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# MASS TRANSFER INTO AN INTERFACE BOMBARDED BY A REGULAR SUCCESSION OF PULSES

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**Abstract**—A tentative model is proposed to describe the rate of transfer of a gas into a liquid whose interface is bombarded with a regular succession of liquid pulses generated from a submerged nozzle. The model, tested experimentally for a range of pulse volume, pulse frequency, nozzle diameter, and nozzle submergence, appears to provide a promising basis for further work. Deviations from the model, interpreted with the aid of visualization studies, occur under conditions of surface rupture or insufficient surface renewal. Suggestions are made regarding further work needed to refine the model.

## NOMENCLATURE

| | |
|---|---|
| $a_n$, | cross sectional area of nozzle; |
| $A_s$, | surface renewed by a pulse; |
| $A_t$, | total area of absorption cell; |
| $\bar{c}$, | bulk concentration of solute; |
| $c^*$, | saturation value of solute in liquid; |
| $c_s$, | solute concentration in pulse on arrival at surface; |
| $D$, | molecular diffusivity of solute in liquid; |
| $f$, | pulse frequency; |
| $k$, | constant in equation (7); |
| $Q$, | total solute absorbed by a pulse; |
| $R$, | rate of transfer of solute into liquid; |
| $t_s$, | residence time of pulse in surface region; |
| $V$, | pulse volume; |
| $V_0$, $V_s$, | initial pulse volume, pulse volume on arrival at surface; |
| $X$, | growth function for pulse species; |
| $X_s$, | value of growth function for given nozzle diameter and submergence; |
| $Y$, | non-dimensional parameter defined under equation (6); |
| $Y'$, | non-dimensional parameter defined under equation (8); |

## INTRODUCTION

MODELS describing the rate of transfer of a gas into a turbulent liquid phase largely stem from the classical work of Higbie [1] and Danckwerts [2]. Essentially, transfer is attributed to an interaction between eddies, generated in the bulk liquid, and the surface region; the process is usually referred to as "surface renewal". Problems arise, though, in using this simple description to relate mass-transfer rates to the state of turbulence in the fluid; the structure of the turbulent field in most practical cases is complex and our physical understanding of it is limited. The current status of turbulent transfer theory reflects this limitation in the form of a number of simplified approaches. Only those based on some kind of "eddy" model are considered here, since it is obviously not possible to do justice to the others without being unduly concise.

"Eddy" based models can conveniently be considered in two groups: the first depending on a well-defined "roll-cell" structure at the surface, the second based on ideas developed by Levich [3] in terms of surface deformation by eddies of known size and velocity characteristics. The "roll-cell" concept enables a tractable solution to be obtained to the convection-diffusion equation by providing a precisely defined velocity field within the cell; in this way the transfer rate into a cell of defined size can be calculated [4–10]. The principal difference between various workers using the "roll-cell" model relates to scale: Fortescue and Pearson [6] maintain that large eddies control transfer and equate cell size to the integral scale of the turbulence; Banerjee *et al.* [9], and Lamont and Scott [10], suggest small eddies, with sizes related to the Kolmogorov length scale; Ruckenstein [7, 8] makes no comment about the relevant scale, though short, deep cells, according to his interpretation, promote surface renewal.

The second group pioneered by Levich [3], and later developed by Davies [11], are more relevant to the work described in this paper. The interaction between an eddy and the interface is described in terms of a balance between the "dynamic pressure" of the eddy and the sum of the "surface tension pressure" and the "gravitational pressure" of the surface deformation it produces. From this the extent of a zone of damped turbulence is deduced. This, in turn, allows a relation to be obtained for the mass transfer coefficient as a function of the approach velocity of the eddy, the molecular diffusivity of the gas–liquid system, the liquid density, and the equivalent surface tension of the interface: details are given in Davies [11].

Levich's model was originally proposed for mass transfer into thin films, though Davies later extended the application to mass transfer into turbulent jets; both represent instances where the surface area is large relative to the bulk liquid volume. Davies then went

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on to study a system where the surface deformation was more well-defined, using a continuous turbulent jet produced from a submerged nozzle in the liquid [11]; the surface area/bulk liquid ratio in this instance is much smaller.

