Because of the discrete nature of our information about $L(k)$, we have, in fact, a set of equations of the form

$$\begin{aligned} L(k_0) &= L_0 = \int_0^\infty e^{-k_0 t} f(t)\,dt \\ L(k_1) &= L_1 = \int_0^\infty e^{-k_1 t} f(t)\,dt \\ L(k_2) &= L_2 = \int_0^\infty e^{-k_2 t} f(t)\,dt \\ L(k_m) &= L_m = \int_0^\infty e^{-k_m t} f(t)\,dt \end{aligned}$$

NOMOGRAPH METHOD

In order to calculate, or 'estimate', $f(t)$ one procedure is to split the time scale

$$0 \leqslant t \leqslant \infty$$

into several intervals

$$(0, t_1),\ (t_1, t_2),\ (t_2, t_3), \ldots\ldots, (t_{n-1}, \infty)$$

where

$$0 < t_1 < t_2 < \ldots\ldots < t_{n-1} < \infty$$

and assume that $f(t)$ has constant values

$$f_1,\ f_2, \ldots\ldots, f_n$$

in each of these intervals respectively. In the last interval the value of $f(t)$ will be zero. The position and lengths of these intervals may be chosen so that they cover the region of interest and are shorter where the function is rapidly varying and longer elsewhere. We require $n \leqslant m$. There is little point in trying to estimate more function values f_i than observations L_j are used to determine them.

A. SOLUTION OF SIMULTANEOUS LINEAR EQUATIONS

The representation of $f(t)$ by a nomograph leads to a relatively simple evaluation of the Laplace transform. Consider the single time interval in which

$$\begin{aligned} f(t) &= f_i, & A_i &\leqslant t \leqslant B_i, \\ f(t) &= 0, & t &< A_i,\quad t > B_i. \end{aligned}$$

The Laplace transform of this step function is

$$\frac{f_i}{k}\left(e^{-kA_i} - e^{-kB_i}\right)$$

Thus the overall transform of $f(t)$ will be given by

$$L = \sum_{i=1}^{n} \frac{f_i}{k}\left(e^{-kA_i} - e^{-kB_i}\right) \qquad (5)$$

By substituting in equation (5) the m experimental values of L and k as well as the chosen values of A_i and B_i, a system of m simultaneous linear algebraic equations with n unknown values of f_i is obtained.

$$L_j = \sum_{i=1}^{n} a_{ij} f_i, \qquad j = 1, 2, \ldots\ldots, m$$

where

$$a_{ij} = \frac{e^{-k_j A_i} - e^{-k_j B_i}}{k_j}$$

If these equations were solved exactly and the f_i's turned out all positive, the problem would be solved.

The method was attempted using 18 values of (L,k) and dividing the time scale for $\frac{\Theta(t)}{t^{1/2}}$ (called $f(t)$, the inverse function) into an equal number of intervals. In each of these intervals $f(t)$ was considered to have a constant value f_i, i varying form 1 to 18.

The coefficients of f_i were evaluated and the equations solved. However it was found that several of the f_i turned out to be negative. Moreover, small variations in the coefficients caused drastic changes in the new answer. This could be explained in terms of the error present in the measured values of the transform and was also the experience of Skoczylas (18). The chief undesirable property of the 'exact' solution was that the transformed function was negative in places while it is required, on physical grounds, to be everywhere positive. In order to ensure positivity of the inverse function, the technique of Linear Programming was used in all succeeding work.

B. SOLUTION BY LINEAR PROGRAMMING

By means of Linear Programming a set of linear algebraic equations expressing inequalities may be solved so that each variable is held positive or zero and the mean modulus of deviation is minimised. The problem may be put in the linear programming form :

$$\begin{array}{lll} \text{Minimise} & D & = \sum |d_j| \\ \text{where} & d_j & = L_j - a_{ij}f_i \\ \text{and} & f_i & > 0 \end{array}$$

The d_j are the deviations from the observations. As linear programming techniques handle positive variables only, we allow the error to be either positive or negative by introducing two 'slack variables' δ_j and δ_j' such that

$$\begin{array}{llll} \delta_j & = d_j & \text{if} & d_j \geqslant 0 \\ & = 0 & \text{if} & d_j < 0 \\ \delta_j' & = 0 & \text{if} & d_j \geqslant 0 \\ & = -d_j & \text{if} & d_j < 0 \end{array}$$

The problem now takes the form:

$$\begin{array}{lll} \text{Min.} & D & = \sum \delta_j + \sum \delta_j' \\ \text{where} & a_{ij}f_i + \delta_j - \delta_j' & = L_j \\ \text{and} & f_i \geqslant 0, \ \delta_j \geqslant 0, \ \delta_j' \geqslant 0. & \end{array}$$

During the inversion process the computer, in effect, fits a smooth curve through the experimental data such that the sum of the absolute values of the deviations is minimised.

