Absorption of Gases Into Drops

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The mass transfer to and from drops is of interest to a number of different fields, including spray and atmospheric systems. For drops falling in a gas the externally controlled mass transfer has been studied by a number of researchers and can be characterized by experimental correlations of Frössling (1938) and Beard and Pruppacher (1971) or numerical modeling by Woo and Hamielec (1971) and Ramachandran (1985). These experimental correlations and models agree quite well. Internal mass transfer has been studied quite extensively, and a number of models have been developed. However, here models and experimental data conflict. That is the focus of this work.

Models that have been developed can be divided into two types: stagnant or steady internal flow, and unsteady or turbulent internal flow. For the former case, a maximum rate of mass transfer can be predicted using the Kronig and Brink (1950) model. The circulation rate within drops is assumed to be much faster than the mass transfer rate, so lines of constant concentration become parallel to the streamlines predicted by a Hill's vortex. Higher mass transfer rates can be predicted if unsteady conditions within the drop are assumed. Handlos and Baron (1957) developed a model for internal mass transfer assuming turbulent conditions within a drop. In terms of k_L, the liquid-side mass transfer coefficient, their model can be expressed as

$$k_L = 0.00375U/(1 + \mu_p/\mu) \tag{1}$$

Ruckenstein (1967) and Ruckenstein et al. (1971) postulated a model in which the drop interior was assumed to be well mixed and the entire resistance to mass transfer restricted to a thin liquid boundary layer. A Hill's vortex solution was linearized near the liquid surface, and the final expression for k_L was found to be

$$k_L = 2/\sqrt{\pi}(UD/d)^{1/2} \tag{2}$$

Angelo et al. (1966) proposed a model for oscillating drops. The authors postulated that during drop oscillation fresh area is formed and returned to the bulk, which is assumed to be well mixed, with k_L given by

$$k_L = 2/\sqrt{\pi}[fD(1 + \epsilon + 3\epsilon^2/(8)]^{1/2} \tag{3}$$

Experimental work has been performed on drops where both types of mass transfer mechanisms might be expected, steady internal circulation and unsteady or turbulent internal flow. Walcek et al. (1984) found that for drops smaller than 1.0 mm dia. falling at terminal velocity, drops exhibited steady circulation patterns and followed the absorption characteristics of the Kronig and Brink model. For drops larger than 1.8 mm dia. the internal flow became unsteady, and the Kronig and Brink model was modified by using an effective diffusivity of 18 times the molecular diffusivity to explain the mass transfer rate. Between these drop sizes the effective diffusivity was a function of drop size. Garner and Lane (1959) measured the absorption rate of two large drop sizes, 4.22 and 5.85 mm. Absorption rates much greater than those predicted by Kronig and Brink were found. The drop oscillation frequency was observed and measured; it was close to that predicted by Lamb (Clift et al., 1978). Recently Kaji et al. (1985) measured mass transfer coefficients for drops of 2.20 mm dia. formed in an unpolluted atmosphere. The drops then accelerated through an absorption zone. Internal turbulence was imparted as the drops were formed. Mass transfer coefficients remained relatively constant throughout the fall, only decreasing from 0.035 to 0.0275 cm/s.

The experiments reported here were conducted to determine liquid-side mass transfer coefficients of drops soon, <0.1 s, after formation for specific ranges of drop sizes. The method of drop production resembled that of sprays, and monosized drops can be investigated.

A separate study of absorption of drops formed from a 1N solution of sodium hydroxide was performed to determine the effective surface area of the drops. This method has been used before with one example being Alper et al. (1980). The reaction rate of hydroxide ion and dissolved carbon dioxide was sufficiently high to eliminate the liquid-side mass transfer coefficient from the expression for the absorption rate.

Carbon dioxide was used as the absorbing gas since the magnitude of the Henry's law constant favors liquid-side control of mass transfer (Ramm, 1968).

