## Interlude: <br> Interphase Mass Transfer

The transport of mass within a single phase depends directly on the concentration gradient of the transporting species in that phase. Mass may also transport from one phase to another, and this process is called interphase mass transfer. Many physical situations occur in nature where two phases are in contact, and the phases are separated by an interface. Like single-phase transport, the concentration gradient of the transporting species (in this case in both phases) influences the overall rate of mass transport. More precisely, transport between two phases requires a departure from equilibrium, and the equilibrium of the transporting species at the interface is of principal concern. When a multiphase system is at equilibrium, no mass transfer will occur. When a system is not at equilibrium, mass transfer will occur in such a manner as to move the system toward equilibrium.

Familiar examples of two phases in contact are two immiscible liquids, a gas and a liquid, or a liquid and a solid. From the standpoint of mathematically describing these processes, each of these situations is physically equivalent. Since oxygen is required for all aerobic life and water is the principal medium of life, the transport of oxygen between air (Phase I) in contact with water (Phase II) is of paramount concern, and this physical situation will be highlighted in the discussion.

Let us imagine the physical and chemical situation where air is first brought in contact with oxygenfree water. There will be a tendency for oxygen to move into the water to achieve equilibrium between the phases. This equilibrium will quickly be achieved "locally" at the interface, but will require more time to become established in the bulk water. In order to predict how quickly oxygen transports, we will need to know a relationship between the gas phase and liquid phase equilibrium oxygen concentrations.

Many equilibrium laws are known. At a fixed temperature and pressure, the equilibrium relationship between the concentrations of a species in two phases can be given by a distribution curve such as that shown in Figure I.1.

The simplest "distribution law" is one which states that the equilibrium concentrations of species between the phases are in proportion. This linear law is usually an appropriate assumption when the equilibrating species is at a low concentration:

$$
\begin{equation*}
c_{j}^{\prime}=K c_{j}^{\prime \prime} \tag{I. 1}
\end{equation*}
$$

In Equation I.1, $\mathrm{c}_{\mathrm{j}}{ }^{\prime}$ is the concentration of species j in phase 1 , and $\mathrm{c}_{\mathrm{j}}{ }^{\prime \prime}$ is the equilibrium concentration of species j in phase $2 . \mathrm{K}$ is referred to as the distribution or partition coefficient. For gases and liquids, the distribution law often used to describe equilibrium at low solute concentration is Henry's Law. For the equilibrium of oxygen between gas and water Henry's Law is:

$$
\begin{equation*}
y_{O_{2}} P=p_{O_{2}}=x_{O_{2}} H_{O_{2}} \tag{I. 2}
\end{equation*}
$$

In this case Henry's Law relates the concentration of oxygen in one phase (mole fraction of oxygen or partial pressure of oxygen in the gas phase) with concentration in the second phase (mole fraction of oxygen in the water). The value of mole fraction in the liquid phase in Equation I. 2 may also be
converted into more familiar concentration units such as mass concentration (e.g., g/L) or molar concentration $(\mathrm{mol} / \mathrm{L})$. At $25^{\circ} \mathrm{C}$, the value of the Henry's Law constant for oxygen, $\mathrm{H}_{02}$, is 43,800 atmospheres. At $10^{\circ} \mathrm{C}$, the Henry's Law constant is 32,700 atmospheres, while at $40^{\circ} \mathrm{C}$, the Henry's Law constant is 53,500 atmospheres.

Figure I. 1 An equilibrium relationship.


Concentration of j in phase II

Question 1: What is the equilibrium concentration (in $\mathrm{mg} / \mathrm{L}$ ) of oxygen in water at $10^{\circ} \mathrm{C}$, $25^{\circ} \mathrm{C}$ and $40^{\circ} \mathrm{C}$ ?

## Solution:

The mole fraction of oxygen in air is 0.21 . The pressure of air will be assumed to be 1.0 atm . Thus, the partial pressure of oxygen in the air is 0.21 atm .

