

MASS TRANSFER STUDIES

1 THE DISTRIBUTION OF SURFACE AGES OF THE LIQUID IN A PACKED COLUMN

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SYNOPSIS

The following expression relating the distribution of surface ages of the liquid in a packed column, $\Theta(t)$, to a number of experimentally measurable quantities (liquid-film mass-transfer coefficient, diffusivity and first-order reaction-velocity constant) has been derived for the process of gas absorption:

$$L \left[\frac{\Theta(t)}{t^{1/2}} \right] = k_L \sqrt{\frac{\pi}{D}} - 2k \frac{dk_L}{dk} \sqrt{\frac{\pi}{D}}$$

The resulting Laplace transforms have been inverted numerically using the technique of Linear Programming to obtain the surface-age distribution functions $\Theta(t)$. It is shown that the transformed functions are in very close agreement with the Danckwerts random surface-renewal model in which $\Theta(t)$ has the form se^{-st} . The values of the parameter s , the fractional rate of renewal of the liquid surface, could be related to the average residence times of the liquid on the packing. It appears that $\Theta(t)$ is affected mainly by the liquid flow-rate and is independent of both the solution viscosity and density. Experimental measurements of the liquid-film mass-transfer coefficient have been carried out in a packed column over a wide range of reaction velocities and at a number of different flow-rates for two first-order reacting systems, the hydrolysis of 1, 1-dimethoxyethane in aqueous solutions and the absorption of carbon-dioxide by sodium carbonate-sodium bicarbonate buffer solutions catalysed by arsenite ions.

INTRODUCTION

The absorption of gases by liquids is one of the basic operations in chemical engineering industry. In spite of this,

however, the methods used for designing industrial absorption equipment are still very largely empirical and of limited application. The Whitman 'two-film' theory has been widely used as a basis for designing and interpreting experiments although its concepts have never been verified. More realistic models, incorporating the concept of 'surface-renewal' and not limited by the Whitman assumption of steady-state conditions, have been suggested for the process of absorption in a packed column but these also lack experimental verification.

Using the 'surface-renewal' model, it is possible, in principle, to predict the performance of a packed column with a knowledge of (1) The rate of absorption into a stagnant liquid (since it is supposed that each element of the liquid surface absorbs gas at the same changing rate as a stagnant liquid of infinite depth, until its ultimate replacement by fresh liquid) and (2) The surface-age distribution function, $\Theta(t)$. The average rate of absorption per unit area of wetted surface is then

$$N = \int_0^{\infty} F(t) \Theta(t) dt$$

where $F(t)$ is the rate of absorption per unit area after exposure for time t .

The purpose of this work was to test the validity of the various surface-renewal models and to determine the actual form of the age distribution function. This would enable predictions of sufficient accuracy for design purposes to be made. An expression relating $\Theta(t)$ to a number of experimentally measurable quantities was derived and this was used to obtain the age distributions for the packing and flow conditions employed in the experimental work.

THEORY - GAS ABSORPTION INTO LIQUID SURFACES OF VARYING 'AGES'

Let $F(t)$ be the rate of absorption per unit area after exposure for time t and $\Theta(t)dt$ be defined as the fraction of surface with 'ages' between t and $t + dt$. Assuming that there is no gas phase resistance and that the concentration of solute at the surface remains at its equilibrium value C^* , then

$k_L(C^* - C_0) = \int_0^{\infty} F(t) \Theta(t) dt =$ Rate of absorption per unit area where k_L is the liquid-film mass-transfer coefficient

and C_0 is the bulk concentration of the solute in the liquid, assumed equal to zero.

For an irreversible first-order chemical reaction (3),

$$F(t) = C^* \sqrt{Dk} \left[\operatorname{erf} \sqrt{kt} + \frac{e^{-kt}}{\sqrt{\pi kt}} \right]$$

where D is the diffusion coefficient of the solute in the liquid and k is the velocity constant of the reaction between the solute and medium.

$$\therefore \frac{k_L}{\sqrt{Dk}} = \int_0^\infty \left[\operatorname{erf} \sqrt{kt} + \frac{e^{-kt}}{\sqrt{\pi kt}} \right] \Theta(t) dt$$

Differentiating,

$$\begin{aligned} \frac{d}{dk} \left[\frac{k_L}{\sqrt{Dk}} \right] &= \int_0^\infty \frac{-e^{-kt}}{k\sqrt{\pi t}} \Theta(t) dt \\ &= -\frac{1}{k\sqrt{\pi}} L \left[\frac{\Theta(t)}{t^{1/2}} \right] \end{aligned}$$

where L is the standard Laplace integral operator.

$$\text{i.e. } L \left[\frac{\Theta(t)}{t^{1/2}} \right] = k_L \sqrt{\frac{\pi}{D}} - 2k \sqrt{\frac{\pi}{D}} \frac{dk_L}{dk} \longrightarrow (1)$$

Properties of the Laplace Transform of $\left[\frac{\Theta(t)}{t^{1/2}} \right]$

(I) At $k=0$,

$$L \left[\frac{\Theta(t)}{t^{1/2}} \right] = (k_L)_{\text{physical}} \sqrt{\frac{\pi}{D}}$$

(II) As $k \rightarrow \infty$,

$$k_L \rightarrow \sqrt{kD}$$

and

$$\frac{dk_L}{dk} \rightarrow \frac{1}{2} \sqrt{\frac{D}{k}} \longrightarrow (2)$$

i.e.