Experimental Method

The feature of the absorption chamber was that mass transfer measurements for different drop contact times could be made.

The chamber consisted of two concentric Lucite tubes. The larger diameter tube was fixed to allow the smaller diameter tube to slide within it, changing the fall distance. The larger tube had a fixed place attached at the top. This plate had a small hole through which the drops passed into the absorption chamber. The inner tube was fitted inside the fixed tube and sealed with two Teflon O-rings. A machined gas distribution system consisting of many small holes was sealed inside the inner tube with two Teflon O-rings. This system distributed the gas around the opening, which allowed drops to exit the absorption chamber and fall into the collection vessel. The system served as the inlet of the carbon dioxide and air mixture to the absorption chamber.

In order to eliminate the drop formation region from the absorption zone, the speaker/hypodermic needle arrangement that produced the drops was positioned above the absorption chamber. The gap between drop formation and the absorption chamber was 13 cm. A compartment was constructed around this area and swept by air of sufficient flow to clear the absorbing gas without altering the trajectory of the drops.

The method of drop production utilized a well-known principle of disintegrating a liquid jet by imposing a frequency disturbance. Without satellite drop production, the drops produced by this method were monodispersed. The drops were formed at the frequency of disturbance, which caused the drops to be closely spaced. To eliminate any interaction between drops a system was constructed to selectively charge and pulse drops from the stream. This system is shown in Figure 1. The pulse charger was based on a design by Russo et al. (1981); however, a number of other researchers have used this method (Sangiovanni and Kesten, 1977; Ochs and Beard, 1978). The particulars of this system are discussed in Lindhjem (1987).

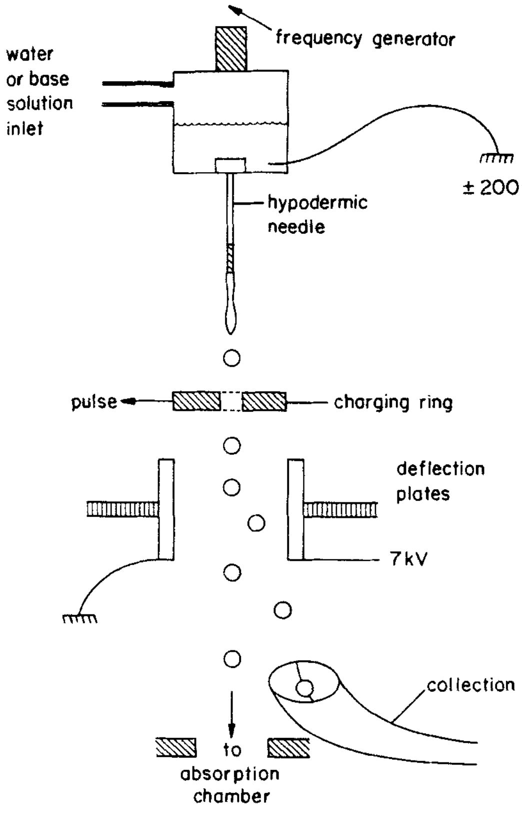

Figure 1. Drop generating and charging system.

Figure 1 shows one of every two drops entering the absorption chamber; however, much lower drop frequencies can be achieved by adjusting the settings on the pulse generator. The frequencies used in this study were 37.9 and 41.5 Hz for drops of 1.20 and 0.60 ±0.01 mm dia., respectively, while the respective drop production frequencies were 303 and 830 Hz. The initial velocities upon production were 120 and 140 cm/s as measured by photographs and calculated using jet velocities. The drops then accelerated due to gravity throughout the fall. Contact times were calculated using the method of Altwicker and Kleinstreuer (1982).

The drops were collected in a basic solution in a vessel constantly swept by nitrogen. Between the absorption chamber and this basic solution a carbon dioxide-free blanket was imposed. The desorption of absorbed carbon dioxide could then occur. This zone was 9 and 2 cm for 1.20 and 0.6 mm drops, respectively; the desorption times were estimated to be 0.025 and 0.01 s. The total absorption was not corrected for this desorption, but desorption was estimated to cause less than 10% bias.

