third of the value obtained for pure oxygen, i.e. that the absorption rate is proportional to the partial pressure.
GRAPH No. 27 (TABLE No. 22)

INITIAL ABSORPTION RATE OF OXYGEN
IN AQUEOUS H₂SO₄ AT 60°C.
Variation of Initial Absorption Rate with Acid Concentration.

The results obtained in the study of this variable at 60°C. are given in Graph 27 (table 22) which employs surface areas taken from Graph 22c. As the acid concentration increases, the initial absorption rate would appear to fall very slowly, within the accuracy of the experimental measurements.
### Table No. 20

Initial Absorption Rate of Oxygen in Aqueous Sulphuric Acid (20.4 gm./l.) at Different Temperatures.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. °C</th>
<th>Calibn. Slope</th>
<th>Slope Diff.</th>
<th>Rate gm.moles /hr.</th>
<th>Total Area cm²</th>
<th>Rate gm.moles /sec./cm² × 10⁸</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30.5</td>
<td>1.732</td>
<td>0.306</td>
<td>0.0385</td>
<td>109</td>
<td>9.81</td>
</tr>
<tr>
<td>2</td>
<td>30.5</td>
<td>1.745</td>
<td>0.302</td>
<td>0.0377</td>
<td>109</td>
<td>9.61</td>
</tr>
<tr>
<td>3</td>
<td>41.2</td>
<td>1.984</td>
<td>0.319</td>
<td>0.0350</td>
<td>114</td>
<td>8.54</td>
</tr>
<tr>
<td>4</td>
<td>30.5</td>
<td>1.734</td>
<td>0.315</td>
<td>0.0396</td>
<td>109</td>
<td>10.09</td>
</tr>
<tr>
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<td>30.5</td>
<td>1.986</td>
<td>0.309</td>
<td>0.0340</td>
<td>114</td>
<td>8.29</td>
</tr>
<tr>
<td>6</td>
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<td>0.0331</td>
<td>114</td>
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</tr>
<tr>
<td>7</td>
<td>59.6</td>
<td>2.202</td>
<td>0.290</td>
<td>0.0287</td>
<td>128</td>
<td>6.38</td>
</tr>
<tr>
<td>8</td>
<td>59.6</td>
<td>2.173</td>
<td>0.275</td>
<td>0.0276</td>
<td>128</td>
<td>5.99</td>
</tr>
<tr>
<td>9</td>
<td>59.6</td>
<td>2.185</td>
<td>0.305</td>
<td>0.0304</td>
<td>128</td>
<td>6.60</td>
</tr>
<tr>
<td>10</td>
<td>59.4</td>
<td>2.204</td>
<td>0.315</td>
<td>0.0312</td>
<td>128</td>
<td>6.78</td>
</tr>
<tr>
<td>11</td>
<td>79.5</td>
<td>2.298</td>
<td>0.175</td>
<td>0.0166</td>
<td>166</td>
<td>2.78</td>
</tr>
<tr>
<td>12</td>
<td>79.5</td>
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<td>0.147</td>
<td>0.0175</td>
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<td>2.93</td>
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<tr>
<td>13</td>
<td>79.9</td>
<td>2.303</td>
<td>0.210</td>
<td>0.0199</td>
<td>166</td>
<td>3.33</td>
</tr>
<tr>
<td>14</td>
<td>79.9</td>
<td>2.312</td>
<td>0.202</td>
<td>0.0191</td>
<td>166</td>
<td>3.20</td>
</tr>
<tr>
<td>15</td>
<td>89.5</td>
<td>1.853</td>
<td>0.087</td>
<td>0.0102</td>
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<td>1.15</td>
</tr>
<tr>
<td>16</td>
<td>89.5</td>
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</tr>
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<td>0.0155</td>
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<td>1.75</td>
</tr>
<tr>
<td>19</td>
<td>89.9</td>
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<td>0.098</td>
<td>0.0117</td>
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<td>1.32</td>
</tr>
</tbody>
</table>

### Table No. 21

Initial Absorption Rate of Oxygen in Aqueous Sulphuric Acid (20.4 gm./l.) at Different Temperatures, from an Inlet Gas Mixture of Nitrogen and Oxygen in the Ratio 2/1.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. °C</th>
<th>Calibn. Slope</th>
<th>Slope Diff.</th>
<th>Rate gm.moles /hr.</th>
<th>Total Area cm²</th>
<th>Rate gm.moles /sec./cm² × 10⁸</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>31.5</td>
<td>1.762</td>
<td>0.133</td>
<td>0.0164</td>
<td>109</td>
<td>4.18</td>
</tr>
<tr>
<td>21</td>
<td>31.5</td>
<td>1.752</td>
<td>0.100</td>
<td>0.0124</td>
<td>109</td>
<td>3.16</td>
</tr>
<tr>
<td>22</td>
<td>31.5</td>
<td>1.771</td>
<td>0.129</td>
<td>0.0159</td>
<td>109</td>
<td>4.05</td>
</tr>
<tr>
<td>23</td>
<td>30.9</td>
<td>1.756</td>
<td>0.084</td>
<td>0.0104</td>
<td>109</td>
<td>2.65</td>
</tr>
<tr>
<td>24</td>
<td>30.9</td>
<td>1.765</td>
<td>0.104</td>
<td>0.0128</td>
<td>109</td>
<td>3.27</td>
</tr>
<tr>
<td>25</td>
<td>60.4</td>
<td>2.136</td>
<td>0.084</td>
<td>0.0086</td>
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<td>1.87</td>
</tr>
<tr>
<td>26</td>
<td>60.4</td>
<td>2.141</td>
<td>0.103</td>
<td>0.0110</td>
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<td>2.83</td>
</tr>
<tr>
<td>27</td>
<td>60.4</td>
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<td>0.0076</td>
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<td>1.65</td>
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<tr>
<td>28</td>
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<td>0.0143</td>
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</tr>
<tr>
<td>29</td>
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<td>0.120</td>
<td>0.0121</td>
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<td>2.63</td>
</tr>
<tr>
<td>30</td>
<td>60.9</td>
<td>2.141</td>
<td>0.102</td>
<td>0.0104</td>
<td>128</td>
<td>2.26</td>
</tr>
</tbody>
</table>
Table No. 22.

*Initial Absorption Rate of Oxygen in Aqueous Solutions of Sulphuric Acid at 60°C.*

<table>
<thead>
<tr>
<th>Run No.</th>
<th>H\textsubscript{2}SO\textsubscript{4} Conc.</th>
<th>Calibn. Slope</th>
<th>Slope Diff.</th>
<th>Rate gm.moles/hr.</th>
<th>Total Area cm\textsuperscript{2}</th>
<th>Rate gm.moles/sec./cm\textsuperscript{2} X 10\textsuperscript{8}</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>20.4</td>
<td>2.202</td>
<td>0.290</td>
<td>0.0287</td>
<td>128</td>
<td>6.23</td>
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<tr>
<td>8</td>
<td>20.4</td>
<td>2.173</td>
<td>0.275</td>
<td>0.0276</td>
<td>128</td>
<td>5.99</td>
</tr>
<tr>
<td>9</td>
<td>20.4</td>
<td>2.185</td>
<td>0.305</td>
<td>0.0304</td>
<td>128</td>
<td>6.60</td>
</tr>
<tr>
<td>10</td>
<td>20.4</td>
<td>2.204</td>
<td>0.315</td>
<td>0.0312</td>
<td>128</td>
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<tr>
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<td>0.366</td>
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<td>0.0360</td>
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<td>101.2</td>
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<td>0.0416</td>
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<td>6.11</td>
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<td>42</td>
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<td>2.312</td>
<td>0.489</td>
<td>0.0461</td>
<td>205</td>
<td>6.25</td>
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</table>
DISCUSSION
Discussion.

On the basis of the present work, the manner in which the reaction rate/unit area varies with temperature (Graph 20) leads to the conclusion that the reaction is absorption controlled over the range of temperatures studied (30 - 90°C.), and also, as excess sulphur dioxide was found to be present in the solution, this view may be extended to specify that it is the absorption rate of oxygen which is the controlling factor. This latter conclusion is supported by the evidence that, while complete oxidation of sulphur dioxide could be obtained at low sulphur dioxide partial pressures, complete conversion of oxygen was never obtained at low oxygen partial pressures (Graph 6).

This idea that the principal controlling factor is the absorption of oxygen is in agreement with the results of previous workers (73, 75, 83, 88). However, in addition to the absorption rate of oxygen, the overall rate of the process would be expected, under certain circumstances to be influenced by the absorption rate of sulphur dioxide, diffusion of sulphur dioxide and sulphuric acid in the liquid phase, and also by the effectiveness of the catalyst. This latter factor has been
been studied and found to be of importance only at very low catalyst concentrations (73, 76) and at comparatively high acid concentrations ($> 20\%$)(82). In Graph 8, for reaction in 20 gm./l. sulphuric acid, this effect would appear to become evident at catalyst concentrations below approximately 0.03\% manganese, which compares favourably with the figure of 0.025\% quoted by previous workers.
Fig. 18  **REPRESENTATION OF THE OXIDATION OF SULPHUR DIOXIDE IN MANGANESE SULPHATE SOLUTION.**
General Interpretation of the Process.

From the standpoint that the absorption rate of oxygen is the major controlling factor, the situation may be represented on the basis of the Two-film theory as shown in figure 18, which is similar to that shown in figure 1, for rapid second order reaction except that both reactants are present in the gaseous phase and must be absorbed by the liquid.

