Gas Absorption Accompanied by Chemical Reaction

P. V. Danckwerts
United Kingdom Atomic Energy Authority, Risley, Warrington, Lancashire, England

This paper is concerned with the processes occurring on the liquid side of the interface when gases are absorbed by liquids, and by reactive liquids in particular. The mechanism of the transport of the solute gas up to the interface on the gas side is not considered. Reference will be made mainly to absorption in the type of equipment often used industrially, in which the absorbing liquid runs over an extended rigid surface, typical examples being ring- and grid-packed towers. However, much of what is said will have some bearing on absorption under other circumstances, for instance at the surface of a stirred liquid or rising bubble.

In the case of packed towers and similar equipment consideration will be confined to the processes occurring in a representative horizontal slice of packing (which will include at least one vertical unit of such ordered packings as grids or stacked rings). The paper will not be concerned with the progressive changes in the bulk compositions of the gas and liquid streams along the axes of flow, although this is of course an important aspect of the problem of designing complete pieces of equipment.

The interfacial partial pressure of the solute gas in the region considered is such that its saturated concentration at the surface of the liquid is c^* (this refers to *unreacted* gas in cases where the solute gas reacts with the absorbent). The effect of an interfacial resistance, which would prevent equilibrium at the interface, will not be considered. There is some evidence that such resistances may exist(*5, 6*); however, their magnitude appears to have little effect under conditions of practical interest(*5*), and their existence would in any case not affect the general conclusions reached here. The bulk concentration of unreacted dissolved gas in the region considered is c_o, and the effective area of liquid-gas interface per unit gross volume of the packed space is a. It is a well-established experimental fact that when no reaction occurs in the liquid the rate of absorption per unit gross volume, aN is given by an expression of the form

$$aN = k_L a\,(c^* - c_o) \qquad (1)$$

For the moment this equation may be taken as defining k_L, which will be used to mean the mass transfer coefficient for physical absorption into a nonreacting liquid. For a given gas and liquid $k_L a$ is constant under given hydrodynamic conditions (e.g., size and shape of packing, liquid flow rate, etc.). However, there is reason to suppose that the effective value of a is in general less than the geometrical surface of the packing and that both a and k_L change when the hydrodynamic conditions are varied. It is therefore not easy to assign values to a and k_L separately, and often only the product $k_L a$ is reported, as this can be directly determined from measurements of the volumetric absorption rate aN and a knowledge of c^* and c_o.

Several different types of model have been proposed for the processes which control the rate of absorption, and hence the value of k_L. Of these the two most familiar lead to the film and penetration theories of absorption.

THE FILM THEORY

The film theory was first put forward by Whitman(*26*); its implications are perhaps most clearly understood if absorption of gas into the horizontal surface of a stirred liquid is considered. Elaborating the original statement of the theory somewhat, one may suppose that the turbulence created in the main body of the liquid by stirring is damped out in the neighborhood of the surface, as it would be near a rigid surface. The scale of turbulence and the magnitude of the eddy diffusivity are supposed to become progressively smaller as the surface is approached, until transport by eddies becomes of negligible importance. There will thus be a region in the immediate neighborhood of the surface through which the solute is transported by molecular diffusion alone. Transport by eddy diffusion becomes increasingly important at greater depths, and the bulk of the liquid is kept virtually uniform in composition by large-scale eddies.

It is convenient for practical purposes to replace this picture by a simpler model (as is often done in the consideration of transfer from rigid surfaces) in which there is supposed to be a completely stagnant surface film of definite thickness B, which offers all the resistance to absorption and which overlies liquid having the bulk concentration c_o. Clearly this model very much oversimplifies the situation described in the preceding paragraph and must therefore be treated with caution if used to simulate the behavior of the real system. If the gas and liquid at the interface are in equilibrium, and steady-state diffusion through the film is assumed, the simplified model gives rise to the expression

$$N = \frac{D}{B}(c^* - c_o) \qquad (2)$$

whence

$$k_L = D/B \qquad (3)$$

D being the molecular diffusivity of the dissolved gas. It is found experimentally that k_L, and hence

B, is not uniquely determined by the hydrodynamic conditions, being roughly proportional to $D^{\frac{1}{2}}$(*21*), but this might reasonably be regarded as a consequence of the simplifying assumption. [Similarly the effective film thickness for *solid*-liquid transfer under forced convection is found to vary as $D^{\frac{2}{3}}$ (*17*).]

The film model has been widely applied, perhaps with less plausibility, to absorption into the liquid running over the packing in an absorption tower.

THE PENETRATION THEORY

The penetration theory, proposed originally by Higbie(*7*) and modified by Danckwerts(*3*), supposes that turbulence extends to the surface of the liquid, so that eddies are constantly bringing macroscopic masses of fresh liquid from the interior to the surface, where they are exposed to the gas for a finite time before being replaced. Between its first exposure and ultimate replacement each element of liquid surface absorbs gas at a rate which is approximately the same as the rate of absorption into a stagnant liquid of infinite depth exposed to the gas for the same length of time; in general the absorption rate decreases with the time of exposure. Thus at a given moment the surface of a stirred liquid is a mosaic of elements of different "ages" which are absorbing at different rates. The average rate of absorption depends on the distribution of the elements of the surface among the various "age groups." In an absorption tower the liquid may be in laminar flow on the continuous surfaces of the packing and may be completely or partially mixed up at the points of discontinuity between packing elements. Each element of surface moving down the packing is supposed to absorb approximately as would a stagnant semiinfinite liquid over the same time interval and to be replaced sooner or later with fresh liquid of the bulk composition as the result of mixing at the discontinuities. Here again a representative slice of the packing will display at a given moment a spectrum of surface ages which will determine the average rate of absorption.