$$L \rightarrow \sqrt{\pi k} - \sqrt{\pi k} = 0.$$

(III) Differentiating equation (1),

$$\begin{aligned} \frac{dL}{dk} &= \sqrt{\frac{\pi}{D}} \frac{dk_L}{dk} - 2\sqrt{\frac{\pi}{D}} \frac{dk_L}{dk} - 2k \sqrt{\frac{\pi}{D}} \frac{d^2k_L}{dk^2} \\ &= -\sqrt{\frac{\pi}{D}} \frac{dk_L}{dk} - 2k \sqrt{\frac{\pi}{D}} \frac{d^2k_L}{dk^2} \longrightarrow (3) \end{aligned}$$

$$\begin{aligned} \text{i.e. } \left(\frac{dL}{dk} \right)_{k=0} &= -\sqrt{\frac{\pi}{D}} \left(\frac{dk_L}{dk} \right)_{k=0} \\ &= -\sqrt{\frac{\pi}{D}} \cdot \frac{1}{C^*} \left\{ \frac{d}{dk} \left[\int_0^\infty F(t) \Theta(t) dt \right] \right\}_{k=0} \\ &= -\sqrt{\frac{\pi}{D}} \cdot \frac{1}{C^*} \left[\int_0^\infty \Theta(t) \frac{d}{dk} F(t) dt \right]_{k=0} \\ &= -\sqrt{\frac{\pi}{D}} \cdot \frac{1}{C^*} \cdot C^* \sqrt{D} \left[\int_0^\infty \Theta(t) \frac{d}{dk} \left\{ \sqrt{k} \left(\operatorname{erf} \sqrt{kt} + \frac{e^{-kt}}{\sqrt{\pi kt}} \right) \right\} dt \right]_{k=0} \\ &= -\sqrt{\pi} \left[\int_0^\infty \Theta(t) \left\{ \frac{2}{\sqrt{k}} \operatorname{erf} \sqrt{kt} \right\} dt \right]_{k=0} \\ &= -\sqrt{\pi} \left[\int_0^\infty \Theta(t) \left\{ \frac{4}{\sqrt{\pi k}} \left\{ \sqrt{kt} - \frac{1}{3} (kt)^{3/2} + \frac{1}{10} (kt)^{5/2} - \dots \right\} \right\} dt \right]_{k=0} \\ &= -\sqrt{\pi} \cdot \frac{4}{\sqrt{\pi}} \int_0^\infty \Theta(t) t^{1/2} dt, \text{ neglecting powers of } kt \text{ higher than the first} \\ &= -4 \int_0^\infty \Theta(t) t^{1/2} dt \end{aligned}$$

i.e. $\left(\frac{dL}{dk} \right)_{k=0}$ is negative and finite if $\left(\frac{dk_L}{dk} \right)_{k=0}$ or

$$\int_0^\infty \Theta(t) t^{1/2} dt \text{ is finite.}$$

IV As $k \rightarrow \infty$,

$$\begin{aligned} \frac{d^2k_L}{dk^2} &\longrightarrow \frac{1}{2} \sqrt{D} \left(-\frac{1}{2} k^{-3/2} \right) \text{ from equation (2)} \\ &= -\frac{1}{4} \sqrt{\frac{D}{k^3}} \end{aligned}$$

and, from equations (3) and (2),

$$\left(\frac{dL}{dk} \right)_{k \rightarrow \infty} \longrightarrow -\frac{1}{2} \sqrt{\frac{\pi}{k}} + \frac{1}{2} \sqrt{\frac{\pi}{k}} = 0.$$

$L \left[\frac{\Theta(t)}{t^{1/2}} \right]$ therefore has the value of $\left[k_L \right]_{\text{physical}} \sqrt{\frac{\pi}{D}}$

when the reaction velocity constant is zero (i.e. for physical absorption) and would be expected to decrease monotonically to zero as k tends to infinity.

Equation (1) is an expression for the Laplace transform of $\frac{\Theta(t)}{t^{1/2}}$ in terms of the liquid-film mass-transfer coefficient, diffusivity and reaction-rate constant for an irreversible first order chemical reaction. In principle, it should therefore be possible to measure absorption rates in a packed column at a number of different reaction speeds for an irreversible first-order reacting system. From these a plot of the Laplace transform against reaction velocity constant can be derived and this, on inversion, should yield $\frac{\Theta(t)}{t^{1/2}}$ and hence the actual age-distribution function, $\Theta(t)$.

REQUIREMENTS AND LIMITATIONS OF THE METHOD

It will be seen that the success of the method is largely dependent on the reliability of estimates of the reaction velocity constant, gas solubility and diffusivity. Moreover, it must be possible to employ a suitable irreversible first-order chemical reaction in which the velocity constant can be varied over a wide range.

Packed column measurements are normally obtained in the form of volumetric mass-transfer coefficients and it is therefore necessary to know precisely the factor 'a', representing the effective wetted area per unit of packed volume, before values of k_L can be isolated from the experimentally determined values of $k_L a$.

The method involves the estimation of slopes from the resulting curve of k_L vs. k and the difference, at high values of k , between two relatively large quantities. It is therefore apparent that the utmost accuracy will be required in the experimental measurements.

The method may, of course, fail if

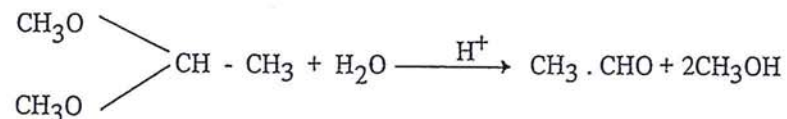
- 1) the surface renewal (or rejuvenation) model does not adequately represent the process of absorption in a packed column;
- 2) should the range of reaction rates obtainable be so limited that an incomplete picture is obtained;
- 3) in the event of coupling between $\Theta(t)$ and k , for example if heat is liberated during the reaction.

Finally, it may be mentioned that the problem of the inversion of experimentally measured Laplace transforms is a difficult one (12).

CHOICE OF ABSORPTION SYSTEMS

Because of the dearth of irreversible first-order chemical reactions fast enough for a study of this kind, the selection of a suitable system with known kinetics proved to be a difficult matter. Before the experimental results can be analysed, an explicit knowledge of the values of certain physico-chemical quantities, viz. the solubility, diffusivity and reaction-rate constant, is required. Information on these is not generally available and is often difficult or impossible to obtain experimentally.

The first reacting system employed was the hydrolysis of dimethyl acetal (1, 1-dimethoxyethane) by water into acetaldehyde and methanol:



This reaction had been studied by Holdcroft (7), who presented data for $C^* \sqrt{D}$ and the velocity constant k . Some independent measurements of the rate constant were also available (2, 10).

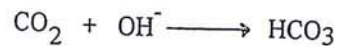
In a large excess of water the reaction is essentially first-order and the rate is given by:

$$\frac{-d}{dt} \left[\text{C}_4\text{H}_{10}\text{O}_2 \right] = k_2 \left[\text{H}^+ \right] \left[\text{C}_4\text{H}_{10}\text{O}_2 \right] = k_1 \left[\text{C}_4\text{H}_{10}\text{O}_2 \right]$$

where k_2 is the second and k_1 the first order velocity constant. The rate of reaction is proportional to the hydrogen ion concentration and is also increased by the addition of inorganic salts such as sodium chloride. It is therefore possible to obtain some variation in the velocity of the reaction by altering the concentrations of, say, hydrochloric acid and sodium chloride in an aqueous solution.