It is possible to weight the deviations if some of the observations are more important than others by introducing 'costs' (or 'weights')

$$\text{Min.} \sum c_j \delta_j + c_j' \delta_j'$$

although in the present case all slack variables were given equal weights of unity

$$c_j = c_j' = 1, \quad \text{all j.}$$

The previously evaluated coefficients of f_i together with the coefficients of δ_j', costs of δ_j', δ_j and f_i, and the experimental (L_j) values were all labelled and arranged in a Linear Programming tableau. All the information in this tableau was then punched on a data tape and the problem specified to the computer (an IBM 1620 model) for solution by the Linear Programming programme. Results showed a limited number of non-zero values for f_i. These solutions, showing several maxima of f_i separated by regions where the value was lower, were obviously physically ridiculous. Distribution functions usually vary smoothly down from a single maximum. This anomaly could be removed by imposing 'shaping' conditions on the function f (t) by means of equations of the type

$$f_i \geqslant f_{i+1} \quad \text{where the function is monotonically decreasing}$$

and by

$$f_i \leqslant f_{i+1} \quad \text{where it is increasing.}$$

The disadvantage of the nomograph method (or equally of any similar point-value representation for f (t)) is that it does not give a smooth function, particularly if there are only a small number of experimental values. An alternative representation was therefore employed.

REPRESENTATION OF THE EXPERIMENTALLY MEASURED FUNCTION BY A SUM OF ANALYTIC FUNCTIONS HAVING KNOWN INVERSES

The Linear Programming method of inversion was finally improved by the use of the following known transformations :

$$L\left[\pi^{-\frac{1}{2}} t^{-\frac{1}{2}} e^{-at}\right] = \frac{1}{(k+a)^{\frac{1}{2}}}$$

$$L\left[2\,\pi^{-\frac{1}{2}} t^{\frac{1}{2}} e^{-at}\right] = \frac{1}{(k+a)^{\frac{3}{2}}}$$

$$L\left[\frac{4}{3}\,\pi^{-\frac{1}{2}}\,t^{\frac{3}{2}}\,e^{-at}\right] = \frac{1}{(k+a)^{\frac{5}{2}}}$$

or, generally,

$$L\left[\frac{\pi^{-\frac{1}{2}}\,t^{n-\frac{1}{2}}\,e^{-at}}{\frac{1}{2}\cdot\frac{3}{2}\cdots(n-\frac{1}{2})}\right] = \frac{1}{(k+a)^{n+\frac{1}{2}}}$$

Thus if the experimentally measured function, $L(k)$, can be expressed in the form :

$$\begin{aligned} L(k) = {} & \frac{A_1}{(k+a_1)^{\frac{1}{2}}} + \frac{A_2}{(k+a_2)^{\frac{1}{2}}} + \frac{A_3}{(k+a_3)^{\frac{1}{2}}} + \cdots\cdots \\ & + \frac{B_1}{(k+b_1)^{\frac{3}{2}}} + \frac{B_2}{(k+b_2)^{\frac{3}{2}}} + \frac{B_3}{(k+b_3)^{\frac{3}{2}}} + \cdots\cdots \\ & + \frac{C_1}{(k+c_1)^{\frac{5}{2}}} + \frac{C_2}{(k+c_2)^{\frac{5}{2}}} + \frac{C_3}{(k+c_3)^{\frac{5}{2}}} + \cdots\cdots \\ & + \cdots\cdots\cdots \end{aligned}$$

then it can be transformed directly into the required function :

$$\begin{aligned} \left[\frac{\Theta(t)}{t^2}\right] = {} & \pi^{-\frac{1}{2}}\,t^{-\frac{1}{2}}\left[A_1 e^{-a_1 t} + A_2 e^{-a_2 t} + A_3 e^{-a_3 t} + \cdots\cdots\right] \\ & + 2\,\pi^{-\frac{1}{2}}\,t^{\frac{1}{2}}\left[B_1 e^{-b_1 t} + B_2 e^{-b_2 t} + B_3 e^{-b_3 t} + \cdots\cdots\right] \\ & + \frac{4}{3}\,\pi^{-\frac{1}{2}}\,t^{\frac{3}{2}}\left[C_1' e^{-c_1 t} + C_2 e^{-c_2 t} + C_3 e^{-c_3 t} + \cdots\cdots\right] \\ & + \cdots\cdots \end{aligned}$$

All the components of the function $L(k)$ have the required monotonic behaviour when all the A's, B's, C's, ... are positive; similarly the transformed function $\left[\frac{\Theta(t)}{t^{\frac{1}{2}}}\right]$ will be everywhere positive and continuous. In other words, both $L(k)$ and $\left[\frac{\Theta(t)}{t^{\frac{1}{2}}}\right]$ are being represented by smoothed functions. This treatment does not exclude the possibility of surface rejuvenation since although $L(k)$ is monotonic, the transformed function, $\left[\frac{\Theta(t)}{t^{\frac{1}{2}}}\right]$, is not limited by this condition.

