The Additivity of Individual Phase Resistances in Mass Transfer Operations

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A basic tool for the design and analysis of interphase mass transfer processes has been the concept of the additivity of individual phase resistances, originally derived from two-film theory:

$$\frac{1}{K_Ga} = \frac{1}{k^*_{Ga}} + \frac{H}{k^*_{La}} \tag{1}$$

The asterisks indicate that the individual phase coefficients employed are those measured in the absence or suppression of resistance in the other phase.* Thus correlations exist for both liquid- and gas-phase resistances in various types of distillation and absorption equipment, and for design they are commonly combined in accordance with Equation (1), (*1*, *13*). It is the purpose of this paper to point out the conditions necessary for Equation (1) to hold true and in view of these criteria to assess the deviations from Equation (1) which can be expected in various situations. Consideration is limited to low net fluxes of mass.

In gas-liquid mass transfer the individual phase coefficients are defined in terms of the fluxes and driving forces as follows:

$$k_G' = \frac{N_A'}{p_G - p_i} \tag{2}$$

$$k_L' = \frac{N_A'}{C_i - C_L} \tag{3}$$

The primed values indicate that the relation applies at any given point of the gas-liquid interface. The overall gas phase coefficient is similarly defined in terms of the overall driving force:

$$K_G' = \frac{N_A'}{p_G - p_{EL}} \tag{4}$$

If $p = HC + b$ defines the equilibrium relation for the solute in the gas and liquid phases, then Equation (3) may be transformed to

$$\frac{k_L'}{H} = \frac{N_A'}{p_i - p_{EL}} \tag{5}$$

Combination of Equations (2), (4), and (5) gives

$$\frac{1}{K_G'} = \frac{1}{k_G'} + \frac{H}{k_L'} \tag{6}$$

which results solely from the definition of the three local coefficients.

Equation (6) will hold true if two conditions are met:

1. H must be a constant, or if it is not, the value of the equilibrium line slope at the properly defined value of C must be employed.
2. There must be no significant resistance present other than those represented by k_L' and k_G'; for example p_i must be in equilibrium with C_i.

In order for the extension of Equation (6) to the form of Equation (1) to be valid when an entire region of interface is considered, additional conditions must be met:

3. The hydrodynamic conditions (interfacial area, etc.) for the case in which the resistances are to be combined must be the same as for the measurements of the individual phase resistances.
4. The mass transfer resistances of the two phases must not interact; that is the magnitude of k_L' at any point must be independent of the relative magnitude of k_G', and vice versa.
5. The ratio Hk_G'/k_L' must be constant at all points of interface.

The first three of the above conditions have been appreciated for some time, and for that reason they will not be considered further. The last two conditions have usually not been stressed or even acknowledged to any extent in mass transfer texts; yet it will be shown that both of these factors are of major importance.

The reason for the fourth condition is apparent; the reason for the fifth is probably less obvious but may be demonstrated as follows:

If k_L' and k_G' vary locally over a given interface for which the bulk gas and liquid concentrations at a distance well removed from the interface are each constant, the apparent or average liquid-phase coefficient in the absence or suppression of gas-phase resistance will be given by

$$k^*_{La} = \iint_a k_L' \, da \tag{7}$$

Similarly

$$k^*_{Ga} = \iint_a k_G' \, da \tag{8}$$

and

$$K_Ga = \iint_a K_G' \, da \tag{9}$$

In view of Equation (6), and if the fourth condition holds true, Equation (9) becomes

$$K_Ga = \iint_a \frac{da}{\dfrac{1}{k_G'} + \dfrac{H}{k_L'}} \tag{10}$$

The value of K_Ga predicted by the two-film relationship, Equation (1), will be denoted as $K_{GF}a$ and may be obtained from Equations (1), (7), and (8):

$$K_{GF}a = \frac{1}{\dfrac{1}{\iint_a k_G' \, da} + \dfrac{H}{\iint_a k_L' \, da}} \tag{11}$$

K_Ga from Equation (10) and $K_{GF}a$ from Equation (11) are identical if and only if Hk_G'/k_L' is a constant at all points of interface. In that event Equation (11) becomes

$$K_{GF}a = \frac{1}{\dfrac{1}{\iint_a k_G' \, da} + \dfrac{(Hk_G'/k_L')}{\iint_a k_G' \, da}} \tag{12}$$

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* For convenience the discussion will be conducted in the terminology of gas-liquid mass transfer; however there is a logical extension to liquid-liquid systems.