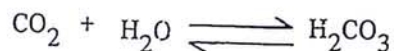
In later work, carbon dioxide was absorbed into sodium carbonate-sodium bicarbonate buffer solutions with added arsenious oxide. In the absence of a catalyst the predominating reaction is an effectively irreversible second-order one of

moderate speed between carbon dioxide and the hydroxyl ions present:



Because of the buffering effect the hydroxyl ion concentration remains approximately constant as absorption proceeds so that this reaction may be regarded as being pseudo-first order.

The slower alternative reaction between carbon dioxide and water molecules:



is, however, catalysed by the arsenite ions formed in an alkaline solution of arsenious oxide. The reaction of carbon dioxide and hence the overall absorption rate is therefore accelerated. Roberts (13) has determined the rate constants of this reaction for various concentrations of arsenious oxide. The increase in reaction rate was found to be directly proportional to the amount of arsenic added.

DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus and experimental procedure were essentially the same as those employed by Kennedy (8). The column consisted of a 4 in. i.d. Pyrex tube, 12 in. long, randomly packed with ½ in. ceramic Raschig rings to a depth of just over 10 in. A packing density of 10,500 rings per cubic foot was used in all experiments. The liquid was distributed evenly over the top of the packing through 35 nozzles.

The column was operated by the 'differential method', i.e. the lower part was filled with liquid and the effective height of the packing could be varied by adjusting the position of a constant-level outlet. At any given position of the free liquid surface, therefore, the rate measured will be that due to mass transfer in the spray zone above the packing, in the packing actually exposed, and in the liquid surface itself. A measurement at some other position will give the rate due to the spray zone, the new volume of exposed packing and the liquid surface in its new position. The difference between the two measure-

ments should give directly the absorption rate due to the section of packing between the two levels assuming that absorption into the free liquid surface may be neglected or that the surface is always equivalent to a constant depth of packing. If the process is repeated in a sufficient number of steps a smooth curve of total absorption-rate, M , against exposed depth of packing, h , can be derived.

If the average rate of absorption per unit wetted area at a given height in the column is R , then

$$\frac{dM}{dh} = AaR$$

where A is the cross-sectional area of the column and a is the wetted surface-area per unit volume. (aR) can therefore be found for a specific level in the column from the slope of the curve of M against h . In the case of absorption without reaction, the bulk concentration of dissolved gas at depth h is given by

$$C_0 = \frac{M}{L}$$

where L is the liquid flow rate. $k_L a$, the volumetric liquid-film mass-transfer coefficient, may be defined by

$$Ra = k_L a(C^* - C_0)$$

or, for the packed column,

$$dM = k_L a(C^* - C_0)A dh$$

$$\therefore \frac{d}{dh} \left[\log_{10} \left(1 - \frac{M}{LC^*} \right) \right] = \frac{A}{2.303L} (k_L a) \quad (4)$$

The value of $k_L a$ can therefore be deduced from the slope of the logarithmic plot according to equation (4).

As is well known, packed column absorption rates are extremely sensitive to the usual operating variables such as liquid properties and flow-rate, packing density and arrangement. In this work, therefore, an attempt was made to standardise the conditions of operation of the packed column. All resistance in the gas phase was eliminated by absorbing from pure gas saturated with water vapour at 25.0°C. Hydrodynamic factors were held constant as far as was possible by using a constant liquid flow-rate and a fixed packing arrangement. The viscosities of all solutions were kept constant and the range

of densities confined to narrow limits. The arrangement of the apparatus used for the measurement of absorption rates into the spiked buffer solutions is shown diagrammatically in Figure 1. With the modifications shown in Figure 2, it was also used for the experiments carried out with dimethyl acetal. Readings were taken at 2 cm. intervals over about 24 cm. of packing.

