

SIMULTANEOUS ABSORPTION AND REACTION OF TWO GASES: ABSORPTION OF CO₂ AND NH₃ IN WATER AND AQUEOUS SOLUTIONS OF ALKANOLAMINES

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(Received 23 April 1974; accepted 29 May 1974)

Abstract—Some aspects of simultaneous absorption and reaction of two gases in an inert medium, and a medium containing species which react with one of the dissolved gases have been considered. Experiments were made on simultaneous absorption of carbon dioxide and ammonia in water and aqueous solutions of mono- and di-ethanolamine in a 5 cm i.d. continuous glass bubble column. A good agreement between the experimental and predicted values was observed.

Simultaneous absorption of two gases in an inert liquid medium where the gases react between themselves, and in a liquid medium which contains a dissolved reactive species which can react with one of the gases is of considerable industrial importance[1]. Roper *et al.*[2] have presented numerical solutions for the case of a fast second order reaction between the dissolved gases in an inert medium. The above analysis is however, based on a restrictive boundary condition; thus, one of the boundary conditions [Eq. (8) of Roper *et al.*] stipulates that the bulk liquid concentration of both the dissolved gases is zero. This situation is possible only in a particular case, that is, when the fluxes of the diffusing gases are in stoichiometric proportion. For the general case of stoichiometrically unequal fluxes, the gas with a higher flux will be present in finite concentration in the bulk liquid phase. The range of variables covered in the above analysis was limited. Teramoto *et al.*[3] have obtained numerical solutions for a wider range of the variables. However, these authors have also used the same boundary conditions as those used by Roper *et al.*[2].

The case of simultaneous absorption and reaction in an absorbent which reacts with one of the gases has apparently not been considered in the literature. In this paper, some situations which are of industrial importance are considered.

THEORETICAL CONSIDERATIONS

1. Absorption into an inert medium

Here, gases *A* and *B* dissolve into the liquid

phase,



and undergo an irreversible reaction:



Gas *B* is considered to have a higher solubility than gas *A*. Reaction (3) is considered to be first order in both the gases *A* and *B*. The above reaction may occur in the slow or fast reaction regime[1]. As regards the slow reaction regime, since there is no interaction between the diffusion and reaction steps, the rates of absorption can be easily predicted.

When the following condition is satisfied, the reaction between the dissolved gases becomes instantaneous:

$$k_G \ll H_A k_{LR} \quad (4)$$

For this case, the ability of the gas phase to supply the gaseous components governs the overall rate of absorption. Thus, for instance, in a particular case, when the gas *A* has a lower solubility than gas *B*, the species *A* will be completely consumed at the interface[4]. The absorption process for both the gases is therefore, gas film controlled. The concentration profiles for this case are shown in Fig. 1a.

In certain cases, the gas *B* may be highly soluble and the following condition for gas film controlled

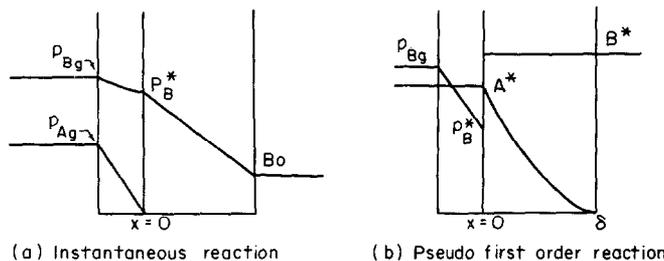


Fig. 1. Concentration profiles for absorption into an inert medium. (a) Instantaneous reaction; (b) pseudo first order reaction.

absorption may be satisfied for the gas *B*:

$$\frac{k_G}{H_B k_L} \ll 1. \quad (5)$$

Under these conditions, there will be no concentration gradients for the gas *B* in the liquid film as shown in Fig. 1b. In addition, if the following inequality is satisfied, then the concentration profile for the dissolved gas *B* is practically unaffected by the reaction with gas *A*:

$$\frac{\sqrt{(D_A k_B B^*)}}{k_L} \ll \frac{B^*}{Z_B A^*}. \quad (6)$$

The reaction (3) can therefore, be treated as a pseudo first order reaction. The following differential equations hold for this case:

Steady state:

$$D_A \frac{d^2 A}{dx^2} = (k_B B^*) A \quad (7)$$

Unsteady state:

$$D_A \frac{\partial^2 A}{\partial x^2} = \frac{\partial A}{\partial t} + (k_B B^*) A \quad (8)$$

The boundary conditions for these equations are different. For Eq. (7) we have:—

$$x = 0, A = A^* \quad (9)$$

$$x = \delta, A = 0 \quad (10)$$

and for Eq. (8)—

initial condition:

$$t = 0, x = x, A = 0 \quad (11)$$

Boundary conditions:

$$t > 0, x = 0, A = A^* \quad (12)$$

$$t > 0, x \rightarrow \infty, A = 0 \quad (13)$$

Analytical solutions for both Eqs. (7) and (8), with the respective boundary conditions are available. However, (as will be shown later) the unsteady state approach is particularly suited for experimental verification and is therefore used here. The volumetric rate of absorption, based on the solution of Eq. (8) is given by[5]:

$$R_A a = a A^* \sqrt{(D_A k_B B^* + k_L^2)} \quad (14)$$

Thus, provided the physical properties remain constant, a plot of $(R_A a / A^*)^2$ against B^* should yield a straight line with slope and intercept equal to $a^2 D_A k_B$ and $(k_L a)^2$, respectively.