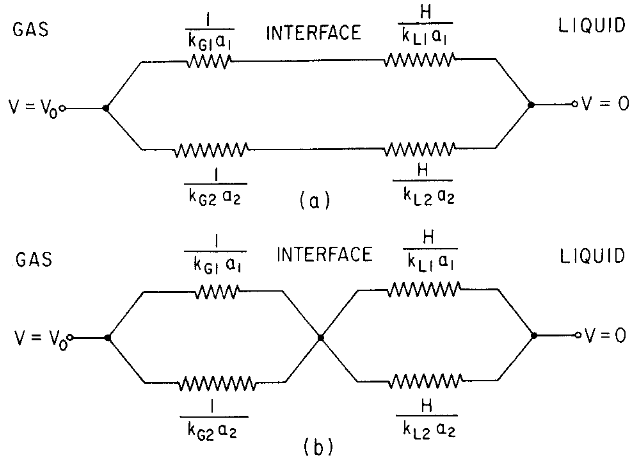

Fig. 1. Electrical resistance analogues for a case where local mass transfer coefficients have different values in two regions of interface.

which can be put in the same form as Equation (10). If Hk_G'/k_L' is not a constant at all points, then Equation (11) is not equivalent to Equation (10), and $K_{GF}a$ is different from K_Ga.*

This point may also be appreciated through consideration of an electrical analogy. In Figure 1*a* the resistances associated with two different regions of interface are depicted. Subscripts 1 and 2 represent the two regions, and it is presumed that values of k_L' and k_G' are constant within each region separately. The bulk gas and liquid concentrations are constant; hence there is a constant potential drop (V_o analogous to $p_G - p_{EL}$) across both sets of resistances in series. The net resistances of the two regions of surface act in parallel. This is the behavior expressed by Equation (10).

On the other hand if the procedure of the two-film model is followed for combining resistances, the situation presented in Figure 1*b* results. Equations (1) and (11) consider the net liquid-phase resistance to be in series with the net gas-phase resistance. Thus there is a common point at the interface in the electrical analogy of two-film theory which is not present in the analogy for the real case. There will be an additional flow of current (or flux of mass) through this effective short circuit unless the potentials at the interface are the same in Figure 1*a* for each region. This will only be the case if Hk_{G1}/k_{L1} is equal to Hk_{G2}/k_{L2}; otherwise the net resistance in Figure 1*b* will be less than that in Figure 1*a* because of the short-circuit. This fact leads to the important general conclusion that the effect of a variation of Hk_G'/k_L' from one point of interface to another will be to make the true K_Ga less than the $K_{GF}a$ predicted from Equation (1). This does not present a conservative basis for design.

SINGLE LIQUID-PHASE EXPOSURE

In any realistic mass transfer device there will be local variations in k_G' and k_L' from point to point of interface. Such behavior is predicted both by the penetration or surface renewal theories and by boundary-layer theory. As a simple case for consideration it is instructive to take a single liquid-phase exposure undergoing unsteady state molecular diffusion and accompanied by a constant gas-phase resistance such as would be predicted by film theory for the gas-phase.

The appropriate differential equation for the liquid phase is

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial y^2} \tag{13}$$

with boundary conditions

$$\begin{aligned}
&\text{(a)} \qquad C = C_L \qquad &&\text{at } y > 0\ ,\ t = 0\\
&\text{(b)} \qquad C = C_L \qquad &&\text{at } y \rightarrow \infty,\ t > 0\\
&\text{(c)} \quad -D\left(\frac{\partial C}{\partial y}\right) = Hk_G(C_{EG} - C_i) \quad &&\text{at } y = 0\ ,\ t > 0
\end{aligned} \tag{14}$$

The solution for the corresponding heat conduction case has been presented by Carslaw and Jaeger (*2*) and has been extended to the mass transfer case by Emmert (*6*) and by Perlmutter (*12*). The change in bulk gas concentration if there is countercurrent flow has been considered by Salvetti and Trevessoi (*15*) and by Lightfoot (*10*).

The local coefficient of mass transfer and the interfacial concentration along the interface are given by the following expression:

$$\frac{K_G'}{k_G} = \frac{C_i - C_{EG}}{C_L - C_{EG}} = \exp\left(\frac{H^2 k_G^2 t}{D}\right) \operatorname{erfc}\left(\frac{Hk_G\sqrt{t}}{\sqrt{D}}\right) \tag{15}$$

This solution may be employed to express the deviation of the true overall mass transfer coefficient, averaged over the contacting interval, from the value predicted by Equation (1):

$$\frac{K_Ga}{K_{GF}a} = \frac{\pi(1+R)}{4R^2} \left[\exp\left(4R^2/\pi\right) \operatorname{erfc}\frac{2R}{\sqrt{\pi}} - 1 + \frac{4R}{\pi}\right] \tag{16}$$

R represents the group Hk_G^*/k_L^*, the ratio of the average coefficients measured independently. This result is shown graphically in Figure 2, where it is seen that the deviation from the overall mass transfer coefficient predicted by two-film theory is always positive but never greater than 5%.

This close agreement is however the result of two compensating effects. If k_L' were unchanged locally by the presence of the gas-phase resistance, the average overall coefficient could be derived through Equation (10), and the result would be

$$\frac{K_Ga}{K_{GF}a} = (1+R)\int_0^1 \frac{d(t/\theta)}{1 + 2R(t/\theta)^{1/2}} \tag{17}$$

or

$$\frac{K_Ga}{K_{GF}a} = \frac{(1+R)}{2R^2}\left[2R - \ln\left(1 + 2R\right)\right] \tag{18}$$

K_Ga is always less than $K_{GF}a$ if Equation (18) is followed, the negative deviation being in accord with the above con-