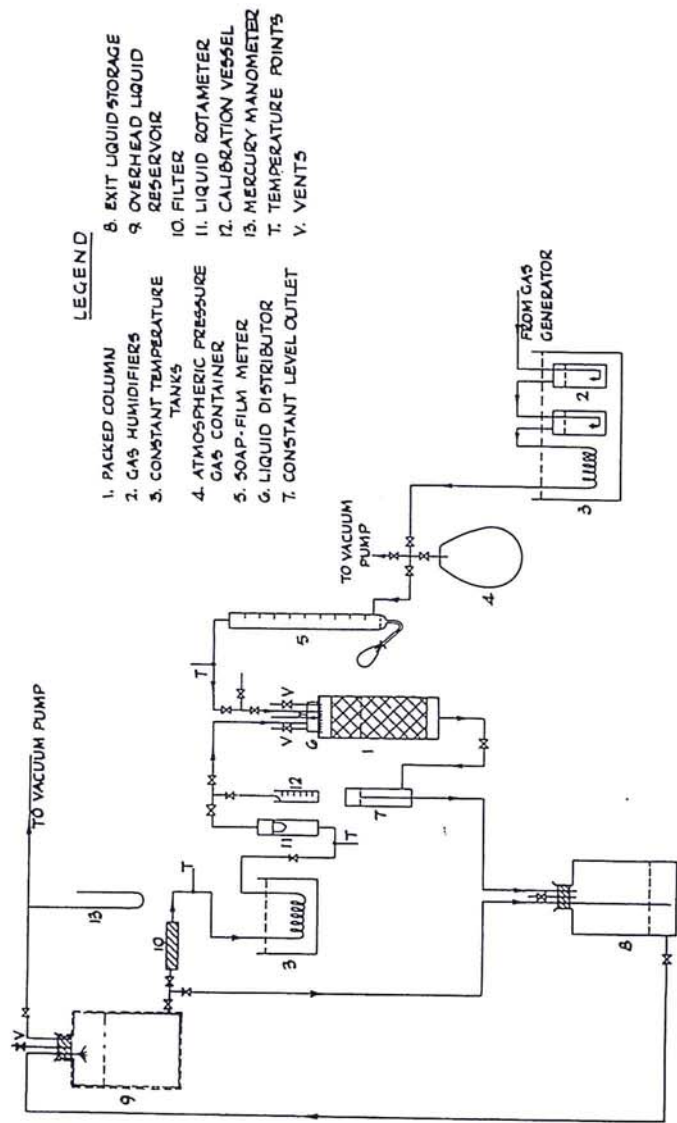


FIG. 1 FLOW DIAGRAM OF APPARATUS FOR ABSORPTION OF CARBON DIOXIDE

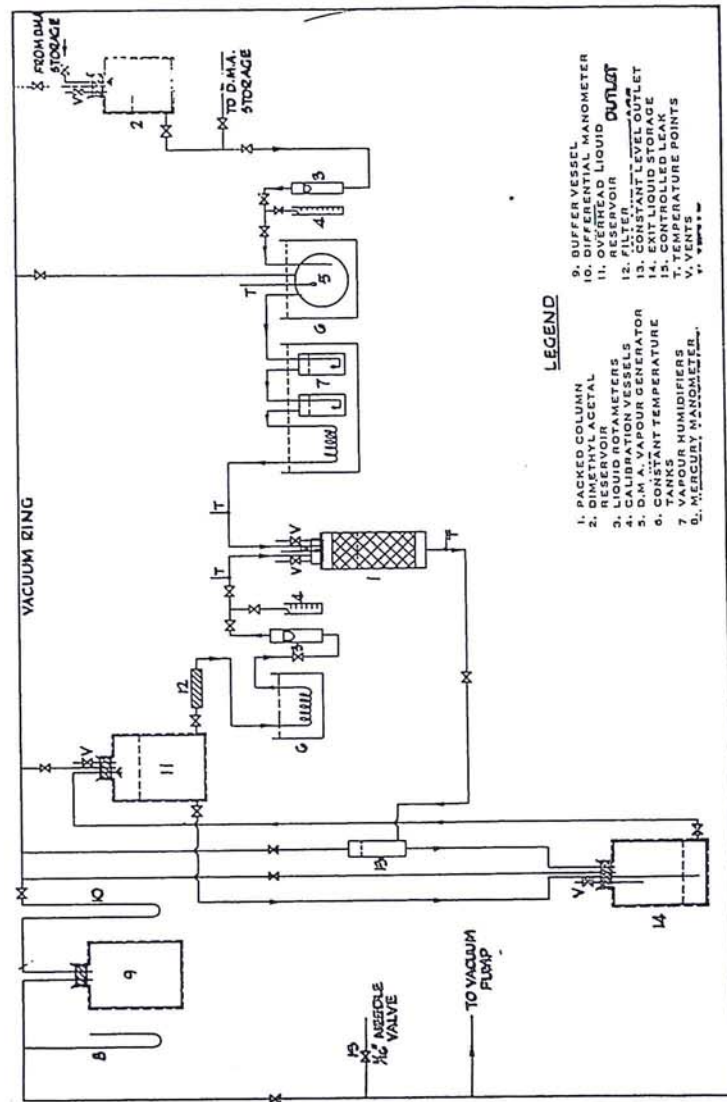


FIG. 2 FLOW DIAGRAM OF APPARATUS FOR ABSORPTION OF DIMETHOXYETHANE

(A) THE ABSORPTION OF 1, 1-DIMETHOXYETHANE INTO AQUEOUS SOLUTIONS

Since dimethyl acetal is a liquid at 25°C and atmospheric pressure, it was decided to work at a partial pressure of 11 mm dimethoxyethane of 120 mm Hg. The required pressure was obtained by employing a water vacuum pump and a controlled leak consisting of a 1/16 in. needle valve, and was maintained constant to within 1 per cent. Fluctuations in the pressure were reduced by the use of a 20-litre buffer vessel in the system.

Liquid dimethyl acetal was metered through a rotameter and then 'flushed off' in a 1-litre Pyrex flask at 80°C. The vapours were saturated with water, cooled to 25.0°C and then passed to the absorption column. All experiments took place in a constant temperature room maintained at 25.0 ± 0.7°C.

Both the dimethyl acetal and absorbing solution were deaerated by spraying repeatedly into their respective overhead vessels under vacuum. At the start of a run the whole apparatus was completely evacuated and the absorbing section (column and flash vessel) isolated. The pressure in the rest of the apparatus was then adjusted to the desired figure and that in the column brought up to this level by the addition of dimethyl acetal. The flow of absorbing liquid was then begun and the level in the column allowed to come to its equilibrium position after making any necessary adjustment to the height of the constant-level outlet. For any given pressure and dimethyl acetal flow-rate there is a unique position of the liquid level in the column. Readings were taken of this level over a wide range of acetal flow rates.

By a suitable choice of the sodium chloride and hydrochloric acid concentrations the solution viscosity could be held constant while the reaction velocity constant was varied. In the main series of experiments the viscosities of the solutions relative to that of water were kept within the limits of 1.57±0.005. The liquid flow-rate was 11.8 cu. cm/sec. Densities varied from 1.145 to 1.155 gm per cc. The entire practical range of reaction velocities from 0 to 7 sec⁻¹ was covered. In addition, measurements were carried out on the purely physical absorption of dimethyl acetal into non-reacting aqueous solutions of sodium chloride having the same viscosity as the acid solutions.

ESTIMATION OF PHYSICO-CHEMICAL VARIABLES

In the absence of independent solubility and diffusivity data for the system, the value of D was, at first, estimated from the semi-empirical correlation of Wilke and Chang (22). Estimates of the solubility were then obtained from the values of $C^*\sqrt{D}$ interpolated from Holdcroft's data (7). There was considerable uncertainty in these predicted values of the solubility and diffusivity. This was, however, largely resolved by measurements of $C^*\sqrt{D}$ (in solutions corresponding to those used in the absorption experiments) coupled with determinations of the solubility of dimethyl acetal in neutral solutions. Details of these measurements may be obtained from the author on request.

Estimates of the reaction velocity constant were obtained from the data of Olson and Tong (loc. cit.). They have reported values of the second-order velocity constant, k_2 , for various concentrations of sodium chloride, but only at very low hydrogen ion concentrations. No allowance was therefore made for the effect of hydrochloric acid on k_2 . Although Holdcroft's results appear to show that this effect may be neglected it is possible, as in the case of the higher acetals, that there is some dependence of the rate constant on the hydrogen chloride concentration. This would lead to less accurate predictions at high hydrochloric acid concentrations. A further upper practical limit to the reaction velocity constant obtainable is imposed by the solubility of sodium chloride. Under the conditions employed this was approximately 7 sec⁻¹. It later transpired that this was quite inadequate.