The rates of transfer of oxygen and sulphur dioxide from the bulk gas phase to the interface CD, namely $R_0$ and $R_S$, are given by:

$$R_0 = k_{\text{O}_2} \cdot (p_0 - p_{10}) \quad (59)$$

and

$$R_S = k_{\text{SO}_2} \cdot (p_S - p_{1S}) \quad (60)$$

At the interface, the concentration of free manganese ions will be at a minimum owing to the formation of an intermediate compound. On penetrating the liquid film, the concentration of this compound will decrease due to the oxidation reaction, until at EF (distant $s'_L$ from the interface) the concentration of oxygen and of the intermediate compound will approach zero. As the concentration of the intermediate compound decreases, the concentration of free manganese ions will increase, so that at EF the concentration will be similar to that in the bulk liquid phase.
The rates of transfer of oxygen and sulphur dioxide in the liquid film will be given by:

\[ R_O = k_{L0} (c_{i0} - 0) = \left( \frac{D_0}{s_{L0}} \right) (c_{i0} - 0) \]  \hspace{1cm} (61)

and

\[ R_S = k_{Ls} (c_{iS} - c_{iS}) = \left( \frac{D_s}{s_{Ls}} \right) (c_{iS} - c_{iS}) \]  \hspace{1cm} (62)

The concentration of sulphuric acid in the liquid film will be at a constant value, \( c_{iA} \), from the interface to the plane \( EF \), and the rate of transfer into the bulk solution will be given by:

\[ R_A = k_{L_A} (c'_{iA} - c_{iA}) = \left( \frac{D_A}{s_{L_A}} \right) (c'_{iA} - c_{iA}) \]  \hspace{1cm} (63)

By assuming Henry's Law and the additivity of resistances (equations 8 & 9), the absorption rate of oxygen during reaction, in terms of overall coefficients may be expressed by:

\[ R_O = (K_{C0})_0 (n_0) = \left( \frac{K_{C0}}{n_0} \right) (c_0) \]  \hspace{1cm} (64)

where \( c_0 \) is the concentration of oxygen which would be in equilibrium with the gas phase.

Previous workers have expressed their results both in terms of \((K_{C0} \cdot n)\) values \((75, 88)\), and also in terms of \((K_{L0} \cdot a)\) values, where \( a \) is the surface area per unit volume.
of absorption apparatus. In the present discussion reference will be made to both methods of representation.

Effect of Diffusion of Sulphuric Acid.

On the assumption of zero oxygen concentration in the bulk liquid, the effect of sulphuric acid concentration on the absorption rate of oxygen during reaction may be considered from two different aspects:

(a) If the concentration of sulphuric acid, $c'_A$, in the reaction zone is considered constant, then the rate at which sulphuric acid is transferred from the reaction zone into the body of the liquid will be twice the absorption rate of oxygen. Thus:

$$2P = R_A = \left(\frac{D_A}{8''L}\right)(c'_A - c_A)$$

(65)

If now $D_A$ and $8''_L$ are assumed constant, then the absorption rate of oxygen should decrease linearly with $c'_A$, which it has in fact been found to do. (Graph 19).

(b) If $c'_A$ increases during reaction, a reduction in the values $D_0$ and $c'_1$ (equation 61) will occur thus again predicting a reduction in the reaction rate with increasing acid concentration.

Thus on the basis of the above it may be stated that the absorption /
absorption rate of oxygen during reaction is a linear function of the diffusion of sulphuric acid from the reaction zone.

Effect of Diffusion of Sulphur Dioxide.

When the partial pressure difference for sulphur dioxide is such that the absorption rate of sulphur dioxide exceeds that of oxygen during the reaction, a proportion of the sulphur dioxide will be 'physically' (as compared with absorption by oxidation) absorbed into the main body of the solution. This effect is evident in the early stages of the reaction depicted in Graph 5.

The calculation of the absorption rate of sulphur dioxide during reaction is however prohibited owing to lack of the requisite equilibrium data. Alternatively, however, the absorption rate of sulphur dioxide may be expressed as:

$$ R_S = 2.0 + R' $$

where $R'_S$ is the rate at which sulphur dioxide diffuses from the reaction zone into the body of the liquid.

When the overall rate of the process is limited by the reaction rate, as at very low catalyst concentrations ($< 0.025\text{M Mn}$), a similar state of affairs will exist as regards oxygen absorption, free oxygen becoming present in the main body of the solution.
Discussion of Process Variables.

In all runs where oxygen absorption is the controlling factor, the measured reaction rate must be due to the imposition of changes of surface area upon the linear variation of reaction rate with acid concentration. Consequently, the results will be discussed, as indicated previously, in terms of $K_La$ values, so that, when excess sulphur dioxide is present in solution, over the range of acid concentrations studied, apart from when the reaction rate is controlling, the comparison of $K_La$ figures at a constant acid concentration is, in essence, the comparison of surface areas available for mass transfer. The effects of the degree of circulation within the bubbles will, for the present, be ignored.

The calculation of $K_La$, and also of $K_Ga$ values are based on:-

$$K_La = \frac{1000.R_0}{A.h.(c_0)_m} \quad \text{and} \quad K_Ga = \frac{1000.R_0}{A.h.(p_0)_m}$$

where $A =$ cross section area of column, (cm.$^2$),

$h =$ column height (cm.), $a =$ surface area/unit volume, (cm.$^2$/l.),

$(p_0)_m =$ log. mean partial pressure of oxygen in the bulk gas phase between inlet and outlet gas streams, (atm.),

$(c_0)_m =$ $(p_0)_m/\Pi$, (gm. moles/cm.$^3$).

The /
The application of the above is shown for reaction at 60°C, at an acid concentration of 20gm/l, when the reaction rate is 0.099 gm.moles SO₂/hr. (Run P.15): –

<table>
<thead>
<tr>
<th></th>
<th>Inlet</th>
<th>Outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Rate (gm.mole/hr.)</td>
<td>0.218</td>
<td>0.168</td>
</tr>
<tr>
<td>Sulphur dioxide Rate (gm.mole/hr.)</td>
<td>0.458</td>
<td>0.359</td>
</tr>
<tr>
<td>Total Dry Gas Rate (gm.mole/hr.)</td>
<td>0.676</td>
<td>0.527</td>
</tr>
<tr>
<td>Total Pressure (mm.Hg)</td>
<td>778</td>
<td>752</td>
</tr>
<tr>
<td>Vapour Pressure (mm.Hg)</td>
<td>14.9</td>
<td>14.8</td>
</tr>
<tr>
<td>Oxygen Partial Pressure (atm.)</td>
<td>0.267</td>
<td>0.253</td>
</tr>
</tbody>
</table>

Log. mean partial pressure of oxygen = \( p_0' \) = 0.260 atm.

Thus employing the solubility data given in Appendix 2: –

\[
K_{La} = \frac{1000 \times 0.0495}{12.22 \times 33.43 \times 0.260} \times 10^6 = 5.97 \times 10^5,
\]

the units of \( K_{La} \) being gm.moles hr⁻¹ atm⁻¹ (gm.moles/cm³)⁻¹.

Note: – (a) In the above, the volume of solution contained by the side-arm of the reaction vessel has been ignored. This is repeated in all calculations of \( K_{La} \).

(b) When the gas stream was not initially saturated, the calculation of \( K_{La} \) was performed assuming that it had been. This is justified by the absence of any significant change in rate on saturating the gas stream.

**Effect of Inlet Gas Ratio.**

The /
GRAPH No. 28

VARIATION OF $K_a$ WITH INLET GAS RATIO.

($K_a = 10^{-5}$ [g mole/hr-l] [g mole/cm$^3$] $^{-1}$)

SO$_2$ Conc. = 20 g/m$. l.$

H$_2$SO$_4$ Conc. = 60 g/m$. l.$

(Proc. from Graph 6)
The maximum reaction rate obtainable with varying inlet gas ratios up to those containing 66.7% sulphur dioxide is obviously the inlet rate of that gas. With gas mixtures containing up to 20% sulphur dioxide, this maximum rate was attained (Graph 6), and as expected, no free sulphur dioxide was present in solution. Thus in this region, the reaction rate must be controlled by the availability of sulphur dioxide. As would be expected, the increase in $K_p$ (Graph 28) is directly proportional to the sulphur dioxide percentage up to about 20% sulphur dioxide.

At still higher inlet sulphur dioxide ratios, up to about 35%, while complete oxidation of the sulphur dioxide was no longer obtained, the absence of sulphur dioxide from the solution would indicate that the reaction is controlled by diffusion of sulphur dioxide in this region. It is well known that in the normal 'physical' absorption of sulphur dioxide in water, an appreciable resistance to diffusion is encountered in both the gaseous and liquid phases, whereas, in the case of oxygen absorption the resistance is substantially due to the liquid phase alone. In view of the absence of unreacted sulphur dioxide in solution up to 35% inlet sulphur dioxide, it would appear that the liquid phase resistance to diffusion of sulphur dioxide is reduced to a value /
value below that for oxygen, so that the actual factor controlling the rate will be the diffusion of sulphur dioxide in the gaseous phase.

In the initial stage of the reaction, when less than 35% sulphur dioxide is present, oxygen absorption may however be the controlling factor if the absorption rate of sulphur dioxide exceeds that of oxygen, so that, according to equation (66), excess sulphur dioxide will be present in solution. However, as the surface area increases, the potential reaction rate will exceed the absorption rate of sulphur dioxide so that this excess will diffuse from the bulk liquid to the reaction zone thus reducing the bulk concentration to zero.

The concentration of sulphur dioxide in solution is thus a reflection of the reaction rate, the liquid phase driving force \((c_{lS} - c_{lS}^-)\) always being such that it tends to maintain the absorption rate of sulphur dioxide at twice the absorption rate of oxygen. Thus \(P_{S}^1\), the diffusion rate of sulphur dioxide from the reaction zone into the body of the liquid, may have a positive or negative value depending upon the demands of the reaction. This is in fact illustrated in Graph 5, where a slow increase in the concentration of sulphur dioxide is evident as the reaction rate decreases, and also by the increasing concentration with amount of sulphur dioxide in the inlet gas stream.
In view of the large excess of sulphur dioxide present in the final solution when the inlet gas contains more than 45% sulphur dioxide, and the fact that the reaction rate never approaches the maximum possible value, it may reasonably be assumed that excess sulphur dioxide is everywhere present in solution. Thus in this region the absorption rate of oxygen is the controlling factor at all acid concentrations studied, whence it may be concluded (Graph 28) that in 20g/l. acid the surface area increases linearly with sulphur dioxide ratio, whereas in 60 g/l acid the surface area reaches a maximum and then decreases slowly with increasing sulphur dioxide ratio. This effect will be discussed more fully later.