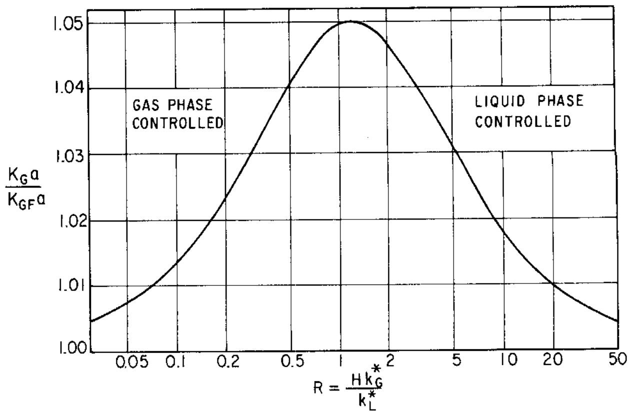

Fig. 2. Deviation from Equation (1) for liquid penetration and stagnant no holdup gas film, plot of Equation (16).

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[*] Strictly speaking, the requirement is that k_G'/k_L' be constant at all points, since H has already been assumed constant. H is included to preserve nondimensionality.

clusion regarding the effects of a distribution in values of Hk_G'/k_L'. The maximum negative deviation would be 10.4%.

On the other hand the true local liquid-phase coefficient defined by Equation (3) can be obtained from Equations (4) and (15)

$$\frac{k_L'}{k_L^*} = \frac{R \exp\,(4\,R^2 t/\pi\,\theta)\ \mathrm{erfc}\ (2\,R\sqrt{t}/\sqrt{\pi\theta})}{1 - \exp\,(4\,R^2 t/\pi\theta)\,\mathrm{erfc}\ (2\,R\sqrt{t}/\sqrt{\pi\theta})} \tag{19}$$

and is plotted in Figure 3 with R as a parameter. The local liquid-phase coefficient is raised because of the presence of a gas-phase resistance by an amount which more than offsets the effect of the variation of Hk_G'/k_L' in lowering the overall coefficient. Violation of the fourth condition in this instance overcompensates for the effect of violation of the fifth condition. An examination of Equations (13) and (14) reveals that an interaction of the individual phase resistances was to be expected, since k_G enters into the third boundary condition used for determining the liquid-phase behavior.

Numerical solutions have been carried out by the author (*9*) for two simplified models representing a single exposure between two fluid phases in countercurrent flow. Transient behavior is considered for both phases rather than for only one phase as was the case in the foregoing example. Plots similar to Figure 2 are obtained, with the deviations from Equation (1) being positive and reaching a maximum of 20%.

For the case of concurrent flow of gas and liquid and a developing laminar gas-phase boundary layer the solution of Potter (*14*) may be interpreted to show that Equation (1) would be exactly obeyed for a given exposure. Exact agreement is also shown by the solution of Marshall and Pigford (*11*), which represents transient contact of two phases near a stationary interface. This latter solution may also be applied to a concurrent flow situation with a simple penetration model obeyed by each phase. In these schemes it should be noted that both individual phase coefficients vary inherently with the −½ power of age or distance along the interface; thus Hk_G'/k_L' is constant. The interfacial concentration is therefore constant, and the mathematical solution for the mass transfer in either phase is the same as for when that phase is considered alone in the absence of resistance in the other phase. Thus in these two cases both the fourth and fifth conditions are satisfied.

The possibility of a mismatch in surface renewal intervals has been considered by Szekely (*18*), who presents a solution for the case where two phases are in contact at a stationary interface with the surface renewal rate for phase 1 being twice the rate prevailing for phase 2. This model also applies to concurrent flow of two phases obeying a simple penetration model, with the flow of phase 1 being interrupted by a surface renewal midway along the exposure interval. Szekely's solution may readily be converted to the form

$$\frac{K_G a}{K_{GF} a} = (1 + R)\left(\frac{1}{1 + \frac{R}{\sqrt{2}}} - \left\{\frac{1}{\frac{R}{\sqrt{2}} + 1 + \frac{\sqrt{2}}{R}}\left(\frac{2 - \sqrt{2}}{2}\right)\right\}\right) \tag{20}$$

which varies from 0.96 to 1.01.

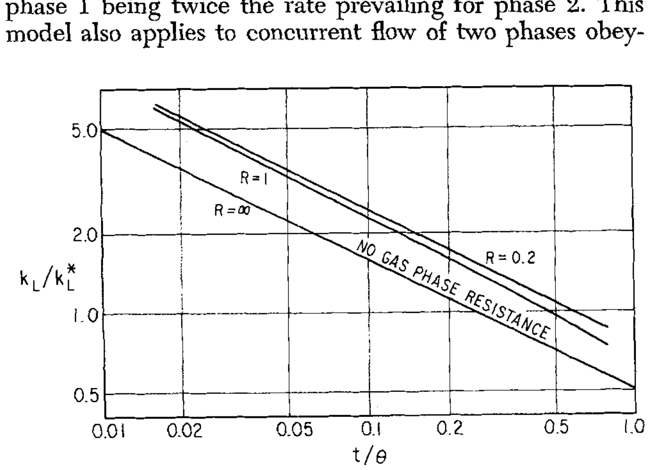

Fig. 3. Local variation of k_L' for liquid penetration and stagnant no holdup gas film.