The Linear Programming technique was used to select suitable positive values of the A's, B's, C's . . . . The a's, b's, c's,. . . . . must also be positive. The number of experimental points, M(18 in most cases), defined the maximum number of non-zero coefficients A, B, C, ... A comprehensive set, N, of a's, b's, c's, ... (usually 36) was chosen to cover the full range of t over which $\left[\frac{\Theta(t)}{t^{\frac{1}{2}}}\right]$ was expected to be significant - the total number exceeded M and, in fact, was limited only by the capacity of the Linear Programme for the computer. It is desirable to make N very much larger than M in the matrix of coefficients i.e. offer a relatively large number of possible functions from which the Linear Programme selects those J ($\leqslant$ M) which make the error a minimum, the aim being to offer if possible such terms as allow of an exact solution corresponding to an error of zero.

The matrix coefficients' for any particular choice were calculated as follows: suppose that one of the experimental values was at $k = k_j$, then the contribution to $L(k_j)$ from a term, say,

$\pi^{-\frac{1}{2}}\,t^{-\frac{1}{2}}\,e^{-a_2 t}$ would be $\frac{1}{(k_j + a_2)^{\frac{1}{2}}}$ and that from a term

$2\,\pi^{-\frac{1}{2}}\,t^{\frac{1}{2}}\,e^{-b_2 t}$ being $\frac{1}{(k_j + b_2)^{\frac{3}{2}}}$ Thus as far as the

matrix coefficients were concerned, they were calculated from the a_1, b_1 or c_1 ....and the index $(n + \frac{1}{2})$ corresponding to $t^{(n-\frac{1}{2})}$ in the relevant term of $\left[\frac{\Theta(t)}{t^{\frac{1}{2}}}\right]$. The row number of the coefficient was given by j. These coefficients formed part of the linear programme matrix, the remainder, as before, being made up of the 'costs' of f_i, δ_j and δ_j', the coefficients of σ_j and the original experimental data.

The numbers referred to above were then converted, as before, into the form necessary for the data-input to the Linear Programming programme and the resulting problem solved on the IBM 1620 computer. Much of the labour involved, from a purely computational point of view, arose because all the coefficients, of which there were several hundred, had to be calculated and provided in a particular numerical form. It was therefore necessary to write a separate computer programme to generate them in the right form.

The resulting function $\left[\frac{\Theta(t)}{t^{1/2}}\right]$ was described in terms of the individual components mentioned earlier. The 'solution' given after applying the relevant algorithm the requisite finite number of times consisted, in general, of $J (\leqslant M$, the total number of rows in the tableau) non-zero values of A, B, C, ...and (M - J) non-zero values of the slack variables δ_j and δ_j. The problem was solved using different values of a's, b's, c's, ...(selected by trial and error), until the solution with the best 'fit' was obtained. A measure of the accuracy of the 'fit' of any particular solution could be obtained from the 'activities' of the slack variables brought into the Linear Programme solution (i.e. from the value of the cost function). Ideally, these should be as low as possible.

The problem, as described, assumed that deviation was allowable from any of the experimental measurements L_j which are, of course, subject to observational errors. However, it is possible to specify that certain conditions should be exactly specified. For example, one condition might be that the area under $\Theta(t)$ be unity. This is an a priori condition and not an observation. We can insist that such a condition be identically satisfied by specifying that its associated slack variables should be zero in the solution. This is equivalent to insisting that the weights are infinity. However it was considered better not to apply this condition initially but rather to check the feasibility of the solution by observing how far this deviated from the condition that $\int_0^\infty \Theta(t)\,dt = 1$

The solutions obtained for $\Theta(t)$, the surface-age distribution function, are given on page 47.

Absorption of 1, 1–Dimethoxyethane in Aqueous Solutions

Flow-rate = 11.8 cu. cm./sec.		Mean Deviation
$2.4805\pi^{-1/2}e^{-1.41t}$	i.e. $1.399e^{-1.41t}$	0.042

Absorption of Carbon Dioxide in Arsenious Oxide-Sodium Carbonate/Sodium Bicarbonate buffer solutions

Series I - Flow-rate = 5.9 cu. cm./sec.		
$1.5938\pi^{-1/2}e^{-0.75t}$	i.e. $0.899e^{-0.75t}$	0.037
Series II - Flow-rate = 11.8 cu. cm./sec.		
$2.5494\pi^{-1/2}e^{-1.41t}$	i.e. $1.438e^{-1.41t}$	0.042
Series III - Flow-rate = 17.7 cu. cm./sec.		
$3.3581\pi^{-1/2}e^{-1.86t}$	i.e. $1.895e^{-1.86t}$	0.055
Series IV - Flow-rate = 23.6 cu. cm./sec.		
$4.2985\pi^{-1/2}e^{-2.52t}$	i.e. $2.425e^{-2.52t}$	0.064
Series V - Flow-rate = 29.5 cu. cm./sec.		
$4.6061\pi^{-1/2}e^{-2.57t}$	i.e. $2.599e^{-2.57t}$	0.063