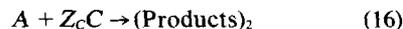
For the gas *B*, the volumetric rate of absorption is given by:

$$R_B a = k_G a [p_G - p_i]_B. \quad (15)$$

Thus, from the Danckwerts' plot [Eq. (14)] and Eq. (15) the data obtained from experiments in a contactor should yield representative values of k_L , a and $k_G a$, respectively.

Absorption into a reactive medium

In the scheme considered here, in addition to the reaction between the dissolved gases [reaction (3)], the following reaction between the gas *A* and a reactant *C*, already present in the liquid phase, occurs.



This reaction is also considered to be irreversible and first order in the gas *A* and reactant *C*. The aim

here, is to predict the rate of absorption of the gas A when absorbed from a mixture with gas B. In certain cases it will be desirable to absorb species A selectively. Therefore, a selectivity factor or index (defined elsewhere) is required to be predicted. The following cases are considered:

Both reactions fast pseudo first order

When the condition given by the following expression along with inequalities (4) and (5) is satisfied, both the reactions (3) and (16) can be considered to be fast and pseudo first order with respect to the gas A:

$$\frac{\sqrt{D_A k_C C_0}}{k_L} \ll \frac{C_0}{Z_C A^*} \tag{17}$$

The concentration profiles for this case are shown in Fig. 2a on the basis of the film model. The following differential equation will hold:

$$D_A \frac{d^2 A}{dx^2} = (k_C C_0 + k_B B^*) A \tag{18}$$

The solution of this equation satisfying boundary conditions (9) and (10) is given by:—

$$A = \frac{A^* \sinh \left[\sqrt{\left(\frac{k_C C_0 + k_B B^*}{D_A} \right) (\delta - x)} \right]}{\sinh \left[\sqrt{\left(\frac{k_C C_0 + k_B B^*}{D_A} \right) \delta} \right]} \tag{19}$$

The specific rate of absorption of the gas A is given by the flux at the interface. Therefore:

$$R_A = -D_A \left(\frac{dA}{dx} \right)_{x=0} = \frac{A^* \sqrt{[D_A (k_C C_0 + k_B B^*)]}}{\tanh \left[\frac{\sqrt{[D_A (k_C C_0 + k_B B^*)]}}{k_L} \right]} \tag{20}$$

For the case when:

$$\frac{\sqrt{[D_A (k_C C_0 + k_B B^*)]}}{k_L} > 3$$

$$R_A = A^* \sqrt{[D_A (k_C C_0 + k_B B^*)]}. \tag{21}$$

The above equation gives the rate of absorption of species A influenced by both reactions (3) and (16). However, in certain situations, a selective absorption of the gas A may be desired. Selectivity of absorption in this case will be governed by the amounts of A chemically combined with species C and B, respectively. Inoue and Kobayashi[6] and Pangarkar and Sharma[7] have discussed the selectivity of consecutive reactions. A selectivity index factor, S, similar to that used by the above authors, is defined as follows:—

$$S = \frac{k_C C_0}{k_B B^*} = \frac{D_A k_C C_0}{D_A k_B B^*} = \frac{M_{01}}{M_{02}} \tag{22}$$

In Eq. (22) the subscript 1 refers to reaction (2) and subscript 2 refers to reaction (3).

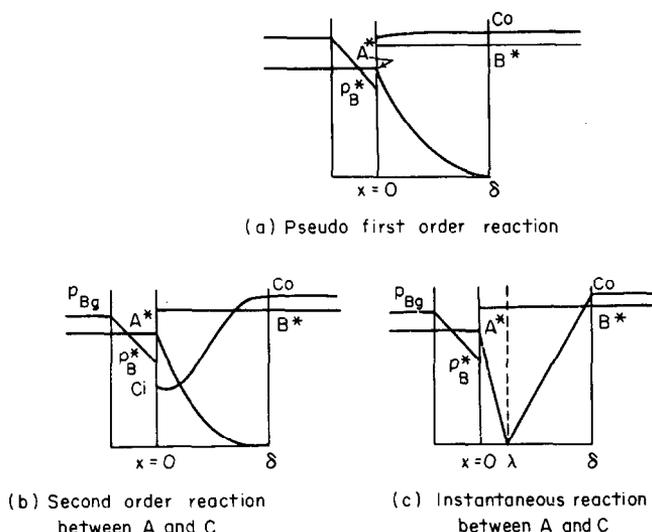


Fig. 2. Concentration profiles for absorption into a reactive medium. (a) Pseudo first order reaction; (b) second order reaction between A and C; (c) instantaneous reaction between A and C.

