Generalization of the Penetration Theory for Surface Stretch: Application to Forming and Oscillating Drops

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A method is developed for predicting rates of mass or heat transfer through stretching or shrinking phase boundaries of finite lifetime at low mass transfer rates. The primary result of this development, Equation (43), may be considered as a generalization of penetration theory. It includes as special cases similar expressions developed for more restricted situations, notably those of Ilkovic (7) and of Beek and Kramers (1).

This general development is then used to refine the Rose-Kintner analysis (13) of mass transfer to large oscillating liquid drops for the limiting case of all heat or mass transfer resistance in the droplet phase. It is found that convection normal to the phase boundary tends to offset the direct effect of surface stretch, and that the postulated mass transfer behavior can be expressed adequately by a very simple expression, Equation (68). This result yields slightly lower predictions of mass transfer rates than the correlation of Rose and Kintner, but available data are not sufficiently accurate to indicate which is the more reliable.

The surface-stretch model is also applied to drop formation at submerged nozzles. Experimentally it was found that the growth of surface during this process is essentially linear, which simplifies calculations. The model gives predictions of the mass transfer coefficient which are in reasonably good agreement with the predictions based on the assumption of continual formation of fresh surface first used by Groothuis and Kramers (18), and later by Beek and Kramers (1). Both models show that the mass transfer coefficient is at least fifteen times as high as predicted by boundary-layer calculations alone. Finally, the surface-stretch model indicates that the mass transfer behavior druing the rise period is approximately fourteen times as important as during the formation period for the equipment used in this study.

An expression was also developed for the more general situation of appreciable resistance in each phase, Equation (62), by assuming the surface-stretch model to describe the transfer processes in both phases. The two-resistance theory (10) is exact under such circumstances. This result was also found to correlate available data reasonably well.

More data, however, are needed if meaningful tests of the above, or other, correlations are desired.

THE SURFACE-STRETCH MODEL

It is our purpose here to extend the penetration theory of heat or mass transfer to systems in which the area of the mass transfer surface is a function of time. We thus begin by considering an interface between two fluid phases which are quiescent except for the convection resulting from shrinkage or expansion of the interfacial surface area. We limit consideration to situations in which the interface is formed suddenly at zero time between two immiscible solutions of uniform composition and to very short contact times. We shall also assume negligible diffusion in directions parallel to the interface. Under these circumstances behavior in the neighborhood of any surface element may be considered one-dimensional, and the continuity equation for any solute species A in either of the two phases takes the form

$$\frac{\partial \rho_A}{\partial t} + v_y \frac{\partial \rho_A}{\partial y} = -\frac{\partial}{\partial y} j_{Ay} \tag{1}$$

If the mass density ρ of the solution is constant and the net rate of mass transfer is small, the fluid velocity in the neighborhood of the interface may be expressed as (see Appendix A)

$$v_y = -y\,(\partial \ln S/\partial t)_{u,w} \tag{2}$$

where u, w are reference coordinates of a point in the interfacial surface and the derivative represents the local fractional rate of change (stretching) of interfacial area for a moving surface element. For high net mass transfer rates Equation (2) must be modified. This situation is of specialized interest and will be discussed in a later communication.

For isothermal isobaric systems with no forced diffusion the mass diffusion flux may be expressed as

$$j_{Ay} = -\sum_{i=1}^{n-1} D_{Ai} \frac{\partial \rho_i}{\partial y} \tag{3}$$

where n is the total number of species in the mixture. From a practical standpoint, it will suffice here to consider only the simple special case of a binary solution (containing species A and D), since the behavior of most multicomponent systems is readily estimated with good accuracy if that of the corresponding binary is known (17, 16, 3). For simplicity we shall also assume that the binary diffusivity $\mathcal{D}_{AD}$ is constant.

Equations (1) through (3) may then be combined to give

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$$\frac{\partial \rho_A}{\partial t} - y\left(\frac{\partial \ln S}{\partial t}\right)_{u,w} \frac{\partial \rho_A}{\partial y} = \mathfrak{D}_{AD}\frac{\partial^2 \rho_A}{\partial y^2} \qquad (4)$$

This equation will be solved with the aid of the boundary conditions

$$\text{I.C.} \quad \rho_A = \rho_{A\infty} \quad \text{at } y > 0 \quad \text{for } t = 0 \qquad (5)$$

$$\text{B.C. 1} \quad \rho_A = \rho_{A\infty} \quad \text{at } y \to \infty \quad \text{for } t \text{ finite} \qquad (6)$$

$$\text{B.C. 2} \quad \rho_A = \rho_{A0} \quad \text{at } y = 0 \quad \text{for } t > 0 \qquad (7)$$

Equations (5) and (6) follow from the assumed rapid formation of the interface and short contact times. Equation (7) is justified below in the discussion of interphase mass transfer. Description of our system is now complete except for the specification of $(\partial \ln S/\partial t)_{u,w}$. For the moment it will be considered an arbitrary but known function of time for any region of the interface. Restrictions on this function and some specific examples are discussed below. We now define the following dimensionless variables:

$$\chi = \frac{\rho_A - \rho_{A0}}{\rho_{A\infty} - \rho_{A0}} \quad \eta = \frac{y}{\sqrt{\mathfrak{D}_{AD}\, t_0}} \quad \tau = \frac{t}{t_0} \qquad (8), (9), (10)$$

where t_0 is a constant with units of time characteristic of the system being considered. Hence, our system of equations in dimensionless form becomes

$$\frac{\partial \chi}{\partial \tau} - f(\tau)\, \eta \frac{\partial \chi}{\partial \eta} = \frac{\partial^2 \chi}{\partial \eta^2} \qquad (11)$$

$$\chi = 1 \ \text{at } \eta > 0 \ \text{for } \tau = 0 \qquad (12)$$

$$\chi = 1 \ \text{at } \eta \to \infty \ \text{for } \tau \text{ finite} \qquad (13)$$

$$\chi = 0 \ \text{at } \eta = 0 \ \text{for } \tau > 0 \qquad (14)$$

where

$$f(\tau) = \left(\frac{\partial \ln S(\tau)}{\partial \tau}\right)_{u,w} \qquad (15)$$

SOLUTION

To solve these equations we attempt a combination of variables by assuming a solution of the form

$$\chi = \chi(\zeta); \ \zeta = \eta \cdot g(\tau) \qquad (16)$$

We thus find

$$\frac{d^2\chi}{d\zeta^2} + \zeta\left[\frac{f}{g^2} - \frac{g'}{g^3}\right]\frac{d\chi}{d\zeta} = 0 \qquad (17)$$

where the prime indicates the partial derivative of g with respect to τ at constant η.