Absorption of Carbon Dioxide in Sodium Carbonate/Sodium Bicarbonate Buffer Solutions (Kennedy)

Flow-rate = 11.8 cu. cm./sec.		
$2.4393\pi^{-1/2}e^{-1.39t}$	i.e. $1.376e^{-1.39t}$	0.050

DISCUSSION OF RESULTS AND CONCLUSIONS

The main conclusion which can be drawn from this work is that, under the conditions employed, the Danckwerts random surface-renewal model provides an excellent representation of the process of liquid film mass transfer in packed absorption columns. The results of the inversions show that, over a wide range of liquid flow-rates, the surface-age distribution function, $\Theta(t)$, is of the form:

$$S_1 e^{-S_2 t}$$

in which $S_1 \approx S_2$. When $S_1 = S_2$, $\int_0^\infty \Theta(t)\,dt = 1$, and S_2 can be identified with the parameter 'S', the fractional rate of renewal of the liquid surface in the Danckwerts model. The coefficients of all terms other than $e^{-S_2 t}$ were zero in each of the inversions carried out. In all cases excellent 'fits' were obtained, demonstrating that the experimental data were not being merely forced into a form which did not reasonably describe them. The failure to satisfy $\int_0^\infty \Theta(t)\,dt = 1$ exactly may be attributed to small errors in the chosen values of the diffusivity, D.

TABLE 1

Absorption system	Flow-rate, cu. cm. / sec.	S_1, sec.-1	S_2, sec.-1	Average vertical velocity, cm. / sec.	$\frac{S_2}{\text{Average vertical velocity}}$
Carbon dioxide into arsenious oxide-buffer solutions	5.9	0.899	0.75	2.08	0.36
	11.8	1.438	1.41	4.15	0.34
	17.7	1.895	1.86	6.23	0.30
	23.6	2.425	2.52	8.31	0.30
	29.5	2.599	2.57	10.39	0.25
1,1-dimethoxyethane into aqueous solutions	11.8	1.399	1.41	4.15	0.34
Carbon dioxide into uncatalysed buffer solutions (Kennedy)	11.8	1.376	1.39	4.15	0.33

Table 1 shows that the values of S_2 can be approximately related to the average residence times on the packing at the various flow-rates employed. The residence times vary inversely with the average vertical velocities of the liquid in the column and the latter were calculated from the liquid flow-rate and 'operating' hold-up in the column. In fully-developed laminar flow the surface velocity of the liquid on the packing would be $\frac{3}{2}$ x average vertical velocity.

In view of the limited ranges of reaction rates employed, less weight was attached to the inversions carried out for the 1,1 - dimethoxyethane and uncatalysed buffer systems. The agreement with the results for the spiked buffer system at the same liquid flow-rate (11.8 cu.cm./sec.) does, however, seem significant. In spite of the wide variation in the physical properties of the three systems, Θ (t) was effectively constant. The range of relative viscosities employed with the dimethyl acetal and uncatalysed buffer systems was 1.57 ± 0.01 while that for the spiked buffer solutions was 1.17 ± 0.01. The average densities were 1.15, 1.10 and 1.04 gm./cu.cm. respectively. It would appear, therefore, that the age-distribution function is not critically dependent on either the solution viscosity or density. The liquid flow-rate seems to be the only major variable which affects Θ (t) although it might be expected that the characteristics of the packing play some role. It will be further observed that the exponential form of the surface-age distribution function remained unchanged over the five-fold range of liquid flow-rates employed.

The experimental results for the catalysed buffer solutions show that for physical absorption the liquid-film mass-transfer coefficients, after resolution of the interfacial areas, were proportional to (liquid flow-rate)$^{1/3}$. They were, however, independent of the liquid flow-rates at high reaction velocities. Both these results are illustrated in Table II. The former is in agreement with, for example, Davidson's theoretical analysis (6) of absorption rates assuming complete mixing at discontinuities, from which it can be shown that k_L is proportional to $L^{1/3}$ for physical absorption. However, when kt is very large, $k_L \approx \sqrt{Dk}$ and would therefore be expected to be independent of the liquid flow-rate.

