Interfacial Resistance in the Absorption of Oxygen by Water

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Transient absorption rates of oxygen into water have been measured by passing a laminar jet through the pure gas for contact times varying from 0.8 to 11.8 msec. The absorption rate is significantly lower than the theoretical value corresponding to no interfacial resistance, if a diffusivity of 2.20 × 10^{-5} sq. cm./sec. at 22.2°C. is used for comparison. The available evidence indicates that this diffusivity is about correct and that the lowered rate may be caused by an interfacial resistance described by an interfacial transfer coefficient equal to 0.6 cm./sec. This resistance is small enough to be neglected in most gas absorbers.

Interfacial resistance in gas absorption has recently come under intensive study because of its fundamental importance in mass transfer. Higbie (*8*) in developing his penetration theory for mass transfer demonstrated a possible method of measuring interfacial resistance. Although his technique failed, the principle has proved to be valid. In essence a pure gas is contacted with a liquid which is stationary or in laminar flow, and the rate of absorption is compared with the rate calculated from Fick's second law for unsteady state diffusion. An interfacial resistance may cause the absorption rate to be lower than the theoretical value, but unfortunately a lower rate may also be caused by secondary effects such as a boundary layer or interfacial contamination. Consequently interfacial resistance has turned out to be quite elusive, and, as techniques have been refined, reported interfacial resistances have become smaller and smaller.

In the carbon dioxide-water system, for example, Higbie first found what appeared to be an appreciable interfacial resistance by passing gas bubbles through a water-filled tube. Emmert and Pigford (*7*) later observed about the same value in short and long wetted-wall columns, but Danckwerts and Kennedy (*5*), using a rotating drum, obtained more self-consistent data and an appreciably lower resistance.

More recently Cullen and Davidson (*2*), using a laminar jet, found a negligible interfacial resistance in the same system and showed that the high values which had been reported were most likely due to secondary effects, such as boundary layers and surface contamination. These results were substantiated by a number of other independent studies with different laminar-jet techniques (*2, 11, 12, 13*).

The foregoing history of an interfacial resistance is very similar to that of condensation coefficients for pure materials, a very closely related subject; again, as techniques have been refined, the measured condensation coefficients have approached 1 (*10*), equivalent to the interfacial resistance approaching a very small value.

Oxygen-water has been studied much less extensively than carbon dioxide–water. Emmert and Pigford found a large resistance in a wetted-wall column, but Davidson and Cullen (*6*), using a wetted sphere, later concluded that interfacial resistance was negligible in this system. Both these studies were made at relatively long contact times, where rate measurements are not very sensitive to an interfacial resistance.

The object of this work is to examine further the oxygen-water system at very short contact times by means of a previously reported laminar-jet technique (*12*), since it is theoretically possible to observe an interfacial resistance at short times which cannot be observed at longer contact times.

THEORY AND EXPERIMENT

The simplest mechanism for the transfer across an interface is described by

$$N_A = k_s(C^* - C_i) \qquad (1)$$

The interfacial transfer coefficient is then the reciprocal of the interfacial resistance. It can never be infinite, since gas molecules can transfer across the interface only at a finite rate. The upper limit for k_s can be obtained from the kinetic theory of gases (*4*):

$$k_s = \frac{\alpha H}{\sqrt{2\pi RTM}} \qquad (2)$$

If the condensation coefficient is 1, and there is no other interfacial resistance, k_s is so large that interfacial resistance is practically zero, and interfacial equilibrium will be very closely approached during practical mass transfer operations.

However it is possible to conceive of a region of exceptionally high diffusional resistance in the liquid adjacent to the interface, and an equation of the same form as Equation (1) may also be used to describe this transfer (*12*); therefore presently it is convenient to consider k_s defined by Equation (1) with an upper limit set by Equation (2), when $\alpha = 1$.