To find the average absorption rate per unit area of surface N, one multiplies the fraction of surface which has the age t by the stagnant-liquid absorption rate for an exposure time t and sums the product over all surface ages. It is convenient to define a distribution function $\phi(t)$ such that the fraction of the surface having ages between t and $(t + dt)$ is $\phi(t) \cdot dt$. If the amount of gas absorbed by unit area of stagnant surface at time t is $Q(t)$, we have then

$$N = \int_{t=0}^{\infty} \phi(t) \frac{dQ(t)}{dt} dt = \int_{t=0}^{\infty} \phi(t)\, dQ(t) \qquad (4)$$

Before the penetration theory can be used, the form of the surface-age distribution function $\phi(t)$ must be known or postulated. The two simplest models each lead to expressions for $\phi(t)$ characterized by a single parameter. Higbie postulated a simple situation in which each element of surface is exposed for the same length of time, θ, before being replaced. Thus $\phi(t) = 1/\theta$ for $t < \theta$, and $\phi(t) = 0$ for $t > \theta$. The average rate of absorption is then

$$N = Q(\theta)/\theta \qquad (5)$$

where $Q(\theta)$ is the amount of gas absorbed by unit area of stagnant surface in time θ (Figure 1).
For physical absorption

$$Q(\theta) = 2(c^* - c_o)\sqrt{D\theta/\pi},$$

and Higbie's model therefore leads to

$$k_L = 2\sqrt{D/\pi\theta} \qquad (6)$$

Danckwerts suggested that it might be more realistic, at any rate in the case of randomly arranged packings and stirred liquids, to suppose that there was no correlation between the age of an element of surface and its chance of being replaced. The distribution function $\phi(t)$ then has the form

$$\phi(t) = se^{-st} \qquad (7)$$

where s is the fractional rate of surface renewal. Inserting this expression for $\phi(t)$, and $Q(t)$ for physical absorption, into Equation (4), one finds

$$k_L = \sqrt{Ds} \qquad (8)$$

The distribution of ages in the Danckwerts model corresponds to that in a population in which the death rate s is independent of age; whereas Higbie's model corresponds to a population in which everyone dies at the same age θ. The Higbie and Danckwerts forms of $\phi(t)$ are compared in Figure 2, and it may be noted that they overlap to a considerable extent. Whatever form the age-distribution function is assumed to have, the penetration theory will always predict that k_L is proportional to $D^{\frac{1}{2}}$ and will give rise to the conventional rule for the addition of "resistances" in series(*19*).

EFFECTS OF CHEMICAL REACTION

In order to calculate the effect of a chemical reaction between absorbed gas and liquid on the basis of any one of the three models described, it is necessary to use the quantity k_L, which is the hypothetical mass transfer coefficient for absorption without reaction. The value of $(k_L a)$ may be found by measuring the absorption rate of a gas of known solubility and diffusivity into an inert liquid under identical hydrodynamic conditions; a liquid of the same viscosity and density as the reacting liquid must be used. The value of $(k_L a)$ thus found must be multiplied by the factor $(D_2/D_1)^{\frac{1}{2}}$, where D_1 is the diffusivity of dissolved gas in the inert liquid and D_2 that of unreacted dissolved gas in the reacting liquid. In view of the uncertainty involved in estimating D_2 (*see* below) and the fact that the diffusivities of many solutes in, for instance, aqueous solutions of equal viscosity are approximately equal, this correction may in practice often be omitted. Alternatively $(k_L a)$ may be estimated by means of some empirical formula, such as that of Sherwood and Holloway(*21*), based on experiments made under fairly similar hydrodynamic conditions. The value of k_L can be found from $(k_L a)$ only if there is some independent method of measuring a. Since a represents not necessarily the total wetted surface but that part of it which is effective in gas absorption, measuring it independently is clearly a matter of some difficulty. Various methods of measurement have been suggested, and the results embodied in formulas involving the hydrodynamic variables(*10*). The results are of doubtful significance, particularly in view of the conclusions reached later in the present discussion. An alternative method, described later, is the measurement of (aN) by use of, for instance, both an inert and a reacting solution. It will be assumed for the moment that unambiguous values of k_L and a can be determined for a given system.

A knowledge of the following quantities is also required: c^*, the solubility of *unreacted* gas in the reacting liquid; D, the diffusivity of *unreacted* dissolved gas; the velocity constant of the reaction; and equilibrium constants (if reversible reactions occur). The quantities c^* and D are not accessible to direct measurement and must be estimated as well as possible; both will be influenced by the concentration and composition of the solution. The mechanism of the reaction between the dissolved gas and the solution may often be open to doubt. If it is known, the equations for diffusion accompanied by chemical reaction can be solved analytically only in certain simple cases. The reaction-velocity constant is often strongly dependent on the concentration and composition of the solution, and its value may have to be estimated by extrapolation from very different conditions. The calculation of equilibrium concentrations, particularly in systems involving ions, is complicated by the nonideal behavior of the reactants.