DISTRIBUTION OF LIQUID SURFACE LIFETIMES

For the cases which have been solved it appears that Equation (1) is obeyed to a remarkably close extent during a single liquid exposure following a penetration model. On the other hand in any large-scale apparatus which provides mass transfer through successive penetrations and liquid surface renewals there will be a distribution of liquid surface lifetimes within the apparatus. This distribution will result in a variation of the ratio $Hk^*_G a/k^*_L a$ between surface areas where the liquid is engaged in reaching different lifetimes. Thus even though Equation (1) is closely obeyed for a liquid surface reaching a given single lifetime, there could still be marked deviations from Equation (1) when all surface lifetimes are considered together. A variation in k_G from point to point of interface will have a similar complicating effect.

If the liquid surface lifetime distribution is denoted by a frequency factor $\psi(\theta_i)\, d\theta_i$, giving the fraction of the total surface area[*] that is engaged in reaching a lifetime θ_i, and k_G is taken to be a constant, Equation (10) may be applied as follows:

$$K_G a = a \int_0^\infty \frac{\delta_i \psi(\theta_i)\ d\theta_i}{\frac{1}{k_G} + \frac{H}{2}\sqrt{\frac{\pi\theta_i}{D}}} \tag{21}$$

δ_i is the value of $K_G a/K_{GF} a$ for the surface reaching a lifetime θ_i. δ_i may be taken from Figure 2, or it can be taken as always equal to 1.0 in order to simplify the integration.

Figure 4 shows three liquid surface lifetime distributions which have been suggested as models for large-scale equipment; two other distributions are also offered for comparison. The coordinates have been made dimensionless in the manner suggested by Danckwerts et al. (*4*).

The Higbie model postulates that all liquid surfaces are engaged in reaching the same lifetime. If a constant k_G is applied to the gas phase, $K_G a/K_{GF} a$ is given by Equation (16) and Figure 2. There is a positive deviation from Equation (1), but it is always less than 5%.

The Danckwerts random surface renewal model pictures a constant rate of surface renewal, independent of the age of the surface. For the case where k_G is constant at all points of gas-liquid interface Danckwerts (*3*) has shown that Equation (1) is obeyed exactly. The effect of the distribution of surface lifetimes in lowering ($K_G a/K_{GF} a$) exactly offsets the positive deviations of Figure 2.

Davidson (*5*) has suggested three lifetime distribution models for the liquid phase in packed towers. The first, or vertical surfaces, model is akin to the Higbie constant lifetime case. The second, or random angle, model is represented in Figure 4, where it may be noted that the distri-

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[*] A clear distinction should be drawn between this form of frequency factor and either the fraction of the total surface with an age t_i (*3,4*) or the fraction of total exposures reaching a lifetime θ_i (*12*).

bution resembles the constant lifetime model. Davidson's third model, random angles and random lengths, has been shown by Danckwerts et al. (*4*) to be similar to the Danckwerts random surface renewal distribution. Thus it is to be expected that all three of Davidson's models, when coupled with a constant k_G, will give close agreement with Equation (1), probably within 5%.

Also shown in Figure 4 is a triangular distribution, corresponding to equal probabilities of any lifetime during every exposure, from zero up to a certain maximum lifetime. This situation corresponds to a vertical surface, random length packed tower model of the Davidson type. If it is assumed that $\delta_i = 1$ and that the average k_G per exposure is uniform, then Equation (21) in combination with Equation (1) reduces to

$$\frac{K_Ga}{K_{GF}a} = 2(1+R)\int_0^1 \frac{\left(\frac{\theta}{\theta_u}\right) d\left(\frac{\theta}{\theta_u}\right)}{1+\frac{4R}{3}\left(\frac{\theta}{\theta_u}\right)^{1/2}} \qquad (22)$$

or

$$\frac{K_Ga}{K_{GF}a} = \frac{1+R}{R}\left[1-\frac{9}{8R}+\frac{27}{16R^2}-\frac{81}{64R^3}\ln\left(1+\frac{4R}{3}\right)\right] \qquad (23)$$

which is always less than 1.00, but never by more than 2%.

Yet another surface lifetime distribution worth consideration is the block distribution of Figure 4, denoting an equal probability that any element of liquid surface is engaged in reaching any lifetime between zero and a given upper limit. If again δ_i is taken as 1.00 and the average k_G per exposure is uniform, Equation (21) and Equation (1) yield

$$\frac{K_Ga}{K_{GF}a} = (1+R)\int_0^1 \frac{d\left(\frac{\theta}{\theta_u}\right)}{1+2R\left(\frac{\theta}{\theta_u}\right)^{1/2}} \qquad (24)$$

$$\frac{K_Ga}{K_{GF}a} = \frac{1+R}{2R^2}\left[2R-\ln(1+2R)\right] \qquad (18)$$

K_Ga is less than $K_{GF}a$, but never by more than 10.4%.

The above liquid surface lifetime distribution models all afford surprisingly close agreement with Equation (1). It is also apparent that a wider distribution gives a more negative deviation, the maximum effect occurring for the block distribution. The deviation from Equation (1) can be made still greater however by considering a binodal, or dumbell distribution of surface lifetimes.