Reaction between the dissolved gases fast pseudo first order and that between the gas A and reactant C fast second order

When the terms in expression (17) are comparable, the assumption of a constant reactant concentration equal to the bulk liquid concentration is not valid (Fig. 2b). The following equation holds for this case:

$$D_A \frac{d^2 A}{dx^2} = (k_C C + k_B B^*) A. \quad (23)$$

An exact analytical solution of Eq. (23) is not possible. van Krevelen and Hoftijzer[8] have shown that for the case of a non-volatile reactant, the zero interfacial flux condition implies a constant reactant concentration, C_i , in the neighbourhood of the interface. The same assumption has been proved to be valid for the case of a volatile reactant for which there is a finite flux through the interface[4]. Equation (23) then assumes the following form:

$$D_A \frac{d^2 A}{dx^2} = (k_C C_i + k_B B^*) A. \quad (24)$$

The boundary conditions for Eq. (24) are the same as those given by Eqs. (9) and (10). The solution of Eq. (24) is similar to Eq. (19), the only difference being, the substitution of C_0 by C_i . Therefore:

$$A = \frac{A^* \sinh \left[\sqrt{\left(\frac{k_C C_i + k_B B^*}{D_A} \right)} (\delta - x) \right]}{\sinh \left[\sqrt{\left(\frac{k_C C_i + k_B B^*}{D_A} \right)} \delta \right]}. \quad (25)$$

The specific rate of absorption is now readily obtained as follows:

$$R_A = -D_A \left(\frac{dA}{dx} \right)_{x=0} = \frac{A^* \sqrt{[D_A (k_C C_i + k_B B^*)]}}{\tanh \left\{ \sqrt{\left[\frac{D_A (k_C C_i + k_B B^*)}{k_L} \right]} \right\}} \quad (26)$$

For the case when:

$$\frac{\sqrt{[D_A (k_C C_i + k_B B^*)]}}{k_L} > 3$$

$$R_A = A^* \sqrt{[D_A (k_C C_i + k_B B^*)]}. \quad (27)$$

In order to calculate the rate of absorption from Eq. (27) a knowledge of C_i is required. We have two

differential equations, namely Eq. (23) and

$$D_C \frac{d^2 C}{dx^2} = Z_C k_C C. \quad (28)$$

Equations (23) and (28) can be used to eliminate one of the kinetic terms (that is $k_C C_A$). For eliminating the other kinetic term, Eq. (25) is used. Thus, subtracting Eq. (28) from Eq. (25) and then substituting for A in the term $k_B B^* A$ by Eq. (25) the following equation is obtained:

$$D_A \frac{d^2 A}{dx^2} = \frac{D_C \frac{d^2 C}{dx^2} + \frac{k_B B^* A^* \sinh \left[\sqrt{\left\{ \frac{k_C C_i + k_B B^*}{D_A} \right\}} (\delta - x) \right]}{\sinh \left[\sqrt{\left\{ \frac{k_C C_i + k_B B^*}{D_A} \right\}} \delta \right]}. \quad (29)$$

The boundary conditions for the reactant C are

$$x = 0, C = C_i, \frac{dC}{dx} = 0 \quad (30)$$

$$x = \delta, C = C_0. \quad (31)$$

The solution of Eq. (29) is obtained by integrating twice. When boundary conditions (30) and (31) are used, a relation between the various variables in Eq. (29) is obtained. On simplification we get the following equation[9]:

$$\frac{C_i}{C_0} = \frac{D_A k_C C_i}{D_A k_C C_0} = \frac{M_{i1}}{M_{02}} = \frac{1}{(\phi_{a1} - 1)} \left[\phi_{a1} - \sqrt{(M_{i1} + M_{02})} \right] + \frac{M_{02}}{\sqrt{M_{i1} + M_{02}}} \left\{ 1 - \frac{1}{\sqrt{(M_{i1} + M_{02})}} \right\}. \quad (32)$$

For the case when:

$$\sqrt{(M_{i1} + M_{02})} \gg 1$$

Equation (32) can be written as:

$$\frac{M_{i1}}{M_{02}} = \frac{1}{\phi_{a1} - 1} \left(\phi_{a1} - \frac{M_{i1}}{\sqrt{[M_{i1} + M_{02}]}} \right). \quad (33)$$

The enhancement factor for the gas A is now given by:

$$\phi_A = \sqrt{(M_{i1} + M_{02})}. \quad (34)$$

The asymptotic enhancement factor, ϕ_{a1} , is obtained as follows:

Equation (33) can be written as

$$\frac{C_i}{C_0} = \eta^2 = \frac{1}{\phi_{a1} - 1} \left[\phi_{a1} - \frac{M_{i_{1a}}}{\sqrt{M_{i_{1a}} + M_{0_2}}} \right] \quad (35)$$

where $M_{i_{1a}}$ represents the asymptotic value of M_{i_1} (i.e. for the case when the reaction between species A and C is instantaneous). For this case, $C_i \rightarrow 0$ and also $\eta^2 \rightarrow 0$, therefore,

$$\frac{M_{i_{1a}}}{\sqrt{M_{i_{1a}} + M_{0_2}}} = \phi_{a1}$$

or

$$M_{i_{1a}}^2 - \phi_{a1}^2 M_{i_{1a}} + \phi_{a1}^2 M_{0_2} = 0. \quad (36)$$

The above quadratic equation gives the value of $M_{i_{1a}}$. The asymptotic enhancement factor, ϕ_a , is now given by:

$$\phi_a = \sqrt{M_{i_{1a}} + M_{0_2}}. \quad (37)$$

Reaction between the dissolved gases fast pseudo first order and that between the gas A and reactant C instantaneous

The reaction between the gas A and reactant C can be considered to be instantaneous when the converse of the condition given by expression (17) is valid. The concentration profiles for this case are shown in Fig. 2c.

Jhaveri [10] has considered the case of absorption of a single gas into a solution containing two reactants, with a similar scheme. The specific rate of absorption for this case is given by

$$R_A = \frac{A^* \sqrt{(Dk_B B^*)}}{\tanh \left[\frac{\sqrt{(D_A k_B B^*)}}{k_L} \frac{\lambda}{\delta} \right]} \quad (38)$$

To obtain R_A from Eq. (38) it is necessary to know the value of (λ/δ) . At the reaction plane, $(x = \lambda)$, by stoichiometry we have:

$$-D_A \left(\frac{dA}{dx} \right)_{x=\lambda} = \frac{D_c}{Z_c} \frac{C_0}{(\delta - \lambda)} \quad (39)$$

$$\frac{A^* \sqrt{(D_A k_B B^*)}}{\sinh \left[\frac{\sqrt{(D_A k_B B^*)}}{k_L} (\lambda/\delta) \right]} = \frac{D_c C_0}{Z_c (\delta - \lambda)}. \quad (40)$$

When Eq. (40) is simplified the following equation is obtained

$$\frac{1 - (\lambda/\delta)}{\sinh \left[\sqrt{M_{0_2}} (\lambda/\delta) \right]} = \frac{\phi_{a1} - 1}{\sqrt{M_{0_2}}}. \quad (41)$$

Equation (41) can be solved by a trial and error procedure to obtain (λ/δ) . Substitution of (λ/δ) in Eq. (38) gives the specific rate of absorption.

An inspection of Eq. (38) shows that when $[\sqrt{(D_A k_B B^*)}/k_L (\lambda/\delta)]$ is greater than three, the rate of absorption of the gas A is practically unaffected by the reaction between A and C. The condition for which the latter reaction (i.e. the reaction between A and C) significantly enhances the rate of absorption of A above that, which prevails when the gases A and B are absorbed in an inert medium, is given by the following equation:

$$\frac{\sqrt{(D_A k_B B^*)}}{k_L} (\lambda/\delta) < 3 \quad (42)$$

or

$$(\lambda/\delta) < \frac{3}{\sqrt{M_{0_2}}}. \quad (43)$$

The minimum value of ϕ_{a1} , below which, no significant enhancement in the rate of absorption of the gas A is achieved, can be obtained by combining Eqs. (41) and (43). Thus:

$$(\phi_{a1})_{\min} = 1 + \frac{\sqrt{M_{0_2}} - 3}{\sinh(3)}. \quad (44)$$

The enhancement factor for the gas A, ϕ_A , is given by:

$$\sqrt{M_{0_2}} (\lambda/\delta) < 3: \phi_A = \frac{\sqrt{M_{0_2}}}{\tanh \left[\sqrt{M_{0_2}} (\lambda/\delta) \right]} \quad (45)$$

$$\sqrt{M_{0_2}} (\lambda/\delta) > 3: \phi_A = \sqrt{M_{0_2}}. \quad (46)$$

In the case when ϕ_{a1} is very much greater than $\sqrt{M_{0_2}}$, Eq. (41) indicates that (λ/δ) is very small as compared to unity. Thus, for finite values of $\sqrt{M_{0_2}}$, $\sqrt{M_{0_2}} (\lambda/\delta)$ is considerably small. In the limit, when $\sqrt{M_{0_2}} (\lambda/\delta)$ is very much lesser than unity we have:

$$\tanh \left[\sqrt{M_{0_2}} (\lambda/\delta) \right] \rightarrow \sqrt{M_{0_2}} (\lambda/\delta)$$

$$\lim \sqrt{M_{0_2}} (\lambda/\delta) \rightarrow 0$$

Therefore, Eq. (38) reduces to

$$R_A = A^* k_L (\delta/\lambda). \quad (47)$$

But $(\delta/\lambda) = \phi_{a1}$ and thus, Eq. (47) becomes

$$R_A = k_L \phi_{a1} A^*. \quad (48)$$

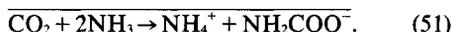
Equation (48) gives the rate of absorption of the gas

A for the case when only the reactant C is present and the reaction between species A and C is instantaneous. Consequently, according to Eq. (48), when ϕ_a is far greater than $\sqrt{M_{O_2}}$, the presence of the gas B does not affect the rate of absorption of the gas A. The amount of A chemically combined with species B is negligible and therefore, the selectivity of absorption of the gas A is maximum.