As explained later, explicit knowledge of the physicochemical quantities mentioned in the last paragraph may be unnecessary if the penetration theory in one of its forms is accepted as a valid basis for the calculation.

First-Order Reactions

As an example of the calculation of the effect of a reaction on the absorption rate N, the case of an irreversible first-order reaction (velocity constant r) may be considered. It leads to the destruction of the dissolved gas, the bulk concentration of this being taken as zero. The steady state and transient diffusion equations have been solved for this case and lead to the following expressions for N for the different models.

Film model (22)

$$N = c^* \sqrt{Dr} / \tanh B \sqrt{\frac{r}{D}} \qquad (9)$$

$$N = c^* \sqrt{Dr} / \tanh \sqrt{\frac{Dr}{k_L}} \qquad (9a)$$

Penetration model [*Higbie* (2)]:

$$N = c^* \sqrt{Dr} \left(1 + \frac{1}{2r\theta}\right) \times$$

$$\operatorname{erf} \sqrt{r\theta} + e^{-\theta r} / \sqrt{\pi r \theta} \qquad (10)$$

$$N = c^* \sqrt{Dr} \left(1 + \frac{k_L{}^2}{8Dr}\right) \times$$

$$\operatorname{erf} \frac{2}{k_L} \sqrt{\frac{Dr}{\pi}} + \frac{2}{k_L} \sqrt{Dr} \times$$

$$\exp\left(-4Dr/\pi k_L{}^2\right) \qquad (10a)$$

Penetration model [*Danckwerts* (3)]:

$$N = c^* \sqrt{D(r+s)} \qquad (11)$$

$$N = c^* \sqrt{Dr + k_L{}^2} \qquad (11a)$$

Equations (9a), (10a), and (11a) are obtained by substituting for B, θ and s respectively in terms of k_L for the appropriate model as given by Equations (3), (6), and (8).

The effect of this or any type of chemical reaction on the rate of absorption can be expressed as the ratio of the rate of absorption with chemical reaction to the rate of absorption in the absence of reaction, other things being equal; this ratio will be denoted by α. In the present case α is obtained by dividing the foregoing expressions for N by $(k_L c^*)$, which is the hypothetical rate of physical absorption when c_o is zero. Each of the three models predicts that α will depend on k_L as well as on (Dr), being greatest when k_L is small, and vice versa. In fact the effect of the reaction depends on the single parameter $(Dr/k_L{}^2)$; α varies in each case from unity when this is small to $(\sqrt{Dr}/k_L)$ when it is large. In spite of the difference in mathematical form of the expressions based on the three models, they give numerically almost equal values for α, with a maximum divergence of less than 10% over the entire range of $(Dr/k_L{}^2)$ from 0 to ∞ (*5*).

The dependence of α on k_L, and the numerical agreement among the three models, are also found in the expressions for irreversible first-order reaction with a finite value of c_o or for reversible first-order reaction (*5*).

Second-Order Reactions

If the dissolved gas is assumed to undergo a second-order reaction with a reagent which can diffuse through the liquid, the resulting diffusion equations cannot in general be solved analytically for either the steady state or the transient cases. However, van Krevelen and Hoftyzer (*11*) have used a step-by-step method to obtain solutions for the film model, and Perry and Pigford (*20*) have obtained expressions for transient absorption rates by means of an electronic computer. In both cases the calculations were simplified by assuming the diffusivities of the dissolved gas and the reagent to be equal. As with first-order reactions, there appears to be general numerical agreement among the predictions based on the film model and the two penetration models (*8, 12*).

Three extreme types of behavior are predicted under limiting conditions. If c'_o is the bulk concentration of the reagent (c^* and c'_o should be expressed in chemical equivalents) and r' is the second-order reaction-velocity constant between dissolved gas and reagent (c_o being assumed equal to zero), then

$$(a)\ \text{if} \quad \sqrt{Dr' c_o'}/k_L \ll 1$$

$$\text{then} \quad N = k_L c^* \qquad (12)$$

$$\text{i. e.,} \quad \alpha = 1$$

$$(b)\ \text{if} \quad \sqrt{Dr' c_o'}/k_L \gg c_o'/c^*$$

$$\left.\begin{aligned} \text{then} \quad & N = k_L (c^* + c_o') \\ \text{i. e.,} \quad & \alpha = 1 + c_o'/c^* \end{aligned}\right\} \qquad (13)$$

$$(c)\ \text{if} \quad 1 \ll Dr' c_o'/k_L \ll c_o'/c^*$$

$$\left.\begin{aligned} \text{then} \quad & N = c^* \sqrt{Dr' c_o'} \\ \text{i. e.,} \quad & \alpha = \sqrt{Dr' c_o'}/k_L \end{aligned}\right\} \qquad (14)$$

In case a the reaction is so slow or k_L so large that the reaction does not appreciably affect the absorption rate. In case b the reaction between the dissolved gas and the reagent is exceedingly fast, and the rate of absorption is controlled by the diffusion of the two substances to the site of the reaction within the film. In case c the concentration of the reagent is so high that the reaction is pseudo first order and so fast that the absorption rate is independent of k_L, as in the case of a true first-order reaction when $Dr/k_L{}^2 >> 1$. In cases which do not fall into any of these limiting categories the value of α is in general dependent on k_L.