k_s is examined by the passage of a laminar jet through a pure gas for a short distance. The rate of absorption of gas is compared with the rate calculated from Fick's law for unsteady state diffusion into a liquid in rodlike flow, with Equation (1) as the boundary condition at the interface. The solution for the average absorption rate over the jet is (*5*)

$$\bar{N}_A = \frac{D(C^* - C_0)}{k_s\theta}\left[e^{k_s\theta/D} \cdot \text{erfc}\, k_s\sqrt{\frac{\theta}{D}} + 2k_s\sqrt{\frac{\theta}{\pi D}} - 1\right] \qquad (3)$$

and when k_s is infinite the equation reduces to the well-known form

$$\bar{N}_A = 2(C^* - C_0)\sqrt{\frac{D}{\pi\theta}} \qquad (4)$$

The total amount of gas absorbed per unit area in the absence of interfacial resistance is then given by

$$\frac{Q}{A} = 2(C^* - C_0)\sqrt{\frac{D\theta}{\pi}} \qquad (5)$$

There are a number of conditions which must be satisfied for these equations to apply (*3*), the most important being that the jet is in rodlike flow. Since a boundary layer must exist when the jet is formed, it is necessary that the surface of the jet accelerate rapidly to the bulk velocity. If this does not occur, the absorption rate will be lower than these equations predict; if there is a significant boundary-layer effect, the rate will then

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vary with jet length (*12*). This fact allows hydrodynamic effects to be separated from purely time-dependent effects such as diffusion, interfacial resistance, chemical reactions, etc., and affords a method of checking for self-consistency. Thus it was shown that when carbon dioxide was absorbed by a water jet formed with a very thin sharp-edged orifice plate, the absorption rate per unit area depended only upon contact time and was independent of jet length (*12*). This indicated that such a jet was essentially in rodlike flow and that the assumptions made in deriving Equations (3) and (4) were satisfied over wide ranges of jet length and velocity. A theoretical analysis of some of the hydrodynamic factors has been presented by Scriven (*13*).

The present work is based on a technique described previously (*12*). A laminar jet formed by a thin-orifice plate is passed through 99.5% oxygen saturated with water vapor, and, as the oxygen is absorbed, fresh gas is fed to the absorber from a constant-pressure source. The absorption rate is measured directly by the timing of the motion of a soap film moving in a capillary tube which is in the line connecting the absorber and constant-pressure source.

The absorption rate is quite small because of the relatively low solubility of oxygen in water, and the absorber was insulated to reduce the temperature fluctuations during a run to the order of ±0.03°C. (The absorber and soap bubble make an excellent thermometer.) The system was in a constant-temperature room held at 22.2 ± 0.25°C.

The orifice plates used were 0.01-cm.-thick stainless steel, and the orifices were 0.0914 and 0.0825 cm. in diameter. This type of thin orifice was shown previously to give essentially rodlike flow in the jet (*12*). The jet was removed from the absorber by being passed into a water-filled 0.11-cm.-diameter hole in a Lucite rod.

The water used was obtained by the condensation of steam and was titrated for the oxygen content before being used. The inlet concentration averaged about 1% of saturation (relative to pure oxygen at 1 atm.), and the water leaving the system had a concentration very close to the inlet value because of the short contact times used. The nitrogen/oxygen ratio in the feed water was assumed to be the same as the ratio in water in equilibrium with air, and the dissolved nitrogen was treated in Equations (3) and (4) as if it were oxygen; this gave an average inlet concentration of total gas of about 3% of saturation. This treatment can be justified by the following analysis.

Gas-phase resistance is negligible, and if nitrogen interfacial resistance is also small, Equation (4), with suitable physical constants, describes the nitrogen desorption. The nitrogen accumulated in the gas phase during a run is very small, and if the trace of nitrogen present in the gas feed is neglected, the rate of transfer of nitrogen is

$$\bar{N}_A' = -2C_0'\sqrt{\frac{D'}{\pi\theta}} \qquad (6)$$

Adding this to Equation (4) for oxygen and taking the two diffusivities as equal, one gets

$$(\bar{N}_A)_{net} = 2(C^* - C_{0T})\sqrt{\frac{D}{\pi\theta}} \qquad (7)$$

where

$$C_{0T} = C_0 + C_0' \qquad (8)$$

and since the net rate of absorption of total gas is measured in the experiment, the nitrogen in the feed water can be treated as oxygen.

The jet area and contact time were calculated directly from measurements of jet length, diameter, and water flow rate, and the measured absorption rates were corrected to correspond to a total oxygen pressure of 1 atm. and an oxygen content in the feed water of zero.

