THE ABSORPTION OF GASES IN LIQUIDS

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INTRODUCTION

For over 100 years chemical engineers have been interested in the factors which govern the rate of absorption of gases by liquids. In about 1830, for instance, William Gossage filled a derelict windmill with brushwood and ran water over it in order to absorb hydrochloric acid vapour from the manufacture of alkali. This perhaps marks the invention of the first practical absorption tower. The principle, incidentally, was protected by a British patent of 1836.

In the chemical and process industries there are many occasions on which a gas must be absorbed by a liquid. A few examples will illustrate their diversity:

Absorption of nitrous gases in water or nitric acid, during nitric acid manufacture.

Absorption of chlorine by alkaline solutions to give hypochlorites.

Absorption of oxygen by fermentation broths.

Removal of carbon dioxide from water-gas by absorption in water or in solutions of alkalis or amines.

Removal of carbon monoxide from water-gas by absorption in solutions of copper complexes.

Absorption of hydrogen by petroleum fractions in processes to remove sulphur as hydrogen sulphide.

Absorption of chlorine and propylene in water to give the chlorhydridin.

In order to carry out the absorption process efficiently and compactly, it is generally necessary to provide a large surface of contact between gas and liquid, and to keep both phases in vigorous motion to promote stirring. Some types of equipment used in various circumstances are:

Packed columns, in which the liquid runs as a film over the extensive surface of the packing, while the gas is blown through the open space.

Spray columns, in which the liquid rains down through the gas in the form of drops.

Stirred vessels, in which the gas is entrained and dispersed in the liquid in the form of bubbles.

Gas absorption is an example of a topic which does not fall entirely within the province of either the chemist or the conventional engineer, because it requires the simultaneous consideration of molecular diffusion, fluid mechanics and chemical reaction kinetics. Gas absorption has thus become a typical, indeed a classical, chemical engineering topic and it is surprising that in spite of all the work done and papers published in the field since the work of Whitman in 1923, we are still far from a thorough understanding of the process.
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The reasons for wanting to understand the process are essentially economic. We want to know if there is any possibility of radically reducing the cost of the process; even if this is not possible, we want to be able to choose the optimum conditions of operation, which will minimize the cost; we want to be certain that the plant we design is capable of doing the work required of it, but does not incorporate wasteful factors of safety; and we want to be able to do the design by calculation based on tabulated data and aided perhaps by small-scale experiments, without doing expensive pilot-scale experiments. The problems of industrial gas absorption are essentially practical, and our approach to them should be pragmatic. This by no means rules out the value of scientific insight into the phenomena involved, but my lecture may leave you with the feeling that the contemporary climate of applied science sometimes leads us to be over-analytical in our methods, and to spend too much time on the elucidation of mechanisms, while we may lose sight of the essence of the practical problem.

A lecture which tried to deal with all the different phenomena related to gas absorption would be too diffuse. I shall therefore concentrate my attention principally on absorption in packed absorption columns, and on the absorption of carbon dioxide by various solutions. Many of the conclusions are applicable to other types of equipment and to other solutes. The kinetics of the reactions accompanying the absorption of carbon dioxide are relatively well understood; if we cannot reduce the phenomena to order in the case of carbon dioxide, we shall certainly not be able to do so in more complicated cases, such as the absorption of nitrous gases.

PHYSICAL ABSORPTION

Let us consider first of all "physical absorption", i.e., the absorption of carbon dioxide into water or some other liquid with which it does not react. The liquid flows down over the pieces of packing in a layer which varies from point to point in thickness, velocity and inclination to the vertical. There may be regions of the surface where the layer moves slowly, or not at all, or is very thin; the layer at these points may become saturated with carbon dioxide, so that it is not contributing to the overall rate of absorption. In other regions the layer is thick and flows briskly and the liquid is agitated by the flow. The agitation causes mixing of the liquid, but we do not know for certain what the nature of the mixing process is. The so-called "film model" pictures a situation in which the liquid flowing over the surface is kept thoroughly mixed by turbulence except in the immediate neighbourhood of the free surface, where the turbulence is supposed to be damped-out, leaving a "stagnant film" across which the dissolved molecules of gas can pass only by molecular diffusion.

The various "surface renewal" models suppose that parts of the liquid surface are from time to time replaced by fresh liquid brought up from the bulk of the layer. In general a freshly formed surface absorbs rapidly, and the rate of absorption thereafter falls off progressively as the concentration of solute in the neighbourhood of the surface rises. In some circumstances the liquid in the layer may be in turbulent flow, so that eddies bring fresh liquid to the surface. In other circumstances the layer may be in undisturbed laminar flow except at the discontinuities between pieces of packing, where
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it is thoroughly mixed; fresh liquid surface is continually formed at the top of a piece of packing and moves downwards, absorbing gas at a decreasing rate until it meets a discontinuity, when it is replaced once more by fresh liquid brought up from the body of the layer. Thus the surface renewal models suggest that in any representative sample of the space in the packed column the surface of the liquid will be a mosaic of elements which have been exposed to the surface for different lengths of times and which will therefore in general be absorbing at different specific rates. Various versions of this model lead to different distributions of exposure times about the mean value. The form of the surface renewal model due to Higbie\(^3\) assumes that every element of liquid surface is exposed to the gas for the same length of time before being replaced with fresh liquid. That due to Danckwerts\(^4\) assumes that the chance of replacement is independent of the length of time for which the element has already been exposed.