RESULTS

The results for absorption into reacting solutions are expressed in terms of the liquid-film mass-transfer coefficient defined by the equation :

$$Ra = k_L ac^*$$

This can be rewritten for the packed column as

$$dM = k_L ac^* A. dh$$

i.e.

$$k_L a = \frac{1}{AC^*} \cdot \frac{dM}{dh}$$

The mass transfer coefficients were therefore obtained directly from the slope of the straight lines of M against h , using the method of least squares. Figure 3 is a plot of the absorption rate against column height for a typical run. The results are expressed graphically in Figure 4 as a plot of the volumetric liquid-film mass-transfer coefficient against reaction velocity constant.

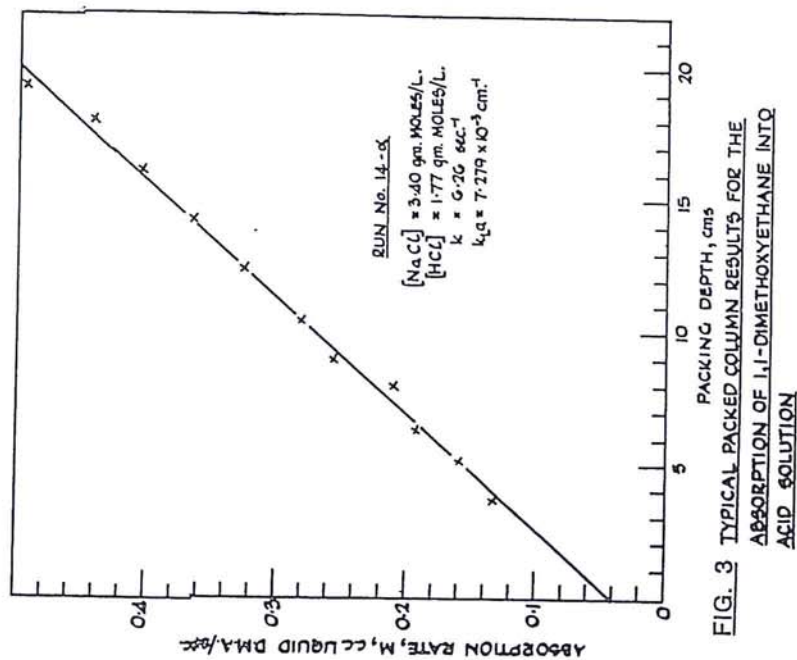


FIG. 3 TYPICAL PACKED COLUMN RESULTS FOR THE ABSORPTION OF 1,1-DIMETHOXYETHANE INTO ACID SOLUTION

(B) THE ABSORPTION OF CARBON DIOXIDE INTO SODIUM CARBONATE-SODIUM BICARBONATE BUFFER SOLUTIONS WITH ADDED ARSENIOS OXIDE

The bulk of the experimental work was carried out on the absorption of carbon dioxide into sodium carbonate - sodium bicarbonate buffer solutions catalysed by arsenite ions. This was mainly because of the wide range of reaction velocities possible with this system. Using the apparatus shown in Figure 1, measurements were made with additions of arsenious oxide to the absorbent ranging from 0 to 0.2 gm. atoms of total arsenic per litre (the reaction velocity constant being varied

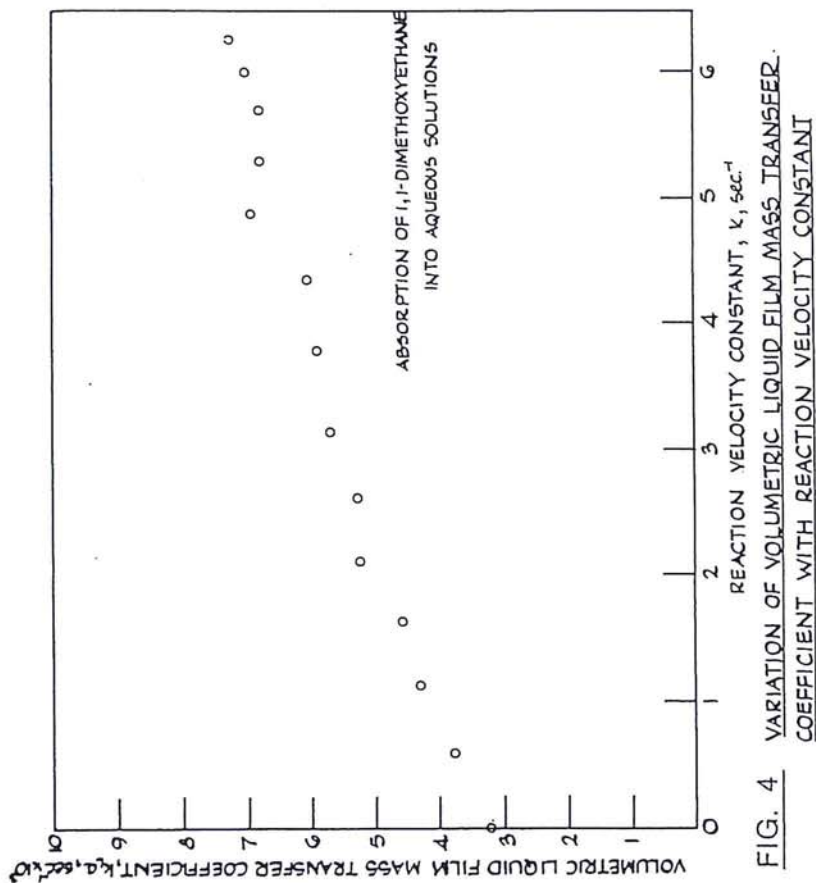


FIG. 4 VARIATION OF VOLUMETRIC LIQUID FILM MASS TRANSFER COEFFICIENT WITH REACTION VELOCITY CONSTANT

from 0.55 to 30 sec⁻¹. The concentrations of carbonate and bicarbonate ions were 0.207 and 0.215 gm ions per litre respectively and the buffer ratio was 0.96. In addition, a number of purely physical absorption runs were carried out using non-reacting aqueous solutions of sodium chloride having the same viscosity as the alkaline solutions.