As a consequence of the foregoing, the effect of increasing column height at constant acid concentration and gas ratio may be predicted, and effects being presumed negligible. At low column heights, excess sulphur dioxide will be present in solution and the rate will be controlled by oxygen absorption. On increasing the height, the process will pass through a region where sulphur dioxide diffusion in the gaseous phase is the dominant factor, until eventually, when the column is sufficiently high, complete conversion will be obtained. The work of Chi-Kwang Chen (88) on the variation of column height would appear to support the above, the rate having been found to
to increase at a decreasing rate with height, until 100% oxidation was achieved.

Effect of Inlet Sulphur Dioxide Rate.

In Graph 9, at the lower sulphur dioxide rates, the existence of this gas phase resistance to absorption of sulphur dioxide would appear to be more clearly evident. At the lowest sulphur dioxide rate (29% sulphur dioxide), after the initial sharp increase due to the changing surface area, the reaction rate remained approximately constant and below its potential value, and excess sulphur dioxide was absent from the solution. Similarly at an inlet sulphur dioxide rate of 0.125 gm.moles/hr. (37%), the rate remained approximately constant and below its potential value up to about 190 gm./l. acid, when a marked reduction in rate was observed.

At all higher sulphur dioxide rates, the reduction in rate occurred at acid concentrations of approximately 130 - 150 gm./l., and is due to diffusion of oxygen and sulphuric acid in the liquid phase, and possibly to some reduction in surface area (88). If the linear reduction in reaction rate with acid concentration at 0.125 gm.moles sulphur dioxide per hour be extrapolated back to 150 gm./l., the rate obtained is considerably /
GRAPH No. 29

VARIATION OF K LA WITH SULPHUR DIOXIDE RATE

(Calc. from Graph 10)

[Graph showing variation of K LA with sulphur dioxide rate]
considerably greater than the measured rate. Thus the acid concentration of 190 gm./l. apparently marks the change-over from control by diffusion of sulphur dioxide in the gaseous phase to control by diffusion of oxygen and sulphuric acid in the liquid phase.

The variation of $K_L a$ with sulphur dioxide rate, as calculated from Graph 9 is shown in Graph 29. In the region where the effect of sulphur dioxide diffusion is negligible, i.e. when the sulphur dioxide content of the inlet gas exceeds 40%, $K_L a$ and thus the surface area, increase almost linearly with sulphur dioxide rate. When the bubble diameters are still comparatively large (20 gm./l. acid), the surface area increases but slowly with gas rate. However when the bubbles are much smaller, i.e. at acid concentrations in the range 60 - 120 gm./l., the surface area, as would be expected, increases at a much greater rate.

This approximately linear variation of surface area with inlet gas rate is in agreement with the work of Macrae(35) on bubble swarms in toluene. The increase in surface area is in general due to a small increase in diameter and to a large increase in gas hold-up with increasing gas rate, but in the present work, the sulphur dioxide content of the solution might be expected to exert some influence.
At still higher acid concentrations (200 gm./l.), the rate of increase of $K_a$ is somewhat reduced. If the results at 120 and 200 gm./l. be expressed in terms of $K_a$ values, they remain of similar form, but the 200 gm./l. curve now falls slightly below that for 120 gm./l., owing to the changed Henry's law constant. A similar effect was obtained by Chi-Kwong Chen (88), in whose work the bubble diameter in the initial stages was reduced to a very low value by the presence of aluminium sulphate in the solution. As the reaction proceeded, Chen observed a gradual increase in bubble diameter attributed to changes in the liquid medium. It would therefore appear that the reduced rate of increase of $K_a$ in 200 gm./l. acid might be due to a slight increase in bubble diameter.

In the photographic measurements carried out during reaction (Graph 17), no change in bubble diameter could be detected after the maximum rate was achieved. From the above it would appear that a slight change in the diameter over the range of concentrations studied beyond the maximum rate, might exist, but would be negligible over this range.

Effect of Inlet Oxygen Rate.

During the study of this variable (Graph 11), a large /
GRAPH No. 30

VARIATION OF $K_{L,a}$ WITH OXYGEN RATE

($\text{Calc. from Graph 12}$)

$\text{H}_2\text{SO}_4$ Contn. = 10 gm./l.

60 gm./l.

120 gm./l.

OXYGEN RATE (gm.moles/hr.)

$\left[10^{-5} \text{ gm.mole/hr.} \cdot \text{cm}^{-3} \cdot 1 \left(\text{gm.mole/cm}^3\right)^{-1}\right]$
large excess of sulphur dioxide was always present in the final solution, so that the reaction may be regarded, as before, as being controlled by oxygen absorption. At low acid concentrations (Graph 30), $K_{La}$ increases linearly with oxygen rate as would be expected, the effect being solely due to the change in surface area. However, at high acid concentrations (60 and 120 gm./l.) the surface area increases much more rapidly with oxygen rate, as was also observed during the variation of sulphur dioxide rate, and reaches a maximum at an inlet oxygen rate of 0.4 gm.moles/hr. after which the $K_{La}$ value falls off quite appreciably with further increase in oxygen rate.

This change in the variation of $K_{La}$ with oxygen rate at these higher acid concentrations and oxygen rates could be due either to the process becoming controlled by the reaction rate or by a change in the characteristics of the bubble swarm. In view of the large amount of catalyst present (1.724 gm.Ln/l.), which is greatly in excess of the optimum concentration of 0.025 gm.Ln, it is unlikely that the former is the controlling factor. Thus reverting to the other alternative, the change in the variation of $K_{La}$ with oxygen rate must be due to changes in the bubble swarm. This was in fact evident, many large bubbles being seen to rise through the column, so that the increase in the density of the bubble swarm was much less pronounced than at the lower oxygen rates. It would therefore appear /
GRAPH No. 31

VARIATION OF $K_a$ WITH CATALYST CONCN.

(Calc. from Graph 8)

$H_2SO_4$ Conc. = 140 gm./l.
80 gm./l.
20 gm./l.

CATALYST CONCENTRATION (gm. Mn/l.)

$K_a$: 10$^{-5}$ [g.mole/hr-l] (g.mole/cm.$^-3$-l$^-1$)
appear that at the higher acid concentrations and gas rates, the effect of increased superficial gas velocity tends to nullify any changes in the bubbles brought about by changes in the properties of the liquid.

**Effect of Catalyst Concentration.**

The profound effect which the concentration of manganese sulphate exerts on the surface area of bubble swarms has been illustrated previously (figure 6). This is further apparent in Graph 31 which depicts the variation of $K_a$ with catalyst concentration, sulphur dioxide being everywhere present in solution, so that the absorption rate of oxygen is once again the controlling factor, except at the lowest catalyst concentrations. In this region (Graph 8) a rapid increase in rate occurred with no corresponding increase in surface area being apparent.

It would therefore appear that the effect of increasing amounts of catalyst at very low catalyst concentrations (below approximately 0.1 gm. Mn/l.) is to increase the reaction rate, whereas at higher catalyst concentrations the overall rate of the process is due to the great changes in surface area. At very high catalyst concentrations ($> 3$ gm. Mn/l.), it would seem that the process resembles
that of Chi-Kwang Chen\(^{88}\), in that the rate of the process tends to its maximum value in the initial stage, thereafter falling steadily. Thus it would appear that aluminium sulphate, as employed by Chen, and manganese sulphate have similar effects on bubble production and properties.

At high acid concentrations and catalyst concentrations (Graph 31), the \( K_L \) variation would appear to indicate that there may in fact be a slight reduction in surface area at catalyst concentrations greater than \( 1 \text{g Mn/l} \). This phenomenon will be discussed later.

**Effect of Temperature.**

On the basis of the photographic measurements carried out during the study of this variable, it has previously been concluded that the variation in the rate of the process is in general due to the combined effects of changing surface area and a continually falling oxygen absorption rate, due, at a constant temperature to the reduced diffusion rate of oxygen and sulphuric acid with increasing acid concentration. This latter conclusion of oxygen absorption control was based on the variation of rate/unit area with temperature (Graph 20), at a constant acid concentration.
The remainder of this discussion will therefore deal principally with the effect of temperature and the previously mentioned factors on the surface area, and also with the factors influencing the absorption rate of oxygen.
Surface Area of Bubble Swarms.

The available surface area for mass transfer, at a constant inlet gas rate hinges on two principal factors, namely the bubble diameter and the gas hold-up, which factors are in themselves not unrelated. Thus, for example, in the region where Stokes' Law is applicable, they may be related by employing Stokes' Law and equation (57), giving for single bubbles:

\[
\frac{\Delta \rho \cdot \pi d^2}{18 \cdot \gamma} = U = \left(\frac{v_g}{A}\right) \cdot \frac{1}{(1 - l_0)}
\]  

(67)

At higher \(Re\) i.e. when Stokes' Law does not apply, the relation between the diameter and the gas hold-up is not known on such a strictly quantitative basis, but may quite adequately be explained in terms of hydrodynamic and hydrostatic forces, and the consequent distortion of large bubbles from the spherical form. Thus in the present work, the fundamental factor requiring explanation is the bubble diameter, which has been found to depend on the concentration of sulphuric acid and manganese sulphate, and, during reaction, on the combination of these factors with the concentration of sulphur dioxide.

Effect of Sulphuric Acid Concentration.