At $10^{\circ} \mathrm{C}$ :

$$
\mathrm{x}_{\mathrm{O} 2}=0.21 \mathrm{~atm} / 32,700 \mathrm{~atm}=6.42 \times 10^{-6} \mathrm{~mol} \mathrm{O}_{2} / \mathrm{mol} \mathrm{H}_{2} \mathrm{O}
$$

$$
\left(6.42 \times 10^{-6} \mathrm{~mol} \mathrm{O}_{2} / \mathrm{mol} \mathrm{H}_{2} \mathrm{O}\right) \times\left(32000 \mathrm{mg} \mathrm{O} \mathrm{O}_{2} / \mathrm{mol} \mathrm{O}_{2}\right)
$$

$$
\times\left(\mathrm{mol} \mathrm{H}_{2} \mathrm{O} / 18.0 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}\right) \times\left(997 \mathrm{~g} \mathrm{H}_{2} \mathrm{O} / \mathrm{L}\right)=\underline{11.4 \mathrm{mg} / \mathrm{L}}
$$

At $25^{\circ} \mathrm{C}$ :

$$
\mathrm{x}_{\mathrm{O} 2}=0.21 \mathrm{~atm} / 43,800 \mathrm{~atm}=4.79 \times 10^{-6} \mathrm{~mol} \mathrm{O} 2 / \mathrm{mol} \mathrm{H}_{2} \mathrm{O}
$$

$\left(4.79 \times 10^{-6} \mathrm{~mol} \mathrm{O}_{2} / \mathrm{mol} \mathrm{H}_{2} \mathrm{O}\right) \times\left(32000 \mathrm{mg} \mathrm{O} 2 / \mathrm{mol} \mathrm{O}_{2}\right)$

$$
\times\left(\mathrm{mol} \mathrm{H}_{2} \mathrm{O} / 18.0 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}\right) \times\left(997 \mathrm{~g} \mathrm{H}_{2} \mathrm{O} / \mathrm{L}\right)=8.5 \mathrm{mg} / \mathrm{L}
$$

## At $40^{\circ} \mathrm{C}$ :

$$
\begin{aligned}
& \mathrm{x}_{\mathrm{O} 2}=0.21 \mathrm{~atm} / 53,500 \mathrm{~atm}=3.93 \times 10^{-6} \mathrm{~mol} \mathrm{O}_{2} / \mathrm{mol} \mathrm{H}_{2} \mathrm{O} \\
& \left(3.93 \times 10^{-6} \mathrm{~mol} \mathrm{O}_{2} / \mathrm{mol} \mathrm{H}_{2} \mathrm{O}\right) \times\left(32000 \mathrm{mg} \mathrm{O}_{2} / \mathrm{mol} \mathrm{O}_{2}\right) \\
& \times\left(\mathrm{mol} \mathrm{H}_{2} \mathrm{O} / 18.0 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}\right) \times\left(997 \mathrm{~g} \mathrm{H}_{2} \mathrm{O} / \mathrm{L}\right)=\underline{7.0 \mathrm{mg} / \mathrm{L}}
\end{aligned}
$$

Oxygen, like the vast majority of gases, is more soluble in water at low temperature than at elevated temperature.

## A. Two-Resistance Theory

Interphase mass transfer involves three transfer steps. For the specific example of oxygen transporting from air to water, these three steps are:

1. The transfer of oxygen from the bulk air to the surface of the water.
2. The transfer of oxygen across the interface.
3. The transfer of oxygen from the surface of the air to the bulk water.

Whitman (1923) first proposed a "two-resistance theory" which has been shown to be appropriate for many interphase mass transfer problems. The general theory has two principal assumptions, which for the case of oxygen transporting from air to water are:

1. The rate of oxygen transfer between the phases is controlled by the rates of diffusion through the phases on each side of the interface.
2. The rate of diffusion of oxygen across the interface is instantaneous, and therefore equilibrium at the interface is maintained at all times.

In other words, two "resistances" to transport exist, and they are the diffusion of oxygen from the bulk air to the interface, and the diffusion of oxygen from the interface to the bulk water. This physical situation may be depicted graphically by the diagram in Figure I.2.

