

COMMUNICATIONS TO THE EDITOR

Averaging of Mass Transfer Rates

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The average rate of absorption per unit surface area in a steady state apparatus such as a wetted-wall column or a jet is

$$\bar{N}_A = \frac{1}{A'} \int_0^{A'} N_A dA \quad (1)$$

where N_A is the local rate of absorption per unit area, \bar{N}_A is the average rate per unit area, and A' is the total area. This can also be applied to a packed or spray column if \bar{N}_A is considered to be the average at one instant of time over all the interfacial area. If u_s depends only on x ,

since

$$dA = P dx \quad (2)$$

and

$$u_s = \frac{dx}{d\theta}, \quad (3)$$

$$\frac{dA}{d\theta} = Pu_s \quad (4)$$

and

$$A' = \int_0^{\theta'} Pu_s d\theta \quad (5)$$

Thus Equation (1) on a time basis is

$$\bar{N}_A = \frac{\int_0^{\theta'} N_A Pu_s d\theta}{\int_0^{\theta'} Pu_s d\theta} \quad (6)$$

where

P = perimeter of the exposed liquid surface which may be a function of x
 x = distance measured in flow direction
 u_s = velocity of liquid at the surface
 θ' = time of contact

The term Pu_s , which may be called the surface-area velocity, is the rate at which fresh surface passes the perimeter at any point x . Its time integral is the total area, as shown by Equation (5). When Pu_s is constant, Equation (6) reduces to the time average-absorption rate,

$$\bar{N}_A = \frac{1}{\theta'} \int_0^{\theta'} N_A d\theta \quad (7)$$

but when it is not constant, Pu_s is the weighting factor which relates the time and area variables.

In the penetration theories of gas absorption where the local absorption rate is assumed to be the stagnant liquid-absorption rate (2),

$$N_A = \Delta C \sqrt{\frac{D}{\pi\theta}} \quad (8)$$

where D is the diffusivity of the gas in the liquid and ΔC is the difference between the interfacial concentration and bulk-liquid concentration. Both D and ΔC are assumed constant. The average absorption rate is usually obtained by taking the time average as defined by Equation (7) so that

$$\bar{N}_A = 2\Delta C \sqrt{\frac{D}{\pi\theta'}} \quad (9)$$

However use of Equation (7) is justified only if the surface-area velocity is a constant; if it is a variable, \bar{N}_A will depend on the path followed in reaching θ' as well as on θ' itself. The average rate will be less than that given by Equation (9) if Pu_s increases with x and greater if Pu_s decreases with x . An example is the hypothetical case where

$$Pu_s = ax^n \quad -1 < n < 1 \quad (10)$$

When $n = 1/4$ and x is small this would approximately describe the surface-area velocity of a laminar liquid flowing into a gas from a sharp-edged orifice. By use of Equations (4), (6), and (10),

$$\bar{N}_A = \frac{2}{n+1} \Delta C \sqrt{\frac{D}{\pi\theta'}} \quad (11)$$

When $n = 0$, Pu_s is constant and Equa-

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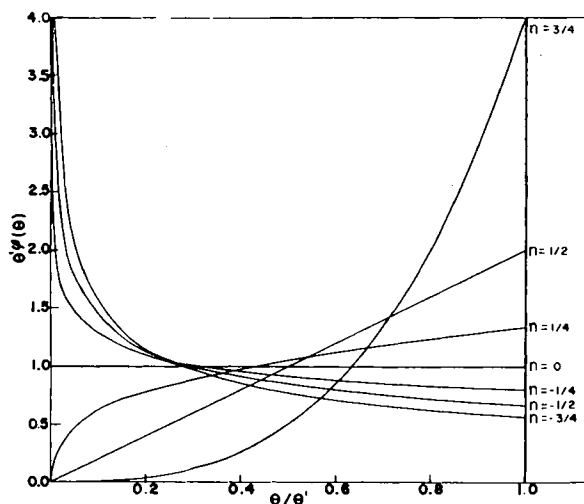


Fig. 1. Surface-age distribution functions with varying surface velocity
Equation (15). No surface renewal

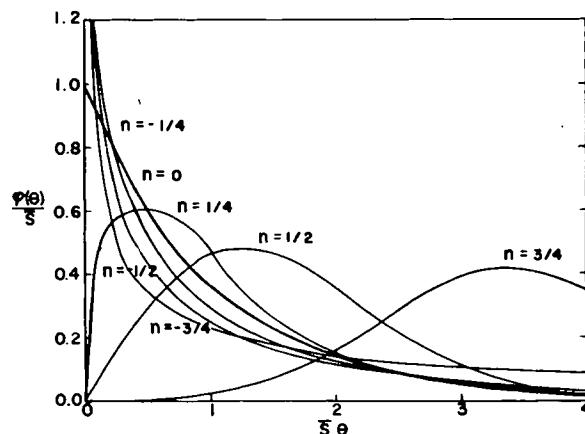


Fig. 2. Surface-age distribution functions with varying surface velocity
Equation (27). Surface renewal

tion (11) reduces to Equation (9). When n is positive, for the same θ' the rate is less than the value given by Equation (9), and when n is negative the rate is greater.

In flow down a wetted-wall column the surface velocity must accelerate from zero or a small value to its final steady value and the average absorption rate over the column will be lower than that given by Equation (9), which in turn will be lower than the average rate obtained by assuming that the average velocity is immediately attained. This lowered rate may have contributed somewhat to the apparent interfacial resistances reported by some authors (3, 5).