At very low gas rates, Maier\(^{(38)}\) stated that the diameter of bubbles actually \textit{produced} assuming complete wetting /
wetting of the orifice was given by equation (37), namely:

\[ R = \left( \frac{3 \pi \sigma}{2 \rho g} \right)^{1/3} \]  

(37)

If this equation is assumed to be applicable to the present work, i.e. for the existing range of gas flows, and if no interaction between bubbles produced from neighbouring pores is assumed, then for solutions of sulphuric acid of concentrations from 0 to 200 gm./l. at 60°C., when the density changes from 0.985 to 1.1 gm./cm³ and the surface tension from 66.2 to 68.3 dynes/cm. (96) (see Appendix 2), the ratio of the diameters would be:

\[ \frac{d_0}{d_{200}} = \left( \frac{\sigma_0 \rho_{200}}{\rho_0 \sigma_{200}} \right)^{1/3} = \left( \frac{66.2 \times 1.1}{0.985 \times 68.3} \right)^{1/3} = 1.03 \]

Thus if the above assumptions are valid, the diameter of bubbles produced at the face of the sinter would remain approximately constant over this range of acid concentrations. This state of affairs is however unlikely owing to the proximity of the pores of the sinter, which would be likely to lead to coalescence and premature detachment of bubbles from the pores due to the restricted growth. It would be expected that this latter factor would be enhanced if coalescence during bubble formation proceeded to any great extent.
In figure 12 it is obvious that coalescence occurs as the bubbles rise through the column, the effect of changes in hydrostatic head being very small, and that the extent of this coalescence decreases with increasing acid concentration. It is therefore quite probable that this decreased coalescence with increasing acid concentration will persist even at, or very close to the sinter during bubble formation and detachment, so that the measured mean diameter (Graph 22a) will bear little resemblance, except at the highest acid concentrations, to the diameter of the bubbles released from the pores of the sinter. This coalescence at the sinter will occur while the bubbles remain in contact in the 'cone' of bubbles on the sinter.

If the diameter of the bubble is calculated according to equation (37), employing a mean pore diameter of 45 microns for the sinter (porosity No. 2), even at the highest acid concentration the measured diameter is only about 50% of the calculated value, so that even when the degree of coalescence is very small, the equilibrium diameter is not achieved. The reason for this removal from the equilibrium diameter will now be examined.

Previously it has been stated that in the production of a bubble from a single orifice, at very low gas rate, buoyancy forces are balanced by surface tension forces until such /
such time as the balance can no longer be maintained, by alteration of the surface tension forces, at which point the bubble commences to neck and becomes detached from the orifice. When the gas rate is increased, this balance is unlikely to be achieved as the viscosity of the liquid may cause the pressure at the point of release to exceed that due to the surface tension and the hydrostatic head so that on release the bubble would be increased in diameter. However, simultaneously with this increased excess pressure there is an increased liquid momentum effect due to the high rate of bubble formation which will cause earlier rupture of the unstable neck of the bubble, thus causing a reduction in diameter. This instability in the neck of the bubble will be further increased during bubble formation on sinters owing to the constriction of the neck of a bubble in an advanced state of development by bubbles being produced at adjacent pores.

Owing to the increase in the surface tension and viscosity with increasing acid concentration, an increase in bubble diameter would be expected as the surface tension forces within the bubble, per unit area, are proportional to \((\sigma/d)\), and also as the high viscosity would lead to an increased pressure excess before release.

The effect of the concentration of sulphuric acid on the surface area (Graph 22c) may therefore be presumed to be due to an increase in the diameter of the bubbles formed at the sinter.
Table No. 23.
Bubble Swarm Velocities and Contact Times in Solutions of Sulphuric Acid at 60°C.

<table>
<thead>
<tr>
<th>H₂SO₄ Conc. (gm./l)</th>
<th>Ht. of Liquid Column cm.</th>
<th>Gas Hold-up cm³</th>
<th>Vapour Press. mm.Hg</th>
<th>Satd. Gas Rate ml/hr</th>
<th>Bubble Swarm Vel. cm/sec</th>
<th>Bubble Diam. cm</th>
<th>Contact Time sec. x 10³</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>32.96</td>
<td>2.72</td>
<td>14.9</td>
<td>7,456</td>
<td>25.09</td>
<td>0.0907</td>
<td>3.61</td>
</tr>
<tr>
<td>20.4</td>
<td>32.96</td>
<td>2.72</td>
<td>14.8</td>
<td>7,444</td>
<td>25.05</td>
<td>0.0813</td>
<td>3.25</td>
</tr>
<tr>
<td>41.4</td>
<td>32.95</td>
<td>2.76</td>
<td>14.7</td>
<td>7,432</td>
<td>24.64</td>
<td>0.0795</td>
<td>3.23</td>
</tr>
<tr>
<td>59.7</td>
<td>32.95</td>
<td>2.80</td>
<td>14.6</td>
<td>7,420</td>
<td>24.27</td>
<td>0.0795</td>
<td>3.28</td>
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<tr>
<td>88.2</td>
<td>32.95</td>
<td>2.86</td>
<td>14.4</td>
<td>7,394</td>
<td>23.67</td>
<td>0.0799</td>
<td>3.38</td>
</tr>
<tr>
<td>101.2</td>
<td>32.96</td>
<td>2.96</td>
<td>14.3</td>
<td>7,382</td>
<td>22.84</td>
<td>0.0802</td>
<td>3.51</td>
</tr>
<tr>
<td>124.8</td>
<td>32.99</td>
<td>3.28</td>
<td>14.1</td>
<td>7,358</td>
<td>20.57</td>
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<td>5.32</td>
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<tr>
<td>145.0</td>
<td>33.00</td>
<td>3.40</td>
<td>13.9</td>
<td>7,335</td>
<td>19.77</td>
<td>0.0810</td>
<td>4.10</td>
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<tr>
<td>172.1</td>
<td>33.00</td>
<td>3.44</td>
<td>13.7</td>
<td>7,311</td>
<td>19.48</td>
<td>0.0815</td>
<td>4.19</td>
</tr>
</tbody>
</table>

Table No. 24.
Bubble Swarm Velocities and Contact Times at Different Temperatures in Sulphuric Acid (20.4gm./l)

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Ht. of Liquid Column cm.</th>
<th>Gas Hold-up cm³</th>
<th>Vapour Press. mm.Hg</th>
<th>Satd. Gas Rate ml/hr</th>
<th>Bubble Swarm Vel. cm/sec</th>
<th>Bubble Diam. cm</th>
<th>Contact Time sec. x 10³</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.0</td>
<td>32.52</td>
<td>2.08</td>
<td>32</td>
<td>5,689</td>
<td>24.70</td>
<td>0.0703</td>
<td>2.85</td>
</tr>
<tr>
<td>40.0</td>
<td>32.65</td>
<td>2.26</td>
<td>55</td>
<td>6,068</td>
<td>23.35</td>
<td>0.0725</td>
<td>2.98</td>
</tr>
<tr>
<td>50.0</td>
<td>32.77</td>
<td>2.48</td>
<td>92</td>
<td>6,606</td>
<td>22.95</td>
<td>0.0751</td>
<td>3.10</td>
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<tr>
<td>60.0</td>
<td>32.91</td>
<td>2.72</td>
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<td>70.0</td>
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<td>3.14</td>
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<td>8,915</td>
<td>24.18</td>
<td>0.0853</td>
<td>3.26</td>
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<tr>
<td>80.0</td>
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<td>3.34</td>
<td>350</td>
<td>11,820</td>
<td>23.58</td>
<td>0.0931</td>
<td>3.43</td>
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<tr>
<td>90.0</td>
<td>33.73</td>
<td>6.00</td>
<td>528</td>
<td>21,640</td>
<td>33.81</td>
<td>0.1290</td>
<td>3.82</td>
</tr>
</tbody>
</table>

Notes:
(1) All inlet gas volumes corrected to existing temperature, pressure and saturation conditions within the column.
(2) Mean bubble velocities calculated from the formula of Verschoor:
\[
U = \frac{\text{Inlet gas rate} \times \text{Ht. of column}}{\text{Gas Hold-up} \times \text{cm}^2}
\]
(3) Bubble diameters taken from smoothed curves.
(4) Contact times according to Higbie, \( \frac{\text{diam.}}{\text{velocity}} \).
sinter together with a gradual reduction in the degree of coalescence, both in the column and at the sinter, the overall result over the range of acid concentrations studied being a reduction in bubble diameter (Graph 22a) to a minimum followed by a slow increase. This latter is in agreement with the manner in which $K_L$ varied with sulphur dioxide rate at high acid concentrations (Graph 29). The increase in gas hold-up (Graph 22b) is due to the reduction in bubble diameter followed by its slow increase, and the steady increase in viscosity with increasing acid concentration, both factors causing a reduced bubble velocity. (Table 23)

**Effect of Manganese Sulphate Concentration.**

It has been noted that the effect of the concentration of manganese sulphate is to cause an appreciable change in the surface area of bubble swarms in water (figure 6); the concentration of manganese sulphate required to bring about a similar change in the bubble swarms as compared with sulphuric acid (figure 12) is however very much smaller.

This change due to manganese sulphate is reflected in the variation of $K_L$ during reaction at low acid concentration (Graph 31). At higher acid concentrations the effect is much less pronounced, and in addition the variation of $K_L$ at high acid and catalyst concentrations, with increasing catalyst concentration /
concentration would appear to indicate a slight reduction in surface area. As a result of the foregoing evidence, it would appear that the efficacy of manganese sulphate in preventing coalescence is many times greater than that of sulphuric acid, and also that their effects are to a certain extent additive. A short digression to examine the reasons for this will now be made.

Coalescence of Bubbles.

As a result of the work of Foulk and Miller, and many others, it has been concluded that the absence of coalescence in many liquids is due to the ability of these liquids to maintain a stable liquid film between the bubbles. The presence of this stable film has been postulated as being due to a difference between the solute concentration in the liquid film and in the bulk liquid. This property is characteristic of solutions exhibiting a difference between the static and dynamic surface tensions, which explains why coalescence occurs most readily in pure liquids, as has been observed.

In a freshly formed liquid surface, it has been proposed that the ions with the strongest fields of force are withdrawn.
withdrawn into the solution, so that the remaining ions are pictured as being adsorbed at the surface \(^{(97)}\). It has furthermore been found that it is the negative ions which are generally adsorbed at the surface. It is therefore evident that with sulphuric acid and manganese sulphate the equilibrium or static surface tension will be achieved much more rapidly with sulphuric acid than with manganese sulphate, owing to the small atomic volume of hydrogen. This therefore may explain the observed efficiency of manganese sulphate, as compared with sulphuric acid, in preventing coalescence.

As the concentration of the solution is increased, this equilibrium surface tension will be attained even more slowly owing to the increased tendency for counter-diffusion of the cations towards the surface.

Effect of Sulphur Dioxide Concentration.