In Figure I.2, the gas phase concentration of oxygen is represented by its bulk partial pressure, $\mathrm{p}^{\mathrm{g}}{ }_{\mathrm{O} 2}$. The liquid phase concentration of oxygen is represented by its bulk molar concentration, $\mathrm{c}_{\mathrm{O} 2}^{1}$. The interface gas and liquid phase concentrations are denoted by $\mathrm{p}_{\mathrm{O} 2}^{\mathrm{i}}$ and $\mathrm{c}_{\mathrm{O} 2}^{\mathrm{i}}$, respectively. Since transport is occurring from the gas to the liquid phase, the value of $\mathrm{p}^{\mathrm{g}} \mathrm{O}_{\mathrm{O}}$ must be greater than the value of $\mathrm{p}_{\mathrm{O} 2}^{\mathrm{i}}$. Similarly, the value of $\mathrm{c}_{\mathrm{O} 2}^{\mathrm{i}}$ must be greater than the value of $\mathrm{c}_{\mathrm{O} 2}^{1}$. Because the interface imparts no resistance to transport, the two interface concentrations will remain in equilibrium, and their values can be related by Henry's Law (Equation I.2) or some other equilibrium relationship. Note that in general these two interface concentrations are not identical, and indeed $\mathrm{p}_{\mathrm{O} 2}^{\mathrm{i}}$ can be less than or greater than $\mathrm{c}^{\mathrm{i}}{ }_{\mathrm{O} 2}$.

Figure I. 2 Two resistance theory


Distance
The distance between the interface and the location in the gas phase at which the oxygen concentration equals the bulk oxygen concentration is the gas phase "film" thickness $\left(\delta_{\mathrm{G}}\right)$, while the similar distance for the oxygen in the liquid phase is referred to as the liquid phase "film" thickness $\left(\delta_{\mathrm{L}}\right)$. Since the shape of the oxygen concentration profile is unknown in both the gas and the liquid, the precise concentration of oxygen at the interface is very difficult to determine. Therefore, the film thicknesses are not known.

Remember, if the transport of oxygen is occurring from the liquid to the gas instead, then the value of $\mathrm{p}_{\mathrm{O} 2}^{\mathrm{i}}$ will be greater than the value of $\mathrm{p}^{\mathrm{g}}{ }_{\mathrm{O} 2}$, and the value $\mathrm{c}_{\mathrm{O} 2}^{1}$ will be greater than the value of $\mathrm{c}^{\mathrm{i}}{ }^{\mathrm{i}}{ }^{2}$.

The molar flux of species $\mathrm{j}\left(\Phi_{\mathrm{j}}\right.$, a vector quantity, having units of moles of material per area per time) is known to be proportional to the concentration gradient of species j . Indeed, this concentration difference is said to be the "driving force" for mass transport. If we consider the onedimensional flux of oxygen across an air-water interface, then we may define a mass transfer coefficient for the gas phase $\left(\mathrm{k}_{\mathrm{G}}\right)$ as:

$$
\begin{equation*}
\Phi_{\mathrm{O}_{2}}=k_{G}\left(p_{\mathrm{O}_{2}}^{g}-p_{\mathrm{O}_{2}}^{i}\right) \tag{I. 3}
\end{equation*}
$$

And, for the liquid phase $\left(\mathrm{k}_{\mathrm{L}}\right)$ :

$$
\begin{equation*}
\Phi_{\mathrm{O}_{2}}=k_{L}\left(c_{\mathrm{O}_{2}}^{i}-c_{\mathrm{O}_{2}}^{l}\right) \tag{I. 4}
\end{equation*}
$$

For the physical situation depicted in Figure I.2, Equations I. 3 and I. 4 represent the flux of oxygen through the gas and liquid phase, respectively. At steady-state, the oxygen flux in one phase must equal the oxygen flux in the other phase (otherwise, there would be accumulation of oxygen somewhere in the system), and therefore these two fluxes equate. These coefficients are often called individual mass transfer coefficients because they refer to transport in individual phases.

The equilibrium distribution curve shown in Figure I. 1 may be redrawn with the particular concentrations found in the physical situation. Figure I. 3 shows this representation, with the point O indicating the two bulk concentrations.

