$m^2 W^{-1}$. It is interesting to note that the final values measured were of the same order of magnitude as the corresponding values suggested by the results of Bakulin, *et al.* [7], Sakhuja and Rohsenow [6] and Wilcox and Rohsenow [10].

5. CONCLUSIONS

The above theory points strongly to the presence of a wall–condensate interface resistance or resistive layer on the nickel condenser surfaces during experiments with condensing liquid metals. Further, preliminary experimental measurements of this resistance tend to support this theory. The authors at this stage make no attempt to explain why such a resistance, or possibly a resistive layer, should exist but merely suggest that all the facts point to the presence of such a phenomenon in liquid metal condensation experiments.

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A THEORY FOR TRANSIENT MASS TRANSFER WITH SUCTION AT THE PHASE BOUNDARY—APPLICATION TO BUBBLES IN FLUIDIZED BEDS

J. R. F. Guedes de Carvalho and J. B. L. M. Campos
Centro de Engenharia Química, Faculdade de Engenharia,
Rua dos Bragas, 4099 Porto Codex, Portugal

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NOMENCLATURE

a,	concentration of diffusing species;
a_0,	concentration of diffusing species far from interface;
D,	gas diffusivity;
D_s,	diameter of slug;
E,	enhancement of diffusive flux due to crossflow;
E_{tr},	as E but for transpiration;
F,	fraction of additive flux contributed by diffusion only;
$k_G S$,	transfer coefficient for slugs due to diffusion only;
L_s,	length of slug;
N,	instantaneous flux of diffusing species across interface;
N_{av}(cross),	average flux of diffusing species across interface due to crossflow only;
N_{av}(diff+cross),	average flux of diffusing species across interface accounting for interaction between diffusion and crossflow;
N^r_{av}(diff),	purely diffusive average flux with random surface renewal, $a_0(Ds)^{1/2}$;
N^r_{av}(diff+cross),	average flux at the interface with random surface renewal, accounting for interaction between diffusion and crossflow;
p,	variable of the Laplace transform domain;
Q,	overall transfer coefficient between slug and dense phase;
R,	ratio between exact value of average flux and the sum of fluxes due to diffusion only and crossflow only;
R^r,	as R but with random surface renewal;
s,	rate of surface renewal;
t,	time;
T_v,	dimensionless time, $v^2 t/D$;
u,	component of gas velocity tangent to bubble surface;
U_{mf},	minimum fluidizing velocity;
v,	fluid velocity perpendicular to the interface;
X,	dimensionless distance from interface, xv/D;
w,	dummy variable;
z,	dummy variable.

Greek symbols

α,	dimensionless concentration, $(a-a_0)/a_0$;
$\bar{\alpha}$,	Laplace transform of α;
θ,	dimensionless time of contact, $v^2/(Ds)$.

Subscripts

av,	average;
0,	far from interface;
s,	refers to slug.

INTRODUCTION

The classical theory of Higbie may be used to predict the mass transfer coefficient at an interface in situations such as that depicted in Fig. 1(a); at $t = 0$ a fresh element of fluid I is brought into contact with the interface and the concentration, a, of the transferred component A undergoes a step change at $x = 0$. (The step change considered is from a_0 to 0 as would be the case if A were consumed by an instantaneous irreversible process.) As time goes on the concentration profile in fluid I changes and for equimolar counterdiffusion or for very dilute mixtures

$$D\frac{\partial^2 a}{\partial x^2} = \frac{\partial a}{\partial t} \tag{1}$$

holds with

$$\begin{aligned} &t = 0\; x < 0 && a = a_0, \\ &t > 0\; x = 0 && a = 0, \\ &t > 0\; x \to -\infty && a = a_0. \end{aligned} \tag{1a}$$

The instantaneous flux across the interface, N, varies with time according to

$$N = -D\left(\frac{\partial a}{\partial x}\right)_{x=0} = a_0(D/\pi t)^{1/2}. \tag{2}$$

If the process of transfer is interrupted after a time t (by taking away the fluid element from the interface), the average flux over that period is given by

$$N_{av}(\text{diff}) = (1/t)\int_0^t N\,\mathrm{d}t = a_0(4D/\pi t)^{1/2}. \tag{3}$$

The process that interests us here is similar to that described above, except that the fluid has a permeation velocity component v (perpendicular to the interface) superimposed on the velocity component along the interface. This situation might be realised in practice by means of a porous plate, under suction, suddenly exposed to the gas mixture with reactant A being instantly consumed at the contact of the porous matrix (e.g. a catalyst). A similar process may be expected to be at work near the bubble surface in a fluidized bed, as described later.