The manner in which the surface area is affected by the concentration of sulphur dioxide is somewhat obscure, as increasing concentrations may greatly affect the surface tension, viscosity, density and mode of coalescence of the bubbles. If, as is likely, the surface tension is reduced, an increased surface area would be expected owing to the reduced bubble diameter. This has already been noted at low acid.
acid concentrations during reaction (Graph 28). However, in view of the reduction of surface area at higher acid concentrations and sulphur dioxide contents, and the lack of the above information no conclusions may be drawn. In addition, the marked heat effect accompanying the absorption of sulphur dioxide and its oxidation will still further complicate the situation.

Effect of Gas Rate.

Increasing gas rate, as has been observed previously, produces an approximately linear increase in surface area (Graph 29 and 30), except at very high gas rates and acid concentrations (Graph 30). This increase in surface area would be expected in view of the increased rate of bubble growth and consequent increased liquid momentum effect (see discussion on 'Effect of Sulphuric Acid concentration'). The reduction in surface area at high gas rates and acid concentrations would appear to be due to some change in the method whereby the bubbles become detached from the sinter, possibly due to some reduction in the stability of the bubble 'cone' due to the high liquid momentum effect and the reduction in coalescence, so that bubble growth becomes less restricted.
Effect of Temperature.

The overall effect of temperature on the surface area, both during reaction and in 20 gm./l. sulphuric acid was to produce an accelerated increase with rising temperature (Graphs 18c and 24a). The bubble diameter during reaction is however decreased (Graph 18a, fig. 11), while that in the sulphuric acid solution is increased (Graph 24a, fig. 13).

These measured bubble diameters cannot be compared, as the inlet gas rate varied with temperature owing to presaturation of the constant inlet dry gas stream to the column temperature. The continued reduction in diameter with increasing temperature in the case of reaction, and the continued increase in the sulphuric acid solution, would appear to indicate that the large bubbles are exceedingly unstable, probably due to the low surface tension at the elevated temperatures, and that a further reduction in the surface tension, as for example by sulphur dioxide or perhaps due to the heat of reaction, will cause a marked reduction in diameter.
The Rate of Absorption of Oxygen from Bubble Swarms.

In the foregoing discussion, it was concluded that the rate of oxidation of sulphur dioxide in manganese sulphate solutions is, in general, controlled by the rate of absorption of oxygen into solutions containing a very low concentration of oxygen, i.e. that the overall rate of the process tends to become limited by the initial absorption rate of oxygen. Consequently, measurements were carried out to determine the initial absorption rate of oxygen into solutions of sulphuric acid, as given in Part III. These results will now be compared with the reaction measurements, and also with the theoretical values predicted by the equations of Higbie (12) and Trossling (28) (equations 12 and 34).

Effect of Temperature.

During the measurement of the initial absorption rate, it was found that this rate was apparently proportional to the partial pressure of oxygen in the gas stream. Graph 32 therefore compares the actual absorption rate during the reaction with the above values corrected to the partial pressures existing during the reaction. (see tables 25, 26 and 27). It is obvious that there is a wide discrepancy between these values.

Graphs 33 and 34 show the variation of $K_L$, the overall liquid
GRAPH No. 32

ABSORPTION RATE v TEMPERATURE IN 20gm./l. ACID AT PARTIAL PRESSURES EXISTING DURING REACTION.

(Tables 25, 26 & 27)
GRAPH No.33 (TABLE No.25)

COMPARISON OF THEORETICAL AND EXPERIMENTAL
KL VALUES FOR PHYSICAL ABSORPTION.

Higbie

Exp.

Frossling

KL \cdot 10^{-2} (cm./hr.)

TEMPERATURE (°C.)
Table No. 25.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>( \frac{d}{d} )</th>
<th>( \frac{d}{D} )</th>
<th>( \frac{d}{D} )</th>
<th>( \frac{d}{D} )</th>
<th>( \frac{d}{D} )</th>
<th>( \frac{d}{D} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.0708</td>
<td>41.70</td>
<td>1.959</td>
<td>1.457</td>
<td>6.72</td>
<td>56.06</td>
</tr>
<tr>
<td>40</td>
<td>0.0728</td>
<td>24.10</td>
<td>0.932</td>
<td>3.06</td>
<td>16.18</td>
<td>55.06</td>
</tr>
<tr>
<td>60</td>
<td>0.0805</td>
<td>26.05</td>
<td>0.959</td>
<td>3.80</td>
<td>19.95</td>
<td>53.76</td>
</tr>
<tr>
<td>80</td>
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<td>28.58</td>
<td>1.35</td>
<td>5.15</td>
<td>22.54</td>
<td>52.21</td>
</tr>
<tr>
<td>100</td>
<td>0.1300</td>
<td>33.81</td>
<td>1.35</td>
<td>6.0</td>
<td>27.58</td>
<td>55.55</td>
</tr>
</tbody>
</table>

Comparison of Experimental Values of \( K \), the Liquid Film Coefficient, with Values Calculated from the Equations of Higbie and Frossling for Oxygen Absorption in 20%, Ca. H₂SO₄.

- \( d = \) mean bubble diameter, (cm.);
- \( \frac{d}{D} = \) absorption rate of oxygen, (gm. moles, sec.⁻¹, cm.⁻²);
- \( \frac{d}{D} = \) mean bubble velocity, (cm./sec.);
- \( \frac{d}{D} = \) oxygen partial pressure, (atm.);
- \( D = \) diffusion coefficient, (cm.²/sec.).

Frossling's equation expressed in the form:

\[
K = 2.0 (1 + 0.276 \frac{\rho_1}{\rho_2})
\]

where \( \rho_1, \rho_2 = \) equilibrium oxygen concentration, (gm. moles, cm.⁻³); \( K = \) absorption rate of oxygen, (gm. moles, sec.⁻¹, cm.⁻²).
liquid film coefficient, with temperature, at an acid concentration of 20 gm./l. during the physical absorption of oxygen and during reaction, together with values calculated from the equations of Higbie and Frossling. The data for the physical absorption are given in table 25, and the values of $K_L$ during reaction are interpolated from those given in tables 26 and 27. Bubble velocities and contact times were obtained from the experimental data given in Part II, as exemplified in table 24; diffusivities were estimated from the nomograph of Othmer, and solubilities and viscosities are given in Appendix 2. It was assumed that the above data were applicable during reaction, but it is appreciated that the values for the diffusion coefficients, in particular, may be extremely inaccurate.

In Graph 33, the values of $K_L$ for physical absorption are seen to agree reasonably well with those predicted for circulating bubbles from Higbie's equation, at the lower temperatures, but at temperatures greater than 55°C, the values fall appreciably, apparently tending towards Frossling's equation for non-circulating spheres.

While it is appreciated that a bubble swarm is likely to consist of bubbles possessing varying degrees of circulation, ranging from fully developed to static, the above would appear to /
GRAPH No.34 (TABLES No. 26 & 27)

COMPARISON OF THEORETICAL AND EXPERIMENTAL

$K_L$ VALUES FOR OXYGEN DURING REACTION

- Higbie
- Exp.

$K_L \cdot 10^{-2}$ (cm./hr.)

TEMPERATURE ($^\circ$C.)
Table No. 26.

Comparison of Experimental Values of $K_L$, the Liquid Film Coefficient, with Values Calculated from the Equations of Higbie and Frossling during Reaction at 60°C.

<table>
<thead>
<tr>
<th>$\text{H}_2\text{SO}_4$ Conc. gm./l</th>
<th>$d$ cm.</th>
<th>$U$ cm./sec.</th>
<th>$P_1 \times 10^8$ atm.</th>
<th>$P_0_2 \times 10^6$</th>
<th>$c_e \times 10^6$</th>
<th>$D \times 10^5$</th>
<th>$N_0.5 \Re$</th>
<th>$N_0.33 \Sc$</th>
<th>$A$</th>
<th>$K_L$ (cm/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.75</td>
<td>0.1016</td>
<td>46.68</td>
<td>3.76</td>
<td>0.258</td>
<td>0.212</td>
<td>4.50</td>
<td>31.52</td>
<td>4.66</td>
<td>83.06</td>
<td>638</td>
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<tr>
<td>13.35</td>
<td>0.0920</td>
<td>35.42</td>
<td>3.72</td>
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<td>0.206</td>
<td>4.45</td>
<td>25.90</td>
<td>4.71</td>
<td>69.34</td>
<td>650</td>
</tr>
<tr>
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<td>0.200</td>
<td>4.40</td>
<td>20.72</td>
<td>4.75</td>
<td>56.34</td>
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<td>0.259</td>
<td>0.194</td>
<td>4.35</td>
<td>18.58</td>
<td>4.79</td>
<td>51.14</td>
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<td>4.30</td>
<td>18.31</td>
<td>4.82</td>
<td>50.72</td>
<td>673</td>
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</table>

Exp. | Fros. | Hig.
Comparison of Experimental Values of $K_L$, the Liquid Film Coefficient, with Values Calculated from the Equations of Higbie and Frossling during Reaction at Different Temperatures.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$H_2SO_4$ Conc. gm./l.</th>
<th>d cm.</th>
<th>$U$ cm./sec.</th>
<th>$R_1$ X 10^8</th>
<th>$P_0_2$ atm.</th>
<th>$c_e$ X 10^6</th>
<th>D $X 10^5$</th>
<th>$N_0.5$</th>
<th>$N_0.33$</th>
<th>A</th>
<th>$K_L$ (cm./hr.)</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>Exp.</td>
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<td>0.331</td>
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</tr>
<tr>
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<td>33.45</td>
<td>3.70</td>
<td>0.308</td>
<td>0.311</td>
<td>2.27</td>
<td>16.89</td>
<td>7.08</td>
<td>68.00</td>
<td>428</td>
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<tr>
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<td>4.74</td>
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<td>773</td>
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<td>31.31</td>
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<td>0.173</td>
<td>0.123</td>
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<td>20.67</td>
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<td>46.58</td>
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<td>0.106</td>
<td>5.3</td>
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<td>47.74</td>
<td>591</td>
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<td>43.70</td>
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<td>0.101</td>
<td>0.067</td>
<td>6.3</td>
<td>24.74</td>
<td>3.87</td>
<td>54.64</td>
<td>586</td>
</tr>
</tbody>
</table>
to indicate that some reduction in the mean circulatory conditions of bubbles within the swarm might occur at the higher temperatures. This effect will be a compromise between the increased bubble diameter and velocity (table 25) and the decreased surface tension tending to favour circulation, and the reduced viscosity tending to reduce circulation. This apparent reduction in the degree of circulation would therefore appear to indicate that the viscous forces on the bubble decrease more rapidly than do the surface tension forces, with increasing temperature.

