Mass Transfer in Drops Under Conditions That Promote Oscillation and Internal Circulation

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Single drops supported on hypodermic tubing have been studied in a wind tunnel to determine the effect of drop oscillation on mass transfer. The systems studied for the case where internal resistance controls consisted of absorption of sulfur dioxide gas by drops of glycerine, propylene glycol, and ethylene glycol. The results may be expressed in terms of effective diffusivity.

No significant effect was noted in glycerine, whereas the glycols gave effective diffusivity values two to eight times greater than theoretically calculated values of molecular diffusivities.

Frequencies, amplitudes, and internal circulation velocities in the drops were studied by cinematography.

The effect of oscillation on external mass transfer coefficients was studied by sublimation of naphthalene spheres in air. In the cases where the vibrational velocity was less than the stream velocity, no effect was noted; this is in agreement with heat transfer studies.

A technique has been developed for studying the effect of internal circulation on effective diffusivity by the use of forced circulation through a drop suspended on hypodermic tubing. A pseudofilm thickness is determined as a function of circulation velocity and presents a means of predicting effective diffusivities for the systems studied. This technique has been demonstrated, giving results in fair agreement with the correlation of Garner and Lane.

The phenomenon of mass transfer between drops and their surrounding medium has been the subject of many studies. Most of this work has been carried out on drops falling freely through a gas or another liquid phase.

Falling drops generally undergo distortion from the spherical shape and at times exhibit internal circulation. One would expect that transport rates would be enhanced if a greater contacting area and/or bulk transport within the drop occurred. Various observers have confirmed this result in cases where deformation of the drop occurred or where internal circulation existed (*4, 7, 9, 10, 14, 16, 18, 19, 20, 26*).

Literature, extensively reviewed by Finlay (*11*), shows that oscillation has only small effects on surface area and thus does not contribute significantly to mass transfer by this means. Studies on heat transfer (*2, 10, 23, 25, 28*) indicate that the effect of oscillation on outside heat transfer coefficients should be small or negligible under the conditions being considered, and one might expect this to also apply to mass transfer. Finally most previous work indicates that internal circulation is a significant mechanism.

It is possible to make rough estimates of frequency and amplitude of oscillations, based on free falling liquid spheres (*24*). The relationship between oscillation and internal circulation is inadequately characterized, but one may calculate an approximate circulation velocity as a function of oscillation as well as an approximate velocity due to skin friction (*20*). Finally relationships exist that may be used to predict in a limited fashion the effect of internal circulation on mass transfer coefficients (*4, 18, 22*).

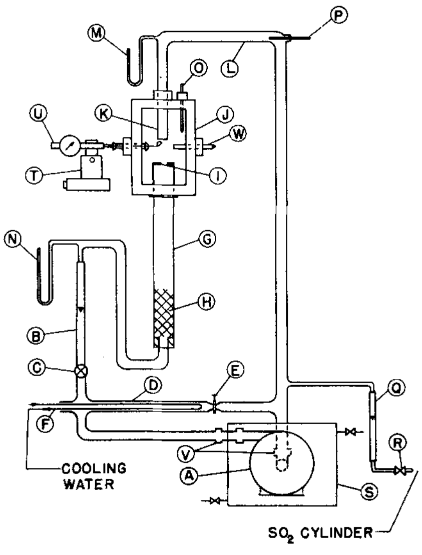

Fig. 1. Wind tunnel assembly for internal circulation studies. A—centrifugal blower, 15,000 rev./min., high efficiency, miniature; B—rotameter; C—flow control needle valve; D—bypass line; E—screw clamp flow control on flexible connection; F—cooling coil, 3/16-in. copper tubing, 4 ft. long; G—aluminum approach tube 1.75-in. diameter by 18 in. long; H—woven copper packing; I—orifice plate, 1/8-in. thick, 3/8-in. orifice, 1/8-in. radial curvature suction flare; J—working section; K—exit tube, 10-mm. I. D.; L—return line; M—mercury U-tube manometer; N—mercury U-tube manometer; O—mercury thermometer; P—mercury thermometer; Q—sulfur dioxide makeup rotameter; R—makeup sulfur dioxide flow control needle valve; S—sealed box for blower; T—traversing stand; U—microburette; V—flexible connections between blower assembly and loop.

In previous studies of falling drops internal circulation was most pronounced at the time of drop formation and disengagement, followed by rapid damping during the drop fall. The short duration of high circulation rates in these cases makes their measurement impractical.

In the case of supported drops the drop distortion and circulation is caused by the action of the gas stream and would persist as long as the gas stream was sustained. Thus an extended duration is provided for studying the behavior of the drop, and the end effects become less important.

The specific aim of this study was to define the relationship of mass transfer to oscillation and internal circulation for the case of gas absorption by supported liquid drops. To this end it was necessary to determine how drops oscillate under different conditions, and how internal circulation behaves in oscillating drops.

This study is based on single drops supported on tubular elements and exposed to a stream of gas so as to create drop oscillation and internal circulation. An auxilliary technique of forced circulation through a drop suspended on tubing has been employed to measure and predict the effect of internal circulation of mass transfer. Finally the validity of applying heat transfer conclusions on effect of drop oscillation to external mass transfer coefficients is verified.

All studies utilized sulfur dioxide as the gas phase, with the exception of the sublimation of naphthalene which was conducted in air.

