The prediction of mass transfer rates during bubble growth in the presence of an instantaneous reaction on the liquid side

Chemical absorption of a solute from a gaseous mixture has received the attention of several authors due to the considerable enhancement of the mass transfer rates when compared with its physical counterpart (Perry *et al.*, 1984). For the case where the gaseous solute undergoes a very fast reaction in the liquid phase and the liquid reactant exists in large excess, the reaction takes place on the gas–liquid interface only (Danckwerts, 1970). Rocha and Guedes de Carvalho (1984) emphasized that most of the mass transport in such cases occurs during bubble formation rather than during bubble rise. The attempt to theoretically model the mass transfer behavior during bubble growth from first principles is, therefore, of both academic interest and industrial significance.

The fundamental interpretations of the available mass transfer data for gas–liquid systems with growing interfaces can be tentatively divided into two major categories according to the underlying fluid mechanics rationale: (i) the growing interface is regarded as a deformable surface accounted for by gas elements sharing the same history (Stewart *et al.*, 1970; Angelo *et al.*, 1966; Howard and Lightfoot, 1968; Fortescue and Pearson, 1967; Bird *et al.*, 1969; Levitch, 1962; Sherwood *et.al.*, 1975), or (ii) the bubble surface in expansion is conceived to be made up of gas elements with different ages (Calderbank and Patra, 1966; Beek and Kramers, 1962; Malcata, 1988). Both types of approach are in essence a generalization to the case of mobile interfaces of the penetration theory introduced by Higbie (1935) and Danckwerts (1951).

The double surface-renewal concept (Malcata, 1988) in its native form was able to semi-quantitatively predict experimental results considerably better than other theoretical approaches. Two major drawbacks were, nonetheless, reported: (i) for very low volumetric flow rates this theory actually leads to amounts of solute desorbed higher than those fed to the system, and (ii) the average percentual deviation between theoretical predictions and experimental observations over the range of industrially relevant volumetric flow rates is fairly high (about −60%).

In this communication the original theory by Malcata (1988) is considerably extended and refined in order to provide a more concise fundamental insight to the physicochemical phenomena taking place. A more powerful designing tool for sparged vessels with sufficiently separated bubbling orifices (Sherwood and Pigford, 1952) aimed at selectively removing a gaseous solute via an instantaneous reaction on the liquid side is, thus, generated. This is accomplished at the expense of two major considerations: (i) the bubble is now assumed to consist of a perfectly stirred pool as the inner core in addition to the outer shell undergoing plug flow in the vicinity of the interface, and (ii) an operational constant that was previously obtained from strict theoretical arguments is now transformed into an adjustable parameter.

According to the double surface-renewal theory the interfacial boundary layer is assumed to consist of gas elements continuously sliding along a toroidal path on the surface of the bubble. Two kinds of surface generation mechanisms are considered: a forced and a natural surface renewal. The former gas elements account for the actual growth of the bubble surface; the latter result from the circulation imposed on the whole bubble by the inlet gas stream, in a way similar to what happens with rising bubbles (Bird *et al.*, 1969; Hammerton and Garner, 1954). Both kinds of gas elements are directly generated from the input gas stream after thorough mixing with the bulk gas, but once at the surface they become totally equivalent. This approach leads to an effective desorption area greater than the area of the actual bubble surface because a gas element is allowed to remain on the surface for a finite time smaller than the lifespan of the growing bubble. In principle a laminar boundary layer should develop near the bubble surface in order to accommodate the approximate non-slip condition at the interface (Schlichting, 1955). It can be shown, however, that for the range of Péclet numbers with physical interest the concentration gradient in the vicinity of the interface does not appreciably depend on whether a parabolic or uniform velocity profile exists on the gas side.

The following postulates are taken as valid in order to define the problem: (i) the solute exists in the gas phase at a very dilute level, so the convective term in Fick's first law is negligible and the overall volumetric flow rate of gas is almost independent of the rate of desorption of solute; (ii) the bulk of the bubble undergoes complete micromixing; (iii) the gas elements on the bubble surface maintain their identity until the wake is reached; (iv) the penetration theory describes the desorption of solute from any gas element on the surface; (v) the bubbles are considered to retain perfect spherical shape; and (vi) the mass flux is essentially unidimensional and normal to the surface at each point, so no mass transfer between adjacent gas elements on the surface is allowed. The mass balance to the solute inside the growing bubble may then be written as