TABLE II

Absorption of Carbon Dioxide into Arsenious Oxide

Sodium Carbonate - Sodium Bicarbonate Buffer Solutions

Liquid flow-rate, L, cu. cm/sec.	Physical absorption			Chemical absorption at a reaction velocity constant of 20.0 sec^{-1}	
	$(k_L a)$ phys. $sec^{-1} \times 10^3$	(k_L) phys. cm. $sec^{-1} \times 10^3$	$\frac{(k_L)\text{ phys.}}{L^{1/3}}$	$k_L a$, $sec.^{-1} \times 10^3$	k_L, cm. $sec^{-1} \times 10^3$
5.9	3.248	3.985	2.21	14.66	17.99
11.8	4.857	4.838	2.13	17.99	17.92
17.7	6.834	5.565	2.14	22.34	18.19
23.6	8.234	6.145	2.14	24.10	17.99
29.5	9.808	6.470	2.09	27.39	18.06

ALTERNATIVE SURFACE RENEWAL AND REJUVENATION MODELS

The Higbie model postulates a surface-age distribution function of a form which is clearly not borne out by the results of the inversions. On the other hand, the distribution function of the Davidson random lengths and angles theory is fairly similar to that of the Danckwerts surface renewal model and would, therefore, be expected to lead to predictions in close agreement with those based on the Danckwerts theory.

The possibility of 'surface rejuvenation', in which complete mixing and the formation of fresh surface at the discontinuities do not occur, has been raised by Danckwerts (5) and Andrew (1). In a process of this kind, $\Theta(t)$ would not decrease monotonically from its maximum value at $t = 0$ as in the Danckwerts surface-renewal model. Instead, surface rejuvenation might be expected to lead to a distribution function with a maximum at some value at $t > 0$. It would then decrease to zero as $t \longrightarrow \infty$. This might be represented by a function which included, for example, terms of the type $\alpha_1 t e^{-B_1 t}$, $\alpha_2 t^2 e^{-B_2 t}$, $\alpha_3 t^3 e^{-B_3 t}$,............. where α_1, α_2, ... and B_1, B_2 .... are constants. The choice of functions to represent $L\left[\frac{\Theta(t)}{t^{1/2}}\right]$ included several which would lead to inverses of this type. However, in no case did the transformed function contain such terms. The experiments described here therefore provide evidence to support the hypothesis of surface rejuvenation.

COMPARISON OF THE EXPERIMENTAL VALUES OF $L\left[\frac{\Theta(t)}{t^{1/2}}\right]$ WITH THEORETICAL SURFACE RENEWAL MODELS

If the concentration of unreacted gas in the bulk of the liquid is assumed to be negligible, the rate equation for absorption with irreversible first-order reaction for the Higbie model is (5) :

$$N = C^* \sqrt{Dk}\left(1 + \frac{1}{2k\tau}\right) \times \operatorname{erf}\sqrt{k\tau} + \frac{e^{-k\tau}}{\sqrt{\pi k\tau}} \qquad (6)$$

where τ is the effective exposure time of liquid on the packing.

Since $L\left[\frac{\Theta(t)}{t^{1/2}}\right] = k_L\sqrt{\frac{\pi}{D}} - 2k\frac{dk_L}{dk}\sqrt{\frac{\pi}{D}}$, the following expression for $L\left[\frac{\Theta(t)}{t^{1/2}}\right]$ can be derived :

$$L\left[\frac{\Theta(t)}{t^{1/2}}\right] = \frac{1}{\tau\sqrt{\frac{\pi}{k}}}\operatorname{erf}\sqrt{k\tau} + \frac{2e^{-k\tau}}{C^*\sqrt{Dk\tau}}(1 + k\tau) . - \frac{1}{\sqrt{\tau}}(1 + 2k\tau)e^{-k\tau} \qquad (7)$$

This expression tends to a value of zero as $k \longrightarrow \infty$ and to infinity as $k \longrightarrow 0$. It cannot, therefore, be fitted to the experimentally determined curves of $L\left[\frac{\Theta(t)}{t^{1/2}}\right]$ against the reaction velocity constant.

For the Danckwerts model, the corresponding rate equation for absorption with irreversible first-order chemical reaction is (4):

$$N = C^* \sqrt{D(k+s)} \tag{8}$$

and it can similarly be shown that

$$L\left[\frac{\Theta(t)}{t^{1/2}}\right] = S\sqrt{\frac{\pi}{k+s}} \tag{9}$$

As $k \longrightarrow \infty$, $L\left[\frac{\Theta(t)}{t^{1/2}}\right] \longrightarrow 0$

and at $k = 0$, $L\left[\frac{\Theta(t)}{t^{1/2}}\right] = \sqrt{\pi S}$

The expression, $S\sqrt{\frac{\pi}{k+s}}$, was fitted, in turn, to the experimental results for $L\left[\frac{\Theta(t)}{t^{1/2}}\right]$ at the different flow-rates by using various trial values of the parameter 'S'. Excellent 'fits' were obtained with the values of S, the Danckwerts surface-renewal factor, given in Table III.