SIMPLE FILM AND PENETRATION MODELS INVALID

It has been pointed out that in cases where the calculations have been made the film model and the two simple penetration models lead to closely similar quantitative predictions concerning the effects of chemical reaction on the absorption rate. It might seem to be immaterial for practical purposes which type of model is used as a basis for calculation, as if any one of the three is valid the use of the others would also be expected to give approximately correct results. However, the penetration models have a great advantage if it is possible to measure in the laboratory the transient rate of absorption of gas into stagnant liquid for short times of exposure (i.e., $Q(t)$ vs. t for small values of t). The Higbie or Danckwerts model can then be used to calculate N for absorption in conditions for which θ or s (i.e., k_L) is known, by use of Equation (4) with the appropriate form of $\phi(t)$. Explicit knowledge of such inaccessible quantities as c^*, D, r, etc., is not required, nor is it necessary to know the mechanism or order of the reaction. If absorption causes a rise in temperature at the surface of the liquid(*4*), this is also automatically allowed for. It is thus possible to make a comparison between the observed and predicted effects of reaction without introducing the uncertainties involved in the estimation of these various factors.

The Higbie model will be used to illustrate the process, since this is the simpler to follow. With the appropriate absorbing liquid and gas (the latter being at the right pressure or partial pressure to give the required value of c^*), $Q(t)$ is determined as a function of t by means of a rotating drum(*5*), a falling film(*6*), or some other technique. Absorption measurements are also made in, for instance, a packed tower by use of the same liquid and gas. If the exposure time of elements of liquid surface in the tower is θ, the average absorption rate N per unit area of interface is $Q(\theta)/\theta$ (Figure 1). The quantity actually measured in the column is the absorption rate per unit volume of packing(aN). There are thus two unknowns, a and θ. Comparing the results for two solutions which give Q vs. t curves of different shapes (e.g., absorption of carbon dioxide into an inert solution and a buffer solution) makes it possible to solve for both a and θ. If the Higbie model is valid, these same values should then enable one to predict the tower absorption rate (aN), under identical hydrodynamic conditions, for any other solution for which the Q vs. t curve is measured.

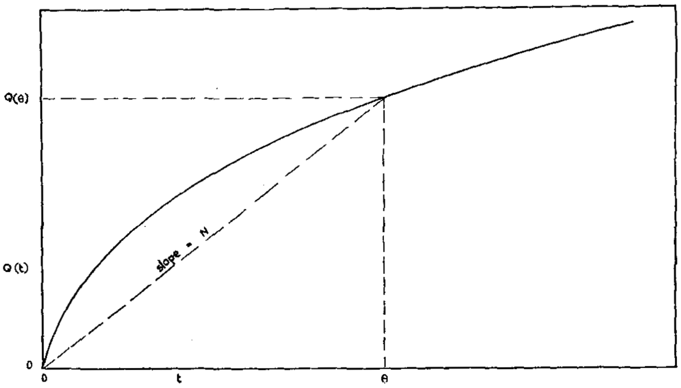

Fig. 1

Kennedy(*5, 9*) has measured the transient rates of absorption of carbon dioxide into inert solutions, alkaline buffer solutions, and caustic soda solutions for times of exposure up to ¼ sec. Measurements were also made of the absorption rate (aN) in a tower packed with ½-in. Raschig rings under carefully standardized hydrodynamic conditions. It appears from these measurements that no single pair of values for a and θ will serve to correlate the observed absorption rates for different solutions in the tower in spite of the constancy of hydrodynamic conditions. For instance, the values of a and θ required to account for absorption into inert solutions and dilute caustic soda solutions appeared to be about 0.5 cm.$^{-1}$ and 0.15 sec. respectively, while the values for absorption into the buffer solutions were about 1.2 cm.$^{-1}$ and 1 sec. Thus the apparent wetted area varied from about 15% of the geometrical surface in the first case to about 30% in the second, and the corresponding apparent values of k_L could be estimated as about 0.13 and 0.05 cm./sec. Very similar conclusions were reached when the Danckwerts model was used as a basis of calculation.

A possible reason for this discrepancy is that the actual distribution of surface ages in the packing departs widely from that postulated in either the Higbie or the Danckwerts models. It seems likely that the "younger" elements of the surface may have a relatively greater rate of replacement than the "older" elements. In other words, there are regions in the packing where the flow is brisk and the rate of turnover high, and other parts where the liquid is relatively stagnant. The distribution of ages then corresponds to that in a population with a high infant mortality rate, and it may give a relatively greater weight to the older parts of the surface than either the Higbie or Danckwerts models, as indicated in Figure 2*c*.

Figure 3 shows calculated curves of $Q/c^*\sqrt{D}$ vs. t for (a) physical absorption, (b) absorption with irreversible first-order reaction ($r =$ 2.2 sec.$^{-1}$), (c) absorption with very fast first-order reaction ($r =$ 22 sec.$^{-1}$). In case (a) the absorption rate into the stagnant liquid falls off rapidly with exposure time, and so the absorption rate in the tower is strongly dependent on the rate of renewal of liquid surface. In case (b) (where the behavior is similar to that calculated and found experimentally for the absorption of carbon dioxide into buffer solutions of *pH* about 10.7) the transient absorption rate falls off at first and then becomes constant; the absorption rate in the tower is then less dependent on the surface-renewal rate. Finally, in case (c), the rate of absorption into the stagnant liquid is virtually constant, and the tower absorption rate is independent of surface renewal. It can be seen therefore that absorption into inert liquids in the tower will take place mainly in the regions where the rate of surface renewal is high. A first-order reaction, by maintaining the rate of absorption into older surfaces, enables a larger proportion of the absorption to occur in regions where the surface-renewal is low. In the limit a very fast first-order reaction gives the same rate of absorption into all regions of the wetted surface.