Other types of model have also been proposed. For instance, Kishinevskii and Pamfilev\(^5\) have suggested that turbulence is not damped-out at the surface; Dobbins\(^6\) and Toor and Marchello\(^7\) have suggested a stagnant film which is replaced piecemeal; Andrew\(^8\) and Danckwerts\(^9\) have discussed "surface rejuvenation". These by no means exhaust the possibilities, and many more models, just about as plausible, could be invented. My guess is that the nature of the flow is so complicated that it does not truly correspond to any of the simple models. However, it is instructive to see what conclusions they lead to, and I shall illustrate the possibilities by considering the film model and the surface renewal models.

Consider the absorption of carbon dioxide in water. The partial pressure of carbon dioxide in the gas at the surface of the liquid is such that the solubility of carbon dioxide is \(C^*\); it is assumed (and the evidence supports this) that the gas and liquid are in equilibrium at the surface, so the concentration of carbon dioxide at the surface is \(C^*\). The concentration in the bulk of the layer is \(C_0\). It is in common ground between the film and the surface renewal models that the concentration falls from \(C^*\) to \(C_0\) in a region close to the surface, the resulting concentration gradient controlling the rate of absorption. The film model predicts that the rate of absorption, \(R_0\), per unit area of surface will be:

\[
R_0 = \frac{D}{\delta} (C^* - C_0) \tag{1}
\]

where \(D\) is the diffusivity of carbon dioxide in solution and \(\delta\) the thickness of the "stagnant film". The surface renewal models lead to expressions of the form:

\[
R_0 = K \sqrt{\frac{D}{\tau}} (C^* - C_0) \tag{2}
\]

where \(\tau\) is a characteristic time (\(e.g.,\) average time of exposure of elements of surface or the reciprocal of the fractional rate of surface renewal) and \(K\) a numerical constant of order unity which depends on the form of model chosen.

Both models thus predict that the rate of absorption is proportional to the "driving force", \((C^* - C_0)\), \(i.e.,\):

\[
R_0 = k_L (C^* - C_0) \tag{3}
\]
where \( k_L \), the "liquid film coefficient", depends on \( D \) and on the hydrodynamic situation (e.g., size of packing, flow rate of liquid). This is well borne out by experimental observations. The main difference between the models is that the film model makes \( k_L \) proportional to \( D \) while the surface renewal models make it proportional to \( \sqrt{D} \). It should be possible to measure rates of absorption of various gases with different values of \( D \) and decide the issue. This has not been entirely convincingly done, because values of \( D \) do not cover a wide range and are difficult to measure accurately. On the whole, however, the evidence favours \( \sqrt{D} \) and the surface renewal model. (The other models mentioned lead to expressions for \( k_L \) involving a power of \( D \) which varies with the circumstances, generally lying between 0 and 1.)

It is not my purpose here to reach a final conclusion about the physical mechanism of the absorption process. In my opinion this is not a question which calls for resolution by extensive research, because on the one hand it is not a matter of profound fundamental interest and on the other it is not necessary to elucidate the mechanism in detail in order to achieve our practical objectives, as I will explain later.

**ABSORPTION WITH CHEMICAL REACTION**

Gases are often absorbed into liquids with which they react chemically. Sometimes (as in the case of propylene chlorhydrin) this is because the products of the reaction are required for their own sake. Sometimes the purpose is to remove one constituent from a mixture of gases. In this case the chemical reaction speeds up the absorption process and the liquid can absorb more gas; both of these factors make for smaller equipment and lower costs. For instance, when carbon dioxide is to be removed from water-gas, it can be physically absorbed by water, the gas being under pressure. Modern practice, however, is to use a solution of potassium carbonate or an amine to increase the absorption rate and the absorptive capacity of the solution. These solutions can be regenerated by stripping out the carbon dioxide with steam or air, a process just as important as the absorption.

When we come to study the reactions which take place during gas absorption, we encounter a complicated situation in which the concentrations of the reactants are in general not uniform and diffusion takes place simultaneously with reaction. If we add the ill-defined effects of convection, due to the motion of the liquid, the problem of making useful predictions from first principles might seem remote. We can start, however, by taking some of the simple models for gas absorption which I have mentioned already, and combining them with reactions having simple kinetics, to calculate the effect which the reactions would have on the absorption rate. Suppose, for instance, that the dissolved gas undergoes an irreversible first order reaction in the solution (the rate constant being \( k \)); at every point in the solution it is being destroyed at a rate proportional to its local concentration. At the same time it is diffusing inwards from the surface, where its concentration is a maximum, to the interior of the liquid where we shall assume it to be zero; the diffusivity of the dissolved gas is \( D \). If we calculate, for three of the models already mentioned, the increase in the rate of absorption due to the reaction, we get the following results, where \( R_0 \) is the rate of absorption in the absence of reaction, \( R \) the rate of absorption into a reacting solution,
and $\alpha = \sqrt{Dk/kl}$, $kL$ being the transfer coefficient for physical absorption, without reaction, in the same hydrodynamic conditions.