Although the dependence of the rate of absorption on the reaction velocity constant is almost the same for both the Higbie and Danckwerts models, it will be seen that the Laplace transform of $\left[\frac{\Theta(t)}{t^{1/2}}\right]$ shows a greater difference and therefore provides a means of comparing the two theories. While it was possible to fit the experimental values of $L\left[\frac{\Theta(t)}{t^{1/2}}\right]$ to the Danckwerts model, no choice of t, with the Higbie model, could yield an $L\left[\frac{\Theta(t)}{t^{1/2}}\right]$ curve which agreed with the experimental data.

TABLE III

Absorption system	Flow-rate, cu. cm. / sec.	Surface renewal factor, S, sec^{-1}
Carbon dioxide into arsenious oxide-buffer solutions	5.9 11.8 17.7 23.6 29.5	1.00 1.44 1.90 2.32 2.57
1,1-dimethoxyethane into aqueous solutions	11.8	1.39
Carbon dioxide into uncatalysed buffer solutions (Kennedy)	11.8	1.36

ANALYSIS OF EXPERIMENTAL VALUES OF THE MASS TRANSFER COEFFICIENT IN TERMS OF THE SURFACE- RENEWAL MODELS

Danckwerts Model

Equation (8) may be rewritten as

$$Na = k_L a c^* = a c^* \sqrt{D(k+s)}$$

Thus a plot of $(k_L a)^2$ against k should give a straight line of slope $a^2 D$ and intercept $a^2 Ds$. The ratio of the intercept to the slope yields S, and a can be calculated from the estimated value of 1.637×10^{-5} cm^2/Sec. for the diffusivity. An example of such a plot (Series 11 - Carbon Dioxide/Arsenious Oxide - Buffer System) is shown in Figure 12 and the values of a and S obtained by this method are listed in Table IV. In each case there was a very good linear relationship. The variation of S with liquid flow-rate is illustrated in Figure 13.

TABLE IV

Absorption System	Flow-rate, cu. cm./sec.	a, cm^{-1}	S, sec^{-1}	t, sec.
Carbon dioxide into arsenious oxide-buffer solutions	5.9 11.8 17.7 23.6 29.5	0.80 0.96 1.18 1.25 1.42	1.04 1.55 2.04 2.65 2.93	1.31 0.89 0.67 0.55 0.50
1,1-dimethoxyethane into aqueous solutions	11.8	1.01	1.57	0.92
Carbon dioxide into uncatalysed buffer solutions (Kennedy)	11.8	1.06	1.45	0.93