In Fig. 1(b), the evolution of the concentration profile is depicted and the dashed area corresponds to the penetration of fluid into the porous wall. It is readily understood that if the suction process goes on for a sufficiently long time ($t \to \infty$), the concentration profile tends to a limiting configuration such that the flux of A across the interface is given by N_{av} (crossflow) $= va_0$; this corresponds to the solution of

$$D\frac{\mathrm{d}^2 a}{\mathrm{d}x^2} = v\frac{\mathrm{d}a}{\mathrm{d}x} \tag{4}$$

with

$$\left.\begin{aligned} &x = 0\;\;, && a = 0, \\ &x \to -\infty, && a = a_0. \end{aligned}\right\} \tag{4a}$$

This flux is that resulting simply from the crossflow.

In the case of transpiration (negative suction) it is obvious that the flux due to crossflow is nil.

PENETRATION THEORY WITH SUCTION AT THE WALL

The exact solution of the problem of diffusion with crossflow corresponding to the situation in Fig. 1(b) at all times is considered next. A material balance on a differential slice with faces parallel to the interface gives

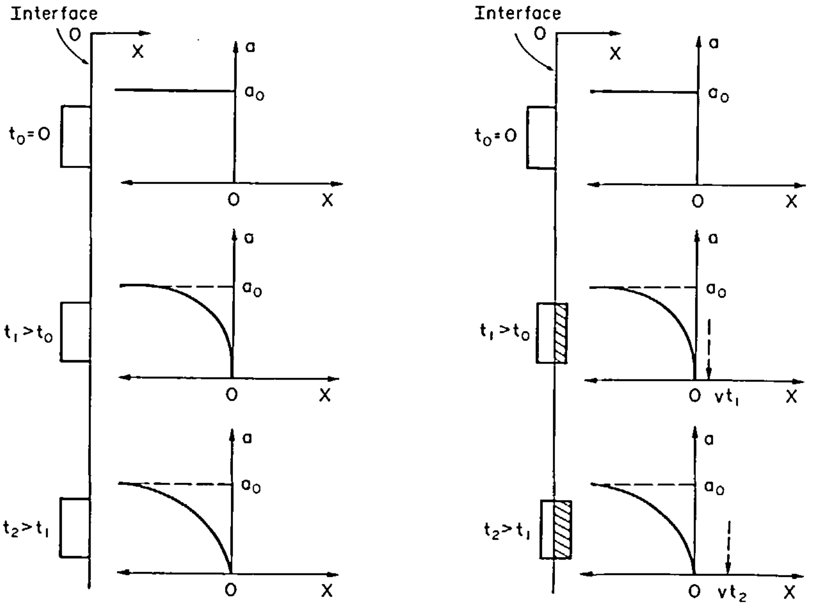
$$D\frac{\partial^2 a}{\partial x^2} - v\frac{\partial a}{\partial x} = \frac{\partial a}{\partial t} \tag{5}$$

and the initial and boundary conditions are

$$\begin{aligned} &t = 0 && x < 0 && a = a_0, \\ &t > 0 && x = 0 && a = 0, \\ &t > 0 && x \to -\infty && a = a_0. \end{aligned} \tag{5a}$$

For constant v, the dimensionless variables $\alpha = (a - a_0)/a_0$, $X = vx/D$ and $T = v^2t/D$ may be defined. Then equations (5) and (5a) reduce to

$$\frac{\partial^2 \alpha}{\partial X^2} - \frac{\partial \alpha}{\partial X} = \frac{\partial \alpha}{\partial T} \tag{6}$$



(a) (b)

Fig. 1. Concentration profiles for transient diffusion; (a) Diffusion only; (b) Diffusion with suction.