Now for a combination of variables to succeed, it is necessary that

$$\left[\frac{f}{g^2} - \frac{g'}{g^3}\right] = C \qquad (18)$$

where C is an arbitrary constant, or more simply

$$fg - g' = C\, g^3 \qquad (19)$$

If Equation (19) is satisfied, Equation (17) can be simplified to

$$\frac{d^2\chi}{d\zeta^2} + C\zeta\frac{d\chi}{d\zeta} = 0 \qquad (20)$$

We have thus reduced Equation (11) to an ordinary differential equation. However, for the assumed combination of variables to be successful it is also necessary that Equation (20) satisfy all three boundary conditions, Equations (12) through (14). Here we shall require that these reduce to

$$\chi(0) = 0 \qquad (21)$$

$$\chi(\infty) = 1 \qquad (22)$$

Equations (19), (21), and (22) thus represent the restrictions that must be met if a combination of variables is to be successful.

For such a situation Equation (20) may be readily integrated to yield

$$\chi = \operatorname{erf} \zeta \qquad (23)$$

where the form of ζ is yet to be determined, and where C has been assigned a value of 2 for convenience. Determination of ζ is facilitated by recognizing that Equation (19) is a Bernoulli equation which can be put into linear form by the substitution

$$g = u^{-1/2}; \quad u = 1/g^2 \qquad (24)$$

Then

$$\frac{dg}{d\tau} = -\frac{1}{2}\, u^{-3/2}\, \frac{du}{d\tau} \qquad (25)$$

which, when substituted into Equation (19), yields

$$\frac{1}{2}\, u^{-3/2}\, \frac{du}{d\tau} + f\, u^{-1/2} = C\, u^{-3/2} \qquad (26)$$

$$\frac{du}{d\tau} = -\, 2fu + 2C \qquad (27)$$

The integrating factor for this equation is

$$e^{2\int f(\tau) d\tau} \qquad (28)$$

Combining Equations (27) and (28) we then obtain

$$e^{2\int f(\tau)d\tau}\, \frac{du}{d\tau} = -\, 2uf(\tau)\, e^{2\int f(\tau)d\tau} + 2C\, e^{2\int f(\tau)d\tau} \qquad (29)$$

When one recalls that $f(\tau) = \left(\frac{\partial \ln S(\tau)}{\partial \tau}\right)_{u,w}$, it follows that

$$e^{2\int\left(\frac{\partial \ln S}{\partial \tau}\right)_{u,w} d\tau} = S(\tau)^2 \qquad (30)$$

Equation (29) then takes the form

$$S^2 \frac{du}{d\tau} = -\, 2uS\frac{dS}{d\tau} + 2C\, S^2 \qquad (31)$$

Putting

$$P = u\, S^2(\tau) \qquad (32)$$

we may readily solve Equation (31):

$$\frac{dP}{d\tau} = 2uS\frac{dS}{d\tau} + S^2\frac{du}{d\tau} \qquad (33)$$

$$P = 2C \int_0^\tau S^2(t)\, dt + C_1 = uS^2(\tau) \qquad (34)$$

where C_1 is an arbitrary constant. It follows then that

$$\frac{1}{u} = \frac{S^2(\tau)}{2C \int_0^\tau S^2(t) dt + C_1} = \frac{S^2(\tau)}{4 \int_0^\tau S^2(t) dt} \qquad (35)$$

The solution obtained by combining Equations (24) and (35) is

$$g(\tau) = \frac{S(\tau)}{\sqrt{4 \int_0^\tau S^2(t)\, dt}} \qquad (36)$$

where C has been assigned a value of 2, and C_1 must be zero to satisfy Equation (22). When one recalls that $\zeta =$

$\eta \cdot g(\tau)$, the complete solution to Equation (11) is

$$\boxed{\chi = \operatorname{erf} \zeta = \operatorname{erf} \frac{\eta S(\tau)}{\sqrt{4 \int_0^\tau S^2(t)\, dt}}} \qquad (37)$$

This expression automatically satisfies Equations (20) through (22) for well-behaved $S(\tau)$. Clearly, it is necessary that $S(\tau)$ be such that Equations (12) through (14) are satisfied. This is true for a very wide class of functions, and, specifically, all of those discussed below.

Equation (37) is sufficient to describe the mass transfer behavior if $S(\tau)$ is known. However, it is often more convenient to work in terms of mass transfer coefficients, which may be obtained from Equation (37) by the methods of the next section.

ESTIMATION OF MASS TRANSFER COEFFICIENTS

Instantaneous local mass transfer coefficients (k_0/ρ) may be defined by

$$j_{A0y} = - \mathcal{D}_{AD} \left.\frac{\partial \rho_A}{\partial y}\right|_{y=0} = (\rho_{A0} - \rho_{A\infty})_D\, \mathcal{D}_{AD} \left.\frac{\partial \chi}{\partial \eta}\right|_{\eta=0} \left(\frac{\partial \eta}{\partial y}\right) = (k_0/\rho)(\rho_{A0} - \rho_{A\infty})_D \qquad (38)$$

where (k_0/ρ) is the mass transfer coefficient at a given time and position on the interface. It follows from Equations (37) and (38) that

$$(k_0/\rho) = \sqrt{\frac{\mathcal{D}_{AD}}{\pi t_0}} \cdot \frac{S(\tau)}{\sqrt{\int_0^\tau S^2(t)\, dt}} \qquad (39)$$

It will be convenient in the following discussion to compare mass transfer behavior for variable surface area to that for the fixed area of the elementary penetration theory. We, therefore, define a dimensionless mass transfer coefficient κ in terms of a reference area S_0 as

$$\kappa = \frac{(k_0/\rho)}{\sqrt{\frac{\mathcal{D}_{AD}}{\pi t_0}}} = \frac{S(\tau)/S_0}{\sqrt{\int_0^\tau \left(\frac{S(t)}{S_0}\right)^2 dt}} \qquad (40)$$

Choices of S_0 and t_0 will be made separately for each special situation considered below.

Normally, it is convenient to work with average mass transfer coefficients. Here this requires averaging both over the mass transfer surface and time since surface formation. Area averaging can be performed in the usual way (2, Chapters 13, 21), but for time varying surface area this must be done carefully. For simplicity we shall assume at this stage of our development that κ is a function only of time.