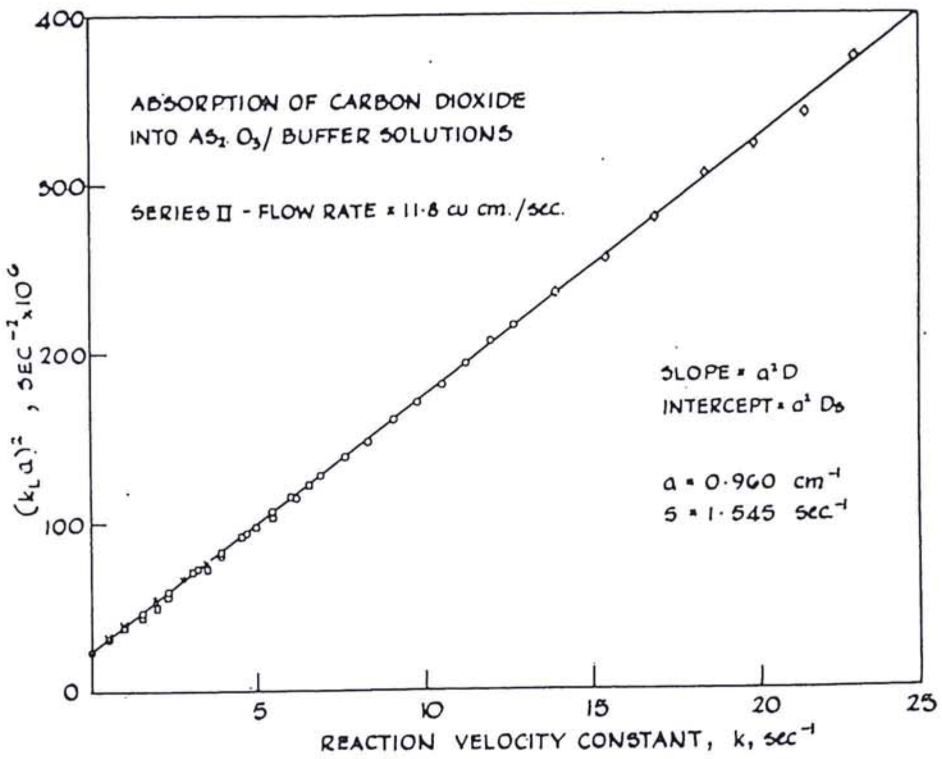

FIGURE 31 ANALYSIS IN TERMS OF DANCKWERTS MODEL

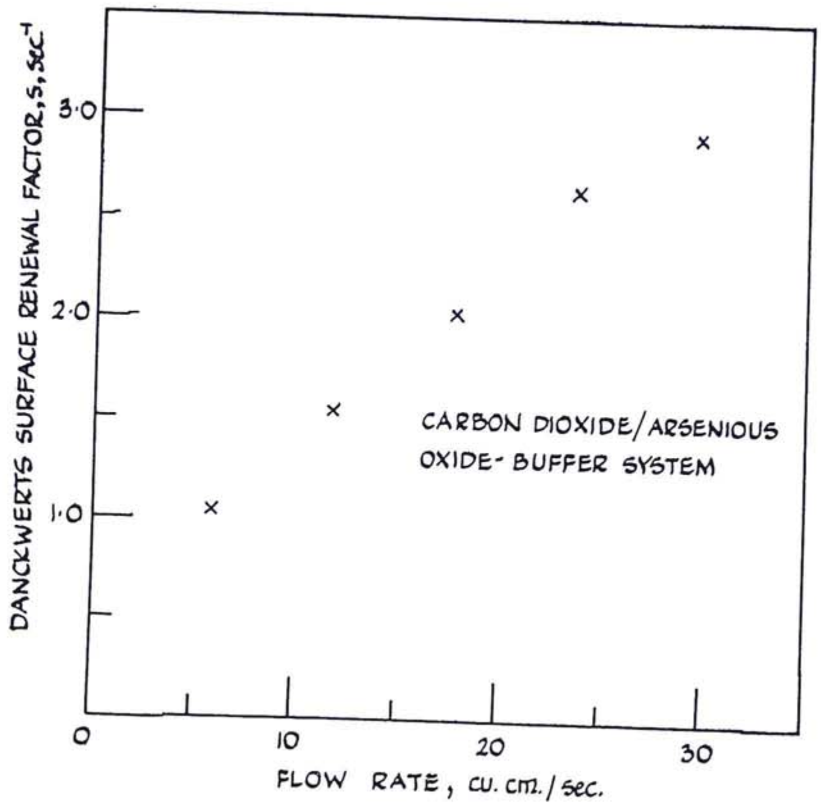

FIG. 13 VARIATION OF DANCKWERTS SURFACE RENEWAL FACTOR WITH LIQUID FLOW RATE

Higbie Model

According to the Higbie model where $k_{Lp} = 2\sqrt{\frac{D,}{\pi \tau}}$ is the liquid-film mass-transfer coefficient for physical Equivalent values of τ, the effective exposure time of the liquid on the packing, can therefore be deduced from the experimental values of k_{Lp} These are given in Table IV.

COMPARISON OF EXPERIMENTAL VALUES OF THE MASS-TRANSFER COEFFICIENT WITH THOSE PREDICTED BY THEORETICAL MODELS

For a first-order irreversible reaction, the Whitman model leads to (15):

$$N = C^{*}\sqrt{Dk} \;/\; \tanh B \sqrt{k/D} \qquad (10)$$

where B is the effective liquid-film thickness. This may be rewritten in the form

$$N_a = k_L a C^{*} = ac^{*} \qquad \sqrt{Dk} / \tanh B \sqrt{k/D}$$

or

$$k_L a = a\sqrt{Dk} / \tanh \sqrt{\frac{Dk}{k^2_{Lp}}} \qquad (11)$$

The corresponding expressions for the Higbie and Danckwerts models (equations 6 and 8) can similarly be expressed in terms of k_{Lp}

Higbie Model

$$k_L a = a\sqrt{Dk}\left(1 + \frac{k^2_{Lp}}{8Dk}\right) \text{ x erf } \frac{2}{k_{Lp}}\sqrt{\frac{Dk}{\pi}} + \frac{2a}{C^{*}k_{Lp}}\sqrt{Dk} \text{ x } \exp\left(\frac{-4Dk}{\pi k^2_{Lp}}\right) \qquad (12)$$

Danckwerts Model

$$k_L a = a \sqrt{Dk + k^2_{Lp}} \qquad (13)$$

With the aid of the expressions 11, 12 and 13, values of $k_L a$ at different reaction velocities can be predicted by the three models for each of the liquid flow-rates employed. Figure 14 represents a typical plot. k_{Lp} was the experimentally determined value for absorption into non-reacting solutions having the same viscosity as the catalysed buffer mixtures.

The three models lead to closely similar predictions about the effect of chemical reaction on absorption rates.