$$Q_{\mathrm{gas}} C_{\mathrm{sol.\,in}} = Q_{\mathrm{gas}} \left(C_{\mathrm{sol.bulb}} + t \frac{\mathrm{d}C_{\mathrm{sol.\,bub}}}{\mathrm{d}t} \right) + 2\left(\frac{D_{\mathrm{sol.\,gas}}}{\pi} \right)^{1/2} \int_0^{A_{\mathrm{surf}}(t)} \frac{C_{\mathrm{sol.bub}}[t_i(\zeta)]}{\sqrt{t - t_i(\zeta)}} \mathrm{d}\zeta \qquad (1)$$

where the LHS arises from the input of solute, the first term in the RHS corresponds to the accumulation of solute, and the remaining integral term accounts for the removal of solute from the gaseous mixture. This term is easily obtained by extending the desorption flux of solute under unsteady-state conditions in a semi-infinite medium to all gas elements existing on the surface at time *t*.

The elementary variation of the area occupied by gas elements desorbing on the surface during an infinitesimal time interval can be expressed as

$$\mathrm{d}A_{\mathrm{des}}(t)=\left[\frac{\mathrm{d}A_{\mathrm{surf}}(t)}{\mathrm{d}t}\right]\mathrm{d}t+v_{\mathrm{ren}}(t)\,\mathrm{d}t. \tag{2}$$

The rate of surface renewal should, in its simplest form, be proportional to the degree of gas circulation within the bubble (measured by Q_{gas}) and also proportional to the availability of a gas element to exist on the surface (measured by the ratio of A_{surf} to V_{bub}). This statement can be mathematically expressed as

$$v_{\mathrm{ren}}(t)=Ma\,Q_{\mathrm{gas}}\frac{A_{\mathrm{surf}}(t)}{V_{\mathrm{bub}}(t)} \tag{3}$$

where Ma is a dimensionless parameter containing the lumped contributions of both proportionality factors. For a gas element that arrived to the surface at time t_i, desorption takes place until time $t_f(t_i)$. During this period the gas element slides on the surface with decreasing v_{ren} spanning an area equal to the actual geometric surface of the bubble at time t_i. The value for $t_f(t_i)$ may then be obtained by solving the integral equation

$$A_{\mathrm{surf}}(t_i)=\int_{t_i}^{t_f(t_i)} v_{\mathrm{ren}}(\xi)\,\mathrm{d}\xi \quad (0\leqslant t_f\leqslant t_{\mathrm{fin}}). \tag{4}$$

Using eq. (3) in eq. (4) and performing the integration with the aid of the geometrical properties of the bubble, one can write

$$t_f(t_i)=\left(\frac{3Ma+2}{3Ma}\right)^{3/2} t_i\left\{H(0)-H\left[\left(\frac{3Ma}{3Ma+2}\right)^{3/2} t_{\mathrm{fin}}\right]\right\}$$
$$+t_{\mathrm{fin}}\left\{H\left[\left(\frac{3Ma}{3Ma+2}\right)^{3/2} t_{\mathrm{fin}}\right]-H(t_{\mathrm{fin}})\right\}. \tag{5}$$

Although the exact equations describing bubble growth exist (Krishnamurthi *et al.*, 1968; Ramakrishnan *et al.*, 1969; Satyanarayan *et al.*, 1969; Khurana and Kumar, 1969; Tsuge and Hibino, 1978, 1981; Pinczewski, 1981; Takahashi and Miyahara, 1981) an alternative relationship suggested by Davidson and Schüller (1960) for constant gas flow rate through a submerged nozzle will be employed due to its simplicity and good agreement with experimental evidence reported elsewhere (Rocha and Guedes de Carvalho, 1984). Such a predictive expression can be formulated as follows:

$$t_{\mathrm{fin}}=\frac{8}{7}Q_{\mathrm{gas}}^{1/5}\,g^{-3/5}. \tag{6}$$

Equations (2) and (3) and (5) and (6) can be combined with eq. (1), yielding

$$1-C^*_{\mathrm{sol,\,bub}}-t^*\frac{\mathrm{d}C^*_{\mathrm{sol,\,bub}}}{\mathrm{d}t^*}-\Xi Op\int_{\left(\frac{3Ma}{3Ma+2}\right)^{3/2}t^*}^{t^*} \times\frac{C^*_{\mathrm{sol,\,bub}}(\xi)\,\mathrm{d}\xi}{\xi^{1/3}\sqrt{t^*-\xi}}=0. \tag{7}$$