EXPERIMENTAL

Discussion of the chemical systems used

Absorption in an inert medium. For this case, ammonia and carbon dioxide were absorbed from a mixture with air (approximate composition: ammonia 45%, carbon dioxide 20% and air 35%) in deionised water. The dissolved gases react according to the following scheme:



Reaction (51) is first order in carbon dioxide and first order in ammonia. The value of the second order rate constant at 30°C is 585 l/g mol sec [11].

Absorption in a reactive medium. For this case a mixture of NH_3 and CO_2 having the same composition as in the above case was absorbed in aqueous solutions of mono- and di-ethanolamine. The reactions of carbon dioxide with these amines are second order and can be written as:



The above reaction is irreversible at lower temperatures and lower levels of carbonation of the amine. The rate constants for both mono- and di-ethanolamine have been reported by Sharma [12] and these values were used.

Apparatus. A 5.0 cm i.d. continuous glass bubble column was used. The gas phase was introduced through a 5 mm i.d. glass tube. The liquid phase was introduced through another 5 mm i.d. glass tube. The operation was carried out in a counter current manner. The operating variables were so adjusted that the ratio of the height of dispersion to the column diameter was about six.

Analytical methods

Absorption in deionised water. The amount of carbon dioxide absorbed was determined by adding a known volume of dilute sulphuric acid (at least 50

per cent in excess of the estimated requirements) to a known volume of the absorbent. The sulphuric acid addition causes a decomposition of the carbamate liberating carbon dioxide. The volume of carbon dioxide evolved was measured in a modified form of Schrötter's apparatus. The total normality of the sample was then determined by titrating a known volume of the sample with standard hydrochloric acid using methyl orange as an indicator. The amount of free dissolved ammonia was found by subtracting the ammonia bound in the carbamate from the total ammonia concentration.

Absorption in aqueous solutions of mono- and di-ethanolamine. The total normality and the amount of dissolved carbon dioxide were determined as described in the preceding section. A part of the sample was then placed in a bubbler and the free dissolved ammonia was stripped off by passing nitrogen, previously saturated with water, for 3–4 hr. At the end of this period the outlet nitrogen was tested for alkalinity due to ammonia. If no alkalinity was indicated, a known volume of the bubbler liquid was titrated with standard hydrochloric acid using methyl orange as an indicator. This reading gave the total concentration of the free and combined (in carbamate) alkanolamine. Subtracting this reading from the reading for total amine and free dissolved ammonia obtained earlier gave the concentration of the free dissolved ammonia. The entire analytical procedure was checked by analysing synthetic samples containing known amounts of alkanolamine, free dissolved ammonia and carbamate and the above procedure was found to be reasonably accurate.

RESULTS AND DISCUSSION

Absorption in deionised water. The value of the second order rate constant for reaction (51) at 30°C is 585 l/g mol sec. The solubility of carbon dioxide in water is relatively very low and that of ammonia in water is relatively very high. Therefore, the conditions given by expressions (5) and (6) are likely to be satisfied. In the solution recycle process used for treating the urea reactor off-gases, the approximate ratio of the gases is 2 mol of ammonia to 1 mol of carbon dioxide. Thus, when water is used as an absorbent, because of the relatively very high solubility of ammonia in water, the following inequality holds:

$$\frac{k_G}{H_{\text{NH}_3}} \ll k_L \quad (5)$$

Also, the solubility of carbon dioxide in water is

relatively very low. The condition for a pseudo first order reaction given by inequality (6) is therefore valid:

$$\frac{\sqrt{(D_{\text{CO}_2} k_{\text{NH}_3} [\text{NH}_3^*])}}{k_L} \ll \frac{[\text{NH}_3^*]}{2[\text{CO}_2^*]} \quad (6)$$

From the above discussion it appears that Eqs. (14) and (15) are likely to be valid under the experimental conditions of this work.

Figure 3 shows the Danckwert's plot for the system carbon dioxide-ammonia-water. The Danckwert's plot is normally obtained by plotting $[R_A a/A^*]^2$ against $[\text{NH}_3]$. In this case however, the temperature of the solution varied slightly (see Table 1). The effect of this slight variation in temperature is relatively more significant on the value of k_{NH_3} than on the physical properties because of the relatively high activation energy for the chemical reaction. To account for this variation in k_{NH_3} , the Danckwert's plot was made between $[R_A a/A^*]^2$ and $k_{\text{NH}_3} [\text{NH}_3^*]$.

The value of the liquid side mass transfer coefficient, k_L , and the effective interfacial area, a , obtained from Fig. 3 are 5.8×10^{-2} (cm/sec) and 1.58 (cm²/cm³), respectively.

