Mass and Heat Transfer from Drops in Liquid-liquid Extraction

A. E. HANDLOS and T. BARON
Shell Development Company, Emeryville, California

Mass and heat transfer rates in extraction are studied theoretically and experimentally for the practical range of the variables involved. For the particular but typical case of liquid drops moving through another liquid a simple correlation for the over-all mass transfer coefficient is presented, which holds with a probable error of 20%.

Included are systems in which the rate is limited by either coefficient, as well as systems in which both coefficients are significant. The correlation, valid for both directions of transfer with either phase dispersed, is useful for the extrapolation of performance from system to system in a given piece of equipment. Also, together with correlations for transfer area and effective driving force, it is part of the information needed for design.

The rate of transfer in any exchange process depends on three factors: the area of contact, the effective driving force, and the transfer coefficient. Occasionally these factors can be evaluated with comparative ease; for example, in a heat exchanger the area is determined solely by the geometry of design, the local driving force is the temperature difference, which may be easily found, and the transfer coefficient in the form of a Nusselt number is known from experiment as a function of the Reynolds and Prandtl numbers.

In principle, rates of mass transfer in an extraction device can be calculated in the same way. The source of the difficulty is that the three factors discussed above cannot be evaluated easily. For instance, no simple relation is known for the contact area and such design variables as throughput of the phases and geometry of distributor and contactor. Actually, the average contact area depends on the frequency distribution of sizes of the dispersed phase and the rate of rise (or fall) of the latter relative to the continuous phase, as well as on the circulation rates of the continuous phase. All these factors are determined by fluid-mechanical processes which are too complicated to be subject to theoretical evaluation. At the same time the large number of experiments necessary for an empirical attack have not yet been carried out.

Similar difficulties are encountered in averaging whatever driving force determines the rate of mass transfer at a given point, because in most extraction apparatus the circulation of the continuous phase results in flow patterns which are neither truly countercurrent nor truly concurrent. The circulation patterns are rarely known and even if they were known, the evaluation of the proper average driving force would be difficult mathematically.

In contrast to the large amount of experimental and theoretical work on transfer coefficients for heat transfer, the experimental and theoretical information available on mass transfer coefficients in extraction is inadequate. This lack of information is due partly to the discouraging results of the earlier investigators. Correlations along patterns well established in heat transfer and simple mass transfer situations have been unsuccessful. Slight differences in experimental conditions have unexplainably large effects. Furthermore, investigators in different laboratories obtain occasionally divergent results.

The three factors controlling extraction rates—the area, the average driving force, and the transfer coefficient—are best considered separately. This paper is a study of the mass transfer coefficient, which was chosen as the first step because simple conditions can be devised in which the transfer area and average driving force are controlled. Specifically, the study is restricted to mass or heat transfer to single drops. In the first phase of the work described below, the data in the literature were examined and correlated on the basis of mathematical models set up for this purpose. These correlations were promising, but some further work was necessary because the range of experimental conditions covered in the literature was small and in some cases the conditions were incompletely specified. The new data agree satisfactorily with the correlations derived, the root mean square percentage error being approximately 30%.

MASS TRANSFER AND THE THERMODYNAMICS OF IRREVERSIBLE PROCESSES

The object of this paper is to study the mass transfer from a liquid drop to the continuous phase of another liquid in which it is freely rising or falling. Observation and theory indicate that during the course of their motion the drops execute small vibrations about an approximately spherical equilibrium configuration. Although this motion may play a significant role in determining the rate of mass transfer, it is hardly significant as far as the area of transfer is concerned. In the range of drop diameters of interest, say from 2 to 5 mm., the amplitude of this motion is small and therefore the area of the drop may be taken as that of a sphere of equivalent volume. If desired, small distortions may be taken into account in the transfer coefficient.

The problem of choosing a proper driving force is a more subtle one. Two general schemes are known for the treatment of irreversible phenomena: the kinetic theory of matter and the thermodynamics of irreversible processes. Unfortunately, the kinetic theory of liquids is not sufficiently advanced to furnish a reliable guide in the evaluation of diffusion in liquids. One must turn, therefore, to the theory of irreversible thermodynamics, which, at least at first glance, appears to furnish a considerable amount of information. In the absence of cross effects, the diffusion flux calculated from the rate of entropy production can be shown to be (*6*)

$$\vec{J}_1 = -L_1 \nabla(\bar{G}_1 - \bar{G}_2) \qquad (1)$$

where J_1 is the diffusion flux of species 1, and $\bar{G}_1$ and $\bar{G}_2$ are the chemical potentials of species 1 and species 2, respectively; L is a coefficient for which the theory furnishes no information. Equation (1) can be put into a more attractive form by use of the Gibbs-Duhem equation,

$$x_1\, d\bar{G}_1 + x_2\, d\bar{G}_2 = 0;\ P,\ T \text{ constant} \qquad (2)$$

and the material-balance relation,

$$x_1 + x_2 = 1 \tag{3}$$

Equation (1) may be put into either one of the following forms:

$$\vec{J}_1 = -\frac{L_1}{x_2} \nabla \bar{G}_1 \tag{4}$$

or

$$\vec{J}_1 = -\frac{L_1}{x_2} \left(\frac{\partial \bar{G}_1}{\partial x_1} \right)_{P,T} \nabla x_1 \tag{5}$$

The difficulty with these apparently useful equations is that the phenomenological coefficient L can by no means be assumed to be constant. This limitation is illustrated by applying the same theory to the familiar process of heat conduction in a solid. In this case the heat flux calculated from the rate of entropy production is given by

$$\vec{Q} = -\frac{L_2}{\theta^2} \nabla \theta \tag{6}$$

which, when compared to Fourier's law of heat conduction,

$$\vec{Q} = -\mathbf{k} \nabla \theta \tag{7}$$

yields the following expression for the phenomenological coefficient L_2:

$$L_2 = \mathbf{k} \theta^2 \tag{8}$$

In most solids the thermal conductivity **k** is known to increase with the temperature; therefore, the coefficient for heat transfer in these cases increases faster than the square of the temperature.

Similarly, the coefficient L_1 may well depend on the chemical potential as well as on other parameters such as the viscosity. In this case the gradient of any "well-behaved" function of the chemical potential may be used as a driving force, as (*46*, *53*)

$$\left. \begin{aligned} \vec{J}_1 &= -L_3 \nabla f(\bar{G}_1) \\ &= -L_3 \frac{df(\bar{G}_1)}{d\bar{G}_1} \nabla \bar{G}_1 \\ L_3 &= \frac{L_1}{x_2} \left[\frac{df(\bar{G}_1)}{d\bar{G}_1} \right]^{-1} \end{aligned} \right\} \tag{9}$$

is equivalent to Equation (4).

From a practical point of view, the function $f(\bar{G}_1)$ is best chosen in such a way that the quantity

$$L_3 \frac{df(\bar{G}_1)}{d\bar{G}_1}$$

remains as nearly constant as possible. The most convenient relationship is $f(\bar{G}_1) = c_1$, where c_1 is the concentration, because the concentrations can be calculated easily and are particularly suitable in the construction of various mathematical models especially when convection phenomena play an important role. On the other hand, as shown below, when the driving force is based on the gradient of activities the correlations improve significantly.

DEVELOPMENT OF CORRELATIONS

The method of correlation by dimensional analysis also has severe limitations in the present case. This is evident when one considers the variables which may be of significance in the mass transfer process. If mass transfer across both "films" is considered as a single problem, the variables are the diameter of the drop; the densities, viscosities, and diffusivities of the two phases; the relative velocity; interfacial tension; distribution ratio; and mass transfer coefficient. Since there are only three fundamental dimensions, one obtains from the Buckingham Pi theorem a relation among eight dimensionless numbers, such as

$$Nu = Nu\left(Re, Sc, We, \frac{\rho'}{\rho}, \frac{\mu'}{\mu}, \frac{D'}{D}, m \right) \tag{10}$$

The form of the functional relationship is unknown. The difficulty with this approach is apparent when one realizes that the number of dimensionless relationships involved is of the order of magnitude of the number of sets of independent data available. Another difficulty arises because the dimensionless ratios cannot be varied independently. Hence the number of combinations to be studied is very large. This difficulty remains when one considers the transfer across the inside and outside films separately. It is still necessary to determine two relations, each of which has the same form as Equation (10) except that the ratio of the diffusivities is eliminated.