with

$$\begin{aligned} &T = 0, \quad X < 0, \quad \alpha = 0, \\ &T > 0, \quad X = 0, \quad \alpha = -1, \qquad \text{(6a)} \\ &T > 0, \quad X \rightarrow -\infty, \quad \alpha = 0. \end{aligned}$$

Laplace transforms may be used to solve equation (6) as shown in the Appendix and the result is

$$(a-a_0)/a_0 = \alpha = -[2/(\pi^{1/2})] \int_{-(X/2T^{1/2})}^{\infty} \times \mathrm{e}^{X/2}\,\mathrm{e}^{-X^2/(16z^2)}\,\mathrm{e}^{-z^2}\,\mathrm{d}z \quad (7)$$

and the instantaneous flux at the interface

$$N = -D\left(\frac{\partial a}{\partial x}\right)_{x=0} = -va_0\left(\frac{\partial \alpha}{\partial X}\right)_{X=0}$$

may be obtained as

$$N = a_0 v[(1/2)+\mathrm{e}^{-T/4}/(\pi T)^{1/2}+(1/2)\mathrm{erf}(T^{1/2}/2)]. \quad (8)$$

It may be seen that equation (8) reduces to

$$N = a_0[D/(\pi t)]^{1/2}$$

for low values of T and to $N = va_0$ for high T as expected. In practice it is important to know the average flux over a period of time t as given by

$$N_{\mathrm{av}} = (1/t)\int_0^t N\,\mathrm{d}t = (1/T)\int_0^T N\,\mathrm{d}T$$

and this is

$$N_{\mathrm{av}}(\mathrm{diff+cross}) = (a_0 v) \times [(1/2)+\mathrm{e}^{-T/4}/(\pi T)^{1/2}+[\tfrac{1}{2}+(1/T)]\mathrm{erf}(T^{1/2}/2)]. \quad (9)$$

It is interesting to compare this value of the exact average flux with the approximate value obtained by simply adding the value for diffusion alone $N_{\mathrm{av}}(\mathrm{diff}) = 2va_0/(\pi T)^{1/2}$ with that for crossflow alone $N_{\mathrm{av}}(\mathrm{cross}) = va_0$. This may be done by defining the ratio

$$\begin{aligned} R &= N_{\mathrm{av}}(\mathrm{diff+cross})/[N_{\mathrm{av}}(\mathrm{diff})+N_{\mathrm{av}}(\mathrm{cross})] \\ &= [(T/2)+(T/\pi)^{1/2}\mathrm{e}^{-T/4}+[1+(T/2)] \\ &\times \mathrm{erf}(T^{1/2}/2)]/[T+2(T/\pi)^{1/2}]. \qquad (10) \end{aligned}$$

Table 1. The effect of crossflow on rate of transfer

T	0.04	0.16	0.36	0.64	1.00	1.96	4.00	9.00	36.0	100
E	1.09	1.19	1.29	1.41	1.52	1.78	2.19	2.95	5.50	8.95
R	0.93	0.88	0.85	0.82	0.81	0.79	0.79	0.81	0.86	0.91
R'	1.08	1.12	1.15	1.14	1.14	1.11	1.08	1.04	1.00	1.00
F	0.85	0.74	0.65	0.59	0.53	0.45	0.36	0.27	0.16	0.10
E_{tr}	0.91	0.84	0.76	0.70	0.64	0.54	0.42	0.29	0.15	0.09

The dependence of R on T is shown in Table 1 and Fig. 2. A slightly more complicated approximate expression for the average flux is

$$N'_{\mathrm{av}} = [N^2_{\mathrm{av}}(\mathrm{diff})+N^2_{\mathrm{av}}(\mathrm{cross})]^{1/2} \qquad \text{(10a)}$$

and the corresponding ratio

$$R' = N_{\mathrm{av}}(\mathrm{diff+cross})/N'_{\mathrm{av}} \qquad \text{(10b)}$$

is shown in Table 1 and Fig. 2 to be closer to unity than R. Also shown are the values of the fractional contribution of diffusion, F, in the approximate additive flux as given by

$$\begin{aligned} F &= N_{\mathrm{av}}(\mathrm{diff})/[N_{\mathrm{av}}(\mathrm{diff})+N_{\mathrm{av}}(\mathrm{cross})] \\ &= [1+(\pi T/4)^{1/2}]^{-1}. \qquad (11) \end{aligned}$$