Diffusivities have been measured by a number of workers in the temperature range of 10° to 25°C., and without temperature correction they vary from 1.8 × 10^{-5} to 2.6 × 10^{-5} sq. cm./sec. These results have been summarized by Davidson and Cullen (*6*). If the measured temperature dependence of Davidson and Cullen is used to correct the values to a common temperature, three independent measurements (*1, 6, 9*) yield a diffusivity in the region of 2.2 × 10^{-5} to 2.4 × 10^{-5} sq. cm./sec. at 22.2°C. with eight other values scattered about equally above and below. It appears probable that the correct diffusivity lies in this intermediate region.

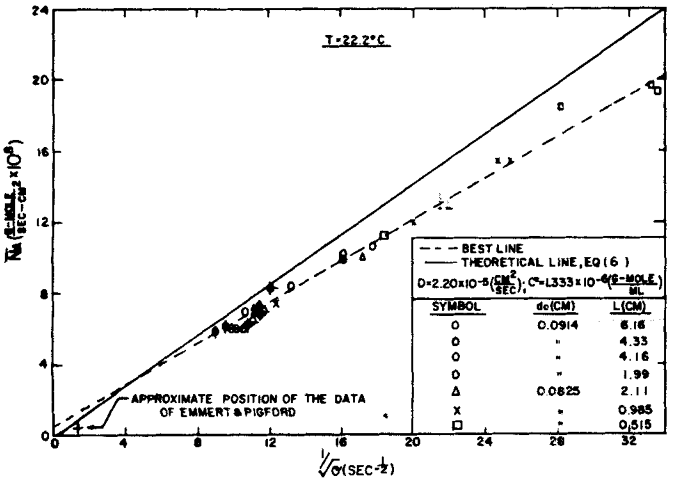

Fig. 1. Rate of oxygen absorption into water.

RESULTS

A range of contact time from 0.833 to 11.8 msec. was obtained when the jet length was varied from 0.505 to 6.16 cm. and the water flow rate from 0.737 to 2.688 cc./sec. The average rate of absorption is shown as a function of $1/\sqrt{\theta}$ in Figure 1, where each point represents the average value of three independent measurements. The original data are available (*3*). The solid line is the equation for no interfacial resistance [Equation (4)]. The solubility was taken from the International Critical Tables, and the diffusivity used was the lowest probable value, 2.20 × 10^{-5} sq. cm./sec.

The dotted line in Figure 1 is the best straight line through the data. The results are replotted in Figure 2 to clarify the long contact-time values. Here the amount of gas absorbed is shown as a function of $\sqrt{\theta}$, and the theoretical line for no interfacial resistance is Equation (5) with the same physical constants as before.

DISCUSSION

The data are more scattered than those reported for the absorption of carbon dioxide because of the extremely low flow rates which had to be measured. The maximum deviation among repeated runs was 10%, and the average was less than 5%. A more critical analysis of the data is shown in Figures 3 and 4. In Figure 3 the amount of gas absorbed is plotted against $\sqrt{\theta}$ for different jet lengths, and the data are fitted by straight lines through the origin. The data are then cross plotted in Figure 4 at a constant contact time, where it is seen that the amount of gas absorbed per unit area is independent of jet length (the maximum deviation from the horizontal line is 5%). This confirms the earlier conclusions that the hydrodynamic effects are negligible in jets formed with a thin-orifice plate and indicates that the data are self-consistent.

Figures 1 and 2 show that the data fall significantly below the theoretical line for no interfacial resistance, when the lowest probable diffusivity is used. The choice of any higher diffusivity would cause an even greater difference between