EXPERIMENTAL

Equipment and Procedures

Wind Tunnel for Internal Coefficients. A modified version of a closed loop wind tunnel used by Garner and Kendrick (*13*) as shown in Figure 1 was employed in this study. This system differs from Kendrick's primarily in the working section, shown in Figure 2, which here has a converging nozzle orifice to provide a flat velocity profile, a hypodermic needle support in conjunction with a precision microburette to measure and support the drop, and a shield or sealing mechanism to isolate the drop from the gas stream during drop formation and drop removal (*6*). The entire unit was housed in a walk-around hood. Potential flow was obtained in the working area by the use of an orifice of suction flare construction, ⅜ in. in diameter. The drops were positioned approximately 1 orifice diam. downstream from the orifice, so as to place them well within the potential cone, at which point a flat velocity profile of 5/16 in. in diameter was measured by a traversing pitot tube. The potential cone diameter at this point was over three times that of the largest drop size used. The microburette was specially fabricated, having a working capacity of 0.1 ml., with subdivisions of 0.0001 ml. The hypodermic tubes had outside diameters of 0.017, 0.028, and 0.037 in., with holes drilled perpendicular 1.5 mm. from the sealed ends, which were 0.006, 0.012, and 0.020 in. respectively.

The procedure consisted of filling the system with sulfur dioxide and then setting the gas flow at a predetermined rate. After the system and the microburette with absorbing liquid were allowed to come to ambient temperature, a drop of desired size was formed outside the box (Figure 2) in air and then positioned in the air-filled shield tube inside the working chamber. The shield could then be removed for exposure. At the end of exposure the procedure was reversed; the drop was rapidly withdrawn and plunged into a measured quantity of hydrogen peroxide solution for analysis. Transfer time amounted to about 2 sec., with no correction being made for this. Analysis consisted of measuring the conductance of the hydrogen peroxide solution containing the sulfur dioxide oxidized to sulfuric acid (*1, 6*). Experimental values of conductance were in agreement with literature (*27*).

The oscillatory motion of drops were studied by means of high-speed photography, with a 16-mm. high-speed motion picture camera at 400 to 1,200 frames/sec., and a 16-mm. camera at 64 frames/sec. with exposure of 1/500 sec. Aluminum particles suspended in the droplets allowed observation of internal circulation.

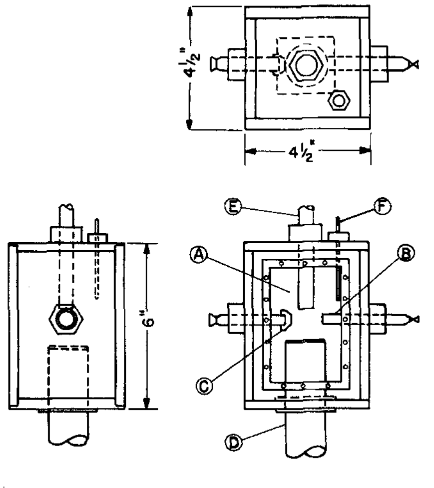

Fig. 2. Working section. A—flat glass windows; B—movable shield, 10-mm. glass tubing; C—guide tube with rubber stop; D—aluminum approach tube; E—exit tube; F—thermometer.

Wind Tunnel for External Coefficients. The effect of oscillation on the outside coefficient was measured by vibrating a solid sphere of naphthalene subliming into the gas stream. Figure 3 is a diagram of the wind tunnel and vibration assembly used. The gas stream was dry air. The naphthalene sphere was cast with a steel support wire imbedded into it (*5*). Amplitudes of ¼ in. and frequencies up to 20 cycles/sec. were employed. Higher frequencies led to disintegration of the spheres. The amount sublimed was measured by weighing on an analytical balance, and the sphere diameter was checked by a micrometer.

Controlled Forced Circulation Through a Drop. One means of creating a controlled amount of circulation in a drop is to suspend a drop from the tip of two concentric tubes and force fresh liquid into the drop through the central tube, withdrawing liquid through the annulus.

An all-glass system was constructed, which eliminated the mechanically moving parts and relied on displacement by density difference. This is shown in Figure 4. Mercury from reservoir (*C*) is allowed to run into reservoir (*E*) which contains the liquid to be exposed. The liquid is displaced through the rotameter (*F*), at a rate controlled by needle valve (*G*) through the center tube of the drop assembly (*I*) into the drop (*K*). As the liquid is forced into the drop, an equal amount is withdrawn through the drop assembly annulus back to the mercury reservoir (*C*) to take the place of the mercury that has left. Sulfur dioxide gas is replaced in the contact chamber (*J*) as it is absorbed by a calibrated syringe reservoir (*M*) whose plunger is advanced manually at a rate necessary to maintain the system pressure as indicated by the U-tube manometer (*L*). A microburette (*H*) is used to adjust the drop to the desired size.

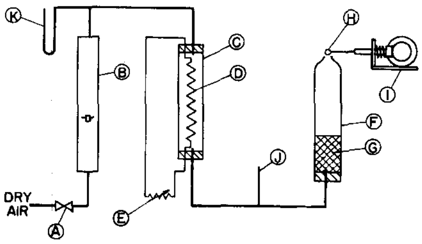

Fig. 3. Wind tunnel assembly for outside coefficient studies. A—air flow control needle valve; B—1 to 15 cu. ft./min. rotameter; C—heating chamber 16 in. long × 1.75 in. O.D. tube; D—250-ohm resistance heating wire; E—variac for heater; F—wind tunnel, Pyrex tube 16 in. long × 1.91 in. O.D., nozzle 0.78 in. I.D.; G—copper wire mesh for temperature and velocity stability; H—naphthalene sphere; I—sphere vibration assembly consisting of 1/10-hp. variable speed motor, eccentric cam, and spring loaded sphere support and guide; J—0° to 100°C. thermometer; K—mercury manometer.