**Film model**

$$R/R_0 = \frac{a\sqrt{\pi}/2}{\cosh(a\sqrt{\pi}/2)}$$

**Surface renewal models**

Higbie

$$R/R_0 = \frac{\sqrt{\pi}}{2} \left[ \left( a + \frac{1}{2a} \right) \text{erfi}a + \frac{e^{-a^2}}{\sqrt{\pi}} \right]$$

Danckwerts

$$R/R_0 = \sqrt{1 + \pi a^2/4}$$

Although these expressions appear very different, their values at a given value of $a$ are very close to one another; in fact, the maximum discrepancy between the models is 7.5 per cent, over the whole range $a = 0$ to $a = \infty^{10}$. In the case of this type of reaction, therefore, almost the same result is obtained, whichever model is used for predicting the rate of absorption.

Another common type of reaction is an irreversible second order reaction between the dissolved gas and a reactant dissolved in the liquid. The concentration of the reactant is greatest in the bulk of the liquid and least near the surface, towards which it diffuses, while the dissolved gas diffuses inwards. The two react at every point at a rate proportional to the product of their concentrations (Figure 1). In this case the equations for simultaneous reaction and diffusion must be solved by numerical methods, and this has been done for the film and Higbie models. It is found$^{11}$ that provided the diffusivities of the dissolved gas and the other reactant are not very different, the two models predict almost the same effect of the reaction. For both film and surface renewal models the reaction of dissolved gas is pseudo-first order (i.e., its rate of reaction is everywhere proportional to its concentration)
when $1 \ll \sqrt{Dk_2C'/k_L} \ll C'/C^*$, where $C'$ is the concentration of reactant in the bulk of the solution, and $k_2$ the second order rate constant for the reaction between carbon dioxide and reactant. This implies that the concentration of the reactant in the absorbing solution is not substantially depleted near the surface, but remains almost uniform. The expressions given above [equations (4), (5) and (6)] can then be used, with $k_2C'$ in place of $k$. Again, for both models, when $\sqrt{Dk_2C'/k_L} \gg C'/C^*$, the reaction between the dissolved gas and the reactant in solution can be regarded as "instantaneous". There is a zone near the surface where the concentrations of both are zero, and both react as fast as they can diffuse to this zone. The rate of absorption is then such that:

$$R/R_0 = 1 + \frac{C'}{nC^*}$$

(7)

where $n$ is the number of moles of reactant which reacts with one mole of dissolved gas.

A number of other types of reaction have been investigated on paper, and in each case the conclusion is the same; it makes very little difference which of the models of gas absorption is adopted, the predicted effect of a specified chemical reaction on the absorption rate is about the same. In some cases this is only true if the diffusivities of the reacting species are not very different; but in practice this is often, one can say usually, the case. The same conclusion applies to the "film renewal" model$^6,7$ and to various other models which have been proposed, so that from a practical point of view, it seems that there is no need to know the physical mechanism of absorption in order to predict the effect of a chemical reaction on the absorption rate. Provided it can be shown that the effect of the reaction in general conforms to the predictions arising from one of the models, one can without much discrepancy use the terminology and mathematics of the other models, as convenient.

When purely physical absorption takes place into gas-free liquid, the rate of absorption per unit of effective interfacial area is:

$$R_0 = k_L C^*$$

(8)

The quantity which can be determined directly from measurements of physical absorption is

$$R_0a = k_L a C^*$$

(9)

where $R_0a$ is the rate of absorption per unit volume of packed space, and $a$ the effective interfacial area per unit volume. For reasons already mentioned, not all the surface of the packing is necessarily effectively involved in the absorption process, so that $a$ is not necessarily the same as the geometrical surface of the packing, or the wetted surface. It must be assumed that both $a$ and $k_L$ for a given type of packing depend on the hydrodynamic conditions and must be determined by experiment. In predicting the effect of a chemical reaction on the absorption rate it is assumed that the effective specific interfacial area $a$ has the same value when a reacting liquid is used as it has in physical absorption. This assumption is suspect; it might appear possible
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that in physical absorption parts of the liquid layer, at points on the packing where the rate of replacement of liquid is slow, may become saturated with gas and thus become ineffective for further gas absorption, while in the case of certain reacting liquids having the capacity to absorb large amounts of gas, these parts of the layer might continue to absorb the gas. One must appeal to experiment to see whether the assumption that $a$ is constant is justified in practice.

Recent systematic experiments in packed columns have in fact shown that the film or surface renewal models can, apparently, be used to make predictions with a useful degree of accuracy. Before describing these experiments I shall consider how reactions of various types affect the rate of absorption of carbon dioxide.