The time average value of κ based on the reference area S_0 is $\overline{\kappa}$, defined by

$$\overline{\kappa} = \frac{1}{\tau} \int_0^\tau \kappa(t) \left(\frac{S(t)}{S_0}\right) dt \qquad (41)$$

$$\overline{\kappa} = \frac{1}{\tau} \int_0^\tau \frac{[S(t)/S_0]^2\, dt}{\sqrt{\int_0^t [S(\theta)/S_0]^2\, d\theta}} \qquad (42)$$

$$\boxed{\overline{\kappa} = \frac{2}{\tau} \sqrt{\int_0^\tau \left[\frac{S(t)}{S_0}\right]^2 dt}} \qquad (43)$$

In these expressions t and θ are dummy integrating variables used in place of τ.

It is perhaps useful at this point to emphasize the physical significance of $\overline{\kappa}$. It is so defined that the total amount of solute $m_A(t)$ passing through the mass transfer surface in the time interval zero to t is given by

$$m_A(t) = \overline{\kappa} \sqrt{\frac{\mathcal{D}_{AD}}{\pi t_0}} (\rho_{A0} - \rho_{A\infty})_D S_0 t \qquad (44)$$

As a specific case we consider the elementary penetration theory for which $S = S_0$. For this condition

$$m_A(t) = \frac{2}{\sqrt{\tau}} \sqrt{\frac{\mathcal{D}_{AD}}{\pi t_0}} (\rho_{A0} - \rho_{A\infty})_D S_0 t \qquad (45)$$

and since $\tau = t/t_0$

$$m_A(t) = 2 \sqrt{\frac{\mathcal{D}_{AD} t}{\pi}} (\rho_{A0} - \rho_{A\infty})_D S_0 \qquad (46)$$

which is a well-known result.

Table 1 defines the dimensionless mass transfer coefficient $\overline{\kappa}$ for several functions $S(\tau)$.

One of these functions of particular interest in the ensuing discussion is that for which

$$S(\tau) = S_0 (1 + \epsilon \sin^2 \tau) \qquad (54)$$

with

$$t_0 = \frac{1}{\pi \omega} \qquad (55)$$

For this situation

$$\overline{\kappa} = \frac{2}{\tau} \sqrt{\int_0^\tau (1 + \epsilon \sin^2 t)^2\, dt}$$

$$\overline{\kappa} = \frac{2}{\tau} \sqrt{\int_0^\tau (1 + 2\epsilon \sin^2 t + \epsilon^2 \sin^4 t)\, dt} \qquad (57)$$

$$\overline{\kappa} = \frac{2}{\tau} \sqrt{(1 + \epsilon_0)\tau - \epsilon_1 \sin 2\tau + \epsilon_2 \sin 4\tau} \qquad (50)$$

where ϵ_0, ϵ_1, and ϵ_2 are defined by Equations (51*a*) through (51*c*), Table 1. Equation (50) will be found useful for oscillating drops and Equation (48) for drop formation. Equation (50) is illustrated in Figure 9 where it is compared with its analog Equation (52).

INTERPHASE MASS TRANSFER AND THE TWO-FILM THEORY

Up to this point we have considered only one of the two phases present. We now turn our attention to interphase transfer. More specifically, we shall extend the above analysis to mass transfer between two adjacent phases across an interface of the above-described type. Equation (4) will be assumed to describe the mass transfer in each of these phases. For one (the dispersed phase) solute diffusivity will be denoted by $\mathcal{D}_{AD}$, whereas in the other (the continuous phase) the symbol $\mathcal{D}_{AC}$ will be used.

Clearly, the total interfacial solute flux n_{A0} and surface movement must be the same for both phases. It, therefore, follows from the above development that

$$\sqrt{\frac{\mathcal{D}_{AD}}{\mathcal{D}_{AC}}} = \frac{(\rho_{A0} - \rho_{A\infty})_C}{(\rho_{A\infty} - \rho_{A0})_D} \qquad (58)$$

TABLE 1. THE DIMENSIONLESS MEAN MASS TRANSFER COEFFICIENT FOR TIME-DEPENDENT VARIATIONS IN SURFACE AREA

$\dfrac{S(\tau)}{S_0}$	ζ	t_0	$\overline{\kappa}$	Equation	Comments
1	$\dfrac{\eta}{2\sqrt{\tau}}$	—	$\dfrac{2}{\tau}\sqrt{\tau}$	(47)	Higbie constant surface model
$1+\beta\tau$	$\dfrac{\eta(1+\beta\tau)}{2\sqrt{\tau+\beta\tau^2+\beta^2\tau^3/3}}$	t_F	$\dfrac{2}{\tau}\sqrt{\tau+\beta\tau^2+\dfrac{\beta^2\tau^3}{3}}$	(48)	Drop formation at submerged nozzles
$1+\beta\tau+\gamma\tau^2$	$\dfrac{\eta(1+\beta\tau+\gamma\tau^2)}{2\sqrt{\tau+\beta\tau^2+\beta_0\tau^3+\beta_1\tau^4+\beta_2\tau^5}}$	t_0	$\dfrac{2}{\tau}\sqrt{\tau+\beta\tau^2+\beta_0\tau^3+\beta_1\tau^4+\beta_2\tau^5}$ $\beta_0=\dfrac{\beta^2+2\gamma}{3}$ $\beta_1=\beta\gamma/2$ $\beta_2=\gamma^2/5$	(49) (49*a*) (49*b*) (49*c*)	—
$1+\epsilon\sin^2\tau$	$\dfrac{\eta(1+\epsilon\sin^2\tau)}{2\sqrt{(1+\epsilon_0)\tau-\epsilon_1\sin 2\tau+\epsilon_2\sin 4\tau}}$	$\dfrac{1}{\pi\omega}$	$\dfrac{2}{\tau}\sqrt{(1+\epsilon_0)\tau-\epsilon_1\sin 2\tau+\epsilon_2\sin 4\tau}$ $\epsilon_0=\epsilon+\dfrac{3}{8}\epsilon^2$ $\epsilon_1=\dfrac{\epsilon}{2}+\dfrac{\epsilon^2}{4}$ $\epsilon_2=\dfrac{\epsilon^2}{32}$	(50) (51*a*) (51*b*) (51*c*)	Approximation to Rose-Kintner surface-time relation
$1+\epsilon\cos^2\tau$	$\dfrac{\eta(1+\epsilon\cos^2\tau)}{2\sqrt{(1+\epsilon_0)\tau+\epsilon_1\sin 2\tau+\epsilon_2\sin 4\tau}}$	$\dfrac{1}{\pi\omega}$	$\dfrac{2}{\tau}\sqrt{(1+\epsilon_0)\tau+\epsilon_1\sin 2\tau+\epsilon_2\sin 4\tau}$ where ϵ_0, ϵ_1, ϵ_2 are defined as above	(52)	Analog to Equation (50) for which shrinkage occurs in the first half of the cycle (see Figure 9)
$e^{\epsilon\sin\tau}$	$\dfrac{\eta\, e^{\epsilon\sin\tau}}{2\sqrt{\int_0^\tau e^{2\epsilon\sin t}\,dt}}$	$\dfrac{1}{\pi\omega}$	$\dfrac{2}{\tau}\sqrt{\int_0^\tau e^{2\epsilon\sin t}\,dt}$	(53)	Small-amplitude capillary oscillations (*20*)

Note: In the limit as ϵ, $\beta \to 0$, all models reduce to Equation (47), the result for constant surface.