This paper describes a study of the rate of transfer of a gas into a liquid whose interface is disturbed by a regular succession of discrete liquid pulses, generated from a nozzle submerged in the liquid. This system, hopefully, represents a simple approximation to the behaviour of an eddy in a turbulent field. The idea of using pulses of reasonably well-defined characteristics in this way is, of course, not new. Linden [12] suggests the use of a discrete pulse system where turbulence is externally imposed and controlled; motions generated by turbulent jets or wakes, or oscillating grids, he argues, are uncontrolled in the sense that details of the eddy structure can be known only in terms of statistical averages. Maxworthy [13] advocates the use of a vortex ring as a model turbulent eddy, as does Scriven [5] in the context of turbulent mass transfer, but Davies [14], and Ruckenstein [15], are not as specific about the precise form of the pulse.

No study in which the mass-transfer characteristics of a pulse system are measured appeared to have been reported when this study was commenced. It seemed worthwhile to proceed, even allowing for the simplicity of the system, in the hope that the results might be useful in interpreting the behaviour of more complex systems.

## A TENTATIVE TRANSFER MODEL

The following represents a first attempt at a possible transfer model, although, as explained later, it contains a number of critical assumptions. Consider the system shown in Fig. 1: pulses of known volume are emitted from a submerged nozzle at a known frequency. The pulses rise to the surface causing deformation; when the deformation subsides liquid is distributed along the surface, ultimately returning to the bulk liquid. Gas is admitted to the system at a rate sufficient to maintain constant pressure in the gas space, while liquid is removed at a rate sufficient to maintain a constant liquid volume.

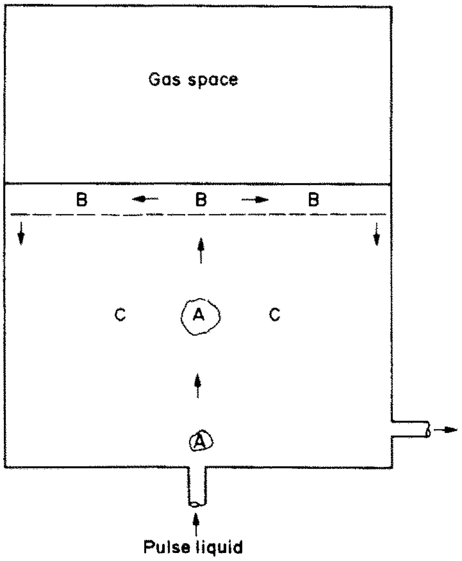

FIG. 1. Schematic diagram of flow field showing: *A*, pulse growth by entrainment; *B*, surface renewal; *C*, bulk mixing.

The overall process can conveniently be considered as a sequence of three stages:

(a) *Entrainment*

Entrainment of ambient fluid into the pulse occurs as it moves towards the interface, due to the velocity difference between the pulse and its surroundings. The quantity entrained depends on the kind of entity formed at the nozzle, as discussed later. The entrained fluid contains dissolved gas, so that the concentration of solute gradually increases inside the pulse. The pulse is assumed to be well-mixed.

(b) *Surface transfer*

After surface deformation, liquid from the pulse is diverted into a motion parallel to the interface, thus accomplishing surface renewal; unsteady-state transfer of gas into the refreshed liquid ensues. Older fluid from previous pulses is gradually displaced along the surface region to the walls of the vessel.

(c) *Bulk mixing*

Liquid displaced from the surface region returns to the bulk phase which, for the sake of simplicity, is assumed to be well mixed; thus the fluid entrained into each pulse, and the fluid leaving the cell, are of the same composition as the bulk fluid.

## DEVELOPMENT OF TRANSFER EQUATION

(a) *Entrainment*

Let the pulse growth due to entrainment be described by

$$V = V_0 \cdot X \tag{1}$$

where $X$ is a function of the pulse species formed by the nozzle. (Arguing by analogy with continuous turbulent jets, $X$ is probably dependent on the ratio of $x$ the distance travelled from the nozzle to $d_n$ the nozzle diameter.)