REATIONS OF CARBON DIOXIDE IN SOLUTION

In discussing the effect of a chemical reaction, I shall use the terminology of whichever model is simplest. I shall assume the diffusivities of all reacting species to be equal (this simplifies the argument without much affecting its validity). Suppose that carbon dioxide is absorbed into a solution of sodium hydroxide, having a concentration $C'$. The reaction which occurs is of second order between dissolved carbon dioxide and hydroxyl ions:

$$\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$$  \hspace{1cm} (10)

followed by the instantaneous reaction:

$$\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$$  \hspace{1cm} (11)

The local rate of reaction, $r$, per unit volume is:

$$r = k_{\text{OH}^-} [\text{CO}_2] [\text{OH}^-]$$  \hspace{1cm} (12)

The value of $k_{\text{OH}^-}$ is 8500 1/g mole sec at 25°C and at infinite dilution. It is substantially affected by the presence of ions in the solution; for instance, it is three and a half times as high in 3M potassium hydroxide solution, and nearly twice as high in 3M sodium hydroxide solution at infinite dilution.

Under certain conditions (specified above) the reaction is pseudo-first order, and if the Danckwerts surface renewal model is used we get:

$$R = k_{\text{L}} C^* \sqrt{1 + \frac{Dk_{\text{OH}^-} C'}{k_{\text{L}}^2}}$$  \hspace{1cm} (13)

or

$$\frac{R}{R_0} = \sqrt{1 + \frac{Dk_{\text{OH}^-} C'}{k_{\text{L}}^2}}$$  \hspace{1cm} (14)

[c.f. equation (6)]. Under certain other conditions, also specified above, one can regard the reaction between carbon dioxide and hydroxyl ions as “instantaneous”. The rate of absorption is then such that:

$$\frac{R}{R_0} = 1 + \frac{C'}{2C^*}$$  \hspace{1cm} (15)

[c.f. equation (7)]; $n = 2$ because two moles of sodium hydroxide react with each mole of carbon dioxide. This expression is only approximately correct, because the diffusivity of carbon dioxide is substantially less than the (effective) diffusivity of hydroxyl ions.
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It should be noted that in the expressions for the absorption rate $G^*, D$ and $k_{OH^-}$ all depend on the composition of the solution. For instance, the rate of absorption of carbon dioxide into sodium hydroxide solutions passes through a maximum when the concentration of the latter is about 2M, and then decreases. This is because the decreasing solubility and diffusivity of carbon dioxide outweigh the increase in reaction rate. Direct measurement of the solubility and diffusivity of carbon dioxide in a solution with which it reacts are impossible and $k_{OH^-}$ depends on the nature as well as the ionic strength of the ions present. In general we cannot assign very precise values to such physico-chemical quantities as gas solubilities, diffusivities and rate constants in the concentrated solutions used industrially for gas absorption, and the calculation of absorption rates from first principles may be subject to errors sufficiently large to make close design impossible (there are, of course, often other and much larger sources of uncertainty in the practical design problem).

The absorption of carbon dioxide by sodium hydroxide solution, being accompanied by an irreversible second order reaction, is a particularly simple case; the effect of the reaction on the absorption rate under various conditions has been calculated for this type of kinetic system, as already mentioned, and its magnitude can be predicted if $k_1$, $a$ and the requisite physico-chemical quantities are known. However, several more complicated types of reaction occur in other processes in which carbon dioxide is absorbed.

When carbon dioxide is absorbed by a solution of potassium carbonate, the principle reaction is that between carbon dioxide and hydroxyl ions (above). The concentration of hydroxyl ions is:

$$[\text{OH}^-] = \frac{K_W}{K_2} \frac{[\text{CO}_2^{2-}]}{[\text{HCO}_3^-]} \quad (16)$$

where $K_W$ is the ionic product of water and $K_2$ the stoichiometric dissociation constant of bicarbonate ions. Thus, in conditions where the ratio $[\text{CO}_2^{2-}]/[\text{HCO}_3^-]$ can be regarded as uniform near the surface, the reaction of carbon dioxide is pseudo-first order, and:

$$R/R_0 = \sqrt{\left(1 + \frac{Dk_{\text{OH}^-}K_W[\text{CO}_2^{2-}]/K_2[\text{HCO}_3^-]}{k_1K_2}\right)} \quad (17)$$

Here again, $k_{\text{OH}^-}$, $K_W$ and $K_2$ vary considerably according to the composition of the solution. The rate of reaction is considerably higher when the cation is potassium than when it is sodium.

Under some conditions the reaction of the carbon dioxide diffusing in from the surface may cause the ratio $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$ to become significantly less near the surface than in the bulk of the solution; the concentration of hydroxyl ions near the surface is correspondingly reduced, the reaction is no longer pseudo-first order, and equation (17) no longer holds. Furthermore, when a sufficient amount of the carbonate originally present in the solution has been converted to bicarbonate, the equilibrium concentration of free carbon dioxide in the bulk of the solution:

$$[\text{CO}_2] = \frac{K_2}{K_1} \frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^{2-}]} \quad (18)$$
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(where \( K_1 = [\text{H}^+] \frac{[\text{HCO}_3^-]}{[\text{CO}_2]} \)) may become significant. The reaction between carbon dioxide and hydroxyl ion must now be treated as reversible, rather than irreversible, and the kinetics are correspondingly more complicated. No calculations covering all the circumstances encountered in practice have so far been published, although certain limiting cases have been dealt with.