Since the interfacial concentrations $(\rho_{A0})_C$ and $(\rho_{A0})_D$ must also satisfy the equilibrium distribution relation for the system (except for improbably high mass transfer rates), these concentrations are constant within the limitations of the above analysis [see particularly Equations (5) and (6)].

It follows then that Equation (7) is reasonable for this system and that all of the above results are valid for interphase mass transfer. It also follows from Equation (58) that the two-resistance theory of mass transfer (*10*) is exact for this model; that is, that the mass transfer resistances of the two phases are additive.

We may thus define an overall mass transfer coefficient in the usual way by

$$j_{A0y} = K_D(\rho_{A\infty}-\rho_A{}^*)_D = k_{D_{\text{loc}}}(\rho_{A\infty}-\rho_{A0})_D = k_{C_{\text{loc}}}(\rho_{A0}-\rho_{A\infty})_C \tag{59}$$

where K_D is the overall mass transfer coefficient and ρ_{AD} is the drop phase concentration in equilibrium with the bulk surrounding phase concentration. These driving forces for interphase mass transfer are defined in Figure 1. It thus follows that

$$\frac{(\rho_{A\infty}-\rho_A{}^*)_D}{1/K_D} = \frac{(\rho_{A\infty}-\rho_{A0})_D}{1/k_D} + \frac{(\rho_{A0}-\rho_A{}^*)_D}{\left(\dfrac{1}{k_C}\right)\dfrac{(\rho_{A0}-\rho_A{}^*)_D}{(\rho_{A0}-\rho_{A\infty})_C}} \tag{60}$$

and

$$\frac{1}{K_D} = \frac{1}{k_D} + \frac{m}{k_C} \tag{61}$$

where

$$m = (\rho_{A0}-\rho_A{}^*)_D/(\rho_{A0}-\rho_{A\infty})_C$$

Since the two intraphase coefficients vary in the same way with time and position, Equation (61) is valid for both instantaneous local and mean coefficients. Furthermore, since the intraphase coefficients differ only in the value of the appropriate diffusivity, we may write for the overall mass transfer coefficient

$$K_D = k_D\left[\frac{1}{1+m\sqrt{\dfrac{\mathcal{D}_{AD}}{\mathcal{D}_{AC}}}}\right] = \kappa\sqrt{\mathcal{D}_{AD}/\pi t_0}\left[\frac{1}{1+m\sqrt{\dfrac{\mathcal{D}_{AD}}{\mathcal{D}_{AC}}}}\right] \tag{62}$$

where the average dispersed phase mass transfer coefficient k_D is defined as

$$k_D = \overline{\kappa}\sqrt{\frac{\mathcal{D}_{AD}}{\pi\, t_0}}$$

The average overall mass transfer coefficient can, therefore, be expressed by

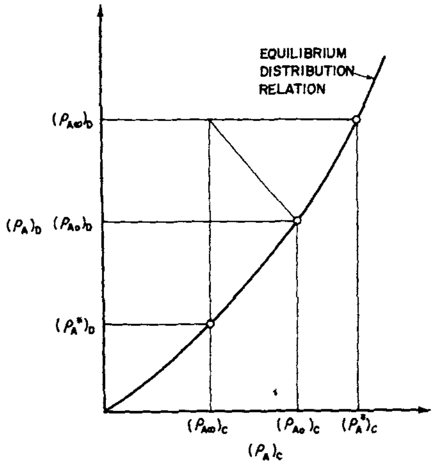

Fig. 1. Driving forces for interphase mass transfer.

$$\boxed{K_D = \frac{2}{\tau}\sqrt{\frac{\mathcal{D}_{AD}}{\pi t_0}}\sqrt{\int_0^\tau \left[\frac{S(t)}{S_0}\right]^2 dt}\;\left[\frac{1}{1+m\sqrt{\dfrac{\mathcal{D}_{AD}}{\mathcal{D}_{AC}}}}\right]} \tag{63}$$

With Equation (63) our general development is complete.* Before we go on to study application of this analysis to systems of practical interest, however, a brief summary seems in order.

In essence, the penetration theory of mass transfer has been extended to surfaces which undergo expansion or contraction during their lifetimes. As in all applications of penetration theory, the above analysis is limited to short exposure times of any surface element, negligible net diffusional or convective transfer of solute parallel to the interface of interest, no circulatory motion (interfacial turbulence) in the interfacial region, constant density, and constant temperature and pressure or incompressibility.

All previous penetration models known to the authors can be developed as special cases of the above treatment, the most important results of which are summarized in Equations (43) and (62). This is clearly true of all models for constant surface area, for which Equation (23) is always satisfied and $\zeta = y/\sqrt{4\,\mathcal{D}_{AD}t}$ for any surface element. The results also include the models of Ilkovic (*7*) and of Beek and Kramers (*1*) for continuously forming surfaces, and, indeed, Equation (43) is very similar to Beek and Kramers' Equation (36). The present development differs from that of Beek and Kramers primarily in our Equation (2), which is more general than their corresponding expression, and in the development between Equations (16) and (37), which greatly increases the class of problems that can be described.

APPLICATION TO CORRELATION OF MASS TRANSFER DATA

The above analysis will clearly be of greatest interest for systems of practical importance in which variations of surface area are large. The examples chosen here are of this type.

Example One: Large Oscillating Drops

We begin by considering a special case of considerable practical importance in liquid-liquid extraction: constant-velocity free fall of liquid drops, of equivalent diameters from about 2 to 10 mm., through a quiescent liquid. Typical Reynolds numbers of such drops relative to the continuous phase are 200 to 2,000 (based on equivalent drop diameter, relative velocity, and kinematic viscosity of the continuous phase). Such drops normally undergo rather large amplitude oscillations which have been attributed to periodic vortex shedding (*14*). The oscillation is typically from nearly spherical to oblate and back, and the drop appears to undergo a rather violent mixing once a cycle (*13*). Similar results have been observed by Kaparthi and Licht (*9*).