The pulse volume at the surface is:

$$V_s = V_0 \cdot X_s. \tag{1a}$$

The entrained volume is therefore $(V_s - V_0)$. A solute mass balance on the pulse gives:

$$V_0 \cdot 0 + (V_s - V_0) \cdot \bar{c} = V_s \cdot c_s.$$

The solute concentration at the surface is therefore:

$$c_{s/\bar{c}} = 1 - X_s^{-1}. \tag{2}$$

An overall solute balance for the cell gives:

$$R = f \cdot V_0 \cdot \bar{c}. \tag{2a}$$

(b) *Surface transfer*

The surface renewal process is idealized as shown in Fig. 2. Each pulse on arrival at the surface renews an area $A_s$ and displaces older fluid radially towards the wall. Assuming the thickness of the surface region to be constant over the total surface, the surface residence

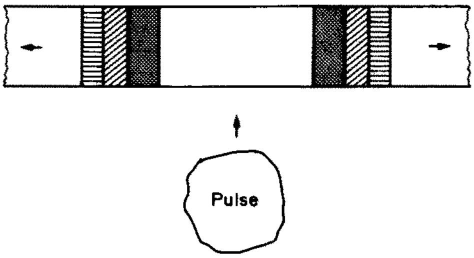

FIG. 2. Schematic diagram of surface renewal model, showing radial displacement of fluid from previous pulses (shown by different cross-hatching).

time, $t_s$, is given by:

$$t_s = A_t/f \cdot A_s. \tag{3}$$

Assuming the Penetration Theory to be valid, each pulse accumulates an amount of solute $Q$, given by:

$$Q = 2\left(\frac{Dt_s}{\pi}\right)^{\frac{1}{2}} \cdot A_s \cdot (c^* - c_s). \tag{4}$$

The rate of transfer, $R$, is given by:

$$R = f \cdot Q. \tag{5}$$

Combining (2), (2a), (3), (4), (5), solving for $R$, and rearranging in non-dimensional form:

$$1/R^* = 1 - (1/X_s) + (1/Y) \tag{6}$$

where $R^* = R/f \cdot V_0 \cdot c^*$

$$Y = 2(D/\pi t_s)^{\frac{1}{2}} \cdot (A_t/f \cdot V_0).$$

$R^*$ can be thought of as the efficiency of transfer into a pulse; $Y$ can be considered to be the ratio of the mean mass-transfer coefficient into a pulse to the average velocity through the system.

Before equation (6) can be used, the surface residence time $t_s$ needs to be related to measurable system variables. In the absence of any direct experimental evidence a dimensional argument is used: let us suppose that $t_s$ is a function of pulse volume, pulse frequency, nozzle submergence, and nozzle area. The simplest function relating these variables is:

$$t_s = k \cdot \left(\frac{x_n \cdot a_n}{f \cdot V_0}\right). \tag{7}$$

Thus $R$ can now be related to known system variables, with $k$ a constant to be determined from experiment.

The model is based on the following assumptions:

(a) A pulse must contain sufficient energy to reach the surface and cause surface renewal, but the energy must not be so great that it leads to surface rupture.

(b) The increase in surface area due to deformation is not considered: the area increase is not large and lasts for only a short time compared with the residence time of the pulse in the surface region.

(c) The thickness of the surface region is large enough for the Penetration Theory to apply.

## EXPERIMENTAL

### *Mass transfer experiments*

The absorption system used was carbon dioxide–water. The absorption cell is a glass cylinder 305 mm long, internal diameter 152 mm; two brass plates with neoprene seals constitute the top and bottom of the cell. The bottom flange is threaded at its centre so that either of two nozzles, diameters 2.38 and 4.76 mm, can be screwed in; each nozzle is flush with the upper surface of the basic flange. An outlet port in the base plate, set close to the wall to minimize disturbance, allows liquid to be removed from the cell. The top flange contains ports, allowing gas addition, temperature measurement, and surface cleaning.

Pulses of solute-free water are injected into the cell by a variable frequency/variable stroke piston pump. Liquid removed from the cell is passed through a de-ionising unit to remove dissolved $CO_2$; the purified effluent from the de-ioniser then passes to the inlet of the piston pump, thus forming a closed circuit. Conductivity cells are used to monitor liquid leaving the cell and liquid leaving the de-ioniser; the first enables a check to be made that steady-state operation has been achieved, the second a check on the removal of solute.