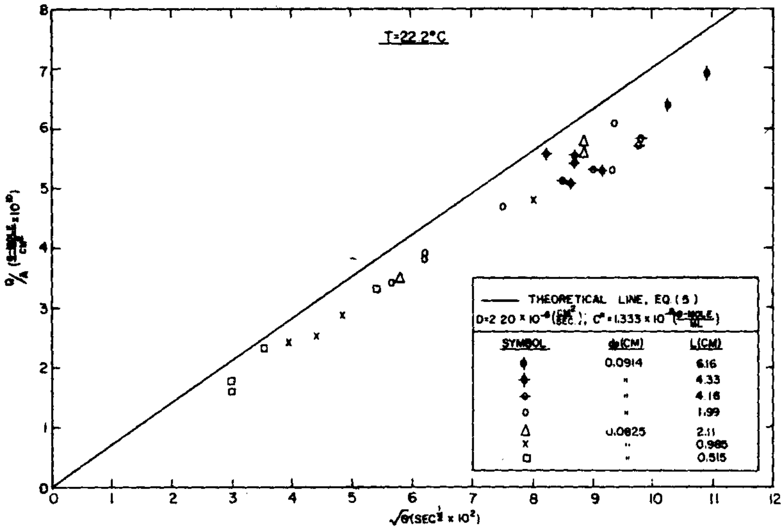

Fig. 2. Amount of oxygen absorbed per unit area.

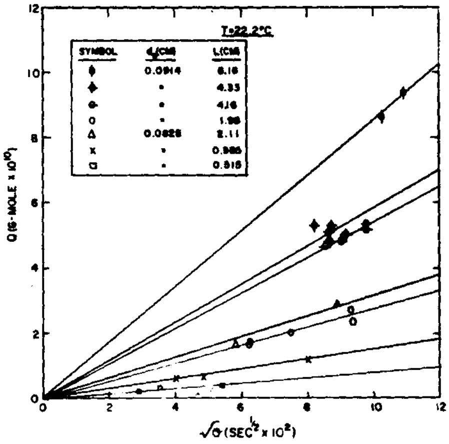

Fig. 3. Amount of oxygen absorbed at different jet lengths vs. square root of contact time.

the theoretical line and the data, and the diffusivity would have to be considerably less than 2.2 × 10^{-5} for the theoretical line to be included in the 95% confidence limits of the data.

The best straight line through the data (the dotted line in Figure 1) is given by $\bar{N}_A = 4.83 \times 10^{-9} + 5.77 \times 10^{-9}/\sqrt{\theta}$, where the standard deviation of the slope is 8.00 × 10^{-11}. Thus the best straight line intersects the y axis at $\bar{N}_A$ = 4.83 × 10^{-9} and the 95% confidence limits of the intercept are 7.34 × 10^{-9} and 2.33 × 10^{-9}; therefore it is improbable that the data fit a straight line passing through the origin as demanded by the equation for no interfacial resistance [Equation (4)]. Since at long times the rate must approach zero under any circumstances, the nonzero intercept implies that $\bar{N}_A$ is not a linear function of $1/\sqrt{\theta}$. Both these factors, the low rate and nonzero intercept, indicate the presence of an interfacial resistance which causes the rate to be lower than the theoretical and the relationship between $\bar{N}_A$ and $1/\sqrt{\theta}$ to be nonlinear, but they are not conclusive.

Figure 5 compares the experimental absorption rates with the theoretical rates for various values of k_s [Equation (4)], and k_s of 0.6 cm./sec. appears to give the best fit to the data. If the interfacial resistance is due entirely to a low condensation coefficient, the value of k_s corresponds to $\alpha = 1.8 \times 10^{-6}$.

If a diffusivity of 2.4 × 10^{-5} sq. cm./sec. is used for comparison, as in Figure 6, none of the constant resistance lines fit the data so well as when the lower diffusivity is used. However the best value of k_s is not changed much by the change in diffusivity, for it is seen to be in the range of 0.4 to 0.6 cm./sec.

There are two possible means of explaining the results without postulating an interfacial resistance (and in view of the history of the carbon dioxide studies, perhaps this would be the prudent viewpoint):

1. There may be secondary effects which cause the absorption rate to be lower than the theoretical value and the time dependence to be somewhat different from the theoretical.

2. The diffusivity of oxygen in water may be appreciably lower than expected, and small secondary effects may explain the nonzero intercept.

The first explanation seems unlikely, for a technique very similar to that used here checked the theoretical value quite closely in the carbon dioxide–water system as well as in other systems (*12*, *3*); moreover Figure 4 eliminates the possibility of any significant hydrodynamic effect such as a boundary layer or a stagnant zone at the receiver.