Without being committed to either the film or penetration models, one can say that the local value of k_L probably varies from one region to another in the packing. When k_L is determined for physical absorption, it is an average value which is obtained. If a reacting liquid is substituted, however, the reaction (if first order, for instance) will have more effect in the regions where k_L is small, and vice versa, and it is not possible to calculate the over-all effect unless the distribution of k_L values is known. In the case of an irreversible first-order reaction in which the reaction is so fast that $Dr/k_L^2 >> 1$ everywhere, the expressions for all three models agree [Equations (9*a*), (10*a*), (11*a*)] that N will be independent of k_L and equal everywhere to $c^*\sqrt{Dr}$.

Physical absorption, however, takes place predominantly in that fraction of the surface where k_L is large. If one takes a series of reacting solutions of increasing r, in effect more and more of the surface participates in absorbing gas. Similarly, in the case of a second-order reaction the effective wetted surface will be least in the cases where the local absorption rate is proportional to k_L [Equations (12) and (13)] and greatest in the case where it is independent of k_L [Equation (14)].

Since dissolved carbon dioxide undergoes, in effect, an irreversible first-order reaction with alkaline buffer solutions and since absorption into the dilute caustic soda solutions is believed to have been controlled by the diffusion of the reactants [the conditions of Equation (13)], Kennedy's observations are in general agreement with the foregoing arguments. Hoftyzer and van Krevelen(*8*) have shown that similar conclusions can be reached by considering some experiments by Tepe and Dodge(*24*) on the absorption of carbon dioxide in solutions of potassium hydroxide and caustic soda and by Comstock and Dodge(*1*) on the absorption of carbon dioxide in solutions of potassium carbonate and sodium carbonate, both in towers packed with Raschig rings. They have used a previous established equation for k_L as a function of flow conditions, packing diameter, diffusivity, etc., and have estimated the values of c^*, D and r' in the solutions considered. They show that certain of the measurements of Tepe and Dodge were made under conditions such that Equation (14) should be obeyed, with $c_o' = [\mathrm{OH}']$. Calculating N on this basis, they used the experimental values of (aN) to calculate a, the effective wetted area per unit volume of packing, which appeared to be 40% of the geometrical surface. For other measurements Equation (13) was applicable, and in this case a was about 2% of the geometrical surface. Certain of the experiments carried out by Comstock and Dodge approached the limiting conditions represented by Equation (14) (with $c_o' = [\mathrm{CO}^{3''}]$), and others by Equation (12). The values of a were again found to be about 40 and 2% respectively of the geometrical surface. The effective wetted surface therefore appears to be much less when the absorption rate is controlled entirely by diffusion, and thus proportional to k_L, than when it is independent of k_L. [The upper limit of 40% suggests that at best only about half the surface of a Raschig ring can be effectively irrigated(*8*).]

PROBLEMS OF INDUSTRIAL DESIGN

The nonuniformity of the value of k_L from one region of the packing to another makes it difficult to devise a generally valid procedure for the design of equipment for absorption accompanied by chemical reaction. If k_L were in fact uniform, and if the performance of the equipment for physical absorption under the appropriate hydrodynamic conditions were known, the effect of the reaction (i.e., the value of α) might be calculated in one of the following ways:

a. If the reaction mechanism is known and values of such physicochemical quantities as c^*, Dr, etc., can be estimated, then a solution of the equations for the film or penetration models leads to formulas such as Equations (9) to (14).

b. If the transient absorption rate of the gas into stagnant liquid is measured, the Higbie or Danckwerts model can be employed [Equation (4)].

c. The value of α, which would be the same for both systems, can be determined in a laboratory model having the same value of k_L as the full-scale equipment.

Modifications of these methods can be used if it is possible to discover the actual distribution of k_L values; this might conveniently be defined by a distribution function $\psi(k_L)$ such that the local value of the liquid-film coefficient lay between k_L and $(k_L + dk_L)$ over parts of the surface having an area corresponding to a fraction $\psi(k_L) \cdot d(k_L)$ of the geometrical surface a_d. The volumetric rate of physical absorption would be given by

$$(aN) = (c^* - c_o)\, a_d \int_0^\infty k_L \cdot \psi(k_L) \cdot d(k_L) = \bar{k}_L\, a_d\, (c^* - c_o) \qquad (15)$$

$\bar{k}_L$ being the average value of k_L over the entire geometrical surface. As already shown, the ratio α which determines the effect of reaction on absorption rate is in general a function of k_L, which may be written $\alpha(k_L)$, and will vary from one region to another. The average value $\bar{\alpha}$ for the surface as a whole would be given by

$$\bar{\alpha} = \int_0^\infty \alpha(k_L) \cdot \psi(k_L) \cdot d(k_L) \qquad (16)$$

There is not necessarily any simple relationship between $\bar{\alpha}$ and $\bar{k}_L$.

