LETTERS TO THE EDITOR

To the editor:

Recently, Sandall and coworkers published series of articles (N.S.Kon and O.C. Sandall, *Can. J. Chem. Eng.*, 56, 685 (1978), E.R. Matheron and O.C. Sandall, *A.I.Ch.E. J.*, 25, 332 (1979)) where they have reported data on the effective interfacial areas, obtained from chemical absorption experiments, in an agitated vessel with an unbroken surface and compared them with the actual contact area. They based their arguments on an article (G.E.H. Joosten and P.V. Danckwerts, *Chem. Eng. Sci.*, 28, 453 (1973)) which explained that when a reactant was added to an absorbing liquid, there were in general two effects. In the first place, the quantity of gas which can be absorbed by unit volume of the liquid is increased by some factor C by virtue of the reaction, and thus it will take longer for thin and slow moving patches of the liquid interface to become saturated; this effect therefore tends to increase the area which is effective for gas absorption. On the other hand, the reaction will increase the rate of absorption by some factor E (the enhancement factor) and this tends to have the opposite effect. The net effect of the reactant on the effective interfacial area may therefore be expected to depend on the quantity ν, which is

$$\nu = \frac{C}{E} = \frac{\text{factor by which reaction increases capacity of absorbent}}{\text{factor by which reaction increases rate of absorption}}$$

They have then carried out experiments in a packed column to test this hypothesis that the interfacial area effective for gas absorption with chemical reaction depends on ν. For physical absorption $\nu = 1$. For absorption of carbondioxide into certain buffer solutions $\nu >> 1$ and the effective interfacial area is much larger than for physical absorption. For absorption with "instantaneous reaction" $\nu \approx 1$, and the effective interfacial area is equal to that for physical absorption.

Although Joosten and Danckwerts have limited their paper to packed columns, it seems reasonable to extend this approach for other industrial and model absorbers too. For instance, Sandall and coworkers have carried out experiments of CO_2 absorption into either hydroxide or buffer solutions. First system was a second order reaction with $\nu = 1$ and the second involved a pseudo first order reaction with $\nu >> 1$. They have then found no difference between the physically and chemically measured k_La values with the first system and considerable difference with the buffer solutions. However as shown by us (E.Alper and W.D. Deckwer, *Chem. Eng. Sci.*, (to be published)), their experiments with buffer solutions containing catalyst did not satisfy the pseudo first order reaction conditions at high catalyst concentrations and the considerable depletion of CO_3^- ions near the interface was the real reason for their apparently unusual results. It is, indeed, easily seen that the factor ν is not itself sufficient to decide whether the effective interfacial area is considerably different for different types of absorption processes. ν is a function of only physicochemical data (such as diffusivities, reaction rate constant), bulk concentration of reactant, interface concentration of dissolved gas and the average value of the physical mass transfer coefficient k_L (or the average contact time), but it does not depend on such important properties as the distribution of contact times (or surface ages) or the distribution of local values of interfacial area per unit volume of absorbent. Some aspects of these properties were already discussed by Porter (K.E. Porter, *Trans. Instn. Chem. Engrs.*, 44, T25 (1966)) and it seems quite clear that these are also very important. For instance, the average values of k_L, for a sieve plate with low liquid content and for a laminar jet (or a falling film) may be in the same order of magnitude, hence for certain systems, such as concentrated buffer solutions etc., the condition of $\nu >> 1$ may hold for all these absorbers. However it seems possible that in froths (which occur at sieve plates with low liquid content) there may be thin films which, in the case of physical absorption of a gas, may become saturated and ceases to contribute to the absorption rate. If the liquid were a reactant solution with a high capacity for absorbing gas, the thin films might contribute to the absorption rate, hence leading to different types of absorption processes (there is however no evidence about this behaviour). On the other hand, no such behaviour would be observed in a laminar jet (or in falling film absorber) even though values of ν may be the same. Alternatively, in the case of a single bubble of a pure gas, rising in a liquid of a large liquid reservoir, the effective interfacial area would not depend on ν or the type of absorption process, but will be the same in each case and equal to the geometrical area.

These examples show—others can be found too—that ν factor cannot be the only criteria, as assumed by Sandall and coworkers, on deciding the effect of chemical reactions on interfacial areas and a knowledge of two other properties—at least qualitatively—i.e. the distribution functions of contact time and the local interfacial area per unit volume of absorbent, is also required. Unfortunately such data are not, in general, available for industrial absorbers.

ERDOGAN ALPER
Chemical Engineering Department
Hacettepe University,
Ankara, Turkey

Reply:

Alper points out that there may be variables other than γ which determine the effect of a chemical reaction on the effective interfacial area. This certainly may be the case. We have shown experimentally [*AIChE J.*, **25**, 332 (1979)] that when $\gamma \doteq 1$ the effective areas for physical absorption and chemical absorption are equal for absorption across the unbroken interface in an agitated vessel. This finding is in agreement with the results of Danckwerts and Joosten for absorption in packed columns. Thus at least for these two contacting devices the parameter, γ, appears to play a significant role.