From Danckwerts's viewpoint (1, 2),

$$\bar{N}_A = \int_0^\infty N_A \varphi(\theta) d\theta \quad (12)$$

where $\varphi(\theta)$ is the surface-age distribution function so defined that $\varphi(\theta) d\theta$ is the fraction of the total surface which has ages between θ and $\theta + d\theta$. From Equation (4),

$$\frac{dA}{A'} = \frac{Pu_s}{A'} d\theta \quad (13)$$

and so

$$\varphi(\theta) = \frac{Pu_s}{A'} \quad \theta < \theta' \quad (14)$$

$$\varphi(\theta) = 0 \quad \theta > \theta'$$

When Pu_s is constant, Equation (14) reduces to $1/\theta'$ for $\theta < \theta'$ and 0 for $\theta > \theta'$.

The surface-age distribution function for the surface-area velocity of Equation (10) is

$$\varphi(\theta) = \frac{1}{1-n} \left(\frac{\theta}{\theta'} \right)^{n/1-n} \frac{1}{\theta'} \quad \theta < \theta' \quad (15)$$

$$\varphi(\theta) = 0 \quad \theta > \theta'$$

Figure 1 shows $\varphi(\theta)$ for various values of n , and these curves typify some distribution functions which could be conceived of when mixing does not take place during the flow.

Since θ , the contact time in the penetration theory [Equation (8)], is the age of the surface, when mixing, i.e., surface renewal, takes place, the surface-area velocity must be known in terms of the surface age. If all the surface elements reach the same age before being replaced, as postulated by Higbie (4) for a packed column, then the equation relating the surface-area velocity to the distance from the point of mixing is sufficient to define $\varphi(\theta)$, and the effect of a varying surface velocity is the same as in the case of no surface renewal.

In Danckwerts's theory the probability that an element of surface is replaced by mixing is assumed to be independent of

its age. This gives the following distribution function (1),

$$\varphi(\theta) = Se^{-S\theta} \quad (16)$$

where S is the fractional rate of surface renewal.

It is interesting to note that the Danckwerts distribution function is also obtained for flow without surface renewal if

$$Pu_s = S(A' - A) \quad (17)$$

(and here S is merely a constant) or when P is a constant

$$u_s = S(L - x) \quad (18)$$

The average absorption rate is then identical with the value given by Danckwerts,

$$\bar{N}_A = \Delta C \sqrt{DS} \quad (19)$$

although the two physical situations are quite different.

Since Danckwerts assumed that the probability of replacement of an element of surface was independent of its age, the velocity does not have any effect on his distribution function. In order to account for velocity variations it is necessary to make another type of assumption concerning the rate of surface renewal, the simplest being that the probability that an element is replaced is independent of x , the distance it has traveled since it was formed. It can be shown by a derivation similar to that of Danckwerts (1) that for a constant perimeter this leads to

$$\varphi'(x) = S'e^{-S'x} \quad (20)$$

where $\varphi'(x)$ is the surface-length distribution function defined so that $\varphi'(x) dx$ is the fraction of the total area between x and $x + dx$, and S' is the constant fraction of the area replaced per unit length of flow. Then in place of Equation (12) one can write

$$\bar{N}_A = \int_0^\infty N_A \varphi'(x) dx \quad (21)$$

Equations (21) and (12) show that in general

$$\varphi(\theta) = u_s \varphi'(x) \quad (22)$$

and so from Equation (20)

$$\varphi(\theta) = u_s S' e^{-S'x} \quad (23)$$

and since

$$S = u_s S' \quad (24)$$

Equation (23) reduces to (16) when u_s is constant. The mean surface velocity in the column is

$$\bar{u}_s = \int_0^\infty u_s \varphi'(x) dx \quad (25)$$

and the average fractional rate of surface renewal is

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$$\bar{S} = S'\bar{u}, \quad (26)$$

It is more likely that there is a unique relationship between u_s and x in a disk or stacked column than in a packed column, but even in the latter case there might be some relationship which would describe the over-all effect. A qualitative picture of the effect of a varying surface velocity may be obtained by using the velocity—distance relationship of Equation (10). This gives in place of Equation (16),

$$\varphi(\theta) = \bar{S} \left[\frac{(1-n)^n (\bar{S}\theta)^n}{\Gamma(1+n)} \right]^{1/1-n} \exp - \left(\frac{1-n}{\Gamma(1+n)} \bar{S}\theta \right)^{1/1-n} \quad (27)$$

Equation (27) is shown in Figure 2 for various values of n . When $n = 0$, Danckwerts's distribution function is obtained, and when n is positive (the velocity increases from zero after mixing) the middle-aged surfaces are given greater weight than when the velocity is constant. When n is negative, so that the velocity is infinite after mixing, greater weight is given to the very young and very old surfaces and less to the middle-aged surfaces.

The average absorption rate with the distribution function of Equation (27) is

$$\bar{N}_A = \Gamma\left(\frac{1+n}{2}\right) \sqrt{\frac{1-n}{\pi\Gamma(1+n)}} \Delta c \sqrt{D\bar{S}} \quad (28)$$

so that for \bar{S} constant, a variation in n changes only the constant in the equation. The rate decreases continuously as n increases; when n is negative (the velocity decreases with distance), the rate is greater than the value corresponding to a constant surface velocity, and when n is positive (the velocity increases with distance), the rate is less than this value.

Since \bar{S} , θ , and n cannot be directly measured in a packed column, Equations (11) and (28) show that the effect of a varying surface velocity is immaterial as far as physical absorption is concerned. However, in absorption accompanied by chemical reaction the particular surface-age distribution function is of importance, and knowledge of it would allow prediction of the effects of chemical reactions on absorption rates (2).

LITERATURE CITED

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