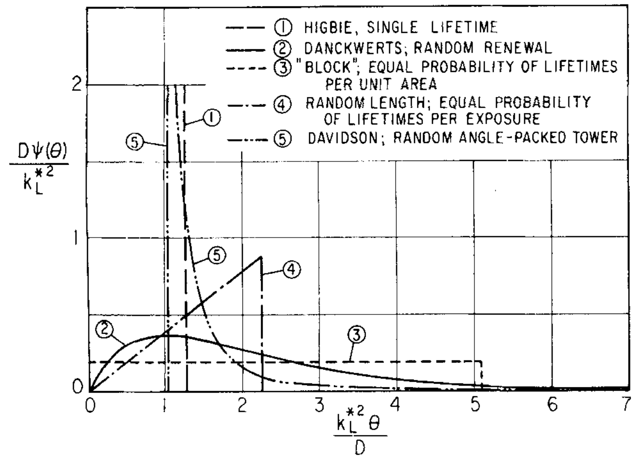

Fig. 4. Liquid surface lifetime distribution models.

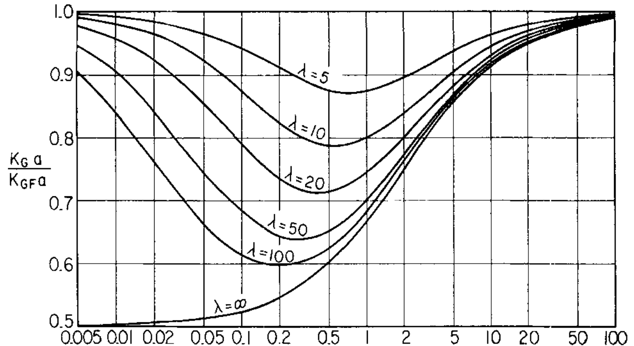

Fig. 5. Deviation from two-film addition with two-lifetime model, plot of Equation (28) for $f = 0.5$.

Two-Surface Lifetime Model

The simplest form of binodal distribution occurs for a model which pictures the liquid surface as being composed entirely of elements reaching either of two lifetimes. Such a distribution would correspond to two vertical lines on Figure 4. A fraction of the surface f is engaged in reaching the shorter lifetime θ_1, and the remainder $1 - f$ is engaged in reaching θ_2. The ratio of average liquid-phase mass transfer coefficients of the two regions k^*_{L1}/k^*_{L2} $(= \sqrt{\theta_2/\theta_1})$ is denoted by λ.

If it is assumed that Equation (1) is obeyed exactly for the surface of each lifetime and k_G is uniform, then it follows that

$$K_Ga = f\,K_{G1}a_1 + (1-f)\,K_{G2}a_2 \qquad (25)$$

and

$$R = \frac{Hk_G^*}{k_L^*} = \frac{Hk_G}{k^*_{L1}\left(f+\frac{1-f}{\lambda}\right)} \qquad (26)$$

Since $k_G/K_{GF} = 1 + R$, Equation (25) becomes

$$\frac{K_Ga}{K_{GF}a} = (1+R)\left[\frac{f}{1+\frac{Hk_G}{k^*_{L1}}}+\frac{1-f}{1+\frac{Hk_G}{k^*_{L2}}}\right] \qquad (27)$$

Combining Equations (26) and (27) one gets

$$\frac{K_Ga}{K_{GF}a} = (1+R)\left[\frac{f}{1+\left(f+\frac{1-f}{\lambda}\right)R}+\frac{1-f}{1+(\lambda f+1-f)R}\right] \qquad (28)$$

Figure 5 depicts Equation (28) for the case where $f = 0.50$, that is where half the liquid surface is engaged in reaching either lifetime. The case of $\lambda = \infty$ corresponds to half the liquid surface being totally inactive for anything except a process such as vaporization where there can be no liquid-phase resistance. From Figure 5 it may be seen that this form of liquid surface lifetime distribution can give substantial negative deviations from the two-film relationship of Equation (1), provided the ratio of the two surface lifetimes is large. Any distribution giving a comparable separation of lifetmes will produce similar effects.

Table 1 presents a summary of the properties of the various liquid surface lifetime distribution models considered in the foregoing discussion.

LOCAL VARIATION OF k_G'

In any real mass transfer situation it is probable that there will be a distribution of k_G^* as well as a distribution