Up to the present time droplet phase mass transfer coefficients for such oscillating drops have normally been estimated from a correlation developed by Handlos and Baron (*6*). However, this correlation is not highly reliable, and it is based on a rather unconvincing physical picture.

More recently, Rose and Kintner (*13*) have suggested a modified penetration model for this system, using the time for one oscillation as the surface lifetime. To take into account the area changes resulting from oscillation they assumed a constant volume for the mass transfer zone. Local instantaneous mass transfer coefficients are considered to vary in direct proportion to thickness of this mass transfer zone. Continuous phase resistance is estimated by using the Garner and Tayeban (*5*) expression for circulating spherical drops. The resulting correlation, described fully by these authors (*13*), has a more appealing physical basis and also appears to be more reliable than that of Handlos and Baron.

However, the allowance for area changes is only an approximate one, and use of different surface lifetimes for the droplet and continuous phases seem open to some doubt. It was, therefore, decided to reanalyze available data on the basis of our own above development to see if any improvement could be obtained.

First, however, it was decided to test the Rose-Kintner method for predicting the effect of surface stretch on

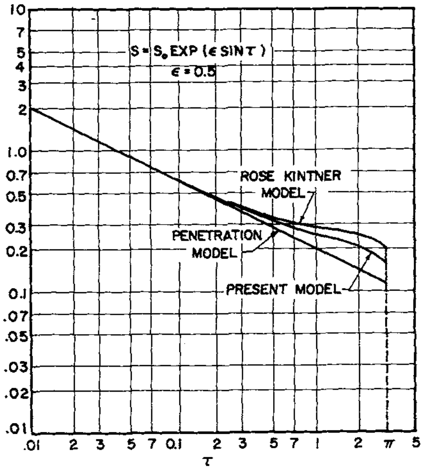

Fig. 2. Comparison of the Rose-Kintner model with the present development for prediction of time-average mass transfer coefficients with an assumed surface-time relation $S = S_0 e^{\epsilon \sin \tau}$ for $\epsilon = 0.5$.

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* During the latter stages of this development it came to our attention that Professor W. E. Stewart had begun a similar analysis. It is our intention to cooperate with him in extending this work.

time-average mass transfer coefficients against the above development. For simplicity the expression

$$S(\tau) = S_0\, e^{\epsilon \sin \tau} \tag{64}$$

was used as a model. Here the constant ϵ determines the magnitude of oscillation. Time-average dimensionless transfer coefficients for the Rose-Kintner analysis then take the form

$$(\bar{\kappa})_{RK} = \frac{1}{\tau}\int_0^{\tau} \frac{(S/S_0)^2}{\sqrt{t}}\, dt \tag{65}$$

$$(\bar{\kappa})_{RK} = \frac{2}{\tau}\int_0^{\sqrt{\tau}} e^{2\epsilon \sin (t^2)}\, dt \tag{66}$$

where (S/S_0) appears to the second power to allow both for the increase in area and the decrease in film thickness. The corresponding expression of the present authors is given by Equation (53) in Table 1.

Results of this comparison for a typical value of ϵ, shown in Figure 2, indicate that Rose and Kintner may have overestimated this effect. However, as we shall see, the effect on average mass transfer coefficients is not large compared with the uncertainty in available data.

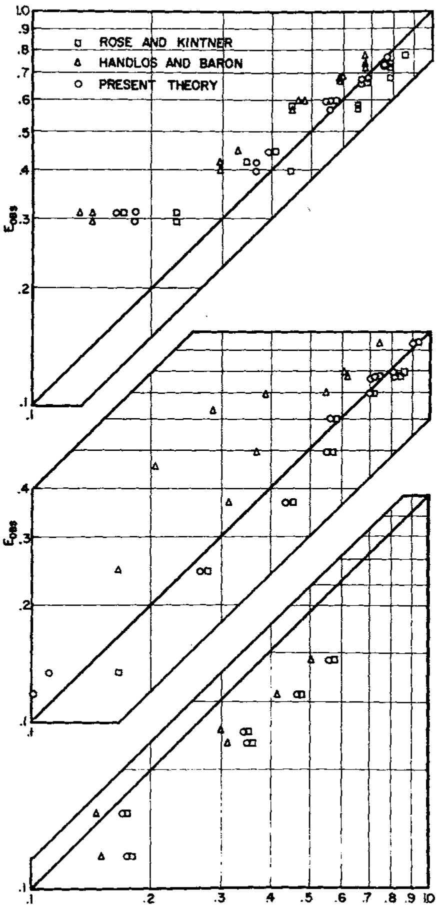

Fig. 3 (*top*). Comparison of predicted and observed extraction efficiency. Data of Johnson and Hamielec (*8*). Water drops in ethyl acetate. All resistance in drop phase. Fig. 4 (*middle*). Comparison of predicted and observed fractional extraction. Data of Skelland and Wellek (*15*). Water drops in ethyl acetate. All resistance in drop phase. Fig. 5 (*bottom*). Comparison of predicted and observed fractional extraction. Data of Skelland and Wellek (*15*). Ethylacetoacetate drops in water. All resistance in drop phase.

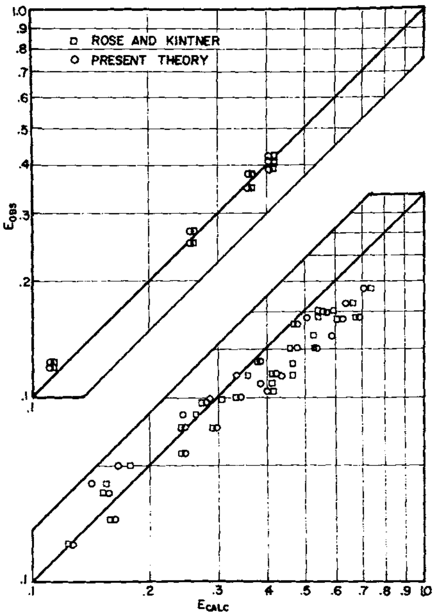

Fig. 6 (*top*). Comparison of predicted and observed extraction efficiency. Data of Garner and Skelland (*4*). Nitrobenzene drops–acetic acid–water. Major resistance in drop phase.

Fig. 7 (*bottom*). Comparison of predicted and observed fractional extraction. Data of Licht and Pansing (*11*). Water drops–acetic acid–methyl isobutyl ketone. Resistance in both phases.

The next predictions based on our above development were compared with both the predictions of Rose and Kintner and available experimental data. These comparisons, shown in Figures 3 through 7, were made by plotting observed vs. predicted extraction efficiencies. Predicted efficiencies were calculated from Equations (43) and (63) in the conventional way. Experimental results were also compared with the Handlos and Baron model when the resistance to transfer was entirely inside the drop phase.