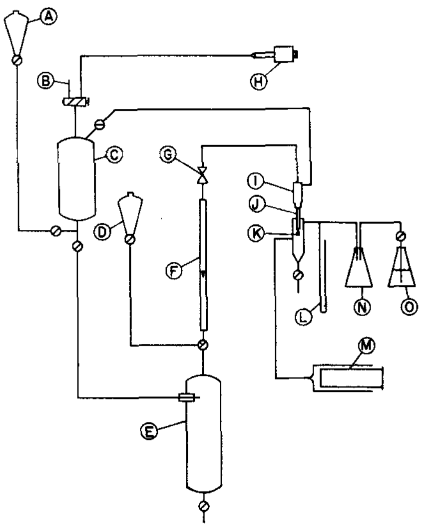

Fig. 4. Assembly for forced circulation through a drop. A—mercury load reservoir, 125 cc.; B—outlet for removing exposed liquid; C—upper reservoir for mercury feed and exposed liquid accumulation 1.8 in. I.D. × 4 in. long, 130 cc.; D—liquid load reservoir, 125 cc.; E—bottom reservoir for mercury accumulation and liquid feed 1.8 in. O.D. × 6 in. long, 200 cc.; F—liquid feed rotameter with special glass float for water, with tantalum float for propylene glycol; G—8-deg. taper needle valve; H—0.1-ml. microburette; I—drop support assembly; J—contact chamber, 10 cc.; K—liquid drop; L—mercury manometer; M—gas reservoir, 50-cc. syringe; N—gas surge chamber, 125 cc.; O—gas absorber, 125-cc. flask with caustic solution.

Materials

Reagent grade glycerine, propylene glycol, and ethylene glycol were used along with anhydrous sulfur dioxide gas.

Physical Properties

The solubility of sulfur dioxide in glycerine, propylene glycol, and ethylene glycol were experimentally determined and are presented in Figure 5 along with the solubility in water as obtained from literature (*21*).

Viscosities and densities were also experimentally determined.* Heats of solution for sulfur dioxide as measured for these liquids, expressed as calories per gram mole sulfur dioxide were 6,240 in propylene glycol, 6,455 in ethylene glycol, and 4,075 in glycerine to an accuracy of ± 2%.

Diffusivity values used in this study were calculated by the method of Wilke and Chang (*30*), with experimentally measured viscosities.

RESULTS

Outside Coefficients

The effect of vibration on outside coefficients is demonstrated by a com-

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* Results have been deposited as document 7353 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

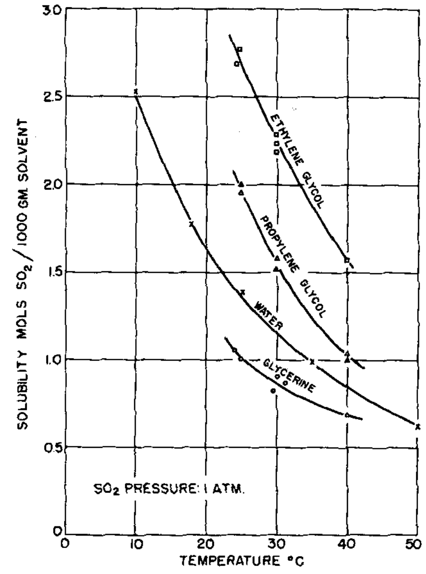

Fig. 5. Solubility of sulfur dioxide.

parison of the experimental coefficients with the theoretically calculated ones.

The experimental coefficients were calculated from data on the average rates of naphthalene subliming into air at 50°C. by means of the steady state relationship:

$$N_A = k_g(p_i - p_g) \qquad (1)$$

The empirical coefficients were calculated from Frossling's correlation (*12*)

$$\frac{k_c d}{D_v} = 2.0\,[1 + 0.276\,N_{Re}^{1/2}\,N_{Sc}^{1/3}] \qquad (2)$$

and

$$k_g = \frac{k_c}{RT} \qquad (3)$$

The theoretical and experimental values of k_g are plotted in Figure 6. No significant difference can be detected between stagnant and vibrating spheres. The experimental data fit the theoretical curves satisfactorily.

Previous investigations on the effect of vibration on heat transfer (*2, 23, 25, 28*) indicate that the vibration has no effect on heat transfer coefficient when the vibration velocity is less than the air flow velocity. It would be reasonable to expect a similar relationship for mass transfer. In the naphthalene experiments the maximum frequency was 20 cycles/sec. with an amplitude of 1/4 in., which yielded a vibration velocity of 0.84 ft./sec. This is much lower than the lowest air flow of 5 ft./sec. that was used.

In the case of oscillating liquid drops in this study the extremes observed were maxima of 75 cycles/sec. and 1/16 in. amplitude, which would yield a vibration velocity of less than 1 ft./sec. Thus one would not expect any significant increase of outside coefficient by virtue of the oscillation when dealing with forced gas convection past drops at moderate or high velocities; this is supported by the experimental results of this study.

Internal Coefficients

Oscillations of Drops. The nature of the oscillations observed falls into two categories which are depicted in Figure 7. Type I and II represent the view perpendicular to the support element which is considered the *XY* plane. Types III and IV represent the head-on view which is considered the YZ plane. Table 1 lists the values observed.