Carbon dioxide can also react with water:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+ \tag{19}
\]

the hydrogen ion reacting instantaneously with the hydroxyl ion in the solution. This is a first order reaction, the local rate being:

\[
r = k_{\text{H}_2\text{O}}[\text{CO}_2] \tag{20}
\]

The value of \( k_{\text{H}_2\text{O}} \) is about 0.026 sec\(^{-1}\) at 25°C\(^{12}\). In a solution containing equal concentrations of carbonate and bicarbonate at 25°C, [OH\(^-\)] is about 10\(^{-4}\) g ion/l., and the pseudo-first order rate constant \( k_{\text{OH}^-} \) [OH\(^-\)] is therefore about 1 sec\(^{-1}\). Thus the reaction with water contributes very little to the total rate of reaction of carbon dioxide in such a solution. However, the reaction with water can be catalysed, notably by anions carrying one ionized and one unionized hydroxyl group attached to a central atom. Examples are the ion of hydrated formaldehyde, \( \text{H}_2\text{COH.O}^- \), and the arsenite ion, \( \text{As(OH)}_2\text{O}^- \). Hypochlorite, \( \text{ClO}^- \), is a very active catalyst, although unsuitable for industrial purposes. Animal blood contains an enzyme, carbonic anhydrase, which catalyses the reaction. In a process which is fairly widely used in industry, potassium arsenite is added to potassium carbonate. The catalysed reaction with water then outweighs the reaction with hydroxyl ions, and the local reaction rate is:

\[
r = k_{\text{As}} [\text{As(OH)}_2\text{O}^-] [\text{CO}_2] \tag{21}
\]

At 25°C, \( k_{\text{As}} \) is about 250 l/g mole sec and at 60°C it is about 3700 l/g mole sec\(^{14}\). If 0.5m arsenic is added to an equimolar mixture of \( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \), the rate of reaction at 25°C is increased about tenfold. \( k_{\text{As}} \) will be seen from the expressions already given, the rate of absorption increases at best with the square-root of the reaction rate.

As carbon dioxide is absorbed into carbonate solution, the ratio \([\text{CO}_3^{2-}] / [\text{HCO}_3^-]\) and the pH fall; the ionization of arsenite will be depressed and it will be converted into arsenious acid, which is not a catalyst. This may occur near the surface of the absorbing liquid, leading to a situation where the concentration of catalyst and the local reaction are less near the surface than in the bulk, and the absorption rate will be correspondingly reduced. This is a situation for which the calculations have not yet been carried out. We find also that the dissociation constant of arsenious acid depends markedly on the concentration of ions present in the solution.

Amines, such as monoethanolamine, diethanoamine and sometimes ammonia, are also used to absorb carbon dioxide. The primary reaction is second order and leads to the formation of a carbamic acid, which reacts instantaneously and completely with another molecule of amine:

\[
\text{CO}_2 + \text{R}_2\text{NH} \rightarrow \text{R}_2\text{N.COOH} \tag{22}
\]

\[
\text{R}_2\text{N.COOH} + \text{R}_2\text{NH} \rightarrow \text{R}_2\text{N.COO}^- + \text{R}_2\text{NH}_2^+ \tag{23}
\]
The local rate of reaction is:

\[ r = k_{Am} [CO_2] [R_2NH] \]  \hspace{1cm} (24)

The rate constant \( k_{Am} \) has the following values at 15°C\(^{15}\):

\[
k_{Am} \left( \frac{1}{g \text{ mole sec}} \right) \quad \text{NH}_3 \quad \text{C}_2\text{H}_5\text{ONH}_2 \quad \text{(C}_2\text{H}_5\text{O})_2\text{NH} \\
420 \quad 7600 \quad 1500
\]

The reaction of carbon dioxide with monoethanolamine is thus about as fast as the reaction with sodium hydroxide. Provided the carbonation ratio (moles of carbon dioxide absorbed per mole of amine present initially) is less than about 0·45, the reaction with an amine can be regarded as second order and irreversible, and the expressions given above for this case can be applied. At carbonation ratios approaching 0·5 however, the rate of the reverse reaction may become appreciable:

\[
\text{R}_2\text{N.COO}^- + \text{R}_2\text{NH}_2^+ \rightleftharpoons 2\text{R}_2\text{NH} + \text{CO}_2
\]  \hspace{1cm} (25)

No general solution to the problem of predicting rates of gas absorption under these circumstances has been published, although the rate can be predicted under certain conditions.