TABLE 1. SURFACE LIFETIME DISTRIBUTION MODELS

No.	Name	Characteristics	Mathematical expression	$K_G a/K_{GF} a$
1	Higbie or Davidson No. 1	Single lifetime	$\psi(\theta_i) = \infty,\ \theta_i = \theta$ $\psi(\theta_i) = 0,\ \theta_i \neq \theta$	1.00 to 1.05* [Equation (16)]
2	Danckwerts	Random renewal	$\psi(\theta_i) = s^2\theta_i e^{-s\theta_i}$	1.00*
3	Block	Equal probability of lifetimes per unit interfacial area	$\psi(\theta_i) = 1/\theta_u,\ \theta_i \lesseqgtr \theta_u$ $\psi(\theta_i) = 0,\ \theta_i > \theta_u$	0.90 to 1.00† [Equation (18)]
4	Random length	Equal probability of lifetimes per exposure	$\psi(\theta_i) = 2\theta_i/\theta_u^2,\ \theta_i \lesseqgtr \theta_u$ $\psi(\theta_i) = 0,\ \theta_i > \theta_u$	0.98 to 1.00† [Equation (23)]
5	Davidson No. 2	Random angles of surface inclination	See reference 5	(1.00 to 1.05)* See text
6	Davidson No. 3	Random angle and random length per exposure	See reference 5	(0.98 to 1.02)* See text
7	Two lifetime	Surface elements reach either of two lifetimes	$\psi(\theta_i) = \infty,\ \theta_i = \theta_1, \theta_2$ $\psi(\theta_i) = 0,\ \theta_i \neq \theta_1, \theta_2$ $\psi(\theta_1)/\psi(\theta_2) = f/(1-f)$	f to 1.00† [Equation (28) and Figure 5]
8	Szekely	Two renewals in phase 1 per renewal in phase 2		0.96 to 1.01 [Equation (20)]

* k_G constant.
† $\delta_i = 1.0$ and uniform average $k_G{}^*$ per exposure interval.

of $k_L{}^*$ from one region to another. If high values of $k_G{}^*$ tend to coincide with high values of $k_L{}^*$, the effect will be compensating; the limit would come when the $k_G{}^*$ distribution coincided exactly with the $k_L{}^*$ distribution in such a way as to make $Hk_G{}^*/k_L{}^*$ a constant ratio. In such an event Equation (1) is obeyed exactly if $\delta_i = 1$. On the other hand if there is a tendency for low values of $k_G{}^*$ to coincide with high values of $k_L{}^*$ and vice versa, then it can easily be shown that negative deviations from Equation (1) will be accentuated.

EXPERIMENTAL STUDIES OF MASS TRANSFER EQUIPMENT

Stirred Flask Absorption

Goodgame and Sherwood (7) have examined the vaporization of water into air and the absorption of carbon dioxide, ammonia, and acetone from air into water in a stirred flask. The results agree within ± 3% with the predictions of Equation (1). It may be inferred that in a stirred flask the distribution of surface lifetimes does not give a sufficiently wide distribution of values of $Hk^*_G a/k^*_L a$ from region to region to cause marked deviations from Equation (1). In addition it should be noted that the arrangement of the paddles in the apparatus employed by Goodgame and Sherwood was such as to present a situation of concurrent flow, which should give close agreement with Equation (1) during a given surface exposure.

Packed Towers

It is well known that $k_G a$ values derived from gas phase controlled absorption data by means of Equation (1) tend to be lower than the $k_G a$ values measured for vaporization processes in packed towers. For example Yoshida and Koyanagi (20) find that $K_G a$ values for methanol absorption, corrected for diffusivity, are 40 to 80% of the $K_G a$ values for water vaporization in beds of 15 and 25 mm. rings, despite the fact that Equation (1) indicates that methanol absorption should be entirely gas phase controlled. Shulman et al. (17) have found $K_G a$ for methanol absorption on 0.5- and 1.0-in. rings to be 55 to 85% of the $K_G a$ values for water vaporization. Results such as these have led to the concept of an effective area for absorption which is less than the effective area for vaporization.

These discrepancies are predicted by a binodal liquid surface lifetime distribution model that provides a sufficiently wide spread of lifetimes. It is probable that a wide lifetime distribution exists in a packed tower in view of the fact that the local liquid flow rate per unit wetted perimeter varies markedly from one point to another on a single piece or a group of pieces of packing, and surface lifetimes will change as this flow rate changes. The frequency factor ψ giving the fraction of the total surface area engaged in reaching a lifetime θ_i may be binodal without necessitating a binodal form for either the distribution of exposures reaching a lifetime θ_i, the distribution of surface area with an age t_i, or the bulk residence time distribution. This point follows from the relatively high weight accorded by the frequency factor ψ to longer times and to surfaces covering areas of lower flow rates. It seems reasonable to attribute the less active surface for mass transfer to regions of thin films and relatively low liquid flow per unit wetted perimeter than to attribute it to stagnant pockets or pools of liquid, since apparently this less active surface must contribute as much as half of the total interfacial area between gas and liquid.

An interesting feature of the consideration of the distribution of liquid surface lifetimes is the prognosis that the effective area for a mass transfer process, as employed by Shulman, Yoshida, and others, should change as R changes, even at fixed flow conditions (see Figure 5 for example). Thus there should be a uniform trend of $K_G a$ with respect to the solubility of the solute under consideration.

It is unfortunate that none of the wealth of packed tower data are suitable for testing this prediction. The studies of Yoshida and Koyanagi (20) and of Shulman et al. (17) give quantitative information on the difference between $K_G a$ for vaporization and $K_G a$ for methanol absorption but consider the absorption of only one solute. Houston and Walker (8) report data for the absorption of methanol, ethanol, ammonia, and acetone from a dilute air stream into water, but there is sufficient scatter and uncertainty in corrections for diffusivity and estimation of liquid-phase resistance to prevent any conclusion regarding the effect of solubility upon $K_G a$ at given flow conditions.