Equation (7) can be integrated from the initial condition

$$\text{at } t^*=0,\qquad C^*_{\mathrm{sol,\,bub}}=1 \tag{8}$$

via a finite-difference method. The integral term can then be evaluated by a trapezoidal rule. The value of $C^*_{\mathrm{sol,\,bub}}(\xi)$ at each intermediate point is calculated either by linear interpolation or by linear extrapolation, depending on whether ξ is smaller or larger relative to the last available step of t^*. The results obtained for three consecutive orders of magnitude for Ma are displayed in Fig. 1 as $C^*_{\mathrm{sol,\,bub}}(t^*=1)$ vs Op.

A careful inspection of Fig. 1 allows one to find linear asymptotes for $C^*_{\mathrm{sol,\,bub}}(t^*=1)$ when Op tends to zero. Their equations are more easily obtained by first rewriting eq. (7) as

$$\frac{\mathrm{d}C^{**}_{\mathrm{sol,\,bub}}}{\mathrm{d}t^*}=\Xi Op\int_{\left(\frac{3Ma}{3Ma+2}\right)^{3/2}t^*}^{t^*}\frac{\mathrm{d}\xi}{\xi^{1/3}\sqrt{t^*-\xi}}$$
$$-\Xi Op\int_{\left(\frac{3Ma}{3Ma+2}\right)^{3/2}t^*}^{t^*}\frac{C^{**}_{\mathrm{sol,\,bub}}(\xi)\,\mathrm{d}\xi}{\xi^{4/3}\sqrt{t^*-\xi}}. \tag{9}$$

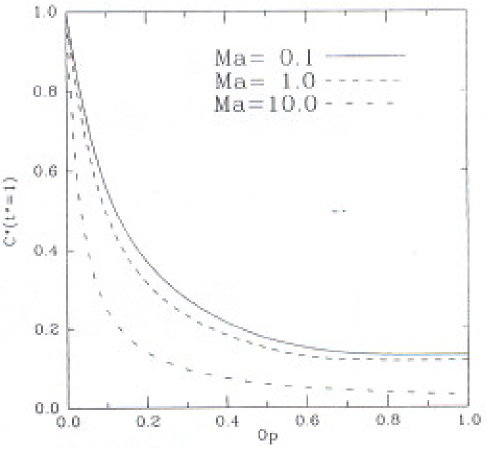

Fig. 1. Normalized concentration of solute in the bulk of the bubble at the time of bubble release, $C^*(t^*=1)$, plotted against the operational parameter, Op, within the range of industrial interest. Three consecutive orders of magnitude are considered for Ma.

For very low values of parameter Op, $C^*_{\mathrm{sol,\,bub}}$ does not significantly differ from unity. Hence the second integral term in eq. (9) can be discarded. Partioning the remaining integral term into two integrals using zero for the lower limit, recalling the definition and mathematical properties of the B and Γ functions (Boas, 1983), employing a McLaurin series expansion in ξ (Spiegel, 1968; Stephenson, 1973), and using eq. (8), one finally gets

$$C^*_{\mathrm{sol,\,bub},\,Op\to 0}=1-\frac{6}{7}\Phi\Xi\,Op\,t^{*\,1/6}. \tag{10}$$

It is interesting to note that large values of Ma gives rise to a linear asymptotic expression for $\Phi\Xi(Ma)$, namely

$$\lim_{Ma\to\infty}\Phi\Xi=2\cdot 3^{2/3}\cdot 4^{1/3}\left(\frac{8}{7\pi}\right)^{1/6}\left[B\left(\frac{1}{2},\frac{2}{3}\right)-\frac{3}{2}-3\sum_{n=1}^{\infty}\frac{\Gamma(n+\frac{1}{2})}{(3n+2)n!}\right]Ma \tag{11}$$

For large Ma, $C^{**}_{\mathrm{sol,\,bub}}(\xi)/\xi$ is approximately given by $C^{**}_{\mathrm{sol,\,bub}}(t^*)/t^*$ over the whole range of integration in eq. (9). The resulting ODE can be solved by first obtaining a general solution for the homogeneous equation counterpart followed by the application of the method of variation of constants in order to find its particular integral (Kreyszig, 1979). Use of eq. (8) coupled with some algebraic manipulation eventually leads to

$$C^*_{\mathrm{sol,bub},Ma\to\infty}=\frac{5}{324}\sum_{j=6}^{\infty}\frac{(-1)^j6^j(Op\,\Phi\Xi)^{j-6}}{j!}t^{*\,j/6-1}. \tag{12}$$

For small values of Op eq. (12) reduces to a linear form consistent with eq. (10) as expected.