## Figure I. 3

Liquid phase driving
force for mass transfer


Concentration of oxygen in water

Many other mass transfer coefficients can be defined depending on the type of concentration gradient being used to describe the mass driving force for mass transfer.

Question 2: A bubble of pure oxygen originally 0.1 cm in diameter is injected into a stirred vessel of oxygen-free water at $25^{\circ} \mathrm{C}$. After 7.0 minutes, the bubble has shrunk to a diameter of 0.054 cm . Assuming no resistance to mass transfer in the gas phase (why would this be reasonable?), what is the liquid phase mass transfer coefficient?

## Solution:

The system is the bubble, and a mass balance must be made around the system. The mass balance is:

$$
\begin{aligned}
& \mathrm{ACC}=\mathrm{IN}-\mathrm{OUT}+\mathrm{GEN} \\
& \frac{d c_{\mathrm{O}_{2}}^{g} V}{d t}=0-\Phi_{\mathrm{O}_{2}} A+0
\end{aligned}
$$

where $\mathrm{c}^{\mathrm{g}} \mathrm{O}_{\mathrm{O} 2}$ is the concentration of oxygen in the system (i.e., the bubble), V is the volume of the system, $\Phi_{\mathrm{O} 2}$ is the flux of oxygen (out of the system) and A is the cross-sectional area of the system. The flux may be represented by Equation I.4, being careful to note that the concentration of oxygen ( $\mathrm{c}^{1}{ }^{1}$ ) refers to the liquid phase oxygen concentration:

$$
\Phi_{O_{2}}=k_{L}\left(c_{O_{2}}^{i}-c_{O_{2}}^{l}\right)
$$

Noting that the concentration of oxygen does not change with time, and that the system volume is $(4 / 3) \pi r^{3}$, while the system surface area is $4 \pi r^{2}$, the material balance becomes:

$$
\frac{4}{3} \pi c_{\mathrm{O}_{2}}^{g} \frac{d r^{3}}{d t}=-4 \pi r^{2} k_{L}\left(c_{\mathrm{O}_{2}}^{i}-c_{\mathrm{O}_{2}}^{l}\right)
$$

Differentiating and canceling terms,

$$
\frac{d r}{d t}=-\frac{k_{L}\left(c_{\mathrm{O}_{2}}^{i}-c_{\mathrm{O}_{2}}^{l}\right)}{c_{\mathrm{O}_{2}}^{g}}
$$

Integrating from $r_{0}$ to $r_{1}$,

$$
r_{1}-r_{0}=-\frac{k_{L}\left(c_{O_{2}}^{i}-c_{O_{2}}^{l}\right)}{c_{O_{2}}^{g}} t
$$

Now values must be determined for each of the parameters in this equation.
$\mathrm{r}_{1}=0.054 \mathrm{~cm} / 2=0.027 \mathrm{~cm}$
$\mathrm{r}_{0}=0.1 \mathrm{~cm} / 2=0.05 \mathrm{~cm}$
$\mathrm{t}=7.0 \mathrm{~min} \times 60 \mathrm{~s} / \mathrm{min}=420 \mathrm{~s}$
$\mathrm{c}^{1} \mathrm{O}_{2}=0$ (The water initially was "oxygen-free")
$\mathrm{c}^{\mathrm{g}} \mathrm{O}_{2}=\mathrm{p}_{\mathrm{O} 2} / \mathrm{RT}$ (Ideal Gas Law)
Since the gas bubble is pure oxygen, we may assume that $\mathrm{p}_{\mathrm{O} 2}=1 \mathrm{~atm}$. Then at $25^{\circ} \mathrm{C}, \mathrm{c}^{\mathrm{g}} \mathrm{O}_{\mathrm{O} 2}=(1$ $\mathrm{atm}) /(0.08206 \mathrm{Latm} / \mathrm{molK})(298 \mathrm{~K})=0.041 \mathrm{~mol} / \mathrm{L}$
$\mathrm{c}^{\mathrm{i}}{ }^{\mathrm{O} 2}$ is found by Henry's Law. At $25^{\circ} \mathrm{C}$ for pure oxygen,