The existence of crossflow enhances the rate of mass transfer and the extent of this enhancement is given by the ratio

$$\begin{aligned} E &= [N_{\mathrm{av}}(\mathrm{diff+cross})/N_{\mathrm{av}}(\mathrm{diff})] \\ &= (\pi T/16)^{1/2}+\tfrac{1}{2}\mathrm{e}^{-T/4} \\ &+[(\pi T/16)^{1/2}+(\pi/4T)^{1/2}]\,\mathrm{erf}(T^{1/2}/2) \qquad (12) \end{aligned}$$

values of which are also shown in Table 1 and Fig. 2.

PENETRATION THEORY WITH TRANSPIRATION AT THE WALL

For the sake of completeness it is interesting to consider the case where gas is blown through the wall (transpiration), while diffusion takes place, thus reducing the rate of mass transfer. If gas is blown steadily at a constant rate, equation (5) still applies, but with negative v. For the same initial and boundary conditions (5a) the expressions for the concentration profile, equation (7), for the instantaneous flux, equation (8), and for the average flux, equation (9), still hold if it is remembered that

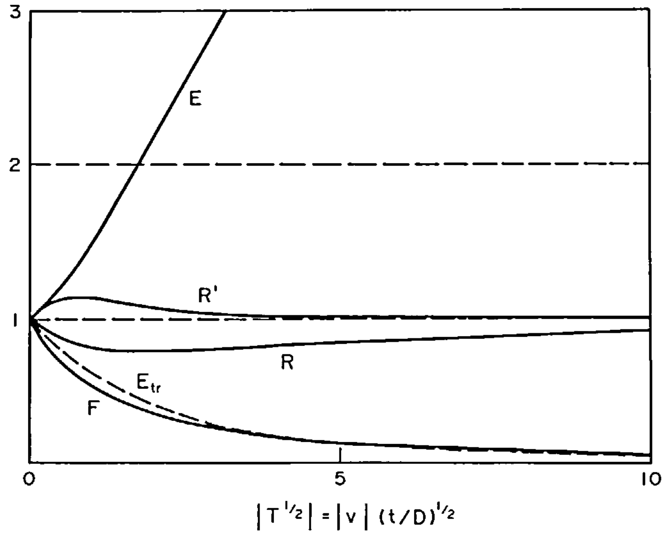


FIG. 2. The effect of suction on the rate of mass transfer; R, given by equation (10); R', given by equation (10b); F, given by equation (11); E, given by equation (12) with positive v (suction); E_{tr}, given by equation (12) with negative v (transpiration).

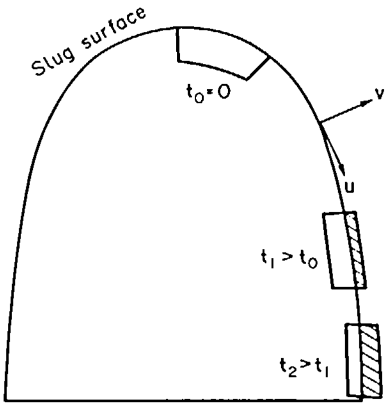


FIG. 3. Trajectory of fluid element near bubble surface.

$T^{1/2} = v(t/D)^{1/2}$ is always negative and $X = vx/D$ is always positive.

In the present case the pure crossflow contribution is nil and, therefore, only the ratio E_{tr} between the average flux and the flux corresponding to diffusion only is of interest and is given in Fig. 2 and Table 1.

MASS TRANSFER ACROSS THE BUBBLE SURFACE IN FLUIDIZED BEDS

The details of gas flow in the neighbourhood of the surface of a bubble (or slug) in a fluidized bed are well understood [1, 2]. As shown in Fig. 3, the gas velocity may be seen as the sum of a tangential component along the slug surface, u (of magnitude equal to the velocity of the particles) and a normal component corresponding to Darcy flow, v. The value of this component just inside the bubble varies from a maximum near the nose (3 U_{mf} for spherical cap bubbles and 2 U_{mf} for slugs) down to zero (and eventually negative values) near the wake.