Once the drops fell into the base, the absorbed carbon dioxide reacted to produce a pH change in the resulting mixture. Using equilibrium constants and the initial concentration of base, a calculation of absorbed carbon dioxide was made (Adewuyi and Charmichael, 1982).

Another study was performed with the 1.2 mm drops produced from a solution of 1N sodium hydroxide. The amount of carbon dioxide absorbed was determined by titration to a phenolphthalein endpoint which corresponded to the pH in which the bicarbonate form of dissolved carbon dioxide predominated (Skoog and West, 1976).

The carbon dioxide gas concentration (5 to 10%) was measured with a gas chromatograph using syringe samples taken at the inlet and exit of the absorption chamber. The temperatures for the absorption measurements were 23 ± 1°C. The water used in this study was obtained from a Millipore Milli-Q system.

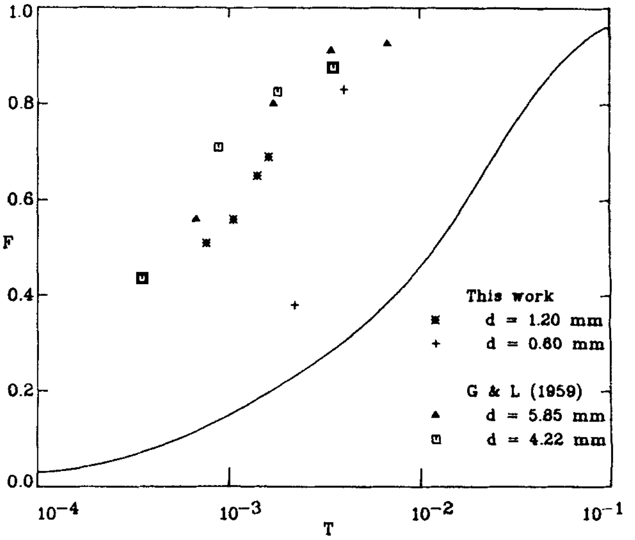

Figure 2. Comparison of Kronig and Brink model with data of Garner and Lane and this work.

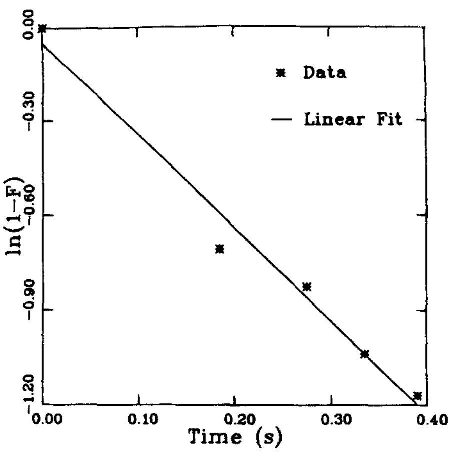

Figure 3. Data and linear fit of data for CO_2 accumulation vs. time.

Results and Discussion

Figure 2 shows data of this work compared with that of Garner and Lane (1959) and the Kronig and Brink (1950) model. The results for the drop sizes used in this study show that the mechanism of mass transfer must follow the unsteady internal flow mechanisms. The drops in the Garner and Lane data were vigorously mixed by steady oscillations produced at terminal velocity for large drops. For the drops in this study the drop oscillations were a result of the method of production. As the frequency disturbance grows on the liquid filament, a long neck forms. Once this neck breaks the drop tries to assume a spherical shape and this motion imparts an oscillation upon the drop. The mass transfer rates from this study are similar to those of Garner and Lane, as shown by Figure 2. At some time after drop production much of this oscillation should decay, especially for drops under 1.0 mm.