The Rose-Kintner predictions are as given by these authors (*13*). Our own were based on the surface-time relation

$$S = S_0\,(1 + \epsilon \sin^2 \tau) \tag{67}$$

with values of ϵ, the amplitude of the surface stretch, calculated from a knowledge of the maximum and minimum surface area per cycle. As shown in Figure 8, Equation (67) is in quite good agreement with the Rose and Kintner results. It in turn yields a very simple relation for the time-average dimensionless mass transfer coefficient for one cycle of oscillation (that is, for $\tau = \pi$):

$$\left.\begin{aligned} \bar{\kappa} &= \sqrt{4(1+\epsilon_0)/\pi} \\ \epsilon_0 &= \epsilon + \frac{3}{8}\epsilon^2 \\ t_0 &= 1/(\pi\,\omega) \\ k_D &= \sqrt{\frac{4\,\mathfrak{D}_{AD}\,\omega(1+\epsilon_0)}{\pi}} \end{aligned}\right\} \text{predicted average mass transfer coefficient for oscillating drops} \tag{68}$$

Clearly, the corresponding overall coefficient, based on dispersed phase units, is

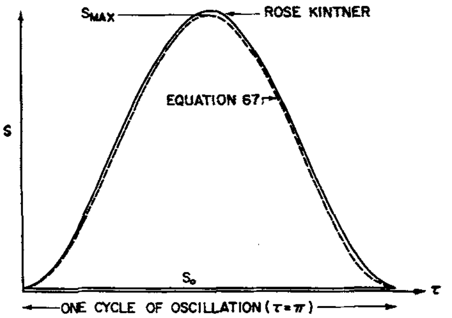

Fig. 8. Comparison of assumed surface-time relation of present analysis with Rose-Kintner variation ($a_0 = 0.304$ cm., $b_0 = 0.301$ cm., $a_p = 0.116$ cm., $\epsilon = 0.199$). Rose-Kintner: $a = a_0\ (1 + a_p/a_0|\sin\ \tau|^2)$. Equation (67): $S = S_0\ (1 + \epsilon \sin^2 \tau)$.

$$K_D = \sqrt{\frac{4\ \mathfrak{D}_{AD}\ \omega(1 + \epsilon_0)}{\pi}} \left[\frac{1}{1 + m\sqrt{\dfrac{\mathfrak{D}_{AD}}{\mathfrak{D}_{AC}}}} \right] \qquad (69)$$

Strictly speaking these expressions are correct only for an integral number of complete oscillations. For a fractional number they will be too low. It may also be noted that different degrees of stretching could be assumed for different portions of the drop surface, and indeed this was done by Rose and Kintner. We both feel, however, that neither of these refinements is justified at present, in view of the scatter of available data.

It can be seen by examination of Figures 3 and 7 that Equations (68) and (69) generally predict somewhat smaller extraction efficiencies than does the Rose and Kintner correlation. This difference is, however, much less than the scatter of the data. On balance the correlations must be considered of equivalent reliability. Our correlation is, however, considerably more convenient to handle, and we feel that it is based on a somewhat firmer foundation.

This close agreement is not unexpected for systems with negligible continuous phase resistance. It is, in fact, predicted by the results shown in Figure 2. It is considerably more surprising for systems with appreciable continuous phase resistance, since we have used a much different model than Rose and Kintner for the external phase.

An attempt was made to test the predicted dependence of the mass transfer coefficient on diffusivity. However, owing to the limited amount of data available, this could not be done successfully.

Thus, although these two rather similar approaches do provide improved reliability and a more appealing picture than previously available correlations, they must still be considered empirical. There is clearly a need for more extensive data and, ultimately, for further analysis.

Example Two: Drop Formation at Submerged Nozzles

Another example of importance to liquid-liquid extraction processes in the mass transfer behavior of forming drops. The drops considered here were of Isopar-H* formed in a continuous water phase. The drops were in a size range of 5 to 10 mm. in diameter and were formed at velocities of about 15 cm./sec. through orifices 3.4 mm. in diameter. Typical Reynolds numbers for these drops were approximately 200 to 300 (based on orifice diameter, dispersed phase flow rate through the orifice, and dispersed phase kinematic viscosity).

Measurements of the surface and volume of the forming drops as functions of time were made from high-speed motion pictures (1,560 frames/sec.) taken of the drops with a Fastax camera. Figure 10 shows a typical cycle of drop growth and detachment.

The drops were considered to be shapes of revolution. The length of the drop along its axis of revolution and its radius perpendicular to this axis at four preselected points were measured from sequences of photographs such as those shown in Figure 10. From these measurements and the fact that the width of the drop is zero at its tip, a Gaussian quadrature scheme was developed and used to approximate the integrals necessary to calculate the surface area and volume of the drops. A test of the quadrature procedure on shapes of known volume and surface gave agreement to an accuracy of one part in a thousand. Because of the possibility of asymmetry of the drop about its assumed axis of revolution, the radius of the drop silhouette on the photograph was measured both to the left and to the right of the assumed axis of revolu-

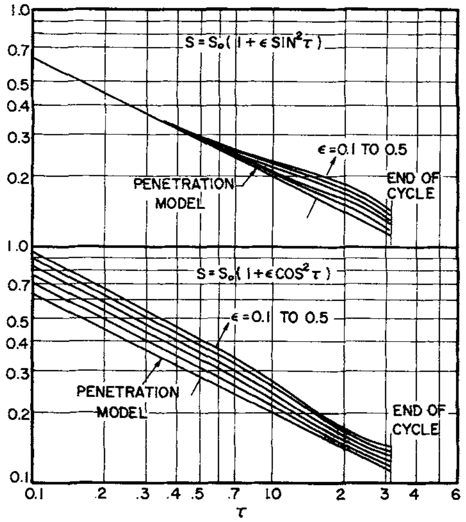

Fig. 9. Time variation of dimensionless time-average mass transfer coefficient for one-half cycle of oscillation ($\tau = \pi$).

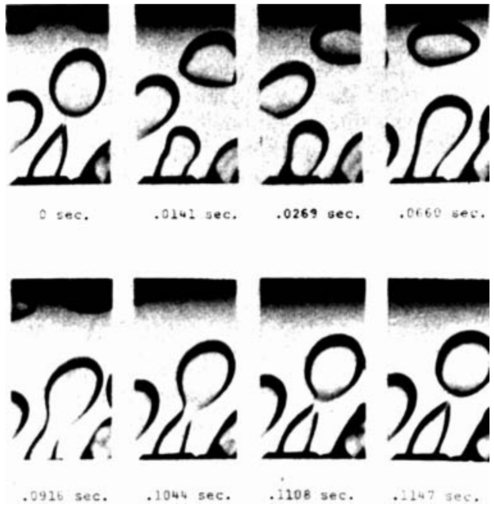

Fig. 10. Cycle of drop growth and detachment at submerged nozzles.