$$
\begin{aligned}
\mathrm{x}_{\mathrm{O} 2}^{\mathrm{i}} & =1 \mathrm{~atm} / 43,800 \mathrm{~atm}=2.28 \times 10^{-5} \mathrm{~mol} \mathrm{O}_{2} / \mathrm{mol} \mathrm{H}_{2} \mathrm{O} \\
\mathrm{c}^{\mathrm{i}} \mathrm{O}_{2} & =\left(2.28 \times 10^{-5} \mathrm{~mol} \mathrm{O}_{2} / \mathrm{mol} \mathrm{H}_{2} \mathrm{O}\right) \times\left(\mathrm{mol} \mathrm{H}_{2} \mathrm{O} / 18.0 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}\right) \times\left(997 \mathrm{~g} \mathrm{H}_{2} \mathrm{O} / \mathrm{L}\right) \\
\quad= & 1.26 \times 10^{-3} \mathrm{~mol} \mathrm{O}_{2} / \mathrm{L}
\end{aligned}
$$

Thus, $\mathrm{k}_{\mathrm{L}}=(0.05-0.027)(0.041) /(0.00126)(420)=\underline{1.78 \times 10^{-3}} \underline{\underline{\mathrm{~cm}} / \mathrm{s}}$

## B. Overall Mass Transfer Coefficients

As previously noted, it is usually not possible to measure the partial pressure and concentration at
the interface. It is therefore convenient to define overall mass transfer coefficients based on an overall driving force between the bulk compositions. For the physical situation of oxygen transporting from air to water, two overall mass transfer coefficients may be defined. An overall mass transfer coefficient may be defined in terms of a partial pressure driving force or it may be defined in terms of a liquid phase concentration driving force. In either case, the coefficient must account for the entire diffusional resistance in both phases.

For the gas phase, an overall mass transfer coefficient may be defined by:

$$
\begin{equation*}
\Phi_{O_{2}}=K_{G}\left(p_{O_{2}}^{g}-p_{O_{2}}^{*}\right) \tag{I. 5}
\end{equation*}
$$

$\mathrm{K}_{\mathrm{G}}$ is the overall mass transfer coefficient, $\mathrm{p}^{\mathrm{g}} \mathrm{O}_{2}$ is the bulk gas oxygen partial pressure (as before) and $\mathrm{p}^{*}{ }^{\mathrm{O}} \mathrm{2}$ is the theoretical partial pressure of oxygen in equilibrium with the bulk liquid phase oxygen concentration. In other words, $\mathrm{p}^{*}{ }_{\mathrm{O} 2}$ is the partial pressure in equilibrium with $\mathrm{c}_{\mathrm{O} 2}^{1}$. Note that this partial pressure does not physically appear anywhere in the system.

For the liquid phase, an overall mass transfer coefficient may be defined by:

$$
\begin{equation*}
\Phi_{\mathrm{O}_{2}}=K_{L}\left(c_{\mathrm{O}_{2}}^{*}-c_{\mathrm{O}_{2}}^{l}\right) \tag{I. 6}
\end{equation*}
$$

$\mathrm{K}_{\mathrm{L}}$ is the overall mass transfer coefficient, $\mathrm{c}_{\mathrm{O} 2}^{1}$ is the bulk liquid oxygen concentration (as before) and $\mathrm{c}^{*}{ }_{\mathrm{O} 2}$ is the theoretical oxygen concentration in equilibrium with the bulk gas phase oxygen partial pressure. In other words, $\mathrm{c}^{*}{ }_{\mathrm{O} 2}$ is the concentration of oxygen in the liquid in equilibrium with $\mathrm{p}^{\mathrm{g}} \mathrm{O}_{2}$. Figure I. 4 shows the equilibrium distribution curve with these new driving forces.