The only other possibility which could account for the lowered rate (aside from a leak in the system, which is ruled out on a number of grounds) is that the nitrogen/oxygen ratio in the entering water was about five times greater than the ratio at equilibrium. This is highly unlikely, for the maximum expected value would be the ratio in air, only 1.5 times greater than the equilibrium value.

Raimondi and Toor's (*12*) data could be interpreted to indicate a very small boundary-layer effect which would tend to give a positive y-axis intercept, and this is also possible in this work. Since there may have been some entrainment in the longest jet (6.16 cm.) the best straight line was recalculated without these points, and the lower limit of the 95% confidence level was found to be 1.76 × 10^{-9}. A small boundary-layer effect might then be used to explain the difference between this value and zero.

Thus if this explanation were used to explain away the nonzero intercept, and the diffusivity were 1.6 × 10^{-5} instead of 2.2 × 10^{-5} sq. cm./sec., the data would indicate no interfacial resistance.

Some support for this argument can be obtained from Emmert and Pigford (*7*), who absorbed oxygen in water in a relatively long wetted-wall column. Based on a diffusivity equivalent to 2.40 × 10^{-5} at 22.2°C. their data were 10 to 20% below the theoretical value for no interfacial resistance. The present data deviate from the theoretical by about the same amount, if this higher value of D is used in Equation (4). This agreement does not prove that the same interfacial resistance existed in both cases; on the contrary it indicates that either there is no interfacial resistance or the magnitude of the resistance is quite different in the two cases. This is due to the contact times used by Emmert and Pigford being of the order of 0.5 sec., 50 to 500 times larger than used here (see Figure 1), and at this long time an interfacial resistance of the magnitude considered here would be completely obscured by the large diffusional resistance in the liquid.

Figure 5, which contains the theoretical lines for various values of k_s, shows that at long contact times a curve passing through the present data is almost indistinguishable from the line for no interfacial resistance. Thus if there is an interfacial resistance present, Emmert and Pigford's value is about fifty times greater than the value reported here. The only line which will fit both sets of

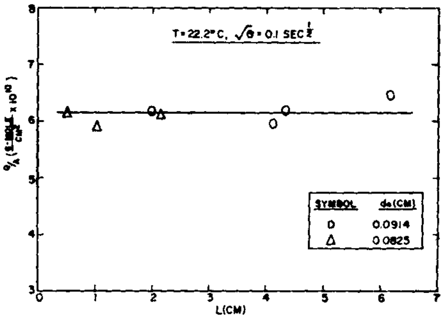

Fig. 4. Comparison of oxygen absorbed per unit area at different jet lengths for same contact time.

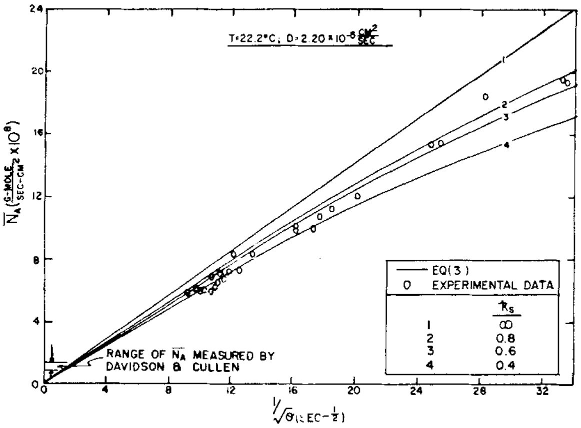

Fig. 5. Comparison of oxygen-absorption data with different interfacial-resistance lines.

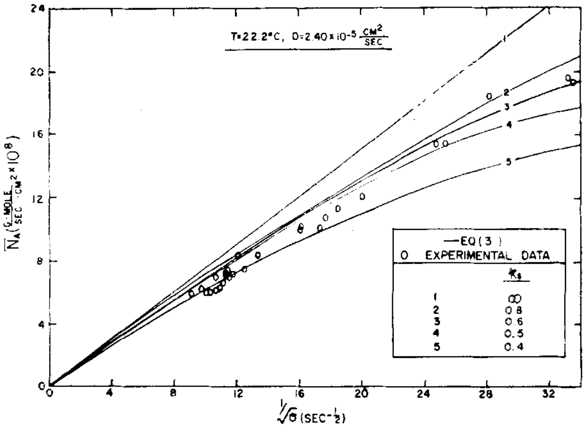

Fig. 6. Comparison of oxygen-absorption data with different interfacial-resistance lines.