The first category of oscillation is one that may be considered a deformation, comparable to an oblate-to-prolate spheroid, and is shown as Types I and III. It is common to free falling drops. The second category is one of displacement, shown as Types II and IV. This type is unique to supported drops and would be expected to contribute significantly to an effect upon mass transfer.

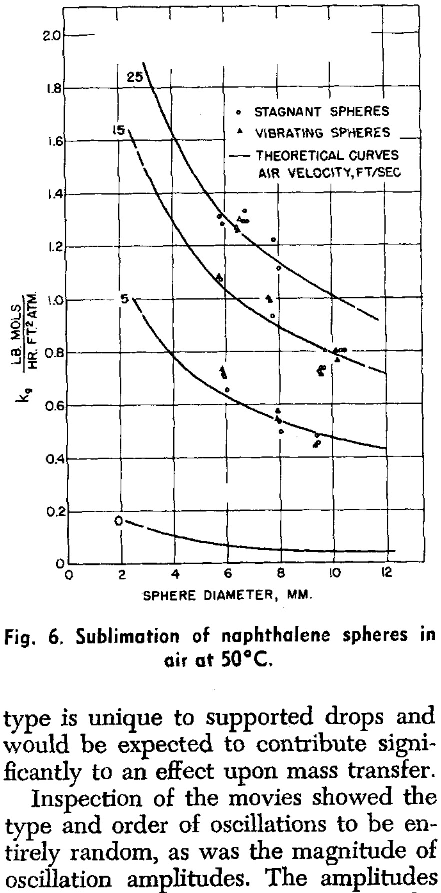

Fig. 6. Sublimation of naphthalene spheres in air at 50°C.

Inspection of the movies showed the type and order of oscillations to be entirely random, as was the magnitude of oscillation amplitudes. The amplitudes are relatively small, increasing as the air velocity is increased. They are generally less than 10% of the drop diameter until blowoff velocities are approached, and then they increase to about 25%. The effect of drop size is not significant, but viscosity appears to play a more prominent role, decreasing the amplitudes as viscosity increases. In the case of glycerine drops the oscillations were too small to allow meaningful measurements.

Attempts to determine frequencies of oscillation from the motion pictures indicated the existence of two frequencies: those of the deformation type which were rapid, and those of the displacement type which were slower. In the case of water only the deformation type were noted. In the case of the glycols both types were noted, but only the displacement type could be accurately measured. These data, shown in Table 1, do not agree with the natural frequencies of spheres oscillating between a prolate and an oblate spheroid calculated by the equation of Lamb (*24*).

No satisfactory means were established to correlate the oscillation to the effective diffusivity.

Effective Diffusivities. Initial attempts to study the system water-sulfur dioxide were abandoned because of two difficulties:

1. The diffusivities were too large for use in this experimental technique because they required short contact times and led to large desorption losses in the transfer process.
2. Increases of a fraction of a degree in the gas stream temperature dropped the humidity below 100% causing significant evaporation of the drops.

Glycerine and the glycols have much smaller diffusivity coefficients and have negligible vapor pressures at the temperatures used; thus they are well suited for this study. The solubility of sulfur dioxide gas in these liquids is large enough to allow reliable analytical measurements on single drops. An extensive literature search failed to reveal any observed chemical reaction in these systems, and there is also reasonable basis not to expect any. Laboratory experiments here supported this. Thus diffusion would be the controlling regime.

Molecular diffusion into a stagnant sphere can be described mathematically, and the equations have been solved (*15*). A solution is presented by Crank (*8*) as a graph of fractional approach to equilibrium vs. the dimensionless time group $\left(\frac{Dt}{r^2}\right)$ for the case of constant surface concentration. Crank's solution is presented here in Figures 8 and 9 as the lines labeled *theory*.

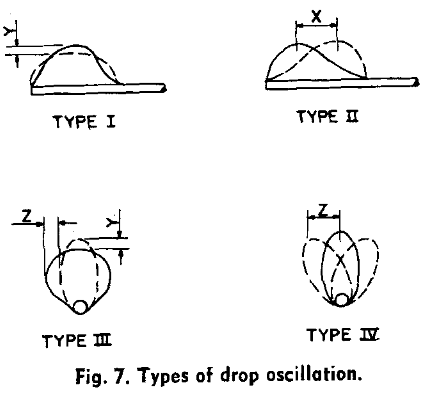

Fig. 7. Types of drop oscillation.

The experimental results have been correlated on the basis of degree of saturation vs. the dimensionless time group. Although the oscillating drop is not a sphere, it was considered to have an effective radius equal to that of a sphere of equivalent volume. The justification of this is that it provides a convenient means of comparing the absorption of the drop with that of a rigid sphere.

The diffusivities used were calculated values based on a mean concentration. This mean was a numerical average of the initial and final average values of the surface and bulk concentrations. The location of the experimental curves relative to theory leads one to believe that the calculated diffusivities may be in error. However this does not affect the comparison of oscillating drops to stagnant drops.

Thermal effects were calculated and shown to cause a temperature rise of 1 to 2 deg. in most cases. This temperature rise was neglected since it could not be accurately measured and since it could be shown that it did not alter the nature of the correlation.

The results are plotted in Figures 8 and 9. Curves were fitted by the least-squares method and the correlation examined by statistical analysis.