The ionic strengths of the solutions were kept at approximately the same value ($I = 0.94$ gm. ions per 1000 gm water) by the addition of varying amounts of sodium chloride. It was therefore hoped that variable salt effects would be eliminated. Moreover, the use of sodium chloride helped to control density and viscosity and thus ensured that the hydrodynamic conditions in the packed column were effectively constant. The viscosities of the solutions were between 1.16 and 1.18 times that of water and the densities varied from 1.035 to 1.045 gm. per cc. When preparing the solutions, enough sodium hydroxide was added to neutralise the acid formed when the arsenious oxide was dissolved. In this way, the addition of the arsenious oxide had little effect on the buffer ratio.

As before, the results for the absorption into reacting solutions were expressed in terms of the volumetric liquid-film mass-transfer coefficient, defined by the equation :

$$k_L a = \frac{1}{A(C^* - C_0)} \frac{dM}{dh}$$

The absorption rates for a typical run are plotted against depth of packing in Figure 5 and it will be noticed that the plot is completely linear. It thus appears that the concentration, C_0 , of unreacted solute in the bulk of the liquid at any level may again be neglected. The mass-transfer coefficients were therefore simply estimated from the slopes of the best straight lines fitted through the points.

Determinations of the mass-transfer coefficient were made at a given liquid flow-rate over a wide range of reaction velocities. These were carried out, in turn, for five different flow-rates, viz. 5.9, 11.8, 17.7, 23.6 and 29.5 cu. cm. per sec. The results are expressed graphically in Figures 6, 7, 8, 9 and 10 as curves of $k_L a$ against the reaction velocity constant. For any given solution and flow-rate three measurements of $k_L a$ were made and the mean value obtained. This was rejected if the separate results were not within 1 per cent of each other. It is

considered that the accuracy of any particular mean value of $k_L a$ is well within 1.5 per cent.