The carbon dioxide transfer rate is measured by metering the gas volume required to maintain constant pressure in the gas space in the cell. The system was adapted from that described by Dobbins [16]. Essentially, a decrease in pressure in the cell caused by gas absorption is sensed by a mercury manometer; this in turn, activates a solenoid, causing the addition of water, saturated with carbon dioxide, from a burette into a gas reservoir connected to the cell, thus compensating the pressure decrease. When the pressure is restored, the liquid flow is cut off.

### *Visualization studies*

Photographic studies, covering the range of conditions over which mass-transfer data were measured, were made of pulse formation and surface deformation. To aid interpretation of the experimental data, the following information was sought:

(a) The nature of the pulse formed.

(b) The extent of surface deformation.

(c) The occurrence of surface rupture.

The studies were carried out in a perspex tank of rectangular cross-section to avoid the distortion associated with a cylindrical surface; a similar clearance was maintained between the path of the pulse and the walls, as exists in the absorption cell. A dilute solution of Aniline Blue was used as the injected fluid to make the pulses visible. A low-speed camera, operating at 32 frames/s, was used to study pulse formation, and a high-speed camera, operating at 1000 frames/s, was used to study surface deformation and surface rupture.

### *Results*

The following experimental conditions were covered:

(a) Pulse volumes: (782, 1564, 2346, 3128, 3910) mm$^3$.

(b) Nozzle diameters: (2.38, 4.76) mm.

(c) Nozzle submergences: (127, 190) mm.

(d) Pulse frequency range: (0.5–2.0) s$^{-1}$.

(e) Temperature: 25°C.

135 combinations of the above variables were studied,

each point being determined from the mean of ten replicates. On average, a period of 60–90 min was allowed for steady-state to be reached.

## DISCUSSION

Equations (6) and (7) may be combined to give:

$$\frac{1}{R^*} = 1 - \frac{1}{X_s} + \frac{k^{\frac{1}{2}}}{Y'} \tag{8}$$

where

$$Y' = \frac{A_t}{2} \cdot \left( \frac{\pi f V_0 x_n a_n}{D} \right)^{\frac{1}{2}}.$$

Figures 3 and 4 show the data obtained for each nozzle size plotted on the basis of equation (8). A regression analysis incorporating all 1350 data points (i.e. including all ten replicate values for each experimental combination of variables) yields a value of 18.0 for the constant $k$.

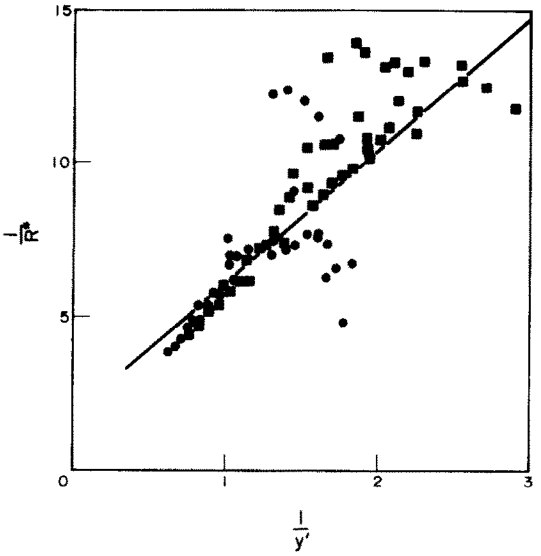

FIG. 3. Data for the 2.38 mm nozzle plotted on the basis of equation (8). ●, 127 mm nozzle submergence; ■, 190 mm nozzle submergence.

Bearing in mind that no attempt has been made to filter out experimental points relating to conditions which do not conform with the assumptions on which the model is based, this initial appraisal of the model appears to be quite promising. Quite clearly, though, several of the data points are not consistent with the model. Further examination indicates that they can be considered in two categories: those associated with extreme surface disturbance or surface rupture, and those associated with low energy conditions of pulse formation, resulting in incomplete surface-renewal. The evidence obtained from the visualization studies, although only preliminary and non-quantitative, may usefully be summarized at this point as an aid to further interpretation.