The system glycerine-sulfur dioxide does not exhibit any significant difference between the stagnant and oscillating drops. A fairly large degree of scatter in the data undoubtedly contributes to the obscuration of any small differences. The data are in good agreement with the theoretical curve.

It might be speculated that no large increases in absorption would be expected in such a highly viscous system that exhibits little or no internal circulation (velocities less than 0.2 cm./sec.).

The system propylene glycol-sulfur dioxide shows that there is a distinct difference between the stagnant and oscillating drops. The oscillating drops attain a given saturation two to eight times as rapidly as the stagnant drops. This could be restated as exhibiting a greater effective diffusivity. The magnitude of the effective diffusivity appears to be dependent on the degree of saturation under consideration and is greatest at low saturations. This is contrary to the effect expected from subsequent studies on forced circulation which predict higher values at the higher saturations.

All the data appear to be above the theoretical curve. Three possible explanations for this follow:

1. The calculated diffusivities are lower than the true diffusivities.
2. The stagnant drops actually exhibit a small amount of circulation as a result of density gradients.
3. Or, the drop is sufficiently deformed so as to present thin sections at the point of contact with the support member to saturate more rapidly. This would be more pronounced for the oscillating drops.

Drop size, gas velocity, and support element diameters were investigated. No significant effect upon the effective diffusivity could be measured for these variables in the ranges studied.

The system ethylene glycol-sulfur dioxide also shows an increased effective diffusivity for the oscillating drops equal to about 2.5 times the molecular diffusivity and is fairly constant with saturation. The magnitude of this increase in diffusivity is smaller than anticipated. The element variable shows no effect. Drop size shows a small effect on effective diffusivity as one might expect from consideration of dependency of internal circulation on gas velocity.

Oscillation of drops does indeed increase mass transfer rates, although to a smaller extent than anticipated. The mechanism appears to be predominantly one of internal circulation, augmented by deformation. The greater effective diffusivity at lower saturations can be explained by the deformation of the drop. At the initial stage of absorption most of the transfer is taking place near the surface and would not be affected by internal circulation. Increased area due to thin sections, such as at the support element would allow greater initial rates and thus higher effective diffusivities. However these sections quickly saturate and then transfer to the major part of the sphere takes over, and internal circulation becomes more important. From the practical standpoint the initial period involves a small amount of liquid, and the longer period is the more important one as higher saturations are approached.

Circulation Velocities Inside Oscillating Drops. Circulation velocities were determined by measuring the travel of aluminum particles near the surface of the drop and represent what are thought to be the maximum velocities.

The results are presented in Table 1 and are compared with the data of Garner and Lane (*14*). The agreement with Garner's results is fair.

As may be seen from these data the circulation velocity is essentially linearly related to the air velocity, as would be expected. The effect of viscosity on circulation velocity is very pronounced, as may be noted in a comparison of the different materials, and would be predicted by theory (*17*). Finally the large drops show greater velocities of circulation for propylene glycol and ethylene glycol, again in accordance with theory. The glycerine data do not show sufficient variation to warrant a similar conclusion in their particular case.

Forced Circulation Inside a Drop

The preceding sections have shown the importance of internal circulation in drops on the mass transfer coefficient. It would be desirable to have a means of relating this increase in mass transfer rate to the internal circulation

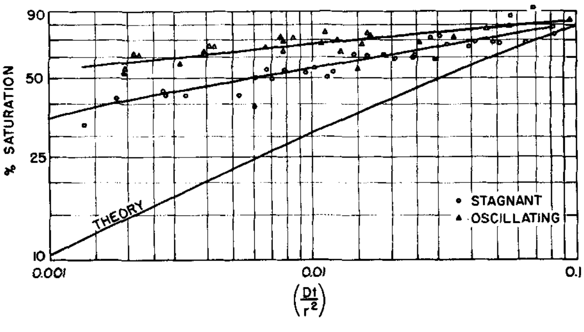

Fig. 8. Absorption of sulfur dioxide by propylene glycol drops.

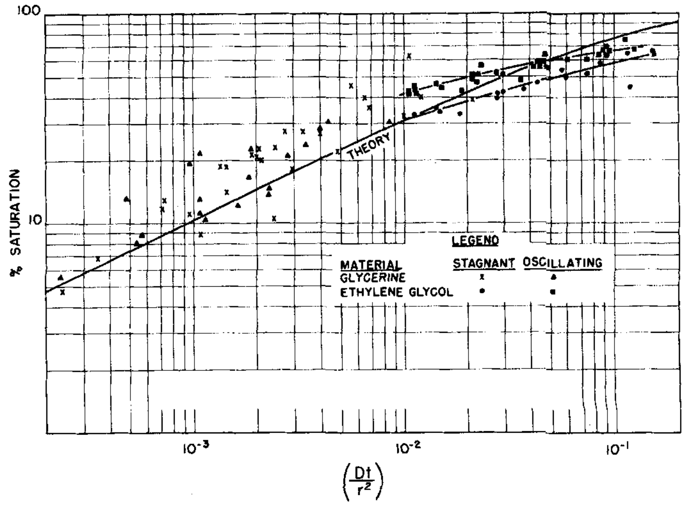

Fig. 9. Absorption of sulfur dioxide by ethylene glycol drops and by glycerine drops.

as would be a method of predicting the magnitude of such an effect.

A convenient way of expressing the increase of mass transfer rate is by means of an effective diffusivity, which would be the value the diffusivity constant would have to assume if the *amount* of material being transferred were transported by molecular diffusion.