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[*] A highly refined straight chain paraffinic hydrocarbon with a boiling range of 340° to 375°F. obtained on special order from Humble Oil and Refining Co., Baytown, Texas.

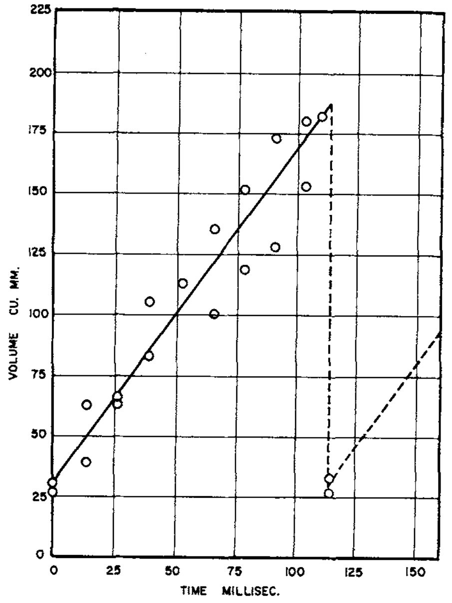

Fig. 11. Surface-time relation for drop formation at submerged nozzles.

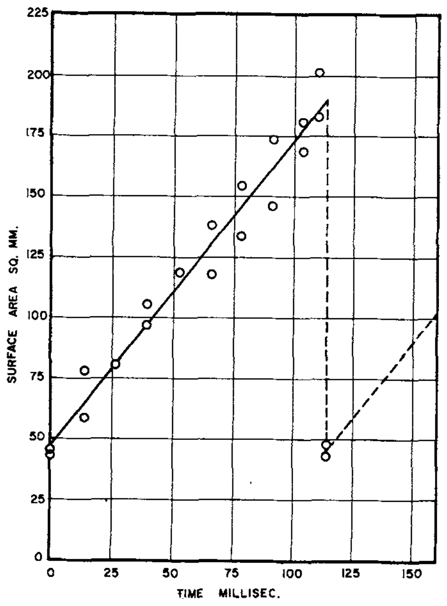

Fig. 12. Volume-time relation for drop formation at submerged nozzles.

tion. This gave two estimates for the true surface and volume which presumably lay somewhere in between.

Figures 11 and 12 show the relationship between the surface area and volume of the drop and the time for one cycle of growth and detachment. The two values of surface area and volume appearing at each time value on the graphs are the values calculated from the left and right radii of the drops. The curves shown on the figures are the best quadratic fit to the data (best in the sense of the minimum sum of squares of deviations). For both the volume and the surface area, the best quadratic was indistinguishable from the best straight line. For the volume, both the straight line and the quadratic gave a correlation coefficient (ratio of the standard deviation of the calculated to the experimental values) of 0.96, and for the surface area both gave a correlation coefficient of 0.98. For this reason, it was assumed for the basis of all subsequent calculations that the volumetric flow rate into the drop and the surface growth rate were linear with time. The determination of linear surface growth is consistent with the findings of Dixon and Russell (*19*), who observed a reasonably constant ratio of surface area to volume.

The application of the surface-stretch penetration model of this paper to this phenomenon is possible because observations made with fine dye filaments injected into the drop during formation indicated that turbulence was absent and that the flow was laminar. This is consistent with the measured orifice Reynolds numbers of 200 to 300. The surface-stretch model is particularly appropriate and appealing because the extreme simplicity of Equation (48) governing surface growth simplifies calculations, and previous calculations of mass transfer during drop formation appear to lack a firm physical and theoretical basis.

Calculations based on the assumption of uniform linear surface growth with the surface-stretch penetration model and Equation (48) used were made for a typical drop. This model predicts a dimensionless mean mass transfer coefficient for the formation period, $\bar{\kappa} = 5.35$. The corresponding value for the simple penetration model with no account taken of the stretching of the surface gave a value of $\bar{\kappa} = 2$.

The assumption of continual formation of completely fresh surface as first proposed by Groothuis and Kramers (*18*) yields

$$\bar{\kappa} = \frac{2}{\sqrt{\tau}} + \frac{4}{3}\beta\sqrt{\tau} \qquad (70)$$

which predicts $\bar{\kappa} = 6.07$. Clearly, continual formation of a fresh surface gives a higher mass transfer coefficient than does the stretching of the already present surface. However, the two results differ from their average by only 6%.

Estimates were made of the relative importance of the formation and rise periods for mass transfer in a sieve-plate extractor operating in this laboratory. These estimates were based on residence-time measurements on this equipment. For a 24-in. tray spacing, the predicted number of transfer units during formation was only 8% of that during drop rise. Although the extractor is of somewhat unusual design (that is, rectangular in cross section), it is believed that comparable results could be expected in conventional cylindrical columns.

Order of magnitude calculations were made to compare the instantaneous mass transfer coefficients for the continuous phase predicted by the surface-stretch and fresh-surface models to that predicted by empirical boundary-layer correlations of flow past a solid cylinder. These calculations show that because of the growth of the surface, the mass transfer coefficient is upwards of fifteen times as high as expected from boundary-layer calculations, even at the end of the formation cycle.

Thus, the surface-stretch model has shown the importance of changing surface area in mass transfer calculations for forming drops and has indicated the inadequacy of boundary-layer approximations for these calculations. The assumption of uniform stretching of the surface gives results which are in reasonably good agreement with the assumption of continual formation of new surface and differs from the results of the latter assumption in the direction expected.

At present there appears to be no suitable data on mass transfer during drop formation which can be utilized for comparison with the above predicted values. Experimental work to obtain such data is in progress.