In order to overcome these difficulties, it is convenient to construct simple mathematical models of transfer and to test these against the available data. It was recognized that the hydrodynamics of the flow pattern is markedly different in the regions inside and outside the drop. Accordingly, the inside and outside regions, i.e., the so-called "inside and outside films," are best treated separately. Of the various models tested, only the most successful ones for each film are presented.

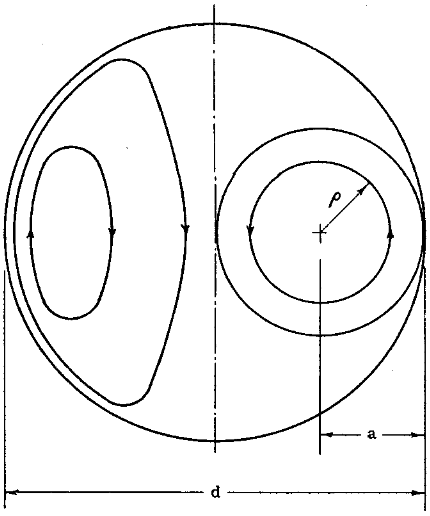

Fig. 1. Circulation patterns in drop.

First the transfer from the main body of the continuous phase to the interface of the drop is considered. A simple expression for the outside coefficient may be obtained in two different ways. If one considers a volume element of the continuous phase coming into contact with the drop at the forward stagnation point, as did Higbie (*20*), and calculates the unsteady state mass transfer for this volume element as it flows around the drop, the mass transfer coefficient turns out to be

$$Nu_0 = c\sqrt{Pe_0} \tag{11}$$

the constant c is determined by the time of contact between the two phases; this procedure is uncertain as the peripheral velocity is not known. On the other hand, the problem may be treated as a steady state boundary-value problem, in which the mass transfer coefficient can be calculated from the solution of the appropriate Fourier-Poisson equations. The difficulty here is that the steady state velocity distribution in the continuous phase is not known exactly and that furthermore the equations can be solved only when the velocity distribution follows some rather simple pattern. One may assume, as Pigford (*23*) did, that the radial velocity at any point is negligible and that the tangential velocity is everywhere equal to the velocity of the drop. With this assumption, the equations may be solved and one again obtains Equation (11) for the transfer coefficient. The constant c depends on the choice of the magnitude of the tangential velocity. Satisfactory agreement with the data are obtained when, as West (*50*) suggests, one calculates the time of contact between phases from the ratio $d/\bar{V}$. In this case Equation (11) becomes

$$Nu_0 = 1.13\sqrt{Pe_0} \tag{12}$$

In the correlation presented below, the mass transfer coefficient for the outside film is always evaluated from this equation.

The problem of mass transfer within the drop is much more difficult. The simplest approach is to assume that the drop is stagnant and to calculate the rate of mass transfer by solving the ordinary equations of diffusion. Unfortunately, the mass transfer coefficients calculated in this way are usually an order of magnitude too small. The reason for this discrepancy must be that there is motion within the drop. Kronig and Brink (*25*) have solved the Fourier-Poisson equations, using Hadamard's (*19*) circulation patterns, which were obtained on the assumption of viscous flow. The results show little improvement, as the only effect of treating the problem this way is to reduce the effective diameter of the drop (by a factor of approximately two) to a length characteristic of the circulation pattern.

The difficulty here is that the motion is highly turbulent. (The Reynolds numbers are about 1,000.) Thus attempts to set up exact equations are futile. A schematic model which takes into account the vibrations of the drop as well as the circulation patterns within the drop is necessary. In the following exposition the tangential motion caused by circulation is combined with the assumed random radial motions due to vibrations in the evaluation of an eddy diffusivity which, with a simplified circulation pattern, is used in the solution of the appropriate Fourier-Poisson equations. While the model may indeed represent the salient physical features of the transfer process within the drop, the justification is, of course, the agreement with experimental data.

The existence of circulation inside the drop has been inferred from a comparison of the drag coefficients of rising (or falling) drops with those of solid spheres at the same Reynolds number (*2*, *22*). Circulation has also been observed directly (*12*, *13*, *39*, *42*) as well as oscillations of the drop (*21*, *27*), which would increase mixing within the drop. Garner, Skelland, and Hale (*11*) have shown that some trace impurities can retard circulation and that the transfer of a solute can promote circulation.

All these observations may be summarized by stating that the circulation which can be inferred from the usual equations of motion (*19*) has been frequently observed; however, in many instances, circulation did not develop. Whether this unexpected occasional rigidity is caused by trace impurities or some other surface effects is not known. No satisfactory criterion for the onset of circulation exists. The extraction model developed below is based on the assumption that the circulation in the drop is fully developed. Examination of the mass and heat transfer data in the light of this correlation showed no evidence of deviations that could be attributed to a lack of circulation.

Figure 1 shows a schematic drawing of the drop in which the streamlines of Hadamard are replaced by a system of tori shown in the cross section at the right. A particle is considered initially at a radius ρ. After a time sufficient for one circuit along a streamline, the particle is displaced to a point ρ' as a result of the assumed random radial motions. In the limiting case of complete mixing in one circulation period, the probability that a particle is found between ρ' and $\rho' + d\rho'$ is the ratio of the differential element of volume at ρ' to the total volume of the torus.

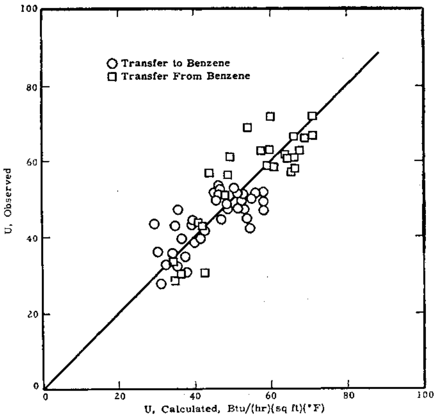

Fig. 2. Correlation of over-all heat transfer coefficients for benzene drops in water.

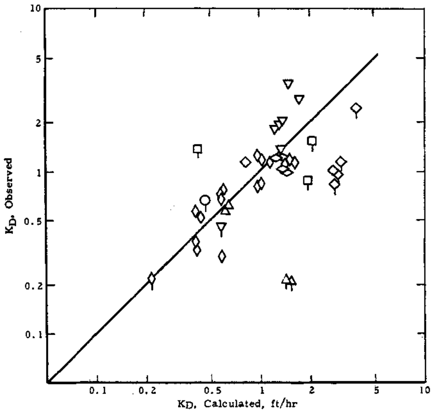

Fig. 3. Correlation of over-all mass transfer coefficients based on literature data; *see* Table 1 for key.

$$P(\rho')\,d\rho' = \frac{32\rho'}{d^2}\,d\rho' \qquad (13)$$

With the substitution

$$r = \frac{4\rho}{d} \qquad (14)$$

Equation (13) becomes

$$P(r')\,dr' = 2r'\,dr' \qquad (15)$$

Accordingly, the square of the displacement is

$$z^2 = \frac{d^2}{16}(r' - r)^2 \qquad (16)$$

If this experiment with the particle is repeated often, the mean square displacement is simply the expectation value of z^2, which is

$$\begin{aligned}\bar{z^2} &= \int_0^1 z^2(r')P(r')\,dr' \\ &= \frac{d^2}{8}\int_0^1 r'(r' - r)^2\,dr' \\ &= \frac{d^2}{96}(6r^2 - 8r + 3) \qquad (17)\end{aligned}$$