The type of entity formed at the nozzle varies from a jet-like mass of fluid (referred to in subsequent discussion as a "jet-pulse") to an unstable vortex ring. The smaller nozzle produces jet pulses at all combinations of pulse volume and frequency used in the experiments; the larger nozzle produces jet pulses only at high pulse volume/pulse frequency combinations. At low volume/low frequency combinations unstable vortex rings are produced from part of the injected fluid, the remainder being left behind as a slower travelling diffuse mass.

The stronger of the jet pulses, those omitted with a relatively high velocity, are capable of causing surface rupture at each of the submergences used in the experiment; they are only produced from the smaller nozzle. None of the jet pulses from the larger nozzle produces surface rupture at any submergence. Conditions leading to extreme surface distrubance with consequent rippling, or surface rupture with possible droplet formation, are those associated with higher transfer rates than those predicted by the model.

At the other extreme, incomplete surface renewal, occurs under conditions of low energy of pulse formation. The behaviour subsequent to formation is variable, although vortex rings are produced in each case. Vortex rings appear to spread radially outward following impact with the surface, as the fluid rotational energy decreased; they then come to rest as a mass of fluid beneath the surface, to be dispersed by the next vortex ring. The slower moving mass of fluid not incorporated into a vortex ring appears to play an insignificant part in surface renewal, sometimes becoming stationary before the surface is reached. Conditions leading to incomplete surface renewal are, then, those associated with lower transfer rates than those predicted by the model.

It is quite clear from the above discussion that further work is needed to clarify the following aspects of pulse behaviour:

(a) The relation between the condition of formation and the pulse species produced.
(b) The subsequent motion of the pulse towards the interface, including velocity and entrainment characteristics.
(c) The degree of surface disturbance produced by the pulse.

Inclusion of all the data into the determination of the intercept by regression analysis yields a value of 1.96, a value inconsistent with equation (6); the anomaly is caused by the inclusion of data obtained under conditions where the model cannot be expected to apply, as discussed above. The intercept, in fact, depends on the value of $X_s$, and should lie between zero and unity; it is therefore a variable, dependent on the pulse species, nozzle diameter and submergence. Information on pulse behaviour, of the kind mentioned above, is required to enable the entrainment characteristic to be related to the observed intercept.

Finally, the relationship suggested for the pulse residence time in the surface region, equation (7), requires further investigation. Based purely on dimensional grounds, it appears to have some support in terms of the general trend shown in Fig. 3. But, again, only a more complete study of pulse motion will enable the problem to be properly explored.