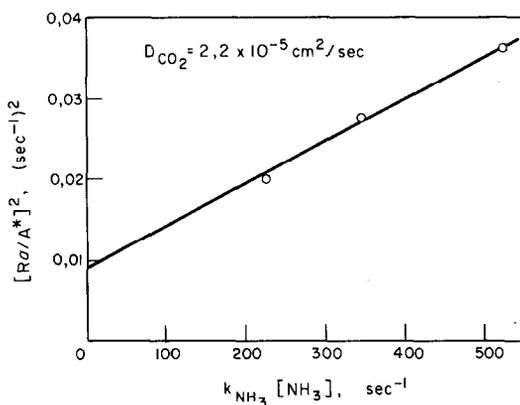


Fig. 3. Danckwert's plot for the system carbon dioxide-ammonia-water.

The inlet gas velocity in all these experiments was 20 cm/sec. However, because of the relatively very high solubility of ammonia in water, a considerable reduction in the gas velocity was observed. The outlet gas velocity was only 13 cm/sec. At relatively high gas velocities (i.e. greater than 10 cm/sec), it has been shown that the liquid phase in a bubble column is completely backmixed[13]. Therefore, the temperature of the liquid phase and the liquid phase concentration are likely to be uniform in a bubble column when the gas velocity is relatively high. The rate constant was thus based on the outlet liquid temperature and the concentration of the dissolved free ammonia and the carbamate were also based on the outlet liquid analysis.

The value of k_L and a obtained with the present system agree reasonably well with those reported by Mashelkar[14] under very similar conditions. Thus, for instance, for inlet and outlet gas velocities of 22 and 13 (cm/sec), respectively the value of a obtained by Mashelkar was 1.75 (cm²/cm³) which is about 15 per cent higher than the present value of 1.58 (cm²/cm³). The system used by Mashelkar was carbon dioxide-aqueous diethanolamine and the temperature was approximately 30°C. In the present case, the temperature was around 36°C and the absorbent was water. Thus, the system used by Mashelkar had a higher viscosity. It is known that absorbents having a higher viscosity usually provide somewhat higher values of interfacial area. Considering the above factors, the agreement between the two values can be considered as good.

The gas side mass transfer coefficient, $k_G a$, for ammonia, obtained simultaneously in this work was approximately 27.5×10^{-5} (g mol/cm³ sec atm). At approximately the same inlet gas velocity, Mashelkar[14] has reported a value of $k_G a$ of 16×10^{-5} (g mol/cm³ sec atm) for the system, sulphur dioxide-air-aqueous sodium hydroxide. Because of the higher diffusivity of ammonia (as compared to sulphur dioxide) in air, the $k_G a$ value for ammonia is expected to be higher than that for

Table 1. Simultaneous absorption of carbon dioxide (≈20% v/v) and ammonia (≈45% v/v) in deionised water

S. no.	$V_{\text{inlet}} = 20$ cm/sec					$V_{\text{outlet}} = 13$ cm/sec			
	Temp. (°C)	C_{NH_3} (g mol/cm ³)	$(\Delta p)_{\text{imCO}_2}$ (atm)	$A_{\text{CO}_2}^* \times 10^6$ (g mol/cm ³)	$(R a)_{\text{CO}_2} \times 10^6$ (g mol/cm ³)	k_{NH_3} (1/g mol sec)	$[k_{\text{NH}_3} C_{\text{NH}_3}]$ (sec ⁻¹)	$\left(\frac{R a}{A^*}\right)_{\text{CO}_2}^2$ (sec ⁻¹) ²	
1	38	5.2×10^{-4}	0.22	5.11	9.72	1000	520	0.036	
2	36	3.9×10^{-4}	0.23	5.47	9.06	900	348	0.027	
3	35	3.2×10^{-4}	0.23	5.78	8.19	820	265	0.02	

the sulphur dioxide-air system. Thus, when the following diffusivity correction is incorporated, a value of 20×10^{-5} is obtained.

$$[k_G a]_{\text{NH}_3} = [k_G a]_{\text{SO}_2} \sqrt{\left(\frac{D_{\text{NH}_3\text{-CO}_2\text{-air}}}{D_{\text{SO}_2\text{-air}}}\right)}$$

Vivian and Behrmann[15] have shown that the gas side mass transfer coefficient varies inversely as the mean partial pressure of the inerts, p_{BM} . In Mashelkar's experiments, p_{BM} had a value of 0.92 atm as compared to a value of 0.5 atm in the present work. Therefore, we would expect a $k_G a$ value 1.8–2 times higher in this case. However, due to the reduction in the gas velocity the value of $k_G a$ is considerably decreased. Unfortunately, data for $k_G a$ under conditions such that the gas velocity varies considerably over the column are not available and therefore, a rational comparison cannot be made.

From the foregoing discussion it is clear that the Danckwerts' model adequately represents the case of simultaneous absorption of carbon dioxide and ammonia in water in a bubble column.