The usual assumption in the derivation of mass transfer coefficients for gas bubbles and slugs in liquids is that of uniform mixing of the gas inside the bubble except for a thin layer near the interface with fresh elements continually taken to the bubble nose and driven down the interface; mass transfer occurs along this descending path at a rate predicted by the penetration theory. In fluidized beds, the wall of the bubble is permeable and in the case of very fast reaction in the particulate phase the situation for each element of gas may be depicted as in Fig. 3. This is very similar to the situation described by equation (5) with boundary conditions (5a). Two important differences arise in that v varies along the bubble surface and therefore for any gas element v decreases with time and also each gas element stretches as it slides along the bubble surface. Under these circumstances a lengthy numerical procedure is required to account for the interaction between diffusion and crossflow and this is being considered at present by the authors. The solution given by equation (7) may help eliminate the initial discontinuity during the process of numerical computation.

The rate of mass transfer from slugs (or bubbles) in fluidized beds may be expressed as

$$n = Q(C_b - C_p) \tag{13}$$

where n is the molar rate of transfer, C_b and C_p are the concentrations of transferred component inside the bubble and in the particulate phase respectively and Q is the transfer coefficient. Hovmand and Davidson [3] developed two simplified theories to predict the value of Q for slugs in fluidized beds. In the 'approximate theory' the value of Q was assumed to be simply the sum of the purely diffusive component ($k_G S$) corresponding to slugs in liquids and the crossflow component ($U_{mf}\pi D_s^2/4$). In the other the interaction between diffusion and crossflow was accounted for, although based on some simplifying assumptions. Matsen [4] made a comparative study of the predictions of the two theories with regard to the effect of crossflow on the overall rate of mass transfer. He considered a slug with length $L_s = 0.60$ m and diameter $D_s = 0.14$ m and studied the effect of variation of U_{mf} on the rate of transfer of a component with diffusivity $D = 0.565 \times 10^{-4}\ \mathrm{m^2\ s^{-1}}$. For the purpose of our discussion his results are best plotted as shown in Fig. 4, where E, the enhancement factor, represents the ratio between the actual transfer coefficient and that corresponding to no crossflow ($U_{mf} = 0$). It may be seen that the line corresponding to the 'approximate theory' follows the trend predicted in Fig. 2 for the effect of crossflow. On the other hand the theory accounting for the interaction between crossflow and diffusion leads to unexpected conclusions; according to this theory it would seem that increased crossflow leads initially to decreased transfer rates ($E < 1$). This is at variance with the conclusions shown in Fig. 2 and is probably the result of neglecting diffusion along the streamlines in the derivation of the theory [3]. Experimental data on mass transfer from slugs with reaction in the dense phase are available from fluidized bed reactor studies. However, entrance effects are generally important and the resulting transfer data for slugs are not very accurate. It is nevertheless noteworthy that in the most extensive study of slugging reactors [3] the experimental values of conversion are shown to fall closer to the predictions of the 'approximate theory'. The present study seems to suggest that the predictions of the 'approximate theory' although higher than the exact values should not be in error by more than 20% and therefore may be used with reasonable confidence.

A probably better approximation to the transfer coefficient is $Q = [(k_G S)^2 + (U_{mf}\pi D^2/4)^2]^{1/2}$ as suggested by a comparison of the ratios R and R' as given in Table 1 [from equations (10) and (10b)]. The coefficient Q predicted in this way is not likely to deviate from the exact value by more than 15% and also it should lead to conservative estimates of conversion.

CONCLUSIONS

The exact solution (derived under appropriate boundary conditions) for the process of transient diffusion with suction

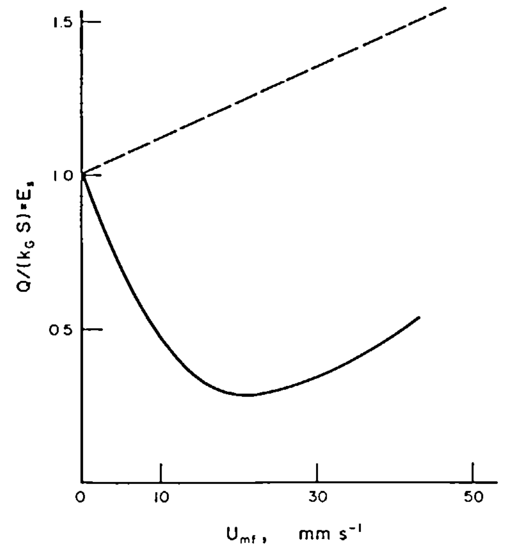


FIG. 4. The effect of crossflow (U_{mf}) on mass transfer from a slug ($L_s = 0.60$ m; $D_s = 0.14$ m; $D = 0.565 \times 10^{-4}\ \mathrm{m^2\ s^{-1}}$), – – – 'approximate theory' [3]; $Q = k_G S + U_{mf}\pi D_s^2/4$, ——— simplified theory accounting for interaction [3].