data is a straight line through the origin, which corresponds to no interfacial resistance, and $D = 1.6 \times 10^{-5}$ sq. cm./sec. Unfortunately this check could easily be fortuitous, since Emmert and Pigford's data for carbon dioxide were later shown to be low, quite possibly because of the hindering effect of a surface-active agent. Since the surface-active agent was present in their oxygen measurements also, the interfacial resistance in their system could well have been much greater than the value found in this work, where the interface is clean.

Davidson and Cullen (*6*) also measured the transient absorption of oxygen in water at relatively long contact times (the order of 0.1 sec.). They used a wetted sphere and reported no interfacial resistance and a diffusivity (by interpolation) of 2.20×10^{-5} sq. cm./sec. at 22.2°C. This technique was also used with other gases, and the measured diffusivities were shown to check known values quite accurately.

Their absorption rate was in the range 0.75×10^{-8} to 1.3×10^{-8} g.-moles/(sq. cm.)(sec.) (corrected to 22.2°C.) which, in the absence of a very large interfacial resistance, corresponds to the long contact-time region in this work, where the effect of interfacial resistance is small (Figure 5). However since the flow in their case was quite different from that used here, the diffusion equation for their system was solved approximately with a constant interfacial resistance described by $k_s = 0.6$ cm./sec. The results showed, as expected, that the interfacial resistance is almost completely obscured by the diffusional resistance and that the convergence of the curves for various values of k_s at long contact times is essentially the same as shown in Figure 5. At their shortest contact time this interfacial resistance would lower the absorption rate about 2% and at their longest contact time by about 1%; even if this resistance were present, the shape of the rate curve would be practically indistinguishable from the curve for no interfacial resistance.

However the diffusivity calculated by the use of the equation for no interfacial resistance would be 2 to 4% low since the diffusivity appears as the square root in the rate equation; therefore the corrected diffusivity would be about 2.25×10^{-5} sq. cm./sec. This change is insignificant and has negligible effect on the value of k_s obtained in this work.

Thus the work of Davidson and Cullen and the present work could be considered as one set of transient experiments covering an effective contact time range of 0.8 to about 900 msec. The entire set of experiments is consistent with a diffusivity of 2.25 sq. cm./sec. and an interfacial transfer coefficient of 0.6 cm./sec.

Since interfacial resistance is in series with a liquid-phase resistance, its effect depends upon the relative magnitude of the two resistances (*12*). As in packed columns the liquid-side resistance is usually appreciably larger than the interfacial resistance reported in this work, the interfacial resistance could be safely neglected in this case. However if k_s is a constant, it would limit the maximum possible mass transfer coefficient which could be obtained; even if the liquid- and gas-phase resistances were reduced to zero, the over-all coefficient could not exceed 0.6 cm./sec. On the other hand, if the experimental data reported here are in error by about 15%, the maximum possible coefficient is set by Equation (2) with $\alpha = 1$, and the maximum over-all coefficient is more than 10^6 times greater than the foregoing limit.

ACKNOWLEDGMENT

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NOTATION

A = surface area, sq. cm.
C_0 = initial gas concentration in liquid, g.-mole/cc.
C_i = interfacial gas concentration in liquid, g.-mole/cc.
C^* = equilibrium gas concentration in liquid, g.-mole/cc.
D = diffusivity of gas in liquid, sq./cm./sec.
H = Henry's law constant erg/g.-mole
k_L = interfacial mass transfer coefficient, cm./sec.
k_s = interfacial transfer coefficient
M = molecular weight
N_A = mass transfer rate, g.-mole/(sec.)(sq. cm.)
$\bar{N}_A$ = average mass transfer rate, g.-mole/(sec.)(sq. cm.)
Q = amount of gas absorbed, g.-mole
R = gas constant, erg./(g./(mole)(°K.)
T = temperature, °K.
α = condensation coefficient
θ = time, sec.
primes = nitrogen

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