Future experimentation to examine the addition of resistances problem in packed towers could follow several lines. The effect of solubility can best be examined by extensive measurements of the rates of absorption of several highly soluble gases from a dilute air stream into water at fixed flow conditions. Data for vaporization and the desorption of a highly insoluble gas should also be obtained in the same apparatus. The pertinent diffusivities should be well established independently. From the results a uniform trend of $K_G a$ with respect to changes in the solubility of the solute could be confirmed or denied, and parameters in the two-lifetime model or any other model could be ascertained. The interfacial area considered in the analysis of the effect of surface lifetime distribution is the total interfacial area, which should remain constant at fixed flow conditions with dilute phases. Since this area is constant, there is no need to separate it from the observed values of K_Ga in order to detect trends in K_G with respect to solubility. It may also be possible to approach the liquid surface lifetime distribution by making measurements of bulk residence times and applying the theory of falling laminar or turbulent films. Measurements would be made for a single layer of packing or for a very few layers, in which case it would be necessary to extrapolate the data toward a single layer. The measurements of the tail of the residence time curve would bear great importance, since a thin, slow-moving film contributes much area but little fluid volume.

Plate Towers

It is apparent that the mass transfer process upon individual plates of a staged distillation or absorption tower again presents a situation where k_G^* and k_L^* can be expected to vary from one location to another. In a recent American Institute of Chemical Engineers plate efficiency project gas-phase data were taken with both vaporization and ammonia absorption systems (*16*, *19*). The k_Ga (or N_G) values obtained from the ammonia absorption data through the use of Equation (1) were markedly lower than the values obtained from vaporization studies. In one case the discrepancy was reported to be about 40% (*19*). Here again the phenomenon can be explained qualitatively in terms of the variation of the group Hk_G^*/k_L^* from one region to another, but a more quantitative understandng must await detailed experimentation of the type suggested for packed towers.

CONCLUSIONS

1. The two-film equation for the addition of individual phase resistances measured in the absence or suppression of resistance in the other phase is subject to several stringent conditions. Among these are the requirements that the mass transfer coefficient for any one phase not be dependent upon the relative magnitude of the resistance in the second phase, and the ratio Hk_G'/k_L' be invariant from point to point along the interfacial area of phase contact.
2. These two conditions are rarely met in common mass transfer geometries. For example in the case of a constant k_G in contact with a penetration model of the liquid phase both conditions are violated, but the effects compensate so as to produce agreement with Equation (1) to within 5%.
3. In equipment which furnishes a wide distribution of liquid surface lifetimes and hence a wide variation in local values of k_L the deviation from the two-film addition of resistances equation is likely to be particularly severe. This concept is capable of resolving the observed discrepancies in k_Ga values calculated from vaporization and from absorption data in packed and plate columns.
4. Consideration of surface lifetime distribution effects in equipment such as packed towers suggests a continuous change in effective area as the solubility of the solute under consideration changes, even at fixed flow conditions.

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NOTATION

a = gas-liquid interfacial area per unit volume of equipment, sq. ft./cu. ft.
C = concentration of solute in liquid phase, lb.-moles/cu. ft.
D = diffusivity of solute in liquid phase, sq. ft./hr.
f = fraction of liquid surface engaged in reaching the shorter lifetme in two-lifetime model
k_G = individual gas phase mass transfer coefficient, lb.-mole/(hr.)(sq. ft./atm.)
k_L = individual liquid phase mass transfer coefficient, ft./hr.
K_G = overall gas phase mass transfer coefficient, lb.-mole/(hr.)(sq. ft./atm.)
N_A = local rate of mass transfer, lb.-mole/(hr.)(sq. ft.)
N_G = number of individual gas phase transfer units
p = partial pressure of solute, atm.
P = total pressure, atm.
R = ratio of individual phase coefficients measured independently = Hk_G^*/k_L^*
t = time, age of surface, hr.
V = electrical potential, volts
y = distance into liquid normal to interface, ft.
δ = $K_Ga/K_{GF}a$
θ = surface lifetime, hr.
λ = ratio of average k_L' for two regions in two-lifetime model = $(\theta_2/\theta_1)^{1/2}$
$\psi(\theta_i)d\theta_i$ = fraction of liquid surface engaged in reaching a lifetime between θ_i and $\theta_i + d\theta_i$

Subscripts

EG = in equilibrium with bulk gas
EL = in equilibrium with bulk liquid
F = predicted by two-film model, Equation (1). See text preceding Equation (11)
G = in bulk gas phase
i = at interface; value within a set
L = in bulk liquid phase
u = upper limit
o = initial value
1, 2 = regions of interface

Superscripts

$'$ = local, at a point of interface
$*$ = measured in the absence or suppression of resistance in the other phase