## Figure I. 4



Concentration of oxygen in water

The overall mass transfer coefficients may be related to the individual mass transfer coefficients. Let us first make the simplification that the equilibrium relationship between the gas phase partial pressure and the liquid phase concentration of the transporting species at the interface is proportional. This assumption is Henry's Law, and it is valid in the case where the transporting species is present in dilute concentration. For mass transport between other types of phases, a similar assumption may often be made.

$$
\begin{equation*}
p_{j}^{i}=m_{j} c_{j}^{i} \tag{I. 7}
\end{equation*}
$$

If the species is oxygen, then Equation I. 7 essentially becomes Equation I.2, with a conversion being necessary to relate mole fraction and concentration. The theoretical partial pressure of oxygen $\left(\mathrm{p}^{*}{ }_{\mathrm{O} 2}\right)$ in equilibrium with the bulk liquid phase oxygen concentration may now be related to the bulk liquid phase oxygen concentration ( $\mathrm{c}_{\mathrm{O} 2}^{1}$ ) by:

$$
\begin{equation*}
p_{\mathrm{O}_{2}}^{*}=m_{\mathrm{O}_{2}} c_{\mathrm{O}_{2}}^{l} \tag{I. 8}
\end{equation*}
$$

Also, the theoretical liquid phase oxygen concentration ( $\mathrm{c}^{*}{ }^{\mathrm{O}}$ ) in equilibrium with the bulk gas phase oxygen concentration may now be related to the bulk liquid phase oxygen concentration ( $\mathrm{p}^{\mathrm{g}} \mathrm{O}_{\mathrm{O}}$ ) by:

$$
\begin{equation*}
p_{O_{2}}^{g}=m_{O_{2}} C_{O_{2}}^{*} \tag{I. 9}
\end{equation*}
$$

Of course, the liquid phase oxygen concentration at the interface is in equilibrium with the gas phase oxygen concentration at the interface:

$$
\begin{equation*}
p_{O_{2}}^{i}=m_{O_{2}} c_{O_{2}}^{i} \tag{I. 10}
\end{equation*}
$$

We would like to find the relationship between $\mathrm{K}_{\mathrm{G}}, \mathrm{k}_{\mathrm{G}}$ and $\mathrm{k}_{\mathrm{L}}$. To accomplish this goal, Equation I. 5 may be rewritten as:

$$
\begin{equation*}
\frac{1}{K_{G}}=\frac{p_{\mathrm{O}_{2}}-p_{\mathrm{O}_{2}}^{i}}{\Phi_{\mathrm{O}_{2}}}+\frac{p_{\mathrm{O}_{2}}^{i}-p_{\mathrm{O}_{2}}^{*}}{\Phi_{\mathrm{O}_{2}}} \tag{I. 11}
\end{equation*}
$$

Substituting Equations I. 8 and I. 10 into Equation I. 11 yields:

$$
\begin{equation*}
\frac{1}{K_{G}}=\frac{p_{\mathrm{O}_{2}}^{g}-p_{\mathrm{O}_{2}}^{l}}{\Phi_{\mathrm{O}_{2}}}+\frac{p_{\mathrm{O}_{2}}^{i}-p_{\mathrm{O}_{2}}^{*}}{\Phi_{\mathrm{O}_{2}}} \tag{I. 12}
\end{equation*}
$$

Substituting Equations I. 3 and I. 4 into Equation I. 12 yields:

$$
\begin{equation*}
\frac{1}{K_{G}}=\frac{1}{k_{G}}+\frac{m}{k_{L}} \tag{I. 13}
\end{equation*}
$$

To relate $\mathrm{K}_{\mathrm{L}}$ with $\mathrm{k}_{\mathrm{G}}$ and $\mathrm{k}_{\mathrm{L}}$, an equation for $\mathrm{K}_{\mathrm{L}}$ may similarly be derived:

$$
\begin{equation*}
\frac{1}{K_{L}}=\frac{1}{m k_{G}}+\frac{1}{k_{L}} \tag{I. 14}
\end{equation*}
$$

Equations I. 13 and I. 14 show that the relative importance of the two individual phase resistances depends on the solubility of the gas in the liquid. If the gas is very soluble in the liquid, such as ammonia in water, then the value of $m$ is very small. From Equation I.13, the overall mass transfer coefficient $\mathrm{K}_{\mathrm{G}}$ is equal to the gas phase mass transfer coefficient, $\mathrm{k}_{\mathrm{G}}$. In other words, the principal resistance to mass transfer lies in the gas phase, and such a system is said to be gas phase controlled. If the gas is rather insoluble in the liquid, such as oxygen or nitrogen in water, then $m$ is large. In this case, from Equation I.14, the overall mass transfer coefficient $\mathrm{K}_{\mathrm{L}}$ is equal to the liquid phase mass transfer coefficient, $\mathrm{k}_{\mathrm{L}}$. Since the principal resistance to mass transfer lies in the liquid phase, such a system is said to be liquid phase controlled.