Absorption in a reactive medium

Both reactions fast pseudo first order. The experiments in this category were carried out in the 5 cm i.d. bubble column. This type of contactor provides relatively high values of the liquid side mass transfer coefficient, k_L . Therefore, for the case of absorption of lean carbon dioxide (about 20 per cent) in faster reacting amines like monoethanolamine, at relatively higher concentrations of the amine (above 1.5 g mol/l), the condition for a pseudo first order reaction [expression (17)] is satisfied. In the case of absorption in aqueous di-ethanolamine, since the value of the reaction rate constant for the reaction between carbon dioxide and di-ethanolamine is much lower than that for mono-ethanolamine, the condition given by expression (17) holds for relatively lower concentrations of di-ethanolamine. The composition of the gaseous feed was the same as in the preceding section. The concentration of the amines was varied between 1.5 to 2 g mol/l in each case. Under these conditions, the reactions between carbon dioxide and the amines can be considered as pseudo first order. Therefore, Eqs. (21) and (22) are applicable. Table 2 gives the values of the selectivity index, S , for absorption in mono- and di-ethanolamine. The experimental values of the ratio of the amount of carbon dioxide combined with the amine and ammonia, respectively were obtained by using the

Table 2. Selectivity index, S , for carbon dioxide for absorption in aqueous solutions of mono- and diethanolamine, respectively

No.	Predicted		Experimental	
	MEA	DEA	MEA	DEA
1	22.6	3.4	25.3	2.77
2	32.1	5.93	35.7	6.15
3	34.7	7.6	37.3	8.62
4	92.8	12.6	—	14.2

following equation:

$$S_{\text{expt.}} = \frac{(Ra)_{\text{CO}_2\text{-amine}}}{(Ra)_{\text{CO}_2\text{-ammonia}}} \quad (52)$$

Theoretical values of the selectivity index were obtained by employing Eq. (22).

It can be seen from Table 2 that the value of selectivity for carbon dioxide absorption obtained with monoethanolamine is about five times that for diethanolamine. The difference between the predicted and experimental values is less than 10 per cent. Therefore, it can be concluded that the fast reacting amine-mono-ethanolamine shows high selectivity for the removal of carbon dioxide. The experimental data can be satisfactorily correlated by the proposed model.

Reaction between the dissolved gases fast pseudo first order and that between the gas A and reactant C fast second order

Experimental verification of the proposed model for this case is difficult. Depletion with respect to the reactant can be achieved by using a packed column which affords relatively low values of k_L (i.e. one-tenth of those obtained in a bubble column). However, in the case of a packed column there is a significant variation in the bulk liquid concentration over the height of the column. The use of a mean concentration is therefore likely to introduce a large error. In this case therefore, only the theoretical aspects are considered.

Figure 4 shows a plot of the enhancement factor, ϕ_A , against $\sqrt{M_{01}}$, for $\sqrt{M_{02}} = 10$ and $\phi_{a1} = 21$. It can be seen that at low $\sqrt{M_{01}}$ values the lower asymptote of ϕ_A (that is $\sqrt{M_{01}}$) is approached and when $\sqrt{M_{01}}$ greatly exceeds ϕ_{a1} and $\sqrt{M_{02}}$, the upper asymptote of ϕ_A given by Eq. (37) is approached. The upper asymptote of ϕ_A for this particular case is 24.8, which is higher than ϕ_{a1} . It thus appears that the presence of the gas B suppresses the depletion of the reactant and increases the overall enhancement factor, ϕ_A .

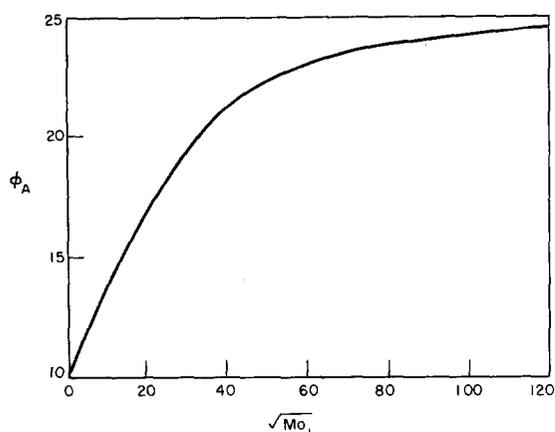


Fig. 4. Plot of ϕ_A against $\sqrt{M_{0_1}}$, for $\sqrt{M_{0_2}} = 10$, $\phi_{a_1} = 21$; Pseudo first order reaction between the dissolved gases and second order reaction between gas A and reactant C.

Selectivity of absorption for the gas A is poor when $\sqrt{M_{0_2}}$ and ϕ_{a_1} are comparable and increase with an increase in ϕ_{a_1} , i.e. as the reaction between gas A and reactant C shifts towards the fast pseudo first order reaction regime.

Reaction between the dissolved gases fast pseudo first order and that between the gas A and reactant C instantaneous

Difficulties similar to those encountered in the preceding section did not allow the experimental verification of the proposed model and therefore, only the theoretical aspects are considered here.