The characteristic time for the average displacement, i.e., the average circulation time is given by Kronig and Brink (*25*):

$$\bar{t} = \frac{16d}{3V}\left(1 + \frac{\mu_i}{\mu_0}\right) \qquad (18)$$

If the transfer process can be described by eddy diffusion, the transfer process is also represented by the Einstein equation, which connects the mean square deviation for a given time to the effective diffusivity:

$$E(r) = \frac{\bar{z^2}}{4\bar{t}} = \frac{dV}{2{,}048}\,\frac{(6r^2 - 8r + 3)}{(1 + \mu_i/\mu_0)} \qquad (19)$$

Multiplying and dividing by the molecular diffusivity, one obtains

$$E(r) = \frac{D \cdot Pe_i'}{2{,}048}(6r^2 - 8r + 3) \qquad (20)$$

where

$$Pe_i' = \frac{Pe_i}{(1 + \mu_i/\mu_0)} \qquad (21)$$

The equation of continuity in the chosen coordinate system is

$$\frac{\partial c}{\partial t} = \frac{16}{d^2}\cdot\frac{1}{r}\frac{\partial}{\partial r}\left(E \cdot r\,\frac{\partial c}{\partial r}\right) \qquad (22)$$

If

$$r = 1 - y \qquad (23)$$

then substituting Equations (20) and (23) into (22) yields

$$\frac{2{,}048d^2}{16DPe_i'}\,\frac{\partial c}{\partial t} \qquad (24)$$

$$= \left[\frac{1}{1-y}\,\frac{\partial}{\partial y}\,(1 - 5y + 10y^2 - 6y^3)\,\frac{\partial c}{\partial y}\right]$$

The boundary conditions are

$$\left.\begin{aligned} c &= c_0 \text{ at } t = 0,\ 0 \le y \le 1 \\ c &= 0,\ y = 0,\ t > 0 \end{aligned}\right\} \qquad (25)$$

The problem is thus reduced to one of finding the solution of Equation (24) with the boundary conditions given by Equations (25). This can be done by the method of separation of variables. If

$$c = T(t)\,Y(y) \qquad (26)$$

Equation (25) can be separated into two ordinary differential equations:

$$\frac{dT}{dt} = -\frac{16\lambda DPe_i'}{2{,}048d^2}\cdot T \qquad (27)$$

and

$$\frac{d}{dy}(1 - 5y + 10y^2 - 6y^3)\,\frac{dY}{dy} + \lambda(1 - y)\,Y = 0 \qquad (28)$$

TABLE 1. SUMMARY OF PUBLISHED MASS TRANSFER DATA

Solute	Continuous Phase	Dispersed Phase	Transfer to:	d cm.	V cm/sec	K_D obs	K_D calc.	Ref.	Symbol[a)]
						ft/hr			
Acetic Acid	Methyl iso-butyl ketone	Water	Water	.161	9.9	1.16	1.02	(29)	◊
				.161	9.9	0.83	1.01		
	"	"	"	.161	9.9	0.81	0.98		
	"	"	"	.161	9.9	1.23	0.98		
	"	"	"	.094	4.9	0.76	0.60		
	"	"	"	.094	4.9	0.30	0.59		
	"	"	"	.094	4.9	0.66	0.58		
	"	"	"	.094	4.9	0.70	0.58		
	"	"	"	.069	3.2	0.52	0.44		
	"	"	"	.069	3.2	0.33	0.42		
	"	"	"	.069	3.2	0.37	0.41		
	"	"	"	.069	3.2	0.57	0.41		
	"	"	"	.206	12.8	1.12	1.14		
	"	"	MIBK	.202	13.2	1.19	1.28		◇
	Water	MIBK	MIBK	.170	7.5	0.66	0.46		♀
	Water	MIBK	Water	.220	10.4	1.39	0.42		□̩
Acetic Acid	MIBK	Water	MIBK	.406	12.3	0.97	1.46	(26)	◇
	"	"	"	.342	11.6	1.00	1.40		◇
	Ethyl Acetate	"	Ethyl Acetate	.406	8.7	1.06	0.82		◇
	Isopropyl Ether	"	Isopropyl Ether	.452	15.9	0.56	0.61		△
	Isopropyl Ether	"	Isopropyl Ether	.344	15.1	0.61	0.64		△
Acetic Acid	MIBK	Water	Water	.295	13.2	1.11	1.62	(34)	◊
	"	"	"	.354	12.5	1.18	1.51		◊
	"	"	"	.418	11.9	1.09	1.42		◊
Acetic Acid	Water	Benzene	Water	.576	11.7	1.12	3.09	(44)	◇̩
	"	"	"	.557	11.1	0.93	2.94		
	"	"	"	.536	10.7	0.81	2.83		
Diethylamine	"	"	"	.554	11.4	0.21	1.53		△̩
	"	"	"	.378	9.4	0.21	1.44		
Acetic Acid	Water	Benzene	Water	.576	13.0	2.42	3.45	(4)	◇̩
	"	MIBK	"	.320	10.3	0.87	1.93		□
Pyridine	"	Benzene	"	.552	12.4	0.45	0.58		▽̩
Acetone	"	"	"	.552	12.9	1.18	1.40		◇̩
Benzoic Acid	"	"	"	.550	12.4	0.22	0.22		◇̩
Ethyl Acetate	Ethyl Acetate	Water	Water	.432	9.9	1.91	1.33	(24)	▽
	"	"	"	.426	10.1	2.03	1.37		
	"	"	"	.472	9.3	1.82	1.26		
	"	"	"	.284	12.9	2.81	1.75		
	"	"	"	.370	11.0	3.54	1.49		◇̩
	"	"	"	.350	10.0	1.38	1.36		◊̩
Acetic Acid	Water	MIBK	Water	.290	11.1	1.52	2.08	(40)	□̩
	"	Benzene	"	.390	10.6	0.98	2.83		◇̩

a) Applies only to Figure 3.

where λ represents any one of an infinite number of eigen values. Accordingly, the general solution of Equation (24) is

$$c(y, t) = c_0 \sum_1^\infty A_n Y_n \cdot \exp\left(-\frac{16\lambda_n DtPe_i'}{2{,}048d^2}\right) \qquad (29)$$

where c_0 is the initial concentration in the drop, A_n is constants to be evaluated from the boundary conditions, and Y_n is the eigen functions corresponding to λ_n.

It turns out that for the purpose of calculating mass transfer coefficients, the evaluation of the functional form of Y_n is unnecessary, as may be seen from the following argument. The ratio of the mass of solute at any time t to that at time 0 is

$$\frac{M(t)}{M(0)} = 2 \sum_1^\infty A_n^2 \exp\left(-\frac{16\lambda_n DtPe_i'}{2{,}048d^2}\right) \qquad (30)$$

A film coefficient may be defined by means of the material-balance relation:

$$\frac{d}{6}\cdot\frac{dc_i}{dt} = k_i(c_{i,in} - c_i) \qquad (31)$$

which, according to the boundary conditions expressed in Equations (25), may also be written as

$$\frac{d}{6}\cdot\frac{dc}{dt} = -k_i c \qquad (32)$$

the solution of which is

$$\frac{M(t)}{M(0)} = \exp\left(-\frac{6k_i t}{d}\right) \qquad (33)$$

Now, according to the general theory of eigen-value problems, each successive eigen value in Equation (30) is larger than the preceding one. In the present case the second eigen value is already large enough to permit use of the first term only in Equation (30) for the free-rise period. Then, by comparison of Equations (30) and (33), the mass transfer coefficient may be expressed as a function of the first eigen value:

$$k_i = \frac{16\lambda_1 DPe_i'}{(6)(2{,}048)d} \qquad (34)$$

The problem is thus reduced to finding the lowest eigen value of Equation (28). This may be done conveniently by the Ritz method (*28*),

$$Y_n = \sum_1^i c_i y^i \qquad (35)$$

being used as an approximate eigen function. With $j = 5$, the value obtained for the lowest eigen value is $\lambda_1 = 2.88$. Equation (34) then becomes

$$k_i = \frac{0.00375V}{(1 + \mu_1/\mu_0)} \qquad (36)$$

which may be rearranged into the more convenient form

$$Nu_i = 0.00375Pe_i' \qquad (37)$$

which is used in the correlation.

Equation (37) indicates that the Nusselt number for the inside is proportional to the Peclet number. In correlating the data, it was found that this proportionality holds and that the proportionality constant is that expected from the model. This unexpected agreement is probably fortuitous.