During reaction, the experimental values of $K_L$ once again show good agreement with Higbie's equation at lower temperatures, but in contrast to those during physical absorption, increase more rapidly with temperature than do the values predicted for circulating bubbles, and are generally greater than those values. The reduction in the values of $K_L$ at the higher temperatures is somewhat uncertain owing to the doubtful accuracy of the surface area measurements in this region (fig. 11). At all temperatures, however, the values are greatly in excess of those predicted for non-circulating spheres.

The effect of the heat of reaction on the surface temperature was examined by assuming the bubbles to be surrounded by a film of thickness 0.004 cm, whence it was found
GRAPH No.35 (TABLE No.26)

COMPARISON OF THEORETICAL AND EXPERIMENTAL

KL VALUES DURING REACTION AT 60°C.

GRAPH No.36 (TABLE No.28)

COMPARISON OF THEORETICAL AND EXPERIMENTAL

KL VALUES FOR THE PHYSICAL ABSORPTION OF OXYGEN AT 60°C.
Table No. 28.

Comparison of Experimental Values of $k_L$, the Liquid Film Coefficient, with Values Calculated from the Equations of Higbie and Frossling during Absorption in Solutions of Sulphuric Acid at 60°C.

<table>
<thead>
<tr>
<th>$H_2SO_4$ Conc. gm./l.</th>
<th>d cm.</th>
<th>U cm./sec.</th>
<th>$P_1$ x 10^6</th>
<th>$P_0$ atm.</th>
<th>$c_e$ x 10^6</th>
<th>$b$ x 10^5</th>
<th>$n_{0.5}$</th>
<th>$n_{0.33}$</th>
<th>$A$</th>
<th>$K_L$ (cm./hr.)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.0813</td>
<td>25.05</td>
<td>6.52</td>
<td>0.805</td>
<td>0.629</td>
<td>4.4</td>
<td>20.33</td>
<td>4.74</td>
<td>55.20</td>
<td>373</td>
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<td>59.7</td>
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<td>6.45</td>
<td>0.808</td>
<td>0.583</td>
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<td>4.98</td>
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<td>0.812</td>
<td>0.543</td>
<td>4.0</td>
<td>18.13</td>
<td>5.18</td>
<td>53.82</td>
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<td>145.0</td>
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<td>19.77</td>
<td>6.30</td>
<td>0.816</td>
<td>0.502</td>
<td>3.8</td>
<td>16.62</td>
<td>5.34</td>
<td>50.96</td>
<td>452</td>
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</table>
that a temperature drop of 0.02°C. across the film was sufficient to provide the required rate of heat transfer. This factor would therefore appear to be relatively insignificant compared with the probable inaccuracies in the estimated diffusion coefficients.

Thus it may be concluded that both the reaction and absorption measurements are in reasonably good agreement with the theoretical values for circulating bubbles, although in the case of physical absorption there is some possibility of a reduction in the degree of circulation with increasing temperature. The difference between the absorption rates with and without reaction would appear from the foregoing to be due principally to the different hydrodynamic conditions existing in the two systems, owing to the presence of manganese sulphate and sulphur dioxide during reaction.

**Effect of Acid Concentration.**

In Graphs 35 and 36 (tables 26 and 28) are shown the variation of $K_T$ with acid concentration during reaction and during absorption, together with values predicted from the equations of Higbie and Frossling. The values of $K_T$ during reaction are approximately constant and greater than those for circulating bubbles, whereas in the absence of reaction, the experimental /
The experimental values of $K_L$ found in this work are compared in Table 29 with those reported in the literature. While there is a great variation in the reported values, the results for the present work are of a similar order of magnitude as the reported values for bubble swarms.
<table>
<thead>
<tr>
<th>Ref.</th>
<th>Conditions</th>
<th>Temp.</th>
<th>$c_0$ gm.mole</th>
<th>Ab. Rate gm.mole/sec.</th>
<th>$K_L$ cm./hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>99</td>
<td>directly into water stirred at 200 r.p.m.</td>
<td>25</td>
<td>1.2</td>
<td>1.1</td>
<td>33</td>
</tr>
<tr>
<td>99</td>
<td>solution of $K_2SO_4$, with suspended $Fe(OH)_2$, stirred at 4000 r.p.m.</td>
<td>25</td>
<td>0.8</td>
<td>0.1</td>
<td>5</td>
</tr>
<tr>
<td>99</td>
<td>directly into water shaken 400 times/min.</td>
<td>25</td>
<td>1.2</td>
<td>2.8</td>
<td>84</td>
</tr>
<tr>
<td>91</td>
<td>directly from sides of 15 c.c. bubbles</td>
<td>25</td>
<td>1.1</td>
<td>1.1</td>
<td>36</td>
</tr>
<tr>
<td>100</td>
<td>solution of $K_2SO_4$, with suspended $Fe(OH)_2$, stirred at 4000 r.p.m.</td>
<td></td>
<td></td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>solutions of $Na_2SO_3$ stirred at 4000 r.p.m.</td>
<td>25</td>
<td>1.17</td>
<td>1.18</td>
<td>36</td>
</tr>
<tr>
<td>9</td>
<td>directly from 0.1 cm. bubbles (extrapolated)</td>
<td>17</td>
<td>-</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>101</td>
<td>0.24 cm. diameter bubbles</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>85</td>
</tr>
<tr>
<td>102</td>
<td>bubble swarms</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>178</td>
</tr>
<tr>
<td>103</td>
<td>bubble swarms from plates of varying porosity</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>182-348</td>
</tr>
<tr>
<td>this work</td>
<td>bubble swarms during reaction in 20 gm./l. $H_2SO_4$</td>
<td>25</td>
<td>0.36</td>
<td>4.04</td>
<td>400</td>
</tr>
<tr>
<td>this work</td>
<td>bubble swarms in 20 gm./l. $H_2SO_4$, without reaction</td>
<td>25</td>
<td>1.15</td>
<td>10.2</td>
<td>320</td>
</tr>
</tbody>
</table>
Correlation of Results.

The results of an attempt to correlate the experimental data in a manner similar to that employed by Frossling(28), i.e. by the use of dimensionless groups, are shown in Graph 37 (table 30). This method of correlation relates the mass transfer coefficient with the flow conditions and diffusional properties of the phase into which transfer occurs.

While the absorption rate during reaction, between the temperatures 30 and 70°C, is reasonably well represented by the equation:

\[ \frac{N}{N_{M}} = 50 + 2.6 N_{Re}^{0.5} N_{Sc}^{0.33} \]  \hspace{1cm} (68)

no similar relation is shown by the physical absorption measurements.

However, in view of the very small range of Reynolds and Schmidt groups encountered in the present work, no conclusion may be drawn as to the reliability of the above type of correlation.
GRAPH No. 37 (TABLE No.30)

ATTEMPTED CORRELATION OF RESULTS BY NUSSELT, SCHMIDT
AND REYNOLDS GROUPS

\[ \frac{N_{Nu}}{N_{Re}^{0.5} N_{Sc}^{0.33}} \]

Reaction

Physical Absorption

80°C

90°C
Table No. 30.

Correlation of Results by Nusselt, Schmidt and Reynolds Groups.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>H₂SO₄ Conc. gm./l.</th>
<th>Kₐ cm./hr.</th>
<th>Diam. cm.</th>
<th>D x 10⁵ cm²/sec.</th>
<th>Nu</th>
<th>Re 0.5</th>
<th>Re 0.33</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Physical Absorption</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>20.4</td>
<td>331</td>
<td>0.0708</td>
<td>2.56</td>
<td>254.4</td>
<td>412.7</td>
<td>152.2</td>
</tr>
<tr>
<td>1.0</td>
<td>20.4</td>
<td>318</td>
<td>0.0728</td>
<td>3.06</td>
<td>230.0</td>
<td>388.8</td>
<td>133.0</td>
</tr>
<tr>
<td>50</td>
<td>20.4</td>
<td>279</td>
<td>0.0752</td>
<td>3.80</td>
<td>196.8</td>
<td>314.5</td>
<td>111.2</td>
</tr>
<tr>
<td>60</td>
<td>20.4</td>
<td>268</td>
<td>0.0782</td>
<td>4.4</td>
<td>176.8</td>
<td>282.9</td>
<td>106.2</td>
</tr>
<tr>
<td>70</td>
<td>20.4</td>
<td>259</td>
<td>0.0812</td>
<td>4.9</td>
<td>152.7</td>
<td>239.9</td>
<td>97.2</td>
</tr>
<tr>
<td>80</td>
<td>20.4</td>
<td>250</td>
<td>0.0842</td>
<td>5.2</td>
<td>138.9</td>
<td>202.9</td>
<td>91.6</td>
</tr>
<tr>
<td>90</td>
<td>20.4</td>
<td>230</td>
<td>0.1028</td>
<td>6.0</td>
<td>120.4</td>
<td>165.9</td>
<td>89.0</td>
</tr>
<tr>
<td>(b) Reaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>9.96</td>
<td>121</td>
<td>0.0918</td>
<td>2.60</td>
<td>112.7</td>
<td>174.9</td>
<td>77.9</td>
</tr>
<tr>
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<td>143</td>
<td>0.0814</td>
<td>2.46</td>
<td>178.8</td>
<td>244.5</td>
<td>89.0</td>
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<td>138.3</td>
<td>199.1</td>
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</tr>
<tr>
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<td>242</td>
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<td>2.08</td>
<td>124.2</td>
<td>174.9</td>
<td>89.0</td>
</tr>
<tr>
<td>4.0</td>
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<td>287</td>
<td>0.0954</td>
<td>3.07</td>
<td>149.1</td>
<td>214.5</td>
<td>88.3</td>
</tr>
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<td>4.0</td>
<td>62.47</td>
<td>351</td>
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<td>324.5</td>
<td>464.5</td>
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<td>2.67</td>
<td>352.7</td>
<td>499.0</td>
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<td>3.82</td>
<td>382.9</td>
<td>532.9</td>
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</tr>
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<td>580</td>
<td>0.0653</td>
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<td>305.7</td>
<td>445.0</td>
<td>96.9</td>
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<td>542</td>
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<td>334.2</td>
<td>474.2</td>
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<td>548</td>
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<td>400.0</td>
<td>540.0</td>
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<td>373.5</td>
<td>423.5</td>
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<td>300.2</td>
<td>350.2</td>
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<td>317.9</td>
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<td>271.2</td>
<td>321.2</td>
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</tr>
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<td>323.0</td>
<td>88.7</td>
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<td>289.2</td>
<td>339.2</td>
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</tr>
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<td>301.0</td>
<td>351.0</td>
<td>90.3</td>
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<td>712</td>
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<td>290.1</td>
<td>340.1</td>
<td>101.7</td>
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<td>307.7</td>
<td>88.8</td>
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<td>773</td>
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<td>4.45</td>
<td>287.5</td>
<td>337.5</td>
<td>91.1</td>
</tr>
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<td>18.95</td>
<td>696</td>
<td>0.0511</td>
<td>6.0</td>
<td>158.4</td>
<td>208.4</td>
<td>80.8</td>
</tr>
<tr>
<td>80</td>
<td>111.83</td>
<td>591</td>
<td>0.0511</td>
<td>5.3</td>
<td>158.2</td>
<td>208.2</td>
<td>82.8</td>
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<td>172.9</td>
<td>92.6</td>
</tr>
<tr>
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<td>41.63</td>
<td>586</td>
<td>0.0508</td>
<td>6.3</td>
<td>131.2</td>
<td>181.2</td>
<td>95.8</td>
</tr>
</tbody>
</table>
Comparison of Results with the Theory of Miyamoto.