at the interface predicts values for the average flux not greatly different from those obtained by mere addition of diffusive and convective fluxes. This result lends support to one of the available theories for mass transfer from bubbles (or slugs) in fluidized beds; the inaccuracy of an alternative theory for mass transfer from slugs is also put in evidence.

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APPENDIX

DIFFUSION WITH SUCTION AT THE WALL

The variables $\alpha = (a-a_0)/a_0$, $X = vx/D$ and $T = v^2t/D$ were defined previously and the Laplace transform of (6) with boundary conditions (6a) is

$$\frac{d^2\bar{\alpha}}{dX^2} - \frac{d\bar{\alpha}}{dX} = p\bar{\alpha} \tag{A1}$$

with

$$\left.\begin{array}{ll} \bar{\alpha} = -p^{-1}, & X = 0, \\ \bar{\alpha} \to 0 \quad , & X \to -\infty. \end{array}\right\} \tag{A1a}$$

where

$$\bar{\alpha} = \int_0^\infty \alpha e^{-pt}\, dt. \tag{A2}$$

The solution of equation (A1) with conditions (A1a) is

$$\bar{\alpha} = -p^{-1} e^{(X/2)[(1+(4p+1)^{1/2}]}. \tag{A3}$$

This may be re-written as

$$\bar{\alpha} = -e^{X/2}\{e^{X[p+(1/4)]^{1/2}}/[p+(1/4)]\} \\ -(1/4p)e^{X/2}\{e^{X[p+(1/4)]^{1/2}}/[p+(1/4)]\} \tag{A4}$$

and making use of tables of transforms, inversion gives

$$\bar{\alpha} = -e^{X/2} e^{-T/4} \operatorname{erfc}[-X/(2T^{1/2})] \\ -\tfrac{1}{4}\int_0^T e^{X/2} e^{-z/4} \operatorname{erfc}[-X/(2z^{1/2})]\, dz. \tag{A5}$$

The second term on the RHS may be calculated by parts and after a change of dummy variable $w = -X/(2z^{1/2})$ there results

$$\alpha = -(2/\pi^{1/2})\int_{-(X/2T^{1/2})}^{\infty} e^{-X^2/(16w^2)} e^{-w^2} e^{X/2}\, dw. \tag{A6}$$

RANDOM SURFACE RENEWAL

The average fluxes calculated above correspond to the situations where all surface elements stay at the surface for the same amount of time, t. It may be of interest to find out the average flux in a situation for which the distribution of contact times is random. In that case the average flux is [5, 6]

$$N^r_{av} = \int_0^\infty N s e^{-st}\, dt$$

where the superscript r refers to random surface and s measures the rate of surface renewal.

If there is suction at the wall equation (8) gives the instantaneous flux and integration gives

$$N^r_{av}(\text{diff}+\text{cross}) \\ = (a_0v)\{(1+\theta/4)^{-1/2}[(\theta^{1/2}/4)+(1/\theta^{1/2})]+\tfrac{1}{2}\} \tag{A8}$$

where

$$\theta = v^2/(Ds).$$

The ratio R^r between the exact solution for the average flux, equation (A8), and the sum of the crossflow flux N (cross) $= a_0v$ and the purely diffusive flux N^r_{av} (diffusion) $= a_0(Ds)^{1/2}$ may again be formed. The values of R^r are tabulated as a function of θ in Table 2.

Table 2. Values of R^r

θ	10^{-3}	10^{-2}	10^{-1}	1	4	6	10	10^2	10^3
R^r	0.98	0.96	0.88	0.81	0.80	0.82	0.83	0.92	0.97