Alternatively, one may use the language of the penetration theory and say that the surface-age dis-

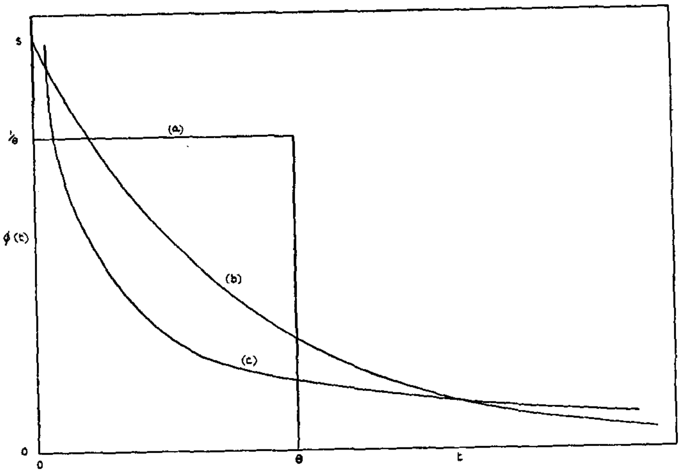

Fig. 2. Surface-age distribution functions $\phi(t)$; (a), Higbie, $\theta = 4D/\pi k_L^2$; (b) Danckwerts, $S = k_L^2/D$; (c) hypothetical case giving greater weight to older parts of the surface.

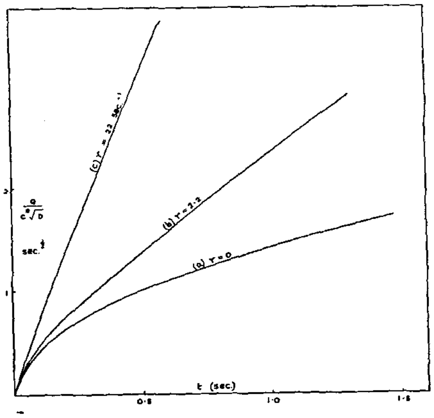

Fig. 3. Effect of first-order reaction on transient absorption.

tribution function $\phi(t)$ is not that of the Higbie or Daanckwerts models, but has some other form; if this were known, and $Q(t)$ known as a function of t by calculation or experiment, then $\bar{\alpha}$ could be found by evaluating Equation (4) for absorption with and without reaction.

An extension of Kennedy's work may make it possible to determine the actual distribution of k_L values or surface ages under the hydrodynamic conditions obtaining in his packed tower. It seems quite likely, however, that a change in hydrodynamic conditions (e.g., flow rate or packing size) might lead to an entirely different form for $\psi(k_L)$ or $\phi(t)$. The labor involved in determining these functions under all conditions of practical interest would then be prohibitive. Hoftyzer and van Krevelen(*8*) point out that investigations carried out under different sets of hydrodynamic conditions have led, for instance, to quite different conclusions about the effect of alkali concentration on the rate of absorption of carbon dioxide. These authors have suggested a simplified approximate design method for the case of second-order reaction, but its usefulness under various conditions requires to be tested by experiment.

The use of a laboratory model cannot be expected to give a value of $\bar{\alpha}$ which will be generally applicable to full-scale equipment, since the functions $\psi(k_L)$ or $\phi(t)$ are likely to have different forms in the two systems, even if the average coefficient $\bar{k}_L$ has the same value in both. Wetted-wall columns, "totem pole" columns, and stirred vessels do not give results which agree well with those for packed towers. Even geometrically similar models are unlikely to give satisfactory results because of the number of conditions which must be satisfied to ensure similarity in other respects. Thus in the case of an irreversible first-order reaction it appears that for a packing of a given shape $\bar{\alpha}$ will be a function of at least three dimensionless groups; for instance,

$$\bar{\alpha} = F\left\{\frac{dL}{\mu}, \frac{\mu^2 d^3}{\rho^2 g}, \frac{rd\rho}{L}\right\} \quad (17)$$

(where d is the particle diameter and L the mass velocity of the liquid).

If surface-tension effects are important, as they will be when the particles are sufficiently small, a fourth group must be added. A second-order reaction will require one or more further groups.

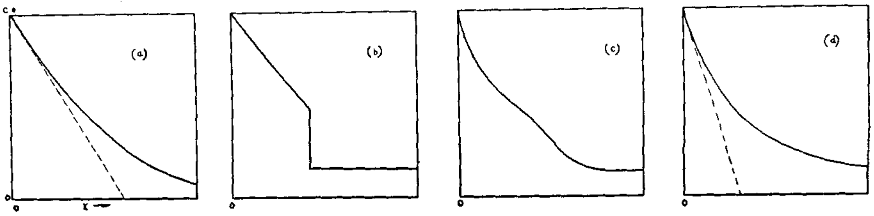

Fig. 4. Effect of discontinuity on concentration profile: (a) before discontinuity, (b) immediately after, (c) and (d) later stages.