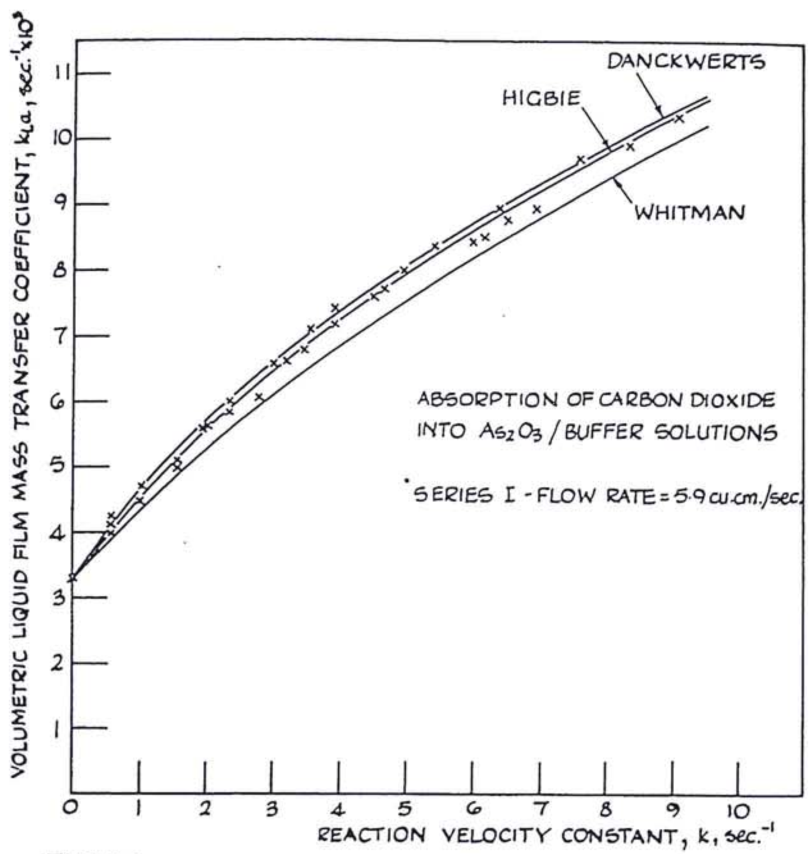

FIG.14 COMPARISON OF EXPERIMENTAL DATA WITH VALUES PREDICTED BY THEORETICAL MODELS

PREDICTION OF ABSORPTION RATES IN PACKED COLUMNS

This work has shown that the actual distribution of surface ages of the liquid in the packing is closely similar to that postulated by the Danckwerts model. In order to predict the rate of absorption in a packed column, therefore, the only further knowledge required is the rate of absorption, F (t), into a stagnant liquid as a function of time for the gas and liquid in question. The integral $\int_0^\infty F(t)\,\Theta(t)dt$ may then be evaluated to obtain the rate of absorption per unit area of wetted surface in the column.

It should also be possible to predict absorption rates in unknown cases by combining $\Theta(t)$ with empirical transient absorption measurements. These measurements of $F(t)$ will allow for such factors as the mechanism and order of the reaction, depletion effects and possible temperature changes at the surface of the liquid due to solution or reaction and these need not, therefore, be taken into account. The Danckwerts model possesses the great advantage over the film model in that an explicit knowledge of the physico-chemical quantities (or, indeed, the orders of any chemical reactions which may take place) is not required. The uncertainties involved in the estimation of these various factors are therefore removed.

SYMBOLS USED

a	Effective interfacial area per unit packed volume	cm^{-1}
A	Cross-sectional area of packed column	cm^2
B	Effective liquid-film thickness (Whitman model)	cm
C^*	Equilibrium concentration of solute in liquid phase	gm. mole/cm^3
C_o	Concentration of unreacted dissolved gas in bulk of liquid	gm. mole/cm^3
D	Diffusivity of solute gas in the liquid phase	cm^2/sec
F (t)	Rate of absorption per unit area after exposure for time t	gm. mole/cm^3 sec
h	Height of exposed packing in column	cm
I	Solution ionic strength	gm. ion/L
k, k_1	First-order reaction velocity constant	sec^{-1}

k_2	Second-order reaction velocity constant	l/gm mole/sec
k_g	Gas-phase mass-transfer coefficient	cm/sec
k_ga	Volumetric gas-phase mass-transfer coefficient	sec^{-1}
k_L	Liquid-film mass transfer coefficient	cm/sec
k_La	Volumetric liquid-film mass-transfer coefficient	sec^{-1}
k_{Lp}	Liquid-film mass-transfer coefficient for physical absorption	cm/sec
L	Liquid flow-rate	cm^3/sec
$L[\ ]$	Laplace integral operator	
M	Total rate of absorption in height h of packed column	cm^3/sec
N, R	Average rate of absorption per unit area of wetted surface in packing	cm^3/sec
S	Fractional rate of renewal of surface (Danckwerts model)	sec^{-1}
t	Time	sec
α, β	Constants	
θ (t)	Surface-age distribution function	sec^{-1}
τ	Effective time of exposure of liquid surface (Higbie model)	sec

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