The following development provides first a description of the transfer process for the case of circulation within the drop and second a relationship between this description and the instantaneous effective diffusivity. It is necessary to distinguish between overall and instantaneous effective diffusivity because they are not necessarily the same for mechanisms not identical with molecular diffusion through a stagnant medium. This is especially true for circulation within the drop and where the velocity is not constant. The latter condition prevailed in the experiments of Garner and Lane (*14*) because of damping effects, and they report instantaneous effective diffusivities evaluated over incremental ranges of fractional saturation.

The transfer process for the case of circulation within the drop might be described in terms of any of several simplified models or by a solution of the transport equations. The authors chose to use the film theory model (*29*) because of a suspicion that it might prove to be a satisfactory correlative framework. (Note: Subsequent work still in progress indicates that there is good physical reason to use a film theory or boundary-layer approach in this situation.) Equations (4) through (9) represent the steps in application of film theory to the unsteady state transfer into a sphere.

For mass transfer through a plane

$$N_A = D\frac{\partial c}{\partial x} \qquad (4)$$

If one assumes the holdup in film is negligible, c = average concentration in sphere, and integrates

$$N_A = D\left(\frac{c_s - c}{x}\right) \qquad (5)$$

The change in concentration may be expressed as

$$\frac{dc}{dt} = \frac{N_A A}{V_s} \qquad (6)$$

Substituting from above, rearranging, integrating, for $t_1 = 0$ and $c_1 = 0$, one gets

$$-\ln\left(\frac{c_s - c_2}{c_s}\right) = \left(\frac{3D}{rx}\right) t_2 \qquad (7)$$

Now let

$$F = \text{fractional saturation} = \frac{c_2}{c_s} \qquad (8)$$

and

$$-\ln\left(\frac{c_s - c_2}{c_s}\right) = -\ln(1 - F) = \left(\frac{3Dt_2}{rx}\right) \qquad (9)$$

Table 1. Amplitudes, Frequencies, and Internal Circulation Velocities

Material	Drop diameter, cm.	Air velocity, ft./sec.	Circulation velocity, cm./sec.	Frequency, cycles/sec.	Amplitude, cm. X	Y	Z
Propylene glycol (100%)	0.20	7.1	0.74		n.	0.014	n.
	0.20	12.3	0.79		n.	0.011	—
	0.20	22.4	1.8	27	—	0.013	0.009
	0.25	7.1	1.5		n.	n.	n.
	0.25	12.3	1.9		n.	sl.	n.
	0.25	22.4	2.8	22	0.027	0.017	0.008
80% propylene glycol	0.287	terminal	1.9[13]		—	—	—
Ethylene glycol	0.20	7.1	3.6		n.	n.	n.
	0.20	12.3	4.4		n.	0.005	0.007
	0.20	22.4	5.2	23	0.024	0.042	0.057
	0.25	7.1	4.8		n.	0.005	n.
	0.25	12.3	5.5		—	0.004	0.004
	0.25	22.4	6.4	25	0.039	0.046	0.047
	0.274	terminal	1.8[13]		—	—	—
Glycerine (100%)	0.20	6.3	0.11				
	0.20	17.1	0.14				
	0.20	22.4	0.19	19			
	0.20	28.7	0.25				
	0.225	12.3	0.13				
	0.225	17.1	0.16				
	0.225	22.4	0.19				
	0.25	6.3	0.09				
	0.25	12.3	0.14				
	0.25	17.1	0.20				
	0.25	22.4	0.18	22			
80% glycerol	0.296	terminal	0.3[13]				
Water	0.20	24.5		73	n.	0.028	—
	0.25	18.5		75	0.011	0.008	—

NOTE:
n. = negligible, less than 0.002 cm.
sl. = slight, less than 0.004 cm.

Instantaneous effective diffusivity can be defined as that which would account for the same rate of change of concentration by the mechanism of stagnant diffusion alone as that rate resulting from the circulation (plus diffusion) mechanism. The rate of change of concentration via the circulation mechanism may be determined either experimentally or through some hypothesis such as that expressed in Equation (9). Because of the necessity for the treatment of experimental data as well as known mathematical relationships, it is convenient to evaluate effective diffusivity by a difference approximation.

For the film resistance model one may determine the following derivative at any value of F:

$$\frac{dF}{d\left(\frac{D_e t}{r^2}\right)} = \left(\frac{rx}{3D}\right)\frac{dF}{dt} \qquad (10)$$

For the stagnant sphere model one may also determine a comparable derivative

$$\frac{dF}{d\left(\frac{D_e t}{r^2}\right)} = \left(\frac{r^2}{D_e}\right)\frac{dF}{dt} \qquad (11)$$

Now combine Equations (10) and (11) on the basis that the effective diffusivity is that which provides the same rate of change of concentration as the circulation case. Thus dF/dt must be the same for both mechanisms and

$$\left(\frac{D_e}{r^2}\right)\frac{dF}{d\left(\frac{D_e t}{r^2}\right)} = \left(\frac{3D}{rx}\right)\frac{dF}{d\left(\frac{3Dt}{rx}\right)} \qquad (12)$$

If difference rather than differential methods are applied to Equation (12), one may state for small increments of F or t

$$\left(\frac{D_e}{r^2}\right)\frac{1}{\Delta\phi_2} = \left(\frac{3D}{rx}\right)\left(\frac{1}{\Delta\phi_1}\right) \qquad (13)$$

where the $\Delta\phi$ terms are increments in dimensionless time for a small change of some fixed size in F. One may evaluate D_e as