To evaluate the models of mass transfer within drops under unsteady flow conditions, mass transfer coefficients were calculated from the data. A constant mass transfer coefficient k_L can be found by plotting $\ln(1 - F)$ vs. t. Assuming spherical geometry the slope then equals $-k_L 6/d$. This is shown in Figure 3 for 1.2 mm dia. drops. The average mass transfer coefficient was then determined from a least-squares fit of the data. The procedure was repeated for 0.6 mm dia. drops.

A comparison of experimental data against models considering well-mixed or turbulent drop interior is shown in Table 1. The table does not include the model of Walcek et al. (1984), which predicts a steady state Sherwood number of near 320 (18 times the steady state Sherwood number for the Kronig and Brink model) for all drop sizes and conditions. This model is theoretically unsatisfying due to the use of an empirically determined effective diffusivity, which may also explain its match of the data. Of the remaining models, the surface-stretch model of Angelo et al. seems to work best over the entire drop size range. A value of zero for ϵ represented a lower limit for the model of Angelo et al. The models of Ruckenstein and of Handlos and Baron both overpredict the mass transfer rate for large drops due to the high drop velocity. In this work and in that of Kaji et al. the drops were accelerating yet the mass transfer coefficient stayed constant or decreased slightly, as shown by the slope of the line in Figure 3, which remains constant throughout the fall despite a twofold increase in drop velocity. Both the Ruckenstein and the Handlos and Baron models predict an increase in the Sherwood number with increased drop velocity. The surface-stretch model predicts a constant mass transfer coefficient and matches the data much better if the frequency of oscillation is approximately one-half that predicted by Lamb (Clift et al., 1978).

The results of the absorption with base showed that the average surface area of the drops was 4.5% greater than the surface area with an equivalent spherical volume, with the experimental uncertainty being of the same magnitude. The ϵ value used in the expression of Angelo et al. was calculated from the experimental results to be 0.09. This indicated that the magnitude of oscillation was minimal.

Conclusions

One conclusion from this work is that even small drops exhibit higher mass transfer than predicted using models assuming steady circulation. The formation of drops in this work should be similar to that in sprays. The necking phenomena with subsequent detachment occurs in sprays also and should impart oscillation and unsteady internal flow. This may explain the results of Frey and King (1986), who found higher mass transfer rates than those predicted by the Kronig and Brink model.

Also, models that predict velocity-dependent mass transfer coefficients do not explain the experimental data. This is important to spray systems in which the drop velocity can be much higher than the terminal velocity. Approximately constant mass transfer coefficients were found for this system although the drops were accelerating. This is consistent with the earlier findings of Kaji et al. (1985).

Notation

D = diffusivity of CO_2 in water, 1.9×10^{-5} cm^2/s
d = drop diameter, cm
F = fractional approach to equilibrium

Table 1. Average Sherwood Numbers

d mm	Angelo et al. (1966) $\epsilon = 0.3$	Angelo et al. (1966) $\epsilon = 0.0$	Ruckenstein (1967)	Handlos & Baron (1957)	Exp.	Ref.
0.60	460	400	920	60	320 +/−80	This work*
1.20	565	489	1,480	150	370 +/−30	This work*
2.20	658	570	1,780	190	275–350	Kaji et al. (1985)
4.22	775	670	5,240	1,920	400–680	Garner & Lane (1959)
5.85	838	727	5,860	2,400	350–920	Garner & Lane (1959)

*Uncertainties given as one standard deviation.

f = frequency of drop oscillation, s^{-1}
k_L = liquid-side mass transfer coefficient, cm/s
Sh = Sherwood number, $k_L d/D$
T = dimensionless or Fourier time, $4Dt/d^2$
t = time, s
U = drop velocity, cm/s

Greek letters

$\epsilon + 1$ = ratio of maximum to minimum surface area during oscillation
μ_p = viscosity of drop, cm^2/s
μ = viscosity of gas, cm^2/s

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