Direct integration of eq. (2) with the help of eq. (3) gives

$$A^*_{\mathrm{des}}(t^*=1)=1+\frac{3}{2}Ma. \tag{13}$$

Ma can be viewed as a direct measure of the turbulence accompanying the formation of the bubble provided that the length scale associated with the most relevant gaseous eddies for mass transfer is of the order of magnitude of the bubble size.

Although similar to the result encountered previously by Malcata (1988) via a numerical approximate method, the result denoted as eq. (10) is now obtained by pure analytical reasoning. Since this result is only valid for low values of Op, a physical inconsistency is likely to be found when the foregoing equation is extrapolated to null volumetric flow rates.

For industrial scale-up eqs (11) and (12) may be used as a short-cut method for an approximate prediction of the mass transfer rates provided that Ma is anticipated to have considerably high values. This reasoning is justified by the large value of Ma (i.e. 1063) found by the least-squares fit of $C^*_{\text{sol, bub}}(t^*=1)$ as given by eqs (7) and (8) using the data reported by Rocha and Guedes de Carvalho (1984). Appreciable changes in the value of Ma lead, however, to small variation of the predicted values for the solute fractional removal. This observation may be partly attributed to the square root dependence of the integrated desorption rates on the surface residence time of the gas elements which tends to damp the effect of Ma.

The fact that very high values of Ma are required for a good fit to observed data is a direct consequence of the stochastic turbulence in the vicinity of the nozzle tip. This behavior may be attributed to the disruptive presence of the injection nozzle and to the strong coalescence between successive bubbles during continuous operation. The extremely enhanced rates of mass transfer during bubble growth are thus understood as a result of an equivalent area available for solute desorption much larger than the actual macroscopically measured area of the bubble surface.

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NOTATION

A	area of surface, m^2
A^*	dimensionless area of surface, $A/A_{\text{surf, fin}}$
C	molar concentration, mol m^{-3}
C^*	normalized concentration, C/C_{in}
C^{**}	dimensionless variable, $t^*(1-C^*)$
D	binary diffusivity, $\text{m}^2\,\text{s}^{-1}$
g	acceleration of gravity, m s^{-2}
H	Heaviside step function
Ma	adjustable dimensionless parameter
Op	dimensionless operating parameter, ${D_{\text{sol, gas}}}^{1/2} \times {Q_{\text{gas}}}^{-3/10} g^{-1/10}$
Q	volumetric flow rate, $\text{m}^3\,\text{s}^{-1}$
t	time elapsed since bubble birth, s
t^*	normalized time elapsed since bubble birth, t/t_{fin}
v	rate of surface renewal, $\text{m}^2\,\text{s}^{-1}$
V	volume, m^3

Greek letters

ζ	dummy variable of integration associated with an area scale
ξ	dummy variable of integration associated with a time scale
Ξ	constant, $\left(\frac{8}{7}\right)^{1/6}\left(\frac{4}{\pi}\right)^{1/2}\left[\frac{8\pi}{3}\left(\frac{3}{4\pi}\right)^{2/3}+3\left(\frac{4\pi}{3}\right)^{1/3}Ma\right]$
Φ	constant, $B\left(\frac{1}{2},\frac{2}{3}\right)-\frac{9Ma}{6Ma+4} - 3\sum_{n=1}^{\infty}\frac{\Gamma\left(n+\frac{1}{2}\right)}{(3n+2)n!}\left(\frac{3Ma}{3Ma+2}\right)^{n+2/3}$

Subscripts

bub	referring to the bubble, or to the bulk conditions in the bubble
des	desorbing on the surface
f	at the moment the gas element is released from the surface of the bubble
fin	when the bubble is released from the submerged nozzle
gas	within the gas phase
i	at the moment the gas element arrives at the surface of the bubble
in	at the inlet conditions
$Ma\to\infty$	when Ma tends to infinity
$Op\to 0$	when Op tends to zero
ren	due to the continuous natural surface renewal
sol	referring to the solute
surf	referring to the actual surface of the bubble

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