DISCUSSION OF RESULTS

In the models discussed above, the tacit assumption was made that the driving force for mass transfer in either phase is identified with the gradient of concentration. Although this is convenient in the formulation of the models, the choice of concentration gradients as driving forces in mass transfer may not be the best choice. The mass transfer problem is also complicated by possible resistances associated with transfer across the interface for which no allowance has been made. In the case of heat transfer to or from liquid drops, these difficulties probably do not exist. The driving force is clearly the temperature gradient. Furthermore, the models developed are directly applicable, with the simple substitution of temperature for concentration and thermal diffusivity for diffusivity.

Garwin and Smith (*14*) present data which may be directly compared with the models used here. In this case heat was transferred to and from benzene droplets rising in water and the results were reported as over-all coefficients of heat transfer. In Figure 2 the over-all coefficients of heat transfer are compared with those calculated from the individual coefficients given by Equations (12) and (37) by use of the usual relation:

$$\frac{1}{U} = \frac{1}{C_{p,0}\rho_0 k_0} + \frac{1}{C_{p,i}\rho_i k_i} = \frac{1}{h_0} + \frac{1}{h_i} \qquad (38)$$

The agreement is highly satisfactory; actually it is about as good as it is in the simple case of heat transfer to solid boundaries. There is no effect of the direction of transfer, which justifies the influence of the viscosity ratio in the mass transfer coefficient as it appears in Equations (37) and (21).

In Figure 3 the literature data on extraction from single drops are compared with values predicted from the correlations. A summary of these data is given in Table 1. The calculated values of the over-all coefficient were evaluated for the mass transfer equivalent of Equation (38):

$$\frac{1}{K_D} = \frac{m_{i,0}}{k_0} + \frac{1}{k_i} \qquad (39)$$

With some notable exceptions, the cor-

TABLE 2. SUMMARY OF EXPERIMENTAL RESULTS

Solute	Continuous Phase	Dispersed Phase	Transfer to:	$d_{3,2}$ cm	V cm/sec	$\bar{m}_{in}$ a)	Concentration		Activity		Calc. K_D ft/hr	Percent Inside Control	Symbol d)
							Observed K_D ft/hr	$R_{N,t}$	Observed K_D ft/hr	$R_{N,t}$			
Acetic Acid	Water	Benzene	Water	.503	11.3	.023	.63	.972	2.51	.998	3.02	95	○̍
	"	"	Benzene	.440	13.9	.043	2.17	.991	2.57	.981	3.60	94	○̩
	Benzene	Water	Water	.407	10.8	13.8	.17	.891	.35	.487	.22	14	○-
	"	"	Benzene	.409	10.8	37.7	.13	.974	.13	.922	.09	5	-○
Benzoic Acid	Water	Benzene	Water	.521	13.8	9.86	.12	.925	-	-	.18	5	□̍
	"	"	Benzene	.533	13.1	3.55	.44	.991	-	-	.45	12	□̩
	Benzene	Water	Water	.414	16.6	.100	1.92	.944	-	-	2.52	92	□-
Phenol	Water	Benzene	Water	.511	11.4	2.69	.63	.991	.56	.981	.59	19	◇̍
	"	"	Benzene	.505	11.2	2.76	.33	.978	.33	.978	.58	19	◇̩
	"	"	Water	.526	14.4	2.58	.59	.987	.57	.988	.63	16	◇̍
	"	"	Benzene	.527	15.1	2.56	.68	.993	.65	.946	.72	17	◇̩
	Benzene	Water	Water	.422	11.3	.362	2.53	.975	1.45	.971	1.68	82	◇-
	"	"	Benzene	.416	12.2	.394	1.56	.999	2.45	.999	1.58	84	-◇
Acetone	Water	Benzene	Water	.481	10.6	.939	1.12	.999	1.49	.998	1.29	44	△̍
	"	"	Benzene	.503	10.8	.970	.68	.949	1.17	.946	1.31	43	△̩
Salicylic Acid	Water	Benzene	Water	.525	12.9	2.12	.54	.999	-	-	.69	19	▽̍
	"	"	Benzene	.525	12.8	1.91	.59	.991	-	-	.75	21	▽̩
Acetic Acid	Water	Ondina 17 b)	Water	.616	13.4	.0012	.69	.975	.27	.945	.28	100	◇
	Water	A oil c)	Water	.581	14.0	.0015	1.11	.996	.59	.995	.66	100	◊

a. $m = c_i/c_0$; b. Ondina 17, $\rho = 0.87$, $\mu = 20$ centipoises; c. mixture of Ondina 17 and kerosene, $\rho = 0.837$, $\mu = 5.9$ centipoises; d. applies only to Figures 4 and 5.

relation appears to be promising. The discrepancies between some of the experimental points and the correlation may be due, at least in part, to any of the following causes:

1. The experimental over-all coefficients were evaluated from the slopes of the curves for the number of transfer units vs. time. For most of the experimental points shown in Figure 3, only two points on the curve were available. Under these circumstances, the accuracy of the observed over-all coefficients cannot be estimated. Moreover, it is not always certain that the data were actually taken in the free-rise period rather than during the period of formation.
2. The distribution coefficient which enters in Equation (39) is often a function of concentration and temperature. The temperature control in the experiments was frequently inadequate, and in many cases the temperature was not even reported. Also, many authors fail to provide information concerning the variation of the distribution coefficient with concentration. This information is necessary in the evaluation of the proper average driving force. In these cases, the single distribution ratio given by the authors has been used and the average driving force evaluated from the logarithmic mean.
3. Failure of the correlation because the concentration gradient is not the true driving force.
4. There may be significant interfacial effects.

In addition to these uncertainties, the data used are not comprehensive. For a given solute and solvent pair, four cases are possible depending on the choice of the dispersed phase and the direction of transfer. For most of the systems only one of these has been studied. Additional experiments under controlled conditions were necessary.

The authors' data, given in Table 2, are compared with the correlation in Figures 4 and 5. In Figure 4 the observed over-all coefficients are evaluated on the basis of concentration differences for the driving force. As shown in Table 2, the new data cover all possible transfer situations and also represent a greater range of the viscosity ratio than the earlier data.

Figure 5 shows that the activity difference is a more suitable driving force than concentration difference. Unfortunately, activity data are not available for all systems used in these experiments. Consequently, there are fewer points in Figure 5 than in Figure 4. It is evident that for those systems for which activity data are available agreement of the experimental data with the theory is much better. Since the data include all possible transfer situations and there is a large range of physical properties and distribution coefficients, the agreement between the experimental and predicted values of the over-all transfer coefficient as shown in Figure 5 and the simplicity of the correlations recommend the methods presented. However, the correlations are limited to the period of free rise and do not apply to the transfer during the formation and coalescence of the drop, which is different from the free-rise period and requires separate study.

TABLE 3. EFFECT OF ADDITIVES ON MASS TRANSFER COEFFICIENT

Solute: acetic acid
Continuous phase: water
Dispersed phase: benzene
Transfer to: water

Additive	Concentration, wt. %*	d_3, cm.†	V, cm./sec.	$m_{in,avg.}$	K_D, ft./hr.	N, initial†
None		0.483	10.6	0.026	2.17	1.09
Dioctyl phthalate	0.05–0.005	0.490	11.5	0.023	2.50	1.07
Santicizer 141	0.05–0.005	0.498	11.3	0.023	1.73	1.06
Dibutyl tin dilaurate	0.05–0.005	0.481	10.6	0.024	0.81	0.74
Barium ricinoleate	0.0002	0.500	10.8	0.024	0.41	0.67

*In benzene phase.
†Based on activity.

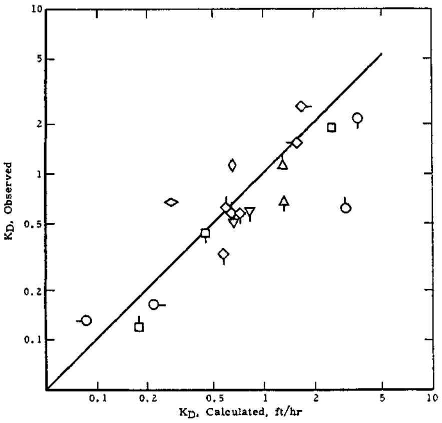

Fig. 4. Correlation of over-all mass transfer coefficients based on concentration; *see* Table 2 for key.