However, there are certain circumstances in which laboratory experiments may be used to predict the effect of chemical reaction in industrial equipment. If the absorption rate per unit volume of packing (aN_A) is known for a given gas-liquid system A under specified hydrodynamic conditions, the absorption rate (aN_B) for some other gas-liquid system B under the same hydrodynamic conditions can be predicted provided the transient absorption curves (Q vs. t) for the two systems are geometrically similar, so that the ratio of Q_A to Q_B is constant. The following simple condition then holds:

$$\left(\frac{aN_B}{aN_A}\right) = \frac{Q_B}{Q_A} \quad (18)$$

The ratio Q_B/Q_A may be determined directly from transient absorption measurements, or it may be calculated if the data are available. Alternatively, the ratio $(aN_B)/(aN_A)$ may be determined in a model absorption apparatus, which need not have the same hydrodynamic characteristics as the full-scale equipment. For example, in the system A the gas might be absorbed in an inert liquid; the Q vs. t curve would then be parabolic:

$$Q_A = 2c^* \sqrt{D_A t/\pi} \quad (19)$$

In system B the dissolved gas might undergo an extremely rapid reaction with a reagent in the solution when

$$Q_B = 2\beta c_B^* \sqrt{D_B t/\pi} \quad (20)$$

β being a constant which is equal to $(1 + c'_0/c^*)$ when the diffusivities of the two reactants are equal(*23*). In such a case the ratio $(aN_B)/(aN_A)$ of the volumetric absorption rates for the two systems would be equal to $\beta c^*_B\sqrt{D_B}/c^*_A\sqrt{D_A}$, but it could be inferred directly from the Q vs. t curves without an explicit knowledge of the physical quantities involved. It could also be measured in a laboratory absorption apparatus if the two curves were known to be geometrically similar.

To take another example, the dissolved gas might in both systems undergo a very fast irreversible first-order or pseudo first order reaction. The Q vs. t curves would then be straight lines through the origin, of slope $c^*\sqrt{Dr}$, or $c^*\sqrt{Dr'c'_o}$, and $(aN_B)/(aN_A)$ would be equal to the ratio of the slopes.

The principle can be applied to all cases in which it is observed experimentally that the Q vs. t curves are geometrically similar, even when the mechanism of the absorption process is unknown. The method is easily justified if the penetration theory, in its most general form, is accepted, since from Equation (4)

$$N_B = \int_{t=0}^{\infty} \phi(t)\, dQ_B(t) = \frac{Q_B}{Q_A}\int_{t=0}^{\infty} \phi(t)\, dQ_A(t) = \frac{Q_B}{Q_A} \cdot N_A \quad (21)$$

The justification does not depend on the form of the surface-age distribution function $\phi(t)$. However, if the two Q vs. t curves are only approximately similar, the accuracy of the method may depend on the form of $\phi(t)$. In such a case, if a model is used to determine the ratio $(aN_B)/(aN_A)$, the results should be treated with caution. Too little information is at present available to enable a more precise statement to be made.

OTHER MODELS OF THE ABSORPTION PROCESS

Since 1949 Kishinevskii and others(*13, 14, 15*) have been developing a theory of gas-absorption which assumes that the liquid surface is constantly being replaced by fresh material. A mean value of the exposure time is introduced, corresponding to the quantity θ in Higbie's model. However, it is assumed that molecular diffusion plays little or no part in determining the rate of absorption; the process envisaged may be described as one of surface renewal without penetration. It is supposed that a layer at the surface of the liquid becomes instantaneously saturated with the gas on exposure, and this saturated layer is subsequently carried away into the bulk of the liquid. If a chemical reaction occurs in solution, the surface layer is kept constantly saturated with *unreacted* gas during the time of exposure, while the concentration of *reacted* gas increases at a rate determined by the kinetics of the reaction. The thickness of the surface layer is not discussed, but it seems necessary for the validity of the theory that it should be confined to an adsorbed film on the surface of the liquid; a deeper layer could be formed only by the diffusion of dissolved gas molecules into the liquid, and this would lead back immediately to the penetration theory. A detailed critical survey of Kishinevskii's theory is not possible here, but it apparently implies that the influence of the diffusivity of the solute gas on k_L should be negligible. Evidence on this point is scanty, but Sherwood and Holloway's measurements (*21*) seem to provide strong evidence that (as between O_2 and CO_2 on one hand and H_2 on the other) k_L varies approximately as $D^{\frac{1}{2}}$. Further evidence on this point would be welcome. It is interesting that recent work by Lewis (*16*) appears to show that rates of transfer across a liquid-liquid interface under turbulent conditions are independent of diffusivity.