LITERATURE CITED

1. "Bubble-Tray Design Manual," American Institute of Chemical Engineers, New York (1958).
2. Carslaw, H. S., and J. C. Jaeger, "Conduction of Heat in Solids," 2 ed., pp. 70-73, Clarendon Press, Oxford, England (1959).
3. Danckwerts, P. V., *Ind. Eng. Chem.*, **43**, 1460 (1951).
4. ———, A. M. Kennedy, and D. Roberts, *Chem. Eng. Sci.*, **18**, 63 (1963).
5. Davidson, J. F., *Trans. Inst. Chem. Engrs. (London)*, **37**, 131 (1959).
6. Emmert, R. E., Ph.D. thesis, Univ. of Delaware, Newark, Delaware (1954).
7. Goodgame, T. H., and T. K. Sherwood, *Chem. Eng. Sci.*, **3**, 37 (1954).
8. Houston, R. W., and C. A. Walker, *Ind. Eng. Chem.*, **42**, 1105 (1950).
9. King, C. J., *Lawrence Radiation Laboratory Report UCRL 11196*, U.S.A.E.C. (January, 1964).
10. Lightfoot, E. N., *A.I.Ch.E. Journal*, **8**, 416 (1962).
11. Marshall, W. R., and R. L. Pigford, "The Application of Differential Equations to Chemical Engineering Problems," p. 134, Univ. of Delaware, Newark, Delaware (1947).
12. Perlmutter, D. D., *Chem. Eng. Sci.*, **16**, 287 (1961).

13. Perry, J. H., ed., "Chemical Engineers' Handbook," 3 ed., McGraw-Hill, New York (1950).
14. Potter, O. E., *Chem. Eng. Sci.*, 6, 170 (1957).
15. Salvetti, O., and C. Trevessoi, *Ann. Chim. (Rome)*, 51, 207 (1961).
16. Schoenborn, E. M., et al., "Tray Efficiencies in Distillation Columns," pp. 8 ff., Final Report from North Carolina State College, American Institute of Chemical Engineers, New York (1959).
17. Shulman, H. L., C. G. Savini, and R. V. Edwin, *A.I.Ch.E. Journal*, 9, 479 (1963).
18. Szekely, J., *Int. J. Heat Mass Transfer*, 6, 833 (1963).
19. Williams, B., et al., "Tray Efficiencies in Distillation Columns," pp. 36, 79, 80, Final Report from the University of Michigan, American Institute of Chemical Engineers, New York (1960).
20. Yoshida, F., and T. Koyanagi, *A.I.Ch.E. Journal*, 8, 309 (1962).

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Statistical Surface Thermodynamics of Simple Liquid Mixtures

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The surface properties of nonpolar liquid mixtures are derived from the application of the grand partition function to a cell model of the vapor-liquid interface. The surface tension and surface composition are expressed in terms of the activity coefficients in the bulk liquid and pure-component properties. The results are in excellent agreement with existing data for the surface tension of mixtures. This treatment provides a sound theoretical basis for the prediction of surface properties of other liquid systems and is especially applicable to cryogenic mixtures.

The surface tension of a liquid or liquid solution is a direct consequence of the molecular structure of the liquid phase and of the intermolecular forces operating within that phase; therefore better understanding of the surface tension is of physicochemical interest. In addition a better understanding of the surface properties of liquid mixtures also has engineering application; for example studies of vapor-liquid mass transfer in distillation columns (*13, 14, 33*) showed that the rate depends on whether the transfer tended to increase or decrease the surface tension of the liquid phase. Also it has been shown (*30*) that in extraction operations the presence or absence of interfacial turbulence is very much influenced by the variation of surface tension with composition. Finally the role of surface tension in heat transfer by nucleate boiling is now being recognized (*19*).

Although the treatment to be discussed is general, it is especially applicable to one class of mixtures, liquefied gases at low temperature. Surface tension data are available for most pure cryogenic fluids, but such data for cryogenic mixtures are very scarce. Since the possible number of mixtures is very large and since experimental measurements at low temperature are difficult to perform, it is of interest to develop a technique for calculating the surface properties of mixtures from more readily available thermodynamic data. Such a technique is provided through the methods of statistical mechanics. This work considers the application of molecular and statistical mechanical concepts to the derivation of a theoretical equation which relates the surface tension and the surface composition of a mixture to the surface energy of the pure components and to the excess free energy of the bulk solution. The final result is quite simple to use and gives exexcellent agreement between calculated and experimental surface properties.

The thermodynamic treatment of a surface liquid solution is considerably more difficult than that of a bulk liquid solution. Although the composition of the bulk solution is a known, independent variable, the composition of the surface is an unknown, dependent variable; as a result of preferential adsorption the mole fractions of the various components at the surface are quite different from those of the bulk. Therefore any attempt to calculate the surface tension of a mixture must be coupled with a calculation of the surface composition.

Previous attempts to apply statistical mechanics to the calculation of surface tensions of mixtures are due primarily to Guggenheim (*15*) and to Prigogine (*11, 12*). Guggenheim uses the lattice model for the liquid state, which necessitates some more or less arbitrary assumptions on the geometry of the liquid structure and which, when applied to mixtures, is valid only for components of very nearly the same size and shape. Prigogine approaches the calculation of the equilibrium surface tension of a mixture as a perturbation on the dynamic surface tension using a smoothed potential model; his technique is applicable only for mixtures which are very nearly ideal and requires the arbitrary choice of a reference substance, which can seriously affect the results. In the present work no lattice model is used, and the equilibrium surface ten-