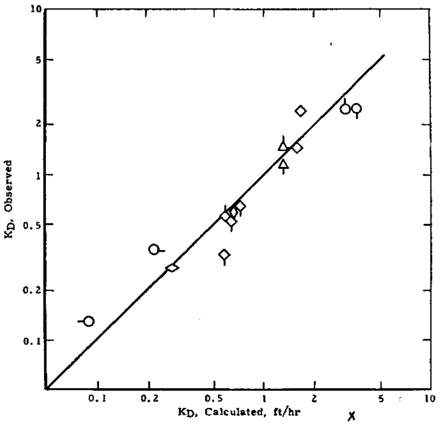

Fig. 5. Correlation of over-all mass transfer coefficients based on activity; *see* Table 2 for key.

EFFECT OF ADDITIVES ON EXTRACTION RATES

The possibility of an additional resistance to transfer at the interface has been mentioned. One type of interfacial resistance is indicated in the work of Drickamer (*9*), who measured in a static system the rates of self-diffusion of sulfur dioxide between normal heptane and sulfur dioxide and of sulfuric acid between phenol and water. A second kind of interfacial resistance is shown by the work of West (*50, 52, 31, 44, 47*) and Coulson and Skinner (*5*). West, who attempted to repeat the work of Sherwood (*40*) on the transfer of acetic acid from benzene drops to water, observed transfer coefficients which were about one-third those reported by Sherwood.

Apparently the reported reduction in over-all transfer coefficients was caused by the presence of certain benzene-soluble substances that were extracted from a Tygon tubing used in the apparatus. Accordingly in the correlations presented here no data obtained in apparatus containing Tygon tubing were used. To study this effect quantitatively, however, the authors obtained data which show the effect of certain high-molecular-weight materials representative of components of Tygon. The data are shown in Table 3, for the extraction of acetic acid from benzene drops to water. There is a marked difference between the extraction rate in the presence of barium ricinoleate as compared with that in the presence of dioctyl phthalate. The data for other additives lie between these two extremes. While all these additives are surface-active agents and reduce the interfacial tension between benzene and water, the concentrations of the additives were kept at such a low level that the reduction in interfacial tension seems hardly significant. Recent experimental work by Garner and Hale (*11*) confirms that the effect of additives is not one of change in interfacial tension.

EXPERIMENTAL METHODS

The experimental techniques used in extraction studies are simple and apart from minor variations are essentially the same for all investigators. A comparison of the data in Figures 3 and 4 suggests that the experimental techniques themselves are not important. In general, the drops are formed at a submerged capillary orifice and rise or fall through a column of the continuous phase. The dispersed phase after collection, is analyzed for the amount of solute transferred from the continuous phase. The drop size is determined by measuring the volume of a known number of drops or by other means, such as photographing the drops and comparing them to a reference scale. Usually an amount of dispersed phase just sufficient for analytical purposes is passed through the column, on the assumption that the concentration of the solute in the continuous phase does not change significantly.

In analyzing their data, previous investigators generally assumed that the distribution coefficient and hence the over-all coefficient of transfer are constants for the system. The equation for transfer is

$$\frac{dc_i}{dt} = -\frac{6K_D}{d}(c_i - c^*) \qquad (1a)$$

where c^* is defined in terms of the concentration of solute in the bulk phase. For a constant K_D simple integration gives

$$N = \frac{6K_D}{d}\,t = \ln\frac{(c_i - mc_0)_1}{(c_i - mc_0)_2} \qquad (2a)$$

As the number of transfer units calculated in this way includes the end effects, at least two column heights must be studied to permit an evaluation of K_D. The over-all transfer coefficient for the free-rise period is then determined by

$$K_D = \frac{d}{6}\left(\frac{\Delta N}{\Delta t}\right) \qquad (3a)$$

When only two column heights are studied, the constancy of the over-all film coefficient, which is implicitly assumed in Equation (3*a*), cannot be examined. K_D may vary because of a choice of column heights such that the formation period is included in the free-rise period or because of variations in the distribution coefficients. Moreover, with only two column heights the accuracy of the data cannot be estimated. The assumption that the concentration in the continuous phase does not change in the course of the experiment is often not valid. While the total amount of solute transferred is usually too small to change the bulk concentration significantly, the possibility of high local concentrations in the path of the drops must be considered. It is surprising that no one has taken two or more samples of dispersed phase in succession and attempted an extrapolation to zero time. When three or more column heights were studied, a regression line of the number of stages against time can be obtained by statistical methods and the slope can be used in Equation (3*a*).

In derivation of Equation (1*a*) the assumption was that the drop is spherical and the ratio 6/*d* is the ratio of area to volume. The validity of this assumption has been examined by several authors. In general, the observed deviations from the sphere do not change the volume-surface ratio by more than 10%, and it is agreed that this error is a secondary one.

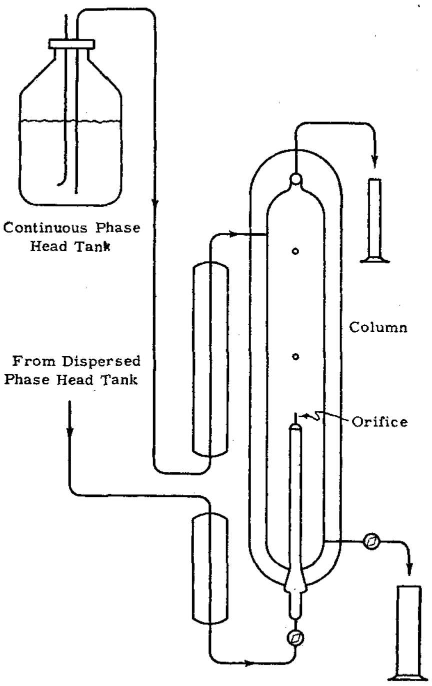

Fig. 6. Schematic drawing of equipment.

The data on the transfer of heat between benzene and water were obtained from data on spray-tower operation. In the calculation of the over-all transfer coefficients the calculated relative velocity of the dispersed phase to the continuous phase was used and it was assumed that there was no circulation within the column. The end effects were avoided by measuring the rate of heat transfer to the continuous phase in the column. A similar technique has been applied to mass transfer (*15, 16, 38*).

The present data were obtained in the equipment which is shown schematically in Figure 6. The extraction column was 3 in. in diameter. Countercurrent flows of the continuous and dispersed phases were used, the flow rate of continuous phase (3 to 5 liters/hr.) being controlled by means of pressure drop in the lines and the constant head supply and dispersed rate being adjusted to give a rate of drop formation of 30 ± 1 drops/min. The exchangers and the column jacket were maintained at constant temperature by circulating water from a thermostat at 25.0 ± 0.1°C.

Four column heights were studied, 35, 55, 75, and 85 cm., obtained by interchanging the orifice support tubes. A glass-capillary orifice, 0.041 in. I.D., was used when the organic phase was dispersed and an orifice of hypodermic tubing, 0.028 in. O.D., was used when the aqueous phase was dispersed. Reference marks were fired on the inner jacket of the column for measurement of the velocity of the drops and as an aid in maintaining the level of dispersed phase. The velocity of the drops was measured by timing ten drops across a distance of 60 cm.

Samples of the dispersed and the continuous phases were taken after 1 and after 1¾ hr. of operation. Analytical results showed that steady state conditions prevailed between the two sample periods. During the sample period the drops were counted.

The acetic, benzoic and salicylic samples were titrated with 0.1 or 0.5*N* sodium hydroxide. The oil-phase samples were diluted with isopropyl alcohol to homogenize them. Acetone was analyzed with hydroxylamine hydrochloride, and phenol by a modification of the method of Koppeschaar (*45*).