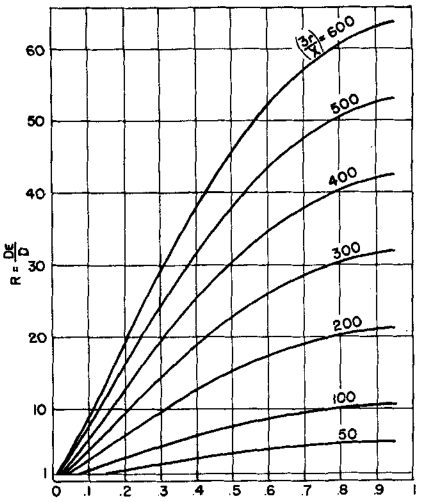

Fig. 10. Diffusivity ratio *R* as a function of fractional saturation.

$$D_e = \left(\frac{3Dr}{x}\right)\frac{\Delta\phi_2}{\Delta\phi_1} \qquad (14)$$

and the diffusivity ratio as

$$R = \frac{D_e}{D} = \left(\frac{3r}{x}\right)\frac{\Delta\phi_2}{\Delta\phi_1} \qquad (15)$$

The relationship of Equation (15) is plotted in Figure 10, a plot of R vs. F with $(3r/x)$ as parameter. Equation (15) indicates that R for a given sphere and F value is dependent on film thickness, which in turn will depend on circulation velocity. One may also note that values of R less than unity at small values of F indicate that the film thickness is not negligible for small F's (short contact times). This is a corollary of the observation that effective diffusivity is actually 1.0 at time zero because the penetration distance is smaller that the laminar sublayer (or film thickness).

The above developments have related to unsteady state transfer to a drop. It it also necessary to describe the steady state absorption by liquid being forced through a drop at constant rate. Film thickness is defined for the steady state case through the following relationships; the rate of absorption of gas by such a sphere is calculated as follows:

$$N_A = \frac{\Delta v_g}{A\Delta t} \qquad (16)$$

Substituting from Equation (5) one gets

$$x = A\,D(\Delta c)\frac{\Delta t}{\Delta v_g} = A\,Dc_s\frac{(1 - F_2)}{(\Delta v_g/\Delta t)} \qquad (17)$$

since

$$\Delta c = (c_s - c_2) = c_s\,(1 - F_2) \qquad (18)$$

The value D can be obtained from literature, the values of Δc and $\left(\frac{\Delta v_g}{\Delta t}\right)$ can be experimentally measured, and x can be calculated.

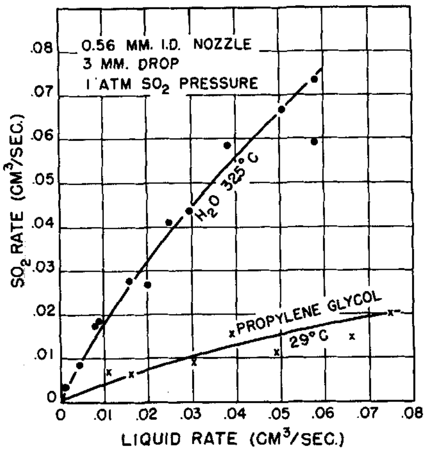

Fig. 11. Sulfur dioxide absorption rate vs. liquid rate.

Rates of absorption of sulfur dioxide by water drops were determined as a function of liquid velocity as shown in Figure 11. By means of Equation (17) the pseudofilm thickness was calculated and values of effective diffusivities were calculated and used to predict absorption by oscillating drops. Absorption data of sulfur dioxide by propylene glycol drops were similarly treated and are shown in Figure 11.

It is evident that the relationship of $3r/x$ vs. velocity is not independent of other variables. An attempt to relate $3r/x$ to N_{Re} was not successful, indicating that other factors (most likely surface tension) play important roles. The questionable nature of the calculated diffusivity for propylene glycol is recognized but could not account for the entire difference. Additional work along this line will be necessary to establish a generalized correlation for $3r/x$.

The validity of any such relationship as the one here depends on how well it is supported by experimental evidence. This can be checked for the sulfur dioxide-propylene glycol system.

Considering the more important region of high saturation one finds the oscillating drops exhibit an R of 1.9 when compared with stagnant drops at 75% saturation. For 0.25-cm. diameter drops at gas velocities of 22.4 ft./sec. the observed internal circulation velocity was 2.8 cm./sec. From Figures 10 and 11 one obtains a predicted value of 1.4. Although somewhat low this value is of the correct order of magnitude. When one considers the general nature of measurements in such an exploratory study as this, especially in the case of circulation velocity and the area of the forced circulation drop, it is significant that good agreement has been obtained.

The prediction technique does not hold as well for lower saturations. Whereas a lower R would be predicted at lower values of saturation, the contrary was obtained in this study. It is possible that at earlier stages other factors may play important roles. This was considered for the factor of increased surface. However this effect becomes of small importance and is obscured once the high saturations are reached. A very likely factor is the error incurred in ignoring the time (about 2 sec.) required to withdraw the sample from the wind tunnel.