Miyamoto (10), who derived equation (23) representing the rate of solution of a gas in a liquid, concluded from his work on the oxidation of sodium sulphite solutions that the concentration of dissolved oxygen in the surface layer was maintained at zero by the reaction. This is most unlikely, as depletion of sodium sulphite in the surface would be expected despite the high rate of stirring employed. Nevertheless, on the basis of the rate of oxidation being the rate of absorption of oxygen at its maximum value, Miyamoto concluded that the minimum molecular velocity $u_o$ for penetration of the liquid surface by a gas molecule remained constant over the temperature range 15 to 35°C.

In contrast, the present work indicates (table 31) that the velocity $u_o$ increases slowly with temperature and is at all temperatures approximately 3.1 times greater than the root mean square velocity of the gas molecules. This value compares well with the factor of 3.4 obtained by Miyamoto, despite the ten-fold difference in absorption rates shown in table 29. In addition, the values of $\beta$ indicate that only about one molecule in every $10^6$ - $10^7$ striking the surface is able to penetrate into the liquid.
Table No. 31.
Calculation of the Minimum Velocity for Absorption and Desorption of a Molecule of Oxygen in 20 gm./l. H$_2$SO$_4$ in the Absence and in the Presence of Reaction.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$R_1$ gm.mole/sec. $^{-1}$ cm. 10$^3$</th>
<th>$P_{O_2}$ atm.</th>
<th>$\beta \cdot 10^7$</th>
<th>$u_o \cdot 10^{-5}$ cm./sec.</th>
<th>$\sqrt{P_i^2 \cdot 10^{-4}}$ cm./sec.</th>
<th>$c_e \cdot 10^4$ gm.mole/l.</th>
<th>$u'_o \cdot 10^{-5}$ cm./sec.</th>
<th>$\beta' \cdot 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>9.73</td>
<td>0.958</td>
<td>2.100</td>
<td>1.553</td>
<td>4.861</td>
<td>10.59</td>
<td>1.355</td>
<td>0.875</td>
</tr>
<tr>
<td>40</td>
<td>8.63</td>
<td>0.928</td>
<td>1.000</td>
<td>1.581</td>
<td>4.920</td>
<td>8.92</td>
<td>1.377</td>
<td>0.865</td>
</tr>
<tr>
<td>50</td>
<td>7.50</td>
<td>0.879</td>
<td>1.957</td>
<td>1.611</td>
<td>5.018</td>
<td>7.93</td>
<td>1.401</td>
<td>0.819</td>
</tr>
<tr>
<td>60</td>
<td>6.26</td>
<td>0.805</td>
<td>1.871</td>
<td>1.640</td>
<td>5.095</td>
<td>6.29</td>
<td>1.422</td>
<td>0.834</td>
</tr>
<tr>
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<td>0.691</td>
<td>1.628</td>
<td>1.669</td>
<td>5.171</td>
<td>5.07</td>
<td>1.445</td>
<td>0.844</td>
</tr>
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<td>80</td>
<td>5.10</td>
<td>0.540</td>
<td>1.378</td>
<td>1.702</td>
<td>5.246</td>
<td>3.83</td>
<td>1.478</td>
<td>0.694</td>
</tr>
<tr>
<td>90</td>
<td>4.35</td>
<td>0.303</td>
<td>1.085</td>
<td>1.740</td>
<td>5.320</td>
<td>2.11</td>
<td>1.516</td>
<td>0.515</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$R_1$ gm.mole/sec. $^{-1}$ cm. 10$^3$</th>
<th>$P_{O_2}$ atm.</th>
<th>$\beta \cdot 10^7$</th>
<th>$u_o \cdot 10^{-5}$ cm./sec.</th>
<th>$\sqrt{P_i^2 \cdot 10^{-4}}$ cm./sec.</th>
<th>$c_e \cdot 10^4$ gm.mole/l.</th>
<th>$u'_o \cdot 10^{-5}$ cm./sec.</th>
<th>$\beta' \cdot 10^5$</th>
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</thead>
<tbody>
<tr>
<td>30</td>
<td>3.99</td>
<td>0.309</td>
<td>2.874</td>
<td>1.520</td>
<td>4.861</td>
<td>3.413</td>
<td>1.355</td>
<td>1.047</td>
</tr>
<tr>
<td>40</td>
<td>3.89</td>
<td>0.299</td>
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<td>1.564</td>
<td>4.920</td>
<td>2.875</td>
<td>1.376</td>
<td>1.197</td>
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<td>1.588</td>
<td>5.018</td>
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<td>1.397</td>
<td>1.321</td>
</tr>
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<td>3.329</td>
<td>1.606</td>
<td>5.095</td>
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<td>1.394</td>
<td>1.574</td>
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<td>0.222</td>
<td>3.626</td>
<td>1.626</td>
<td>5.171</td>
<td>1.625</td>
<td>1.397</td>
<td>1.750</td>
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<td>2.974</td>
<td>1.661</td>
<td>5.246</td>
<td>1.224</td>
<td>1.431</td>
<td>1.429</td>
</tr>
<tr>
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<td>1.74</td>
<td>0.097</td>
<td>2.650</td>
<td>1.686</td>
<td>5.320</td>
<td>0.678</td>
<td>1.452</td>
<td>1.400</td>
</tr>
</tbody>
</table>

\[
\beta' = \sqrt{\frac{2 \pi M R T}{p}} R_i ; \quad u'_o = \sqrt{\frac{2 R T \ln \beta}{M}} \text{ cm./sec.} ; \quad \sqrt{c^2} = \sqrt{\frac{3 R T}{M}} \text{ cm./sec.} ;
\]

\[
u_o^2 - u'_o^2 = -\frac{2 R T}{M} \ln(c_e R T/1000 p) ; \quad \beta' = \frac{M u_o^2}{2 R T}.
\]
APPENDIX

1. Methods of Analysis.

2. Physical Data.
Methods of Analysis.

(1) **Determination of Manganese in Catalyst.**

0.15 gms. of the manganese sulphate \( \text{MnSO}_4 \cdot 5\text{H}_2\text{O} \) obtained from May & Baker, were dissolved in a cooled mixture of 100 ml. water and 20 ml. nitric acid, and shaken for one minute. The solution was then diluted with 100 ml. water and filtered through an asbestos Gooch crucible. After washing with nitric acid diluted with 33 volumes of water, the filtrate and washings were combined with 50 ml. \( \text{N/10} \) ferrous ammonium sulphate and back titrated with potassium permanganate.

The analysis revealed the catalyst to contain 22.98% manganese.

(2) **Determination of Sulphur Dioxide.**

20 c.c. of the cooled reactor solution was rapidly transferred by pipette into a known excess volume of standard \( \text{N/10} \) iodine solution, the excess iodine being determined by titration with sodium thiosulphate in the normal manner.

(3) **Determination of Sulphuric Acid.**

A stream of water-saturated nitrogen was bubbled through 200 ml. of the reactor solution until tests revealed complete absence of sulphur dioxide. 20 ml. of the resulting solution were diluted to one litre. 25 ml. portions of this solution /
solution were then titrated with N/10 sodium hydroxide using methyl orange indicator.

(4) Determination of Dithionate.

The method employed was that of Bassett and Henry (71), in which the filtrate and washings from the normal gravimetric estimation of sulphates, by barium sulphate precipitation, were treated with potassium carbonate in order to convert any dithionate present to the potassium salt, after which the solution was slowly evaporated to dryness. By heating the residue in a hard glass tube in a stream of nitrogen, any potassium dithionate present is decomposed giving off sulphur dioxide which is carried by the nitrogen into a solution of iodine, where it is absorbed and is estimated by back-titration with N/10 thiosulphate. In the present work, no sulphur dioxide was found to be absorbed by the iodine, thus indicating the absence of dithionate.
SURFACE TENSIONS OF AQUEOUS SULPHURIC ACID SOLUTIONS

SURFACE TENSION (dyne/cm.)

H₂SO₄ CONCENTRATION (wt.%)

0° C
25°
30°
50°
60°
(extrapolated)

(96)
VISCOSITY OF AQUEOUS SULPHURIC ACID SOLUTIONS

(Extrapolated from Int. Crit. Tab. 5, 12, (1933)
SOLUBILITY DATA FOR OXYGEN IN AQUEOUS H$_2$SO$_4$, AT AN OXYGEN PARTIAL PRESSURE OF 760 mm.