The entire apparatus was made of glass and no stopcock grease was used in the system. Distilled water was used and the oil phases, benzene, Ondina 17, and *A* oil, were passed over silica gel to remove surface-active agents. These precautions were taken to avoid the effect of additives such as were described earlier. All solutes were chemically pure grades.

In spite of the precautions taken to obtain reproducible drop sizes, a 5 to 10% variation in drop volume was observed. A part of this variation was caused by errors in measuring the total volume of the drops sampled. The Sauter mean diameter (*30*) was used as the average diameter. The root mean square deviation of the observed drop diameters was 2 to 3%.

TREATMENT OF DATA

When the distribution coefficient was independent of concentration the over-all coefficient was calculated by Equation (3*a*). In the general case the distribution coefficient is dependent on concentration and Equation (1*a*) is not valid. The equation of transfer is

$$\begin{aligned}\frac{d}{6}\frac{dc_i}{dt} &= -k_i(c_i - c_{i,in})\\ &= -k_0(c_{0,in} - c_0) \qquad (4a)\end{aligned}$$

The following self-explanatory steps indicate the method of elimination of the interfacial concentrations $c_{i,in}$ and $c_{0,in}$:

$$-k_i(c_i - c_{i,in}) = -k_0(c_{0,in} - c_0) \qquad (5a)$$

$$m_{in} = \frac{c_{i,in}}{c_{0,in}} \qquad (6a)$$

$$c_{0,in} = \frac{k_0c_0 + k_ic_i}{k_im_{in} + k_0} \qquad (7a)$$

$$\begin{aligned}\frac{d}{6}\frac{dc_i}{dt} &= -k_0(c_{0,in} - c_0)\\ &= -k_0\left[\frac{k_0c_0 + k_ic_i}{k_im_{in} + k_0} - c_0\right] \qquad (8a)\end{aligned}$$

or

$$\begin{aligned}\frac{d}{6}\frac{dc_i}{dt} &= -\frac{k_0}{\kappa + m_{in}}(c_i - m_{in}c_0)\\ &= -K_D(c_i - m_{in}c_0) \qquad (9a)\end{aligned}$$

TABLE 4. DISTRIBUTION-DATA PARAMETERS FOR TRANSFER SYSTEMS AT 25°C.

Solute	Solvents*	m_∞	α
Acetic acid	Methyl isobutyl ketone	0.510	0.051
Acetic acid	Isopropyl ether	0.182	0.023
Acetic acid	Benzene	0.0113	0.017
Acetic acid	Ondina 17	0.00119	0.00957
Acetic acid	"*A*" oil	0.00150	0.00120
Benzoic acid	Benzene	1.52	912
Salicylic acid	Benzene	1.31	237
Acetone	Benzene	0.899	0.114
Phenol	Benzene	2.54	6.53
Pyridine	Benzene	2.59	313
Diethylamine	Benzene	0.583	11.6

*Other solvent is water.

where

$$K_D = \frac{k_0}{\kappa + m_{in}} \qquad (10a)$$

and

$$\kappa = \frac{k_0}{k_i} \qquad (11a)$$

It is necessary to relate m_{in}, the distribution coefficient at the interface to the bulk concentrations c_i and c_0. For many systems in which the organic phase is dispersed, the effect of concentration on the distribution coefficient may be described adequately by an equation of the form

$$m = \frac{c_i}{c_0} = m_\infty + \alpha c_0 \qquad (12a)$$

Therefore, also

$$m_{in} = \frac{c_{i,in}}{c_{0,in}} = m_\infty + \alpha c_{0,in} \qquad (13a)$$

Combining Equations (5*a*), (11*a*), and (13*a*) one obtains the quadratic

$$m_{in}^2 + m_{in}(\kappa - m_\infty) - (m_\infty \kappa + \alpha c_i + \alpha \kappa c_0) = 0 \qquad (14a)$$

The physically acceptable solution of this is

$$m_{in} = \frac{m_\infty - \kappa}{2} + \left[\frac{(m_\infty - \kappa)^2}{4} + m_\infty \kappa + \alpha c_i + \alpha \kappa c_0\right]^{1/2} \qquad (15a)$$

A number of stages is defined by integrating Equation (9*a*):

$$N' = \int_{c_{i,1}}^{c_{i,2}} \frac{(\kappa + m_{in})\, dc_i}{(c_i - m_{in} c_0)} = -\frac{6}{d} k_0 \int_1^2 dt = -\frac{6}{d} k_0 t \qquad (16a)$$

The integration must be performed with the aid of Equation (15*a*).

For a given set of values $c_{i,1}$, $c_{i,2}$, c_0, α, m_∞ and t, Equations (15*a*) and (16*a*) can be used to calculate either coefficient if the other is known. Values of m_∞ and α for the systems which are reported here are given in Table 4. No single set of data can give information by which both the inside and outside coefficients can be found. However, consistent correlations can be developed by relying on experiments in which either the inside or the outside resistance is controlling.

For the purpose of comparing the data with the correlations an average experimental over-all coefficient was calculated in the following way. First κ was calculated from the correlations. With this, a series of values of N' were calculated from Equations (15*a*) and (16*a*) for various values of the time t. With the coefficient k_0, evaluated from the relation $k_0 = (d/6)\, dN'/dt$, an average over-all coefficient was calculated from the expression

$$\overline{K_D} = \frac{k_0}{n+1} \sum_n \frac{1}{\kappa + m_{in,n}} \qquad (17a)$$

where n refers to the nth value of t.

When the aqueous phase is dispersed, an analogous procedure may be followed. If

$$m' = \frac{c_0}{c_i} = m_\infty' + \beta c_i \qquad (18a)$$

and therefore also

$$m_{in}' = \frac{c_{0,in}}{c_{i,in}} = m_\infty' + \beta c_{i,in} \qquad (19a)$$

then Equation (20*a*),

$$m_{in}' = \frac{(m_\infty' - 1/\kappa)}{2} + \left[\frac{(m_\infty' - 1/\kappa)^2}{4} + \frac{m_\infty'}{\kappa} + \frac{\beta c_i}{\kappa} + \beta c_0\right]^{1/2} \qquad (20a)$$

and Equation (21*a*),

$$N'' = \int_{c_{i,1}}^{c_{i,2}} \frac{(m_{in}' + 1/\kappa)\, dc_i}{m_{in}'(c_i - c_0/m_{in}')} = -\frac{6}{d} k_i t \qquad (21a)$$

take the place of Equations (15*a*) and (16*a*) respectively. In Table 2 N' and N'' are listed as N as the choice of Equation (16*a*) or (21*a*) is definite.

The use of the activity as the potential in the equations for transfer causes certain difficulties. The transfer equations are derived on the basis of the concentration as the potential, and integration of the equations is possible only because the flux and the potential are expressed in terms of the same conserved quantity. However, the following plausible (although essentially empirical) approach was found to result in a successful correlation.

The activities of the solute in each phase being assumed the same at equilibrium, it is possible to write the transfer equation in terms of the activities at a point. Since the distribution ratio at the interface is approximately equal to the ratio of the activity coefficients $\bar{\gamma}_0/\bar{\gamma}_i$, where $\bar{\gamma}$ is an average coefficient in a given phase,

$$\vec{J} = \frac{1}{\bar{\gamma}_i} k_i(a_i - a_{in}) = \frac{1}{\bar{\gamma}_0} k_0(a_{in} - a_0) = \frac{1}{\bar{\gamma}_i} K_D(a_i - a_0) \qquad (22a)$$

and

$$\frac{1}{K_D} = \frac{m_{in}}{k_0} + \frac{1}{k_i} \qquad (23a)$$

At this point the number of transfer units is defined as

$$N = \int_{a_{i,1}}^{a_{i,2}} \frac{da_i}{a_i - a_0} = -K_D \cdot \frac{A}{v} \int_1^2 dt \qquad (24a)$$

Since the activity of the solute in the continuous phase in the experiments changes very little, a simpler form of Equation (24*a*) is

$$N = \ln \frac{(a_0 - a_i)_1}{(a_0 - a_i)_2} \qquad (25a)$$

The advantage of defining N by Equations (23*a*) and (24*a*) depends on the possibility of a successful correlation for K_D. As Figures 4 and 5 show, these definitions are preferable to the less empirical definitions contained in Equations (2*a*), (16*a*), and (21*a*).