At high carbonation ratios the carbon dioxide present in the bulk of the solution owing to the above equilibrium reacts with hydroxyl ions or water to give bicarbonate. This secondary reaction reduces the back-pressure of carbon dioxide and increases the concentration of free amine, and thus tends to increase the rate of absorption and the capacity of the solution for absorbing carbon dioxide. Because of the low concentration of hydroxyl ions and the inherently slow reaction of carbon dioxide with water, the secondary reaction is normally too slow to proceed to an appreciable extent during the passage of the liquid through an absorption column. However, the reaction with water can be catalysed, as described above, and the addition of (say) potassium arsenite to the amine may speed up the secondary reaction to the point where the equilibrium:

\[
\text{R}_2\text{N.COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{R}_2\text{NH} + \text{HCO}_3^-
\]

is set up in the bulk of the liquid. The advantage to be gained from this depends on the magnitude of the equilibrium constants involved, the carbonation ratio, etc. The effect becomes more marked the higher the carbonation ratio, and is greater for ammonia than for the ethanolamines\(^{16}\). The effect on a batch absorption process in a stirred vessel containing 2·0M ammonia is shown in Figure 2. At a carbonation ratio of 0·5 the absorption rate was increased by a factor of 2·5 by adding 0·1M arsenite; this was apparently enough to bring about the secondary equilibrium, since doubling the concentration of arsenite had no further effect. It has not yet been demonstrated that the addition of a catalyst to an amine will confer advantages in practice.

I will now consider how the designer of plant can take various types of chemical reaction into account in calculating the rate at which carbon dioxide will be absorbed in the plant.
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Figure 2. Effect of arsenite on rate of absorption of carbon dioxide by 2N ammonia solution at 18°C in a stirred vessel. Pressure of carbon dioxide = 1 atm. Volume of liquid per unit surface area = 1.31 cm³

PROCESS DESIGN PROCEDURES

It is not a very difficult or expensive business to determine once and for all the values of $k_{1,a}$ for physical absorption into non-reacting liquids, for various types of packing, liquid flow rates and liquid mechanical properties. Indeed, many such data have already been recorded, particularly for water and liquids which can be regarded as mechanically identical with water. The designer can be supposed to have access to such data for physical absorption. The question considered here is what additional information he needs, and what methods he can use, to predict the rate of absorption into some solution with which the absorbed gas reacts.

My colleagues and I have carried out a number of systematic experiments in packed columns to see whether $a$ can be regarded as constant when reacting solutions of various types are substituted for inert solutions, all having the same physical properties. If carbon dioxide is absorbed into a solution in which it undergoes a first order reaction with rate constant $k$, the rate of absorption per unit volume, $Ra$, is given (according to the Danckwerts surface renewal model) by:

$$Ra = a C^* \sqrt{k_{1,a} + Dk}$$  (26)

whence

$$(Ra)^2 = (aC^*)^2(k_{1,a} + Dk)$$  (27)

Thus if $k$ alone is varied, a plot of $(Ra)^2$ against $k$ should, if $a$ is constant, be a straight line. In some of our experiments we varied $k$ by adding various small concentrations of arsenite to a buffer solution¹⁷. Figure 3 shows that in a series of experiments at different wetting rates in columns packed with ½ in. (1.3 cm) Raschig rings these plots were indeed straight, showing that at any rate under the conditions of the experiments the surface renewal model
could be used and \( a \) could be regarded as constant. By suitable experiments with laminar jets or wetted wall columns\(^{18}\) it is possible to evaluate \( C^* \sqrt{D} \) (and \( k \)) for these solutions. Since the slopes of the lines in Figure 3 can be identified with \( a^2(C^* \sqrt{D})^2 \), the value of \( a \) can be found for each flow rate. Thus the value of \( k_L \) can be deduced from values of \( k_La \) determined for physical absorption at the same flow rates. The values of \( k_L \) and \( a \) can be tabulated for the use of process designers.

![Graph](image)

*Figure 3.* Absorption of carbon dioxide into buffer solutions containing arsenite at various superficial flow rates. Column packed with 1·3 cm Raschig rings

These experiments were carried out in the laboratory in a 4 in. (10 cm) diameter column packed with \( \frac{1}{4} \) in. (1·3 cm) Raschig rings, and the liquid flow rates were rather low by industrial standards. We have recently done measurements on a more realistic scale, using a column of 18 in. (46 cm) diameter, packed with \( 1\frac{1}{2} \) in. (3·8 cm) Raschig rings and employing a wide range of flow rates. The solutions used consisted of mixtures of carbonate and bicarbonate, with hypochlorite (\( \text{ClO}^- \)) as a catalyst. (The first order rate constant for reaction of carbon dioxide at 25°C is about 3000 [\( \text{OCl}^- \)] sec\(^{-1} \) as compared to 450 [\( \text{As(OH)}_2\text{O}^- \)] for arsenite.) The experimental difficulties are considerably greater when working on this scale, but *Figure 4* shows that \( (Ra)^2 \) is linear in \( k \), so it is apparently justifiable to use expressions based on the surface renewal model, with a constant value of \( a \), in all the conditions investigated.

In all these experiments pure carbon dioxide was used, so that there was no resistance to absorption on the gas side of the interface.