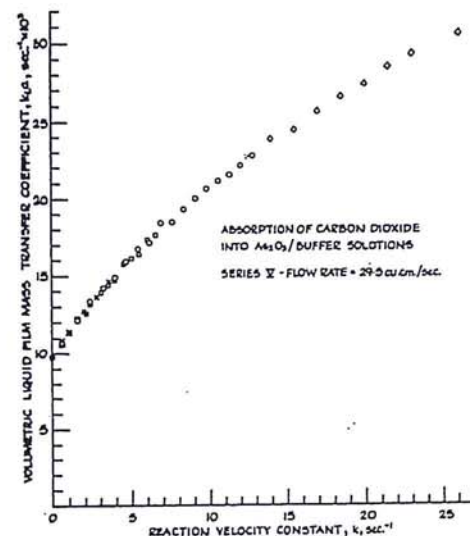


FIG. 6 VARIATION OF VOLUMETRIC LIQUID FILM MASS TRANSFER COEFFICIENT WITH REACTION VELOCITY CONSTANT

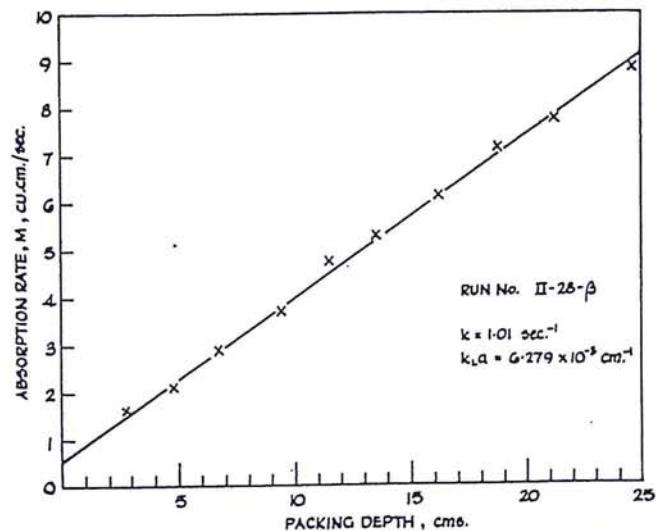


FIG. 5 TYPICAL PACKED COLUMN RESULTS FOR THE ABSORPTION OF CARBON DIOXIDE INTO SPIKED BUFFER SOLUTION AT 25.0°C

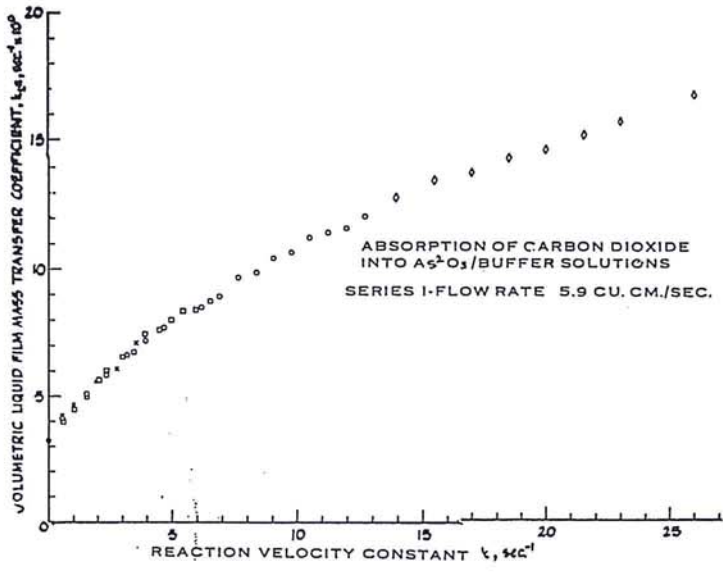


FIG. 7 VARIATION OF VOLUMETRIC LIQUID FILM MASS TRANSFER COEFFICIENT WITH REACTION VELOCITY CONSTANT

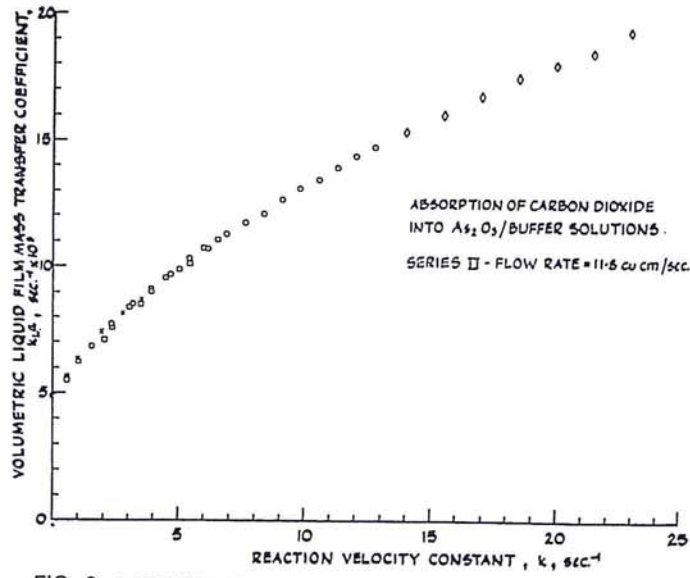


FIG. 8 VARIATION OF VOLUMETRIC LIQUID FILM MASS TRANSFER COEFFICIENT WITH REACTION VELOCITY CONSTANT

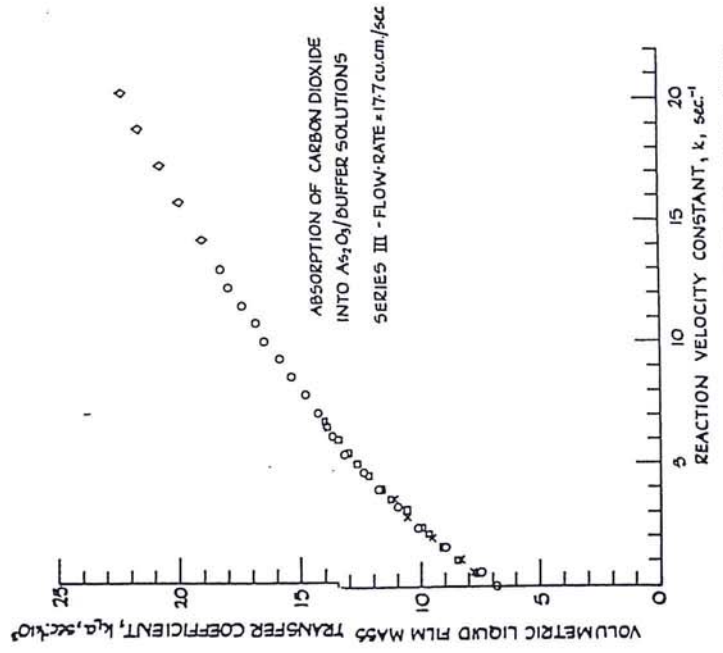


FIG. 9 VARIATION OF VOLUMETRIC LIQUID FILM MASS TRANSFER COEFFICIENT WITH REACTION VELOCITY CONSTANT

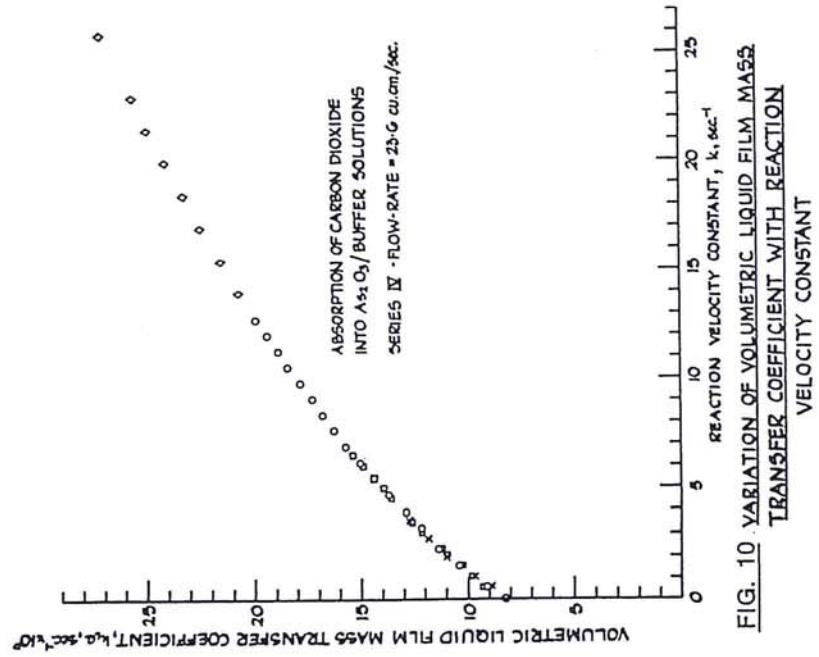


FIG. 10 VARIATION OF VOLUMETRIC LIQUID FILM MASS TRANSFER COEFFICIENT WITH REACTION VELOCITY CONSTANT

DEPLETION OF THE BUFFER

It is possible that depletion of the buffer occurs near the surface of the absorbing liquid and that this will destroy the first-order character of the reaction. This should, however, introduce much less error than in the case of the uncatalysed reaction since the resulting fall in the hydroxyl ion concentration makes little direct difference to the total absorption rate. The effect on the degree of ionisation of arsenious acid to arsenite might be more serious, since a fall in the buffer ratio leads to a reduction in the concentration of the catalysing species, arsenite ions. Roberts and Danckwerts (14) have shown that a decrease of nearly 60 per cent in the buffer ratio from 0.96 to 0.40 causes a reduction in the concentration of arsenite ions of only 11 per cent. Such a fall would lead to a reduction in the pseudo first-order reaction velocity constant of about 14 per cent. In most of the experiments carried out the extent of depletion was not as great but it undoubtedly became important under the extreme conditions of high exposure times (i.e. low liquid flow-rates) and large arsenic concentrations.

The experimental plots of M against h remained linear at the highest exposure times used in the column (except in the extreme cases of very low liquid flow-rates and large depths of exposed packing) and showed no signs of falling-off. This suggests that the influence of depletion on the bulk concentration of the buffer was negligible under the particular conditions employed.

TREATMENT OF RESULTS

An accurate knowledge of the interfacial area for mass transfer in packed towers has long been lacking. This difficulty in estimating the area of contact between gas and liquid flowing in a packed column has necessitated the use, in practice, of the product, $k_L a$, of the transfer coefficient k_L and a , the effective area per unit volume of packing. Separation of volumetric mass-transfer coefficients, such as $k_g a$ and $k_L a$, into their components k_g or k_L and a , has been attempted by several workers (16, 17, 20, 23 and 24). The method used by the present author overcomes the limitations of previous methods used and will be described elsewhere.