The correlation coefficients R for regression lines of the number of stages against time are given in Table 2. In no case has the last significant figure been rounded upward. In general, the values of R are close to unity, an indication of a good correlation. As a measure of the agreement between the observed and the calculated values of K_D based on activity, the root mean square of the percentage error, 100 (observed—calculated)/calculated, was found to be 30%. The correlation coefficient of the observed value of K_D on the calculated K_D is 0.932 and the corresponding standard error of estimate is 0.32.

For the systems with acetic acid as solute, the liquid-liquid equilibrium data were measured. The liquid-vapor data of Othmer, Silvis, and Spiel (*32*) and the infinite-dilution data of Pierotti (*36*) for acetic acid in water were fitted by a Van Laar equation to give activity coefficients. The equilibrium data were used to obtain activity coefficients in the acetic acid–benzene system.

Data for activities for water-acetone were calculated from the liquid-vapor data of Beare, McVicar, and Ferguson (*1*) and correlated in the dilute region by $\ln \gamma_1 = 1.89x_2^2$. The distribution data of Gross and Schwarz (*18*) were used.

In the calculation of activities the effect of mutual solubility of the solvents was neglected. For the system phenol-water-benzene the phases were treated as three component mixtures in terms of the three binary systems. Data for the phenol-benzene system are given by Dickinson and Lassetre (*8*), distribution data are given by Philbrick (*35*), and data for the benzene-phenol system are given by (*7*). The water-phenol system and the water-benzene system were fitted by Van Laar equations from solubility data which are given in the International Critical Tables.

No consistent set of activity data could be developed for the benzoic acid in the benzene-water system in spite of available solubility, freezing-point (*3, 37*), and liquid-vapor data (*48, 49*). The freezing-point data show a molecular weight of 150 to 160 (formula weight = 122) even at the lowest concentrations. Water is reported to increase the association of benzoic acid (*54*), but the distribution data indicate a reduction in degree of association. The distribution data were obtained from Smith (*41*) and Farmer (*10*).

For salicylic acid between water and benzene the distribution data of von Szyskowski (*43*) were used. This solute-solvent system is interesting from the standpoint that the solubility of salicylic acid in benzene increases 31% when the benzene is saturated with water. Available data were insufficient for a calculation of activities.

Diffusivities were calculated by the correlation of Wilke (*52*). In addition, some experimental values for diffusivities were obtained by the diaphragm-cell method, which is described by Gordon (*17*). These data are shown in Table 5 with the values calculated by the Wilke correlation. The correlation proposed by Othmer and Thakar (*33*) was also examined, and the deviation of the calculated values from the experimental values was found to be about the same for both correlations.

TABLE 5: DIFFUSIVITIES FOR TRANSFER SYSTEMS AT 25°C.

Solute	Solvent	D, sq. cm./ sec. × 10^5*	
Acetic acid	Benzene	2.78	(1.97)
	Water	1.15	(1.14)
Acetone	Benzene	2.62	(2.53)
	Water	1.07	(1.25)
Benzoic acid	Benzene	1.76	(1.34)
	Water	0.75	(1.02)
Phenol	Benzene	2.16	(3.27)
	Water	0.88	(0.96)
Salicylic acid	Water	0.75	

*Figures in parentheses are experimental values; other values are based on Wilke correlation.

ACKNOWLEDGMENT

The authors gratefully acknowledge the contributions of R. L. Maycock, whose early studies of extraction from single drops provided them with useful data and thoughtful observations.

NOTATION

A = drop area
a = activity
C_p = specific heat
c = concentration, mass/unit volume
D = diffusivity
d = drop diameter
E = eddy diffusivity
$\bar{G}$ = chemical potential
h = transfer coefficient in heat transfer
$\vec{J}$ = generalized flux
K = over-all mass transfer coefficient
k = transfer coefficient in mass transfer
$\mathbf{k}$ = thermal conductivity
m = phase-distribution ratio
r = $\rho/(d/4)$
t = time
v = drop volume
x = mole fraction
z = displacement or distance
L = generalized conductivity
N = number theoretical stages
N', N'' *See* Equations (16*a*) and (21*a*).
$\vec{Q}$ = heat flux
R = correlation coefficient

$$= \frac{n \sum N_i t_i - \sum N_i \sum t_i}{\sqrt{[n \sum N_i^2 - (\sum N_i)^2][n \sum t_i^2 - (\sum t_i)^2]}}$$

U = over-all heat transfer coefficient
V = drop velocity
α *See* Equation (12*a*).
β *See* Equation (18*a*).
γ = activity coefficient
κ = k_0/k_i
λ = eigen value of Equation (28)
ρ = radius of circulation patterns, also density
θ = temperature
μ = viscosity
Nu = Nusselt number, kd/D or $hd/\mathbf{k}$
Pe_i = inside Peclet number, dV/D
Pe_i^1 = modified inside Peclet number, $Pe_i/(1 + \mu_i/\mu_0)$

Subscripts

i = inside, or dispersed, phase
0 = outside, or continuous, phase
in = at interface
∞ = at infinite dilution
1, 2 = inlet and outlet of column; used as i, 1 to indicate dispersed phase at inlet
D = based on dispersed phase

Superscripts

$\bar{\ }$ = average

LITERATURE CITED

1. Beare, W. G., G. A. McVicar, and J. B. Ferguson, *J. Phys. Chem.*, **34**, 1310 (1930).
2. Bond, W. N., and D. A. Newton, *Phil. Mag.* **5**, No. 7, 794 (1928).
3. Bury, C. R., and H. O. Jenkins, *J. Chem. Soc.*, p. 688 (1934).
4. Clark, R. O., B.S. thesis, Univ. Washington, Seattle (1951).
5. Coulson, J. M., and S. J. Skinner, *Chem. Eng. Sci.* **1**, 197 (1952).
6. De Groot, S. R., "Thermodynamics of Irreversible Processes," pp. 101-105, Interscience Publishers, Inc., New York (1951).
7. Derr, E. L., private communication.
8. Dickinson, R. G., and E. N. Lassetre, *J. Am. Chem. Soc.*, **61**, 54 (1939).
9. Drickamer, H. G., and L. H. Tung, *J. Chem. Phys.*, **30**, 6, 10 (1952).
10. Farmer, R. C., *J. Chem. Soc.*, **83**, 1446 (1903).
11. Garner, F. H., and A. R. Hale, *Chem. Eng. Sci.*, **2**, 157 (1953).
12. Garner, F. H., and A. H. P. Skelland, *Trans. Inst. Chem. Engrs.*, **29**, 315 (1951).
13. ———, *Chem. Eng. Sci.*, **4**, 149 (1955).
14. Garwin, Leo, and B. D. Smith, *Chem. Eng. Progr.*, **49**, 591 (1953).
15. Geankoplis, C. J., and N. A. Hixson, *Ind. Eng. Chem.*, **42**, 1141 (1950).
16. Gier, T. E., and J. O. Hougen, *Ind. Eng. Chem.*, **45**, 1362 (1953).
17. Gordon, A. R., *Ann. N. Y. Acad. Sci.*, **46**, 285 (1945).
18. Gross, P. and K. Schwarz, *Monatsh. Chemie.*, **55**, 287 (1930).
19. Hadamard, J., *Compt. rend*, **152**, 1735 (1911).
20. Higbie, Ralph, *Trans. Am. Inst. Chem. Engrs.*, **31**, 365 (1935).
21. Hu, Shengen, and R. C. Kintner, *A.I.Ch.E. Journal*, **1**, 42 (1955).
22. Hughes, R. R., and E. R. Gilliland, *Chem. Eng. Progr.*, **48**, 497 (1952).
23. Johnstone, H. F., R. L. Pig-ord, and J. H. Chapin, *Trans. Am. Inst. Chem. Engrs.*, **37**, 95 (1941).
24. Kopinsky, S., M.S. thesis, Mass. Inst. Technol., Cambridge (1949).
25. Kronig, R., and J. C. Brink, *Appl. Sci. Research*, **A2**, 142 (1950).
26. Licht, William, Jr., and J. Conway, *Ind. Eng. Chem.*, **42**, 1151 (1950).
27. Licht, William, Jr., and G. S. R. Narasimhamurty, *A.I.Ch.E.Journal*, **1**, 366 (1955).
28. Margenau, Henry, and G. M. Murphy, "The Mathematics of Chemistry and Physics," pp. 253-259, D. Van Nostrand Company, New York (1943)
29. Maycock, R. L., private communication.
30. Mugele, R. A., and H. D. Evans, *Ind. Eng. Chem.*, **43**, 1317 (1951).