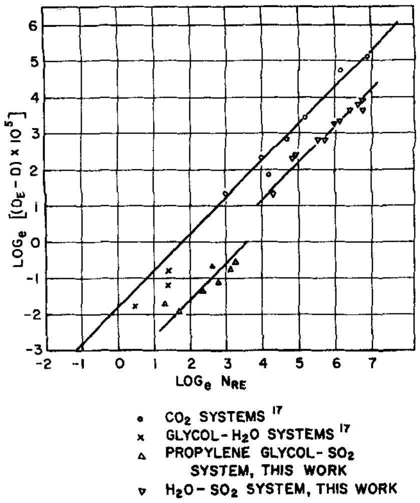

Fig. 12. Effect of internal N_{RE} on effective diffusivity.

Comparison with Other Studies

The other published work reporting absorption of gases by drops that exhibit internal circulation is that of Garner and Lane (*14*). Although other investigators (*9*, *16*) have reported on the effect of turbulence on gas absorption by drops, their data could not be compared since they pertained to growing drops that were formed on the end of a capillary.

Garner and Lane report, among other materials, absorption of carbon dioxide by water, and absorption of water by propylene glycol and glycerol. They have plotted their data for the water-carbon dioxide system as the $\ln_e[(D_E - D) \times 10^5]$ vs. the $\ln_e N_{Re_i}$, and get a straight line relationship. The pseudofilm thickness relationship obtained in this work for sulfur dioxide-water is used to predict the effective diffusivity at a saturation of 50%, which is comparable to Garner's data on carbon dioxide-water and is plotted on Figure 12. The data fall somewhat below the curve. The difference cannot at this time be attributed to any recognized factor.

The propylene glycol-sulfur dioxide data from this study have also been plotted on Figure 12, as have Garner's propylene glycol-water data. The degree of agreement between the two systems is of the same order but not as good as for the carbon dioxide systems. It should be noted that the propylene glycol data are for very low N_{Re} values; it is quite possible that the model being considered is applicable only to the higher N_{Re}.

CONCLUSIONS AND RECOMMENDATIONS

The present study on gas absorption by oscillating drops has shown that oscillation can increase the rate of mass transfer by means of deformation and internal circulation in the cases where liquid phase resistance controls. The increase, expressed as an effective diffusivity, depends on circulation velocity within the drop and can be negligible or small in the cases of viscous materials such as those studied here. Materials such as water would exhibit much greater effects.

Motion picture studies show that the oscillations are random and of two types, one of deformation and one of displacement, and that they increase with gas velocity. Measurements have been made and thus provide at least an order of magnitude that can be expected, but they are not precise enough to allow a generalized quantitative correlation of the effects of oscillation.

No effect of oscillation is noted on the outside resistance when the vibration velocity is less than the gas velocity; this is in agreement with studies on heat transfer. Since the maximum vibrational velocities that can exist in real systems undergoing oscillation are much lower than the gas velocities needed to cause oscillation, it is reasonable to expect that no likelihood exists for an increase of gas film coefficient due to drop oscillation.

Increases in area due to oscillation were expected to be small and to play a relatively minor role. Although it was found that these increases were small, indications are that they may play a fairly important part in the early stages of absorption, especially in systems such as the ones studied where internal circulation is not great. The exploratory nature of this study did not permit further definition of this factor.

Internal circulation was found to exist in oscillating drops, and velocities were measured. However no quantitative relationship was obtained between the circulation velocity and the oscillations. The variables that did seem to affect this velocity in a noticeable fashion were viscosity, drop size, and gas velocity, all in the manner expected. The effect of the internal circulation was to increase the rate of absorption.

The technique of forced circulation through a drop presents a new means of measuring the effect of liquid velocity inside a drop. By such measurements it may be possible to predict effective diffusivities for any material that exhibits circulation in its drop form.

The present state of this technique employs calculation of a pseudofilm thickness which is dependent on the circulation velocity, having a different dependency for each material. It is hoped that additional studies will establish the other important variables so that a generalized correlation may result which will allow prediction of effective diffusivity without the necessity of measurements.

NOTATION

A = area, sq. cm.
c = concentration, g. mole sulfur dioxide/liter solution
c_s = saturated concentration, also surface concentration
d = diameter, cm.
D_E = effective diffusivity, sq. cm./sec.
D = molecular diffusivity in liquid, sq. cm./sec.
D_V = molecular diffusivity in vapor, sq. ft./hr.
f = frequency, cycles/sec.
F = fractional degree of saturation
k_L = transfer coefficient, ft./hr.
k_g = gas phase mass transfer coefficient, lb. mole/hr. sq. ft. atm.
N_A = rate of transfer of component A, lb. mole/hr. sq. ft.
N_{Re} = Reynolds number = $(Du\,\rho/\mu)$
N_{Sc} = Schmidt number = $(\mu/\rho\,D_v)$
p = pressure, atm.
r = radius of drop, cm.
R = ratio of effective to molecular diffusivity (D_E/D)
t = time, sec.
T = absolute temperature, °K.
u = (liquid) circulation velocity, cm./sec.
v_G = volume of gas, cc.
V_1 = molal volume of a solute at its normal boiling point, cc./mole
V_s = volume of sphere
x = film thickness, cm.
X, Y, Z = rectangular coordinates, amplitudes, cm.

$$\Delta\phi_1 = \frac{\Delta\left(\dfrac{3Dt}{rx}\right)}{\Delta F}$$

$$\Delta\phi_2 = \frac{\Delta\left(\dfrac{D_e t}{r^2}\right)}{\Delta F}$$

μ = absolute viscosity, centipoise
ρ = density, g./cc.

Subscripts

1 = initial
2 = final
g = gas
i = interfacial

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