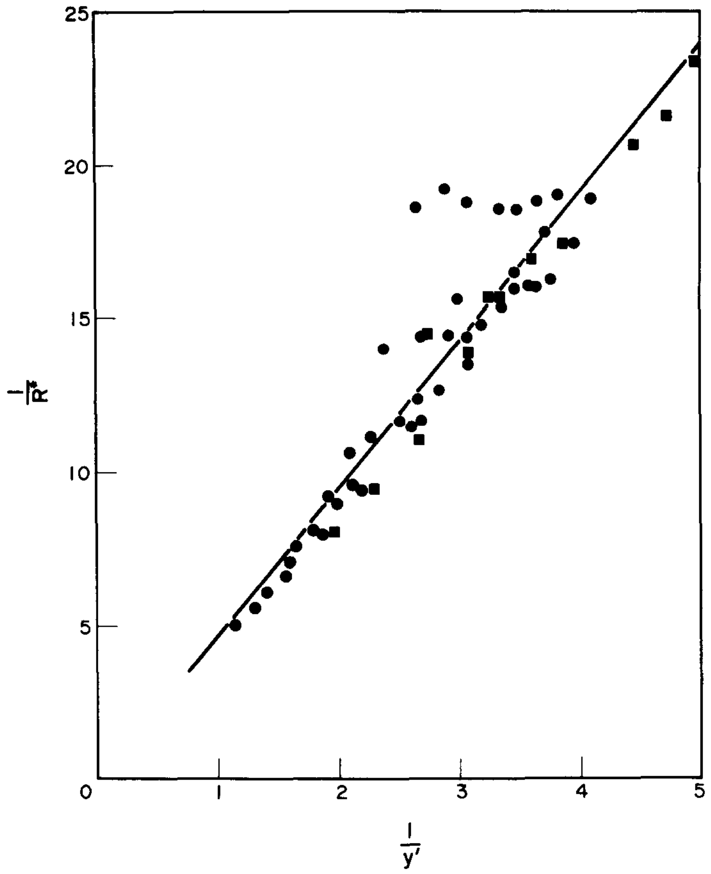

FIG. 4. Data for the 4.76 mm nozzle plotted on the basis of equation (8). ●, 127 mm nozzle submergence; ■, 190 mm nozzle submergence.

## CONCLUSIONS

1. The tentative model proposed to describe mass transfer into an interface bombarded by liquid pulses appears to provide a promising basis for further work.

2. Higher rates than those predicted by the model can be explained in terms of extreme surface disturbance or surface rupture, while lower rates occur when low energy pulses give rise to incomplete surface revewal.

3. Further work is required on the following aspects in order to refine the model:
   - (a) The species of pulse formed under various conditions.
   - (b) The dynamics of pulse motion subsequent to formation.
   - (c) The degree of disturbance caused by the pulse on impact with the surface.

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## TRANSFERT MASSIQUE A TRAVERS UN INTERFACE BOMBARDE PAR UNE SUCCESSION REGULIERE D'IMPULSIONS

**Résumé**—Un essai de modèle est proposé afin de décrire le flux massique d'un gaz vers un liquide dont l'interface est bombardée par une succession régulière d'impulsions du liquide à l'orifice d'une tuyère submergée. Le modèle, testé expérimentalement sur un certain domaine d'intensité et fréquence des impulsions, de diamètre et profondeur de l'orifice, s'avère fournir une base prometteuse pour la poursuite des travaux. Des écarts sur le modèle, interprétés à l'aide d'une méthode de visualisation, se produisent dans des conditions de rupture de surface ou de renouvellement insuffisant de la surface. Des suggestions sont faites concernant la nécessité de perfectionner le modèle dans une étude ultérieure.

## DER STOFFAUSTAUSCH AN EINER PHASENGRENZFLÄCHE, AUF WELCHE IN REGELMÄSSIGER FOLGE IMPULSE AUFTREFFEN

**Zusammenfassung**—Es wird der Versuch unternommen, zur Beschreibung der Transportrate eines Gases in eine Flüssigkeit, deren Phasengrenzfläche in regelmäßiger Folge von Flüssigkeitsimpulsen getroffen wird, ein Modell vorzuschlagen. Die Flüssigkeitsimpulse werden mit Hilfe einer in die Flüssigkeit eingetauchten Düse erzeugt. Das Modell, das experimentell für eine Reihe von Volumina und Frequenzen der Impulse, für verschiedene Düsendurchmesser und verschiedene Entfernungen der Düse von der Phasengrenzfläche überprüft wurde, scheint eine vielversprechende Basis für weitere Arbeiten abzugeben. Abweichungen vom Modell, welche mit Hilfe von Methoden zur Sichtbarmachung der Strömung untersucht wurden, treten in den Fällen auf, in denen die Oberfläche aufgebrochen wird oder die Oberflächenerneuerung unzureichend ist. Im Hinblick auf zukünftige Arbeiten zur Verfeinerung dieses Modells werden Vorschläge gemacht.

## ПЕРЕНОС МАССЫ К ГРАНИЦЕ РАЗДЕЛА, БОМБАРДИРУЕМОЙ РЯДОМ РЕГУЛЯРНО ПОВТОРЯЮЩИХСЯ ИМПУЛЬСОВ

**Аннотация** — Предложена ориентировочная модель для описания скорости переноса газа в жидкость, поверхность которой бомбардируется регулярно повторяющимися импульсами жидкости из затопленного сопла. Проведена экспериментальная проверка модели для различных диапазонов объема и частоты импульсов, диаметра и глубины затопления сопла, что обеспечит основу для проведения дальнейших работ. Наблюдаемые визуально отклонения от модели происходят при разрыве поверхности или недостаточно полном ее восстановлении. Даны предложения по дальнейшему усовершенствованию модели.