Figure 5 shows a plot of ϕ_A against ϕ_{a_1} for $\sqrt{M_{0_2}} = 10$. The lower limit for ϕ_A in this case is $\sqrt{M_{0_2}}$, as can be seen from Eqs. (38) and (41). At low ϕ_{a_1} values (i.e. comparable to $\sqrt{M_{0_2}}$) there is very

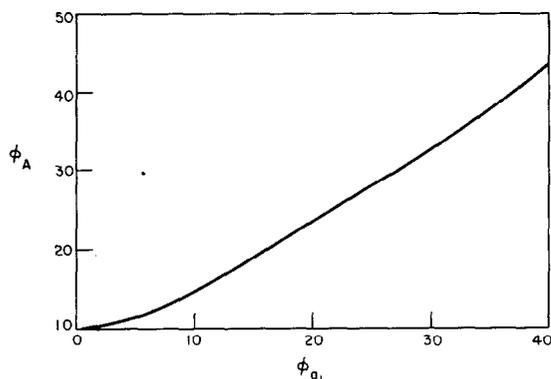


Fig. 5. Plot of ϕ_A against ϕ_{a_1} for $\sqrt{M_{0_2}} = 10$; Pseudo first order reaction between the dissolved gases and instantaneous reaction between gas A and reactant C.

little enhancement above $\sqrt{M_{0_2}}$. Therefore, if the gas A is to be selectively absorbed from a mixture with gas B, addition of the reactant will improve the selectivity only when the concentration of the reactant employed yields a high ϕ_{a_1} value which greatly exceeds $\sqrt{M_{0_2}}$. Equation (44) yields for this particular case a value of $[\phi_{a_1}]_{min}$ equal to 2.48. Thus, for this case, if the concentration of the reactant is such that, ϕ_{a_1} is less than 2.48, there will be no improvement in the selectivity as a result of the addition of the reactant. Figure 5 shows that ϕ_A increases with ϕ_{a_1} and in the limit when:

$$\phi_A \approx \phi_{a_1}$$

the selectivity of absorption for the gas A is maximum as the reaction between the dissolved gases is completely suppressed for all practical purposes.

CONCLUSIONS

(1) For the system carbon dioxide-ammonia-water, Danckwerts' analysis for the case of single gas absorption was extended. The experimental results can be successfully correlated with the proposed model.

(2) For the case of absorption of carbon dioxide and ammonia in aqueous solutions of mono- and di-ethanolamine, the experimental data agree well with the theoretical predictions for the case of fast pseudo first order reactions. It is possible to realize high selectivities with respect to carbon dioxide by employing a faster reacting amine like mono-ethanolamine when both the reactions are pseudo first order. For the other regimes of absorption, the theoretical analysis made here can be used to obtain conditions for maximum selectivity.

NOTATION

- A gas A or the concentration of the dissolved gas A at any point in the liquid film, g mol/cm³
- A* interfacial concentration of the dissolved gas A, g mol/cm³
- a gas-liquid interfacial area, cm²/cm³
- B gas B or the concentration of the dissolved gas B at any point in the liquid film, g mol/cm³
- B* interfacial concentration of the dissolved gas B, g mol/cm³
- C liquid phase reactant or the concentration of the liquid phase reactant at any point in the liquid film, g mol/cm³

- C_i interfacial concentration of the liquid phase reactant, g mol/cm³
 C_0 bulk liquid phase concentration of the liquid phase reactant, g mol/cm³
 D_J liquid phase diffusion coefficient of species J , cm²/sec
 H_J Henry's law coefficient for species J , g mol/cm³ atm
 k_B reaction rate constant for the reaction between the dissolved gases A and B , cm³/g mol sec
 k_C reaction rate constant for the reaction between the dissolved gas A and the reactant C , cm³/g mol sec
 k_G true gas side mass transfer coefficient based on the partial pressure of the solute gas as the driving force, g mol/cm² sec atm
 k_L liquid side mass transfer coefficient in the absence of chemical reaction, cm/sec
- $$\sqrt{M_i} \frac{\sqrt{(D_A k_C C_i)}}{k_L}$$
- $$\sqrt{M_{O_1}} \frac{\sqrt{(D_A k_C C_0)}}{k_L}$$
- $$\sqrt{M_{O_2}} \frac{\sqrt{(D_A k_B B^*)}}{k_L}$$
- p_J partial pressure of species J , atm
 R_J specific rate of absorption of species J , g mol/cm² sec
 t time elapsed since the first contact of the gas and liquid phase, sec
 x distance in the direction of the diffusion measured from the gas-liquid interface, cm
 Z stoichiometric factor

Greek symbols

- ϕ_A enhancement factor for the gas $A = R_A/A^*k_L$
 ϕ_{O_1} asymptotic enhancement factor for the reaction between the dissolved gas A and the reactant C

- λ distance below the interface at which the reaction plane is located, cm

Subscripts

- A species A
 B species B
 C species C
 G denotes bulk gas phase properties
 i denotes interfacial properties
 J species J
 0 bulk liquid phase properties
 λ properties at the reaction plane

Superscripts

- * denotes interfacial properties

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