There is a certain amount of evidence in favor of what may be called "surface rejuvenation" rather than surface renewal. The passage of liquid over a discontinuity between two smooth surfaces, on both of which the flow is laminar, may be considered; as a simple example one may consider the flow over two contiguous spheres. Although it may be expected that over a wide range of flow conditions some type of eddy may form at the junction of the spheres, it appears that complete mixing and renewal of the surface does not occur. Lynn, Straatemeier, and Kramers, for instance, have found (*18*) that the rate of absorption into water flowing over a vertical column of contiguous spheres corresponds more closely to that to be expected if no mixing occurs at discontinuities than to the case of complete mixing. Experiments with totem-pole columns suggest that complete mixing does not occur at the junction points between the disks. Wagstaffe (*25*) (using the Higbie model) has shown that the average exposure time required to account for observed absorption rates is usually greater than the average retention time on a disk (calculated from flow rate and holdup); the ratio of apparent exposure time to retention time depends on the flow rate and the physical properties of the liquid, including its surface tension. Kennedy's measurements on a column packed with ½-in. Raschig rings (*5, 9*) indicate that the effective exposure time may be sufficient for liquid traveling with the mean vertical velocity to traverse several packing diameters. None of these observations are conclusive in themselves, but taken together they tend to suggest that when a film of liquid in laminar flow meets a discontinuity, a surface layer may under certain circumstances travel on relatively undisturbed even though eddying may cause mixing of the liquid beneath it. The liquid leaving the region of the discontinuity may then consist of an outer layer in which the original concentration profile is unchanged, overlying a layer in which the concentration is uniform (Figure 4). The result would be that owing to an increase in the concentration gradient at the surface, the absorption rate after the discontinuity would be higher than if the liquid had continued in undisturbed laminar flow, but not so high as if there had been complete mixing at the discontinuity. We may say that the surface has been rejuvenated rather than renewed. The net effect of passage over a series of discontinuities will be that the average value of the transfer coefficient k_L will remain constant, rather than decreasing progressively as it would in uninterrupted laminar flow. It is possible but by no means certain that the methods of the penetration theory might be applicable to a process of this kind, the surface-age distribution function $\phi(t)$ (unlike those functions discussed previously) having the value zero at $t = 0$. If the flow rate over the packing is sufficiently high and the uninterrupted paths are long enough, convective mixing of the liquid is likely to take place even on the continuous surfaces, either because of turbulence or through the action of ripples, which have a profound effect on liquid-film coefficients in wetted-wall columns (*6*).

Even if a liquid is in completely streamline flow, the fanning out of the stream lines and their subsequent convergence (particularly, for instance, in grid packings and totem-pole columns) are likely to play a major part in the process of gas absorption. As yet, the mechanics of flow of this kind have barely been considered.

CONCLUSIONS

In the present state of knowledge only rough estimates can be made of the performance of absorption equipment when reacting liquids are to be used (except in the special cases cited). The conventional methods fail because they employ oversimplified models of the hydrodynamic behavior of the liquid, involving only two parameters (k_L and a). It is possible that sufficiently accurate methods might be based on a rather more elaborate model, but there is not enough reliable information available to enable the theory to be developed further at the moment.

Much of the past research on absorption with reaction has been difficult to interpret because of lack of knowledge of the mechanism and rate of the reaction and other physicochemical data. It is recommended that any future work on absorption into agitated liquids should be coupled with the measurement of transient absorption rates into the same liquids; in this way many of the uncertainties would be resolved.

Gas absorption in packed towers depends on the flow of a layer of liquid over discontinuous surfaces, and very little is known about the mechanism of such flow. The study of this flow is essential to an understanding of the true mechanism of absorption.

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NOTATION

a = effective wetted surface area per unit volume of packing
a_d = geometrical surface area per unit volume of packing
B = effective liquid-film thickness
c^* = concentration of unreacted dissolved gas at surface of liquid
c_0 = concentration of unreacted dissolved gas in bulk of liquid
c'_0 = concentration of unreacted reagent in bulk of liquid

D = diffusivity of dissolved gas
d = diameter of packing particle
k_L = liquid-film coefficient for physical absorption
$\bar{k}_L$ = average value of k_L over entire surface of packing
L = liquid mass velocity
N = average rate of absorption per unit area of wetted surface in packing
$Q(t)$ = quantity of gas absorbed by unit area of stagnant liquid of effectively infinite depth in time t
r = first-order reaction-velocity constant
r' = second-order reaction-velocity constant
s = fractional rate of surface renewal
t = time of exposure of liquid to gas
α = ratio of N with reaction to N without reaction, other things equal
$\bar{\alpha}$ = average value of α over entire surface of packing
β = constant in Equation (20)
θ = effective exposure time of liquid on packing
μ = viscosity of liquid
ρ = density of liquid
$\phi(t)$ = distribution function for local surface ages
$\psi(k_L)$ = distribution function for local values of k_L

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Heat Transfer in Cylinders with Heat Generation

Leonard Topper
The Johns Hopkins University, Baltimore, Maryland

The prediction of temperatures has been studied for a tubular flow reactor when heat is generated at a rate which is a linear function of the local temperature. Analytical solutions are presented both for the case where the wall is isothermal and for the case where the exterior surroundings are isothermal and the heat transfer coefficient between the tube wall and the surroundings is constant. This analysis should be helpful for estimating local temperatures and also for predicting the transient response to changes in one of the independent operating variables.

One of the fundamental chemical engineering problems is the prediction of temperatures in a flow reactor. The temperature pattern is dictated by the inlet temperature of the fluid, heat generation within the fluid due to chemical or nuclear reaction, heat transfer to the surroundings, the velocity distribution and transport properties of the fluid, and the geometry of the reactor. Every case of this problem has some unique aspects, but there are enough common features to make a simplified theoretical analysis desirable. The present analysis should be helpful for estimating temperatures in a flow reactor and for predicting the transient response to changes in an operating variable.

The assumption that the rate of heat generation depends only on the local temperature is valid for chemical reactions only when they are of zero order. The linear temperature dependence of the heat source may be viewed as an approximation of the exponential variation of chemical reaction rate with temperature.

The reactor is taken to be a tube of radius s, through which the fluid

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Leonard Topper is at present with Esso Research and Engineering Company, Linden, New Jersey.