Sample Calculations

Complete sample calculations (Appendix *B*) for the above cited examples are available elsewhere.[*]

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NOTATION

a_p = amplitude of oscillation of the major axis taken from reference *12*, L
a = length of major semiaxis; a_0 = initial value, L
b = length of minor semiaxis; b_0 = initial value, L
D_{Ai} = multicomponent diffusivity of pair $A - i$ based on free energy driving force, L^2/t
$\mathcal{D}_{Ai}$ = binary diffusivity for pair $A - i$; $i = D$ drop phase; $i = C$ continuous phase, L^2/t
E = extraction efficiency = $\left[\dfrac{\rho_{Ain} - \rho_{Af}}{\rho_{Ain} - \rho_A^*}\right]_D$
$f(\tau)$ defined by Equation (15)
$g(\tau)$ defined by Equation (36)
j_{Ay} = mass flux of species A relative to mass average velocity, M/tL^2
k_0 = instantaneous local mass transfer coefficient at a given time and position on the interface, L/t
k_i = time-average individual phase mass transfer coefficient; $i = D$ drop phase; $i = C$ continuous phase, L/t
K_i = time-average overall mass transfer coefficient; $i = D$ drop phase; $i = C$ continuous phase, L/t
$m_A(t)$ = total amount of A transferred in time t, M
m = $(\rho_{A0} - \rho_A^*)_D/(\rho_{A0} - \rho_{A\infty})_C$
n_{A0y} = y component of the mass flux of species A relative to stationary coordinates, M/L^2t
S = area of time-dependent surface, L^2
S_0 = characteristic reference area for constant surface, L^2
t = time, t
t_0 = characteristic constant for particular system being considered, t
t_F = drop formation time, t
v_y = y component of mass average velocity normal to the boundary for a moving surface element, L/t
x = rectangular coordinate, L
y = distance measured from the interface into the phase of interest, L
z = rectangular coordinate, L

Greek Letters

β = dimensionless surface growth rate, a constant
γ = dimensionless coefficient of the quadratic contribution to surface growth rate, a constant
ϵ = dimensionless amplitude factor characteristic of particular system being considered and of assumed surface-time relation
$\epsilon_0, \epsilon_1, \epsilon_2$ = dimensionless constants defined by Equations (51*a*) through (51*c*)
ζ = dimensionless variable defined by Equation (37)
η = dimensionless position variable defined by Equation (9)
θ = dummy variable in Equation (42)
κ = dimensionless mass transfer coefficient
ρ_i = mass concentration of species i, M/L^3
τ = dimensionless time variable defined by Equation (10)
χ = dimensionless concentration profile defined by Equation (8)
ω = frequency of oscillation, t^{-1}

Overlines and Superscripts

— = time-average value
$*$ = equilibrium value

Subscripts

A = solute species in a binary system
C = continuous phase
D = dispersed phase
loc = local transfer coefficient
F = formation period
0 = interface value except as otherwise noted
∞ = bulk or cup mixing value for given phase
in = initial condition, at start of extraction
f = final condition, at end of extraction

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APPENDIX A: INTERFACIAL VELOCITY DUE TO A CHANGE IN INTERFACIAL AREA

As a simple justification of Equation (2) consider a small flat element of surface $\Delta x \Delta z$ moving with the local fluid velocity. The direction of the y axis is perpendicular to element

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[*] Deposited as document 8886 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

$\Delta x \Delta z$ and pointing into the phase of interest. The fractional rate of change of area of surface element $\Delta x \Delta z$

$$\frac{1}{\Delta x \Delta z}\left(\frac{\partial S}{\partial t}\right)_{\text{avg}} = [\Delta x(v_z|_{z+\Delta z} - v_z|_z) + \Delta z(v_x|_{x+\Delta x} - v_x|_x)]\frac{1}{\Delta x \Delta z} \quad \text{(A1)}$$

By taking the limit as $(\Delta x, \Delta z)$ approach zero, this expression may be rewritten for any point u, w in the interfacial surface as

$$\left(\frac{\partial \ln S}{\partial t}\right)_{u,w} = \frac{\partial v_x}{\partial x} + \frac{\partial v_z}{\partial z} \quad \text{(A2)}$$

For an incompressible fluid this expression may be rewritten with the aid of the continuity relation to obtain

$$\left(\frac{\partial \ln S}{\partial t}\right)_{u,w} = -\frac{\partial v_y}{\partial y} \quad \text{(A3)}$$

Since $(\partial \ln S/\partial t)_{u,w}$ is independent of y, we may write for negligible net transfer across the interface

$$v_y = -y(\partial \ln S/\partial t)_{u,w} \quad (2)$$

For curved surfaces this relation will be only approximately correct and should only be used for small y, more specifically for y small compared with the local radii of curvature. This is consistent with the limitations on the penetration theory of mass transfer.

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The Evaporation of Drops of Pure Liquids at Elevated Temperatures: Rates of Evaporation and Wet-Bulb Temperatures

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The rates of evaporation and the wet-bulb temperatures have been correlated for drops of pure liquids evaporating in streams of high-temperature air. The four liquids studied were acetone, benzene, *n*-hexane, and water. The drops were of the order of a millimeter in diameter and were suspended in a free jet of dry, vapor-free air that ranged in temperature from 27° to 340°C. Reynolds numbers ranged from 24 to 325. Corrections to the Nusselt number to account for the heat lost to the outwardly diffusing vapor ranged up to about 35%.

The correlation of the phenomena characterizing the evaporation of liquid drops under conditions leading to high heat and mass fluxes would be of interest in many fields of commercial importance, but probably the greatest utility of such a correlation would be in relation to spray-drying and droplet-combustion studies. The present paper presents a simplified approach to such a correlation, being concerned solely with the evaporation of isolated pure liquid drops at atmospheric pressure.

DROP EVAPORATION RATES

A heat balance taken on a differential shell about a spherically symmetrical model of a drop undergoing steady state evaporation leads to the differential equation (constant film properties)

$$\frac{d^2T}{dr^2} + \left[\frac{2}{r} - \frac{w\, c_{P,v}}{4\pi\, k\, r^2}\right]\frac{dT}{dr} = 0 \quad (1)$$

with the boundary conditions of $r = R_1$, $T = T_1$, and at $r = R_0$, $T = T_0$. This equation implies that k, the thermal conductivity of the film, is constant. In the general case, however, k will be a function of both composition and temperature. In order to maintain the simple form of Equation (1), it is therefore necessary to define an effective average thermal conductivity of the film, to be evaluated at some appropriate composition and temperature which are as yet undefined. By designating this average thermal conductivity of the film as k_f, the solution of Equation (1) is (*13*)

$$\frac{T - T_1}{T_0 - T_1} = \frac{\exp(-a'(R_1/r)) - \exp(-a')}{\exp(-a'(R_1/R_0)) - \exp(-a')} \quad (2)$$

Equation (2) may now be differentiated to obtain the temperature gradient at the drop surface:

$$\left.\frac{dT}{dr}\right|_{R_1} = \frac{a'\,\Delta T}{R_1}[\exp(a'(1 - R_1/R_0)) - 1]^{-1} \quad (3)$$

The expression for the heat balance at the drop surface is

$$k_f\, A_1 \left.\frac{dT}{dr}\right|_{R_1} = w\,\Delta H_s \quad (4)$$

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