31. Oberholtzer, W., B.S. thesis, Univ. Washington, Seattle (1951).
32. Othmer, D. F., S. J. Silvis, and A. Spiel, *Ind. Eng. Chem.*, **44**, 1864 (1952).
33. Othmer, D. F., and M. S. Thakar, *Ind. Eng. Chem.*, **45**, 589 (1953).
34. Pansing, W. F., Ph.D. thesis, Univ. Cincinnati, Cincinnati, Ohio.
35. Philbrick, F. A., *J. Am. Chem. Soc.*, **56**, 2581 (1934).
36. Pierotti, G. J., private communication.
37. Rodebush, W. H., and J. M. Peterson, *J. Phys. Chem.*, **32**, 709 (1928).
38. Ruby, C. L., Ph.D. thesis, Princeton Univ., Princeton, N. J. (June, 1952).
39. Savic, P., Nat. Research Lab., Rept. MT-22, Ottawa, Canada (1953).
40. Sherwood, T. K., J. E. Evans, and J. V. A. Longcor, *Ind. Eng. Chem.*, **31**, 1144 (1939).
41. Smith, H. W., *J. Phys. Chem.*, **26**, 256 (1922).
42. Spells, K. E., *Proc. Phys. Soc. (London)*, **B65**, 541 (1952).
43. von Szyszkowski, B., *Z. physik. Chem.*, **131**, 175 (1928).
44. Tanaka, T., B.S. thesis, Univ. Washington, Seattle (1951).
45. Treadwell, F. P., and W. T. Hall, "Analytical Chemistry," 9 ed., Vol. II, p. 633, John Wiley and Sons, New York (1942).
46. Ubbelohde, A. R., *Trans. Faraday Soc.*, **33**, 599 (1937).
47. Vinkenes, R. A., B.S. thesis, Univ. Washington, Seattle (1951).
48. Wall, F. T., and F. W. Banes, *J. Am. Chem. Soc.*, **67**, 898 (1945).
49. Wall, F. T., and P. E. Rouse, Jr., *ibid.*, **63**, 3002 (1941).
50. West, F. B., A. J. Herrman, A. T. Chong, and L. E. K. Thomas, *Ind. Eng. Chem.*, **44**, 621 (1952).
51. West, F. B., P. A. Robinson, A. C. Morgenthaler, Jr., T. R. Beck, and D. K. McGregor, *Ind. Eng. Chem.*, **43**, 234 (1951).
52. Wilke, C. R., *Chem. Eng. Progr.*, **45**, 219 (1949).
53. Wirtz, K., *Z. Naturforsch.*, **3a**, 672 (1948).
54. Wright, W. G., *J. Chem. Soc.*, 683 (1949).

Void Fractions in Two-phase Steam-water Flow

H. S. ISBIN, NEIL C. SHER, and K. C. EDDY

University of Minnesota, Minneapolis, Minnesota

The pressure-drop characteristics associated with one liquid and one gaseous phase flowing concurrently in a pipe or tube have yet to be understood. The operation of evaporators, boilers, and condensers has long stimulated interest in the pressure drop of steam-water mixtures, and more recently this specialized case of one-component, two-phase flow has received even greater attention from the applications in cooling nuclear reactors. The two-phase-flow problems have not been amenable to thorough theoretical analyses, and therefore empirical and semiempirical correlations have attained unusual prominence in practical applications. The present investigation employs a new research tool for the study of two-phase-flow structure.

A variety of geometric flow patterns is possible. Bergelin, Alves, and others have classified these patterns according to visual appearance; whereas the Martinelli classifications were based upon whether the flow in each phase was termed *viscous* or *turbulent*. The distinction between viscous and turbulent flow in either phase is rather arbitrary, and if the Reynolds number for one phase, calculated on the basis of the total tube diameter, is greater than 2,000, the flow in the phase is called *turbulent*. This investigation is confined to the study of annular flow, in which most of the liquid is found in an annular ring surrounding the central vapor core and the flow in each phase is turbulent.

Boiling or flashing occurs when superheated water rises in an insulated vertical tube at atmospheric pressure. For a separated two-phase flow geometry, the mean linear steam velocity may exceed that of the water. The fraction of the tube occupied by the steam (void fraction) at a given cross section cannot be obtained directly from a determination of the thermodynamic quality. Void fractions, however, must be known for the estimation of the pressure drops due to head and momentum changes.

Void fractions and pressure drops for steam-water flows were measured in an 0.872-in. I.D. vertical tube at atmospheric pressure over a quality range of 0 to 4%. The test section was the hot leg of a natural-circulation loop, and the inlet liquid flow rate ranged from 1 to 3 ft./sec. A new technique for measuring void fractions was used, and the method utilizes the difference between the gamma-ray absorption coefficients of water and steam.

A comprehensive survey of two-phase frictional pressure drops has been prepared by Isbin, Mosher, and Moen (*9*), and an additional brief survey is given by Marchaterre (*13*). The experimental data of this investigation are compared with the predictions of the homogeneous and Martinelli models.

The treatment of the vapor-liquid mixture as a homogeneous fluid is called the homogeneous, fog, or Woods model (*12*). The two phases are assumed to be in equilibrium, average specific volume and viscosity properties are used, and the mean linear velocities of the vapor and the liquid are assumed to be equal. For example, the total pressure drop for a steam-water mixture flowing vertically upward in a channel of uniform cross section is approximated by the following equation for steady-state conditions:

$$\underbrace{p_n - p_{n+1}}_{\substack{\text{static}\\ \text{pressure}\\ \text{drop}}} = \underbrace{\left(\frac{z_{n+1} - z_n}{\bar{v}}\right)\frac{g}{g_c}}_{\substack{\text{head}\\ \text{pressure}\\ \text{drop}}} + \underbrace{\frac{G^2}{g_c}(v_{n+1} - v_n)}_{\substack{\text{momentum}\\ \text{pressure}\\ \text{drop}}} + \underbrace{\frac{\bar{f}G^2\bar{v}(z_{n+1} - z_n)}{2g_cD}}_{\substack{\text{frictional}\\ \text{pressure}\\ \text{drop}}} \qquad (1)$$

where

$$v_n = q_n v_{sn} + (1 - q_n)v_{wn} \quad \text{and} \quad \frac{1}{\mu_n} = \frac{q_n}{\mu_s} + \frac{1 - q_n}{\mu_w}$$

Fanning friction factor $\bar{f}$ is evaluated at an average Reynolds number average property between stations, for example, $\bar{v} = (v_n + v_{n+1})/2$. $\bar{f}$ and $\bar{q}$ also are average values.

(The use of an arithmetic mean was sufficiently accurate for the conditions selected.)

The Martinelli method is characterized by two basic postulates: (1) for the case of steady, two-phase flow involving no radial pressure gradients, the frictional pressure drop is assumed to be the same in both the liquid and gas phases, and (2) at any instant the sum of the volumes occupied by the liquid and gas must be equal to the total volume of the tube. In terms of the fractional cross-sectional areas occupied by each phase, $R_l + R_g = 1$.

Martinelli and Lockhart (*11*) presented a two-phase frictional pressure-drop correlation in the form of related dimensionless parameters. The param-

---

Neil C. Sher is now at Westinghouse Atomic Power Division, Pittsburgh, Pennsylvania, and K. C. Eddy is at Esso Standard Oil Company, Linden, New Jersey.