Values of the liquid-phase mass-transfer coefficient, $k_L a$,

were resolved into their components, k_L and a . For the results on the carbon dioxide/arsenious oxide-buffer system, the relationship between k_L and k was expressed in polynomial form:

$$k_L = a + bk + ck^2 + dk^3 + \dots$$

by the least squares technique. It was felt that this procedure was justified in view of the comprehensive and accurate data which were available. The equations obtained were:

Series	Flow-rate	Equation for k_L	Standard Error of k_L
Series I	5.9 cu.cm./sec.	$k_L = 3.2990 + 1.3585k - 0.1232k^2 + 0.0092k^3 - 0.0003k^4$	0.123
Series II	11.8 cu. cm./sec.	$k_L = 4.8721 + 1.4179k - 0.1214k^2 + 0.0104k^3 - 0.0006k^4$	0.088
Series III	17.7 cu. cm./sec.	$k_L = 6.8486 + 1.5401k - 0.1043k^2 + 0.0067k^3 - 0.0002k^4$	0.077
Series IV	23.6 cu. cm./sec.	$k_L = 8.2557 + 1.4773k - 0.0858k^2 + 0.0049k^3 - 0.0002k^4$	0.070
Series V	29.5 cu. cm./sec.	$k_L = 9.8373 + 1.5483k - 0.0670k^2 + 0.0024k^3$	0.133

The slopes, $\frac{dk_L}{dk}$, were then obtained at regular intervals

by differentiation of the relationships given above. The Laplace transforms:

$$L \left[\frac{\bar{\theta}(t)}{t^{1/2}} \right] = k_L \sqrt{\frac{\pi}{D}} - 2k \frac{dk_L}{dk} \sqrt{\frac{\pi}{D}}$$

could then be computed at various values of k . A typical curve showing the variation of the Laplace transform with reaction velocity constant is plotted in Figure 11.

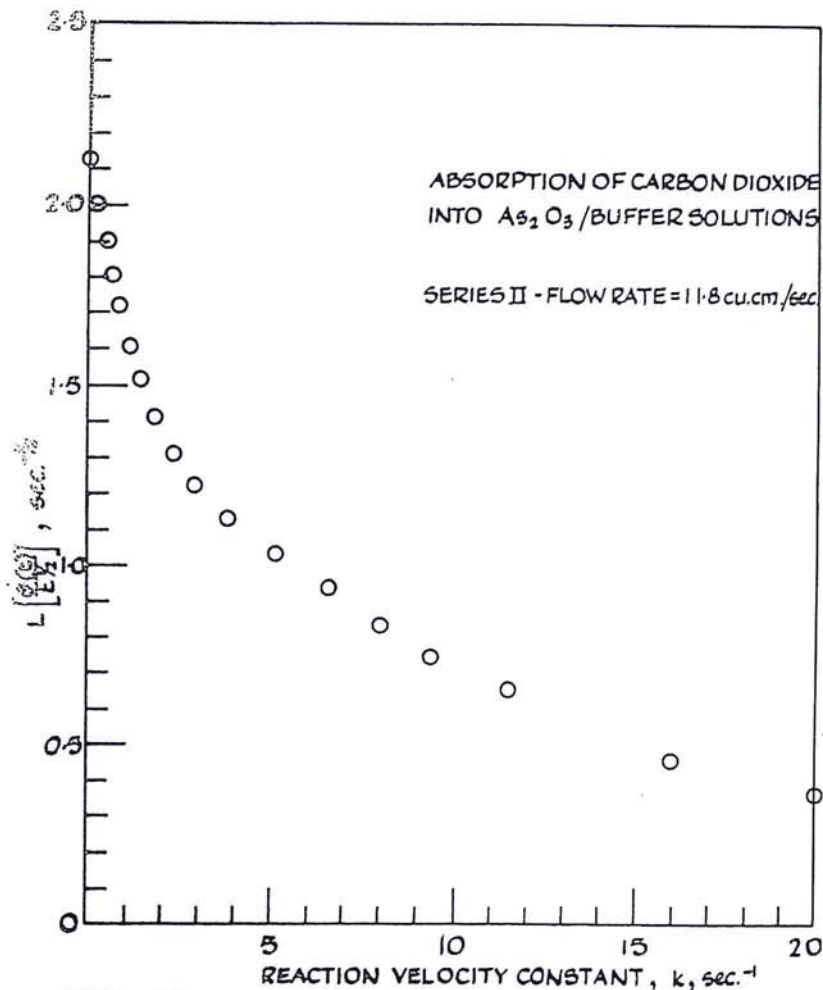


FIG. 11 - VARIATION OF THE LAPLACE TRANSFORM OF $\frac{\Theta(t)}{t^{1/2}}$ WITH REACTION VELOCITY CONSTANT

In the case of the results on the absorption of 1, 1-dimethoxyethane and those of Kennedy (8) there were fewer data points and a certain amount of scatter. The slopes were therefore estimated visually from the curves of k_L against k . The curves of the Laplace Transform against reaction velocity constant were then inverted to obtain the surface-age distribution functions, $\Theta(t)$.

NUMERICAL INVERSION OF THE LAPLACE TRANSFORMS

Experimental observations of the Laplace transform of $\frac{\Theta(t)}{t^{1/2}}$ have been made at various values of k for each liquid flow-rate and reacting system employed.

$$L(k) = \int_0^{\infty} e^{-kt} \left[\frac{\Theta(t)}{t^{1/2}} \right] dt$$

where $\Theta(t)$ is the required surface-age distribution function and k is the reaction-velocity constant. Although many elaborate analytic solutions to the problem of inverse Laplace transformation have been given (19,21) the problem of obtaining physically significant inverse functions from experimentally measured transforms remains (11,18). Lanczos states (9): ". . . . and thus it is demonstrated that physical observations of the Laplace transform can never solve the problem of restoring the indicial functions with any degree of accuracy".

In this paper a brief outline is made of the methods which have been attempted to obtain the inverse Laplace transforms of the experimentally-measured functions and the results are summarised. A more general discussion of the problem of inversion by Linear Programming has been given elsewhere (12).

THE PROBLEM

The problem, in essence, is that given a function $L(k)$ (called the transformed function) in the form of a set of observations, e.g. $L(k_0), L(k_1), L(k_2), \dots, L(k_m)$, it is required to find the function $f(t)$ of the form $f(t) \geq 0$, all t , such that

$$L(k) = \int_0^{\infty} e^{-kt} f(t) dt.$$