For the case of chemical absorption with $\gamma > 1$, Alper claims that we have misinterpreted our experimental data [*Can. J. Chem. Eng.*, **56**, 685 (1978] in that our solutions did not satisfy the pseudo first-order reaction conditions at high catalyst concentrations. I do not agree with this statement. The criteria for a bimolecular reaction to be considered pseudo first-order is given, according to the Danckwerts model, by the inequality,

$$\left(1 + \frac{D_A k}{k_c^{o2}}\right)^{1/2} - 1 << \frac{C_{Bi}}{2\, C_{Ao}}$$

where k is the pseudo first-order reaction rate coefficient [Danckwerts, P.V., "Gas-Liquid Reactions", p. 122, McGraw-Hill (1970)]. This inequality is satisfied under all conditions for our experiment when k_c° is taken to be the value as determined from the chemical absorption experiments. Use of the physical absorption mass transfer coefficient as determined from the chemical absorption experiments is consistent with our model since our experimental results for $\gamma > 1$ indicate that the effective area is much larger for chemical absorption.

ORVILLE C. SANDALL
Dept. of Chemical & Nuclear Eng.
University of California
Santa Barbara, CA 93106

To the Editor:

In a recent R and D note published in this Journal, Liaw et. al. (1979) presented an approximate solution to a fixed bed adsorption problem considered previously by Rosen (1952). The problem is that of adsorption of a single adsorbable species from a fluid stream passing through a fixed bed packed with adsorbents free of adsorbate initially. The isotherm is linear and the rate controlling step is the combination of mass transfer resistances in both fluid and particle phases.

The approximation introduced by Liaw et.al. (1978) is the use of the Glueckauf's linear driving force assumption in describing the diffusion through the particle phase instead of the diffusion equation. Apparently overlooked by the authors was the fact that if the linear driving force assumption is used, the governing equation can be put into a form identical to those of cross flow heat exchanger or heat regenerators whose analytical solution was first given more than half a century ago [Anzelius, 1926]. To demonstrate this, consider Equations (8) and (14) of the note. By eliminating the interphase concentration, q_R, the rate equation becomes

$$\frac{\partial \bar{q}}{\partial \theta} = \left[\frac{R^2}{15D} + \frac{KR}{3k}\right]^{-1}\left(cK - \bar{q}\right) = \frac{cK - \bar{q}}{\xi} \qquad (1)$$

where ξ is the overall resistance or more commonly, the reciprocal of the overall transfer coefficient. Equation (1), together with the macroscopic mass balance equation [i.e. Equation (12) of the Liaw et. al.] are the governing equations which can be put into the following dimensionless form

$$\frac{\partial c^+}{\partial z^+} + \frac{\partial \bar{q}^+}{\partial \theta^+} = 0 \qquad (2)$$

$$\frac{\partial \bar{q}^+}{\partial \theta^+} = c^+ - \bar{q}^+ \qquad (3)$$

where $c^+ = c/c_0$, $\bar{q}^+ = q/Kc_0$, $z^+ = Kz/\xi$ and $\theta^+ = \theta/\xi$.

The initial and boundary conditions are

$$c^+ = 1,\ \text{at}\ z^+ = 0\ \ \theta^+ \geq 0 \qquad (4)$$

$$\bar{q}^+ = 0, \quad z^+ \geq 0\ \ \theta^+ \geq 0 \qquad (5)$$

A thorough literature survey of the solutions of the above system of equations published prior to 1962 was made by Beveridge (1962). The solutions of Equations (2) and (3) with the initial and boundary conditions are known to be

$$c^+ = J(z^+\ \theta^+) \qquad (6)$$

$$\bar{q}^+ = 1 - J(\theta^+, z^+) \qquad (7)$$

where

$$J(\alpha, \beta) = 1 - e^{-\beta} \int_0^{\alpha} e^{-y} I_0(2\sqrt{\beta y})\, dy \qquad (8)$$

The J-function has been extensively tabulated (Opler and Hiester, 1954) and is also given in a recently published text book (Sherwood, Pigford and Wilkes, 1975). Furthermore a number of asymptotic expressions of the J-function are available as summarized by Klinkenberg (1954) and Beveridge (1962). For example, for small values of either z^+ or θ^+, one has

$$c^+ = 1 + e^{-\theta^+ - z^+} \sum_{n=1}^{\infty} \left[\frac{z^{+n}}{n!} \sum_{K=0}^{n-1} \frac{\theta^{+K}}{K!}\right] \qquad (9)$$

$$q^+ = e^{-\theta^+ - z^+} \sum_{n=1}^{\infty} \left[\frac{\theta^{+n}}{n!} \sum_{K=0}^{n-1} \frac{z^{+K}}{K!}\right] \qquad (10)$$

together with

$$c^+ - q^+ = e^{-\theta^+ - z^+} I_0(2\sqrt{\theta^+ z^+}) \qquad (11)$$

A term by term comparison showed that Equation (9) is identical to Equation (3) given by Liaw et. al. The limitation that this expression is valid for either small θ^+ or z^+ results directly from the series expansion method these authors used in inverting the Laplace transfer although this was not stated explicitly in their work.

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CHI TIEN
Department of Chemical Engineering
and Materials Science
Syracuse University
Syracuse, N.Y. 13210

Reply:

Tien missed the point that our Eq. (33), not Eq. (31), is the new solution. Yes, Eq. (31) is in the literature but it is useless as it is impossible to implement on the computer. It does not take very large values of i to blow up calculations of $(i!)^2$ on computers. This problem is eliminated in Eq. (33).

R. A GREENKORN AND
K. C. CHAO
School of Chemical Engineering
Purdue University
W. Lafayette, Indiana 47907