The conclusion reached as a result of our recent work is therefore that it is possible to use the film or surface renewal models to predict absorption rates in packed columns. For this purpose it is necessary to know \( k_L \) for physical absorption and the effective interfacial area \( a \) (these can be found, for instance, by the use of “first order” reactants, as just described).
Method A

Using what may be called Method A it is also necessary to have the required physico-chemical data—the kinetics of the reaction, the solubility of the gas and the diffusivities of the various species—and to carry out the calculations which indicate the effect of the reaction on the absorption rate. It may be very difficult to fulfil all these requirements; the kinetics may be obscure or complicated, and the rate constant, solubility and diffusivities may be only roughly known in the solution and at the temperature in question. As indicated above, in discussing some of the reactions undergone by carbon dioxide, the equations involving simultaneous diffusion and reaction may be very complicated, and in many cases solutions are not available. For all but the simplest types of reaction the calculation of the effect of the reaction on the absorption rate is a matter for an elaborate computer programme.

This suggests the possibility of making simple laboratory experiments with the liquid and gas in question, which will yield all the necessary information about the reaction in a form which can be applied directly to calculation of absorption rates in packed columns. Two different methods of approach have been used with success.

Method B

The first of these, Method B, involves the measurement of transient rates of absorption into liquid surfaces, and the use of the resulting data in one of the surface renewal models. The simplest to consider is the Higbie model, in which every element of surface is assumed to be exposed for the same length of time, \( t \). When a fresh liquid surface is exposed to the gas in the absence of convection, it absorbs gas at a rate which in general decreases with time. Let us say that the amount absorbed in time \( t \) by unit area of surface
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is \( Q(t) \); then the average rate of absorption over time \( t \) is \( Q(t)/t \). In the Higbie surface renewal model of the packed column, this is also the average rate of absorption per unit area of effective interface in the packed column. For physical absorption, the Higbie model leads to:

\[
k_L = 2 \sqrt{\frac{D}{\pi t}} \tag{28}
\]

and thus the exposure time \( t \) is related to the physical mass-transfer coefficient \( k_L \) by

\[
t = \frac{4D}{\pi k_L^2} \tag{29}
\]

where \( D \) refers to the same gas as \( k_L \). Thus \( t \) is determined from a knowledge of \( k_L \) for physical absorption in the packed column, and the absorption rate into a reacting solution in the packed column can then be predicted from the laboratory measurements of transient absorption into that solution, which determine \( Q(t) \) as a function of \( t \).

The most useful methods of measuring transient absorption rates over the range of values of \( t \) typical of packed columns (up to 2 sec) are the wetted-wall column and the laminar jet\(^{19, 18}\). The applicability of Method B has been demonstrated, although only over a limited range of variables\(^2\). Pure carbon dioxide was absorbed in a small column packed with \( \frac{1}{4} \) in. (1.3 cm) Raschig rings, the superficial velocity of the liquid being 0.145 cm/sec. Various inert solutions, carbonate–bicarbonate buffer solutions and sodium hydroxide solutions were used, all having the same density and viscosity. Transient absorption measurements were carried out on the same solutions. Using a single value of \( t \) (1.6 sec) and of \( a \) (1.2 cm\(^{-1} \)) for all solutions, the absorption rates per unit packed volume were calculated as described above. The observed adsorption rates are compared with the calculated rates in Figure 5, and the two agree within about 10 per cent. It seems possible that the method may be generally applicable.

The advantage of Method B over Method A is that it requires no knowledge of physico-chemical quantities, and there is no need to solve complicated diffusion reaction equations.

**Method C**

However, accurate measurement of transient absorption rates requires rather careful experimental techniques. Further reflection suggested that it might not really be necessary to measure transient rates, and that a simple model absorption apparatus, representing the process occurring in the packed column, might be constructed and used instead. This will be called Method C. Suppose, for instance, that the surface renewal process actually occurs in the packed column. As already explained, calculation (for cases where calculation is possible) shows that the predicted effect of a chemical reaction on the absorption rate is influenced very little by the distribution of surface ages which is assumed (\( e.g. \), Higbie or Danckwerts), but is determined within narrow limits solely by the value of \( k_L \). Suppose, on the other hand, that the actual process occurring is most closely represented by the film model.
Figure 5. Comparison of measured values (circles) and predicted values (line) of absorption rates of carbon dioxide into (a) buffer solution and (b) sodium hydroxide solution (below). Column packed with 1.3 cm Raschig rings. Superficial flow rate = 0.145 cm/sec

Again, calculation shows that for a given value of $k_L$, this model leads to much the same conclusions as the surface renewal models (except in cases where the diffusivities of participating species are markedly unequal). It seems likely, therefore, that a laboratory model absorption system, having the same value of $k_L$ as the packed column which it represents, will be influenced in almost exactly the same way by chemical reactions in general as will the packed column. The fact that the model may differ from the column with regard to the mechanism of absorption in some respects (e.g., mechanism of surface renewal or distribution of surface ages) may prove to be immaterial, provided that $k_L$ is the same for both.