(Extrapolated from: Seldell, A., Solubility of Inorganic Compounds, I, 1355, 1940.)
NOMENCLATURE
Nomenclature.

\( A' \) = surface area of solid.

\( A \) = cross section area of column.

\( b \) = major half axis of ellipse.

\( c \) = minor half axis of ellipse.

\( c_x \) = liquid phase concentration, where \( x \) may be \( s, i, o, e, \) or \( l \) (as defined in text.)

\( c_w \) = drag coefficient.

\( d \) = bubble diameter.

\( D \) = diffusion coefficient in liquid phase.

\( D \) = tube diameter.

\( D' \) = orifice diameter.

\( D' \) = absorption rate (molecules/sec.).

\( D_0 \) = absorption rate as above with zero liquid concentration.

\( e \) = base of natural logarithm.

\( e \) = eccentricity of ellipse.

\( g \) = gravitational constant.

\( H \) = Henry's law constant.

\( k_L, k_G \) = film transfer coefficients.

\( k_S \) = surface transfer coefficient.

\( K_L, K_G \) = overall transfer coefficients.

\( l \) = initial height of column.

\( l_0 \) = extended height of column.

\( M \) /
$M =$ molecular weight of solute.

$n =$ moles of absorbable gas.

$N =$ Avogadro's constant.

$N'$ = rate at which gas molecules collide with unit area of liquid phase.

$N'' =$ rate at which gas molecules enter unit area of liquid phase.

$N''' =$ rate at which gas molecules leave unit area of liquid phase.

$p_x =$ partial pressure of gas, where $x$ may be $i$, $o$, or $e$ (as defined in text.)

$p_o =$ pressure component due to surface tension.

$p_h =$ hydrostatic pressure component.

$p_s =$ hydrodynamic pressure component.

$p_o =$ pressure on surface of liquid.

$p_g, P =$ total pressure in bubble.

$Q =$ total gas transferred.

$R =$ gas transfer rate per unit area.

$R'$ = gas constant.

$R =$ bubble radius.

$r =$ first-order velocity constant.

$r =$ orifice radius.

$s =$ rate of surface renewal.

$S =$ surface area.

$t =$ time.

$T =$ absolute temperature.

$T' =$
$T' = \text{time of oscillation of falling sphere.}$

$u_o = \text{minimum molecular velocity for penetration of liquid.}$

$u_o' = \text{minimum molecular velocity for escape from liquid.}$

$U = \text{bubble velocity.}$

$V = \text{flow velocity along a streamline.}$

$V = \text{bubble volume.}$

$V' = \text{volume of solution.}$

$V_g = \text{volume flowrate of gas.}$

$W = \text{fluid frictional resistance.}$

$x = \text{distance from surface.}$

\[ t(e), f(e), j(e), T(e) = \text{functions of } e, \text{ the ellipticity} \]

$N_{Re} = \text{Reynolds number } = \frac{d.U.P}{\chi}.$

$N_{Sc} = \text{Schmidt number } = \frac{\chi}{(\rho.D)}.$

$N_{Nu} = \text{Nusselt number } = \frac{K.d}{D}.$

$s = \text{equivalent film thickness.}$

$\Theta = \text{contact time between phases.}$

$\phi = \text{surface age distribution function.}$

$\beta, \beta' = \text{accommodation coefficients for molecules entering and leaving the liquid.}$

$\gamma = \text{absorption rate per unit area of stagnant liquid surface.}$

$\alpha = \text{}/$
\( \alpha \) = angle of separation of forward flow

\( \rho \) = density of liquid.

\( \gamma \) = viscosity of liquid.

\( \sigma \) = surface tension.

\( \lambda \) = function relating interaction of bubbles.
Bibliography.

(1) Noyes, A.A. & Whitney W.R.

(2) Nernst, W.
    ibid. 47, 52, (1904).

(3) Whitman, W.G.
    Lewis, W.K. & Whitman, W.G.

(4) Higbie, R.

(5) Danckwerts, P.V.

(6) Kishinevskii, M.Kh.

(7) Lynn, S., Straatemeier, J.R., & Kramers, H.

(8) Groothuis, H. & Kramers, H.
    ibid. 4, 17, (1955)

(9) Garner, F.H. & Hammerton, D.

(10) Miyamoto, S. & Nakata, A.

(11) Miyamoto, S.
    ibid. 7, 8, (1932)

(12) Danckwerts, P.V. & Kennedy, A.M.

(13) /
(13) Drickamer, H.C. & Sinfelt, J.H.

(14) Lindland, K.P. & Terjesen, S.G.

(15) Garner, F.H. & Hale, A.E.
    ibid. 2, 157, (1953).

(16) Emmert, R.E. & Pigford, R.L.

(17) Peaceman, D.W.

(18) Danckwerts, P.V.
    Research, 2, 494, (1949).

(19) Sherwood, T.K. & Pigford, R.L.

(20) Danckwerts, P.V. & Kennedy, A.M.

(21) Hoftyzer, P.J. & Van Krevelen, D.W.

(22) Garner, F.H. & Grafton, R.W.

(23) Hadamard
    Comptes Rendus, 52, 1735, (1911).

(24) Boussinesq, L.J.

(25) Garner, F.H.

(26) Garner, F.H. & Skelland, A.H.P.

(27) /
(27) Pattie, R.E.

(28) Frossling, N.

(29) Garner, F.H. & Hammerton, D.

(30) Chilton, T.H. & Colburn, A.P.

(31) Shulman, H.L. & Mølstad, M.C.
    ibid. 42, 1058, (1950)

(32) Coppock, P.D. & Mciklejohn, G.T.

(33) Geddes, R.I.

(34) Aikman, H.R.

(35) Macrae, R.

(36) Danckwerts, P.V.

(37) Sherwood, T.K.

(38) Maier, C.G.

(39) Datta, R.I., Napier, D.H. & Newitt, D.M.

(40) van Krevelen, D.W. & Hoptyzer, P.J.

(401) /
(41) Eversole, W.G., Wagner, G.H., & Stackhouse, E. 

(42) Dixon, B.E. & Russell, A.A.W. 

(43) Schnurmann, R. 

(44) Halberstadt, S., & Prausnitz, P.H. 

(45) Bond, W.M. 
Phil. Mag. 4, 339, (1927).
Bond, W.M. & Newton, D.A. 
ibid. 5, 794, (1928).

(46) Allen, H.S. 
Phil. Mag., 50, 323, (1900).

(47) Siemes, W. 

(48) Miyagi, O. 
Phil. Mag., 50, Ser.6, 112, (1925).

(49) Peebles, F.N., & Garber, H.J. 

(50) Schmiedel, J. 
Physik Z., 22, 593, (1928)

(51) Lamb, H. 
Lehrbuch der Hydrodynamik, Leipsig, p.166, (1931).

(52) Davies, R.M. & Taylor, C.I. 

(53) Bryn, T. 
(54) Luchsinger, W.
    Koll. Z., 84, 180, (1937).

(55) Barr, G.

(56) Stimson, M. & Jeffrey, C.E.

(57) O'Brien, M.F. & Gosline, J.E.

(58) Owens, J.S.

(59) McAdams, W.H.

(60) Verschoor, H.

(61) Eggleston, B.C., Evans, D.F. & Richards, R.E.

(62) Seeliger, R.

(63) Foulk, C.W. & Miller, J.N.

(64) Klinkenberg, A. & Mcq, H.H.

(65) Kaiszling, F.

(66) Leaver, E.S.
    U.S. 1,477,965, (1924).

(67) Whartman, F.S. & Keyes, H.E.

(68) /
(68) Ralston, O.C.

(69) Back, A.E., Ravitz, S.F. & Tame, K.E.
 Bur. of Mines, Repts. of Investigations,
 No. 4931, (1952).

(70) Ephraim, F.
 Inorganic Chemistry, Gurney & Jackson, p. 570
 (1948).

(71) Bassett, H. & Henry, A.J.

(72) Johnstone, H.F.

(73) Johnstone H.F.
 Steam Engineer, 1, 153, 208, (1932).

(74) Johnstone, H.F.
 Combustion, 5, 19, (1933).

(75) Copson, R.L. & Payne, J.W.

(76) Keyes, D.B.
 Chem. & Ind., 692, (1934).

(77) Grodzovskii, M.K.
 Izvestiya Teplotekh. Inst., No. 4, 22, (1933).

(78) Kashtanov, L.I. & Ruizhov, V.P.

(79) Kashtanov, L.I. & Ruizhov, V.P.
 ibid. No. 8, 43, (1935).

(80) Vasil'ev, S.S., Kashtanov, L.I., Kastorskaya, T.L. &
 Nemkova, O.G.
 Novosti Tekhniki, No. 58-9, 12, (1936).

(81) /
(81) Peisakhov, I.I.

(82) Kashtanov, I.I. & Ruzhov, V.P.

(83) Grodzovskii, N.K.

(84) Vasil'ev, S.S., Kashtanov, I.I., & Kastorskaya, T.I.

(85) Kashtanov, I.I. & Ruzhov, V.P.

(86) Kashtanov, I.I. & Ruzhov, V.P.
imibid. 6, 732, (1936).

(87) Kashtanov, I.I. & Oleshchuk, O.N.
imibid. 8, 341, (1938).

(88) Chi-Kwang Chen.

(89) Johnstone, H.E.

(90) Haller, P.

(91) Adeney, W.E. & Becker, H.C.
Phil. Mag., 32, Ser.6, 317, (1919).

(92) Ledig, P.G. & Weaver, E.R.

(93) Ledig, P.G.

(94) Goodridge, F.

(95) /
(95) Anderson, L.B. & Johnstone, H.F.

(96) Suggett, R.M., Aziz, P.M. & Wetmore, F.E.

(97) Adam, N.K.
   The Physics and Chemistry of Surfaces, C.U.P.
   p.106, (1941).

(98) Othmer, D.W.

(99) Davis, H.S. & Crandall, C.S.

(100) Becker, H.G.
   Phil. Mag., 45, 581, (1923).

(101) Scouller, W.D. & Watson, W.

(102) Holroyd, A.

(103) Philpott, J.A.
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