To test this method of prediction we have chosen as the model a stirred vessel. The stirrer has four vertical blades which cut the surface of the water. The value of $k_L$ can be varied by varying the stirring speed, and the highest values of $k_L$ attainable are comparable with, although somewhat less than, the highest values attained in packed columns in practice. Hardly any entrainment of bubbles occurs, and the surface of the liquid remains reasonably flat, so that the total area into which absorption occurs is known.

There are various ways in which the validity of the model can be tested. One of them is as follows. Consider a series of inert and reacting liquids of various chemical types but closely similar physical properties. If each solution in turn is used as the absorbent in a packed column, the flow rate of the liquid being the same in each case, it is assumed that $k_L$ and $a$ will be the same in each case; under these conditions the absorption rates per unit volume are in the ratios $R_1: R_2: R_3$ etc. If the right rate of stirring in the vessel is chosen, so that $k_L$ has the same value as in the packed column, then
for the same series of solutions the absorption rates will be in the same ratios $R_1: R_2: R_3$ etc. as in the packed column. We have tested this idea by absorbing carbon dioxide into a variety of reacting solutions at various flow rates in a column packed with 1½ in. (3·8 cm) Raschig rings, and it proves to be possible to match the behaviour of the column at a given flow rate by using the stirred vessel with a particular stirring speed. The situation in the column using a superficial liquid flow rate of 1·7 cm/sec, for instance, was simulated by a stirring speed of 160 r.p.m. Under these conditions substitution of one solution for another had the same effect on the absorption rate in the column as on the absorption rate in the stirred vessel. The vessel can thus be used as a model for the packed column, and the effect of using various absorbents can be conveniently determined on a small scale in relatively simple apparatus. The accuracy likely to be attained is indicated by Figure 6, which shows the measured and calculated rates of absorption of carbon dioxide with various solutions at a single flow rate, using various heights of packing.

![Graph showing rate of absorption vs. height of packing](image)

*Figure 6. Comparison of measured values (circles) and predicted values (— — — —) of rates of absorption of carbon dioxide in column packed to various heights with 4·3 cm Raschig rings. Superficial flow rate = 0·78 cm/sec. A: 0·37 m sodium hydroxide; B: buffer solution with hypochlorite; C: 0·08 m sodium hydroxide; D: physical absorption.*

I visualize that the way in which this technique might be used by process designers is as follows. As a result of work now in progress, the values of $a$ and $k_L$ (or rather $k_L/\sqrt{D}$, which is probably independent of the gas being absorbed) would be tabulated for various types of packing and various flow rates (and for liquids of different physical properties). It would then be necessary to set up a laboratory model, such as a stirred vessel, with the
same value of $k_L$ as will be encountered in the column under the specified operating conditions. In the stirred vessel $a$ is known (it is simply the area of the liquid surface) and $k_L$ at various stirring speeds is thus easily obtained from physical absorption measurements, which yield $k_{La}$. One chooses the stirring speed to give the right value of $k_L$, and then measures the rate of absorption per unit area, $R_a$, into the specified solution. This is taken to be the value of $R$ in the packed column, and hence the absorption rate per unit packed volume $(Ra)$ is calculated.

It may well be asked why, if one is going to do model experiments, one does not simply set up a small packed column. Indeed, if the plant to be designed is to use a small packing, such as ½ in. (1·3 cm) Rasching rings, this is probably the simplest way to proceed. However, the diameter of the small column should be 8 or 10 times the diameter of the packing pieces, and the experimental facilities required cease to be “bench-scale” and become more of a “pilot plant”, and correspondingly expensive, when larger packings are in question. In principle one could use a small packing to act as a model for a large one, provided that the value of $k_L$ were the same for both; however, the maximum values of $k_L$ attainable in small packings are limited by flooding, and are less than those commonly encountered in large packings. Other types of model which have been used, such as the string of discs and the string of spheres, also give rather low upper values for $k_L$. It should also be mentioned that with the stirred vessel $k_L$ can be varied independently of the residence time of the liquid, which is often an advantage. If a model giving large values of $k_L$ is required, a suitable version of the laminar jet apparatus might be used, since this gives exposure times in the millisecond range.

As yet there is no very firm evidence to show whether the method of approach described above for calculating the effect of a reaction on the rate of absorption can also be applied to absorption on bubble-plates. It is clear, however, that the values of $k_L$ encountered on bubble-plates tend to be much higher than those in packed columns. They may sometimes correspond to exposure times of a few milliseconds. This suggests that the type of model to use would be a laminar jet, or perhaps a small bubble-plate, although in the latter case it would be necessary to establish the value of $a$ as well as $k_L$ for every set of conditions.

CONCLUSION

It seems probable that the film model or the surface renewal models can be used to predict rates of absorption of gases into reacting liquids in packed columns, provided that the necessary data are available. In their absence, it seems probable that rates of absorption can be predicted from very simple experiments in laboratory equipment which reproduces the value of $k_L$, but not necessarily any of the other features of the full-scale plant. This method had been foreshadowed some time ago, but without any very firm theoretical basis or any comprehensive tests. It is interesting that a long intellectual excursion should have brought us back to the “obvious” and simple-minded approach to the problem.
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