Even when the individual coefficients are essentially independent of concentration, the overall coefficients may vary with the concentration unless the equilibrium relationship is linear. Accordingly, the overall coefficients should be employed only at conditions similar to those under which they were measured and should not be employed for other concentration ranges unless the equilibrium relationship for the system is linear over the entire range of interest.

## C. Correlations of Mass Transfer Coefficients

If we consider the transfer of oxygen from air into water, we might imagine that the dissolution process can be hastened by agitating the two phases. This agitation would essentially result in a decrease in the film thicknesses, and hence an increase in the concentration gradient. Indeed, the mass transfer coefficients are dependent on, among other things, the flow conditions on both sides of the interface. Mass transfer coefficients are therefore correlated for various geometries to several dimensionless groups. The principal dimensionless groups used for the correlation of mass transfer coefficients are:

Reynolds Number: $\quad \operatorname{Re}=\frac{L v \rho}{\mu}$

Schmidt Number: $\quad \mathrm{Sc}=\frac{\mu}{\rho D_{A B}}$
Sherwood Number: $\quad \mathrm{Sh}=\frac{k_{L} L}{D_{A B}}$
For these relationships, L is the characteristic length dimension of importance (diameter of a sphere, diameter of a cylinder, or length of a flat surface), $v$ is the mass average velocity, $\rho$ is the fluid density, $\mu$ is the fluid viscosity, $\mathrm{D}_{\mathrm{AB}}$ is the diffusion coefficient of " A " in the fluid, $\mathrm{k}_{\mathrm{L}}$ is the mass transfer coefficient in the liquid phase. These dimensionless numbers each describe the ratio of the importance of two transport phenomena. The Reynolds Number physically describes the ratio of
inertial forces to viscous forces, the Schmidt Number describes the ratio of momentum diffusivity to mass diffusivity, and the Sherwood Number describes the ratio of mass transfer rate to diffusion rate. As noted earlier, there are numerous definitions for mass transfer coefficients. Although all mass transfer coefficients are related, they do have different values. Therefore, one must exercise care when correlations are used that the correct mass transfer coefficient is being correlated.

If the physical situation is the dispersion of bubbles in a liquid-containing vessel, then a more appropriate Reynolds Number might the characteristic dimension of the impeller diameter, $D_{i}$, and a reference velocity of $N_{i} D_{i}$, where $N_{i}$ is the stirrer speed (revolutions/minute). Thus, Reynolds number becomes:

Reynolds Number: $\quad \operatorname{Re}=\frac{N_{i} D_{i}^{2} \rho}{\mu}$
One way to correlate mass transfer coefficient is by the following type of equation:

$$
\begin{equation*}
\mathrm{Sh}=K \operatorname{Re}^{\alpha} \mathrm{Sc}^{\beta} \tag{I. 15}
\end{equation*}
$$

where $\alpha$ and $\beta$ are exponents and K is a constant. Of course, there are many other types of correlations.

Just as an illustration, there are a couple correlations available for the liquid phase mass transfer coefficient of a sphere suspended in that liquid. The sphere may be an oxygen bubble from which oxygen is flowing into the liquid, or the sphere may be a microorganism to which nutrients are flowing from the fluid.

For the case of small spheres (less than 0.6 mm diameter) under mild agitation (where the principal contributor to mass transfer is gravitational forces), the following correlation may be used:

$$
\begin{equation*}
\operatorname{Sh}=2+0.31\left[\frac{\left(\rho_{L}-\rho_{G}\right) \rho g d_{B}^{3}}{\mu^{2}}\right]^{1 / 3} \operatorname{Sc}^{1 / 3} \tag{I. 16}
\end{equation*}
$$

where $\mathrm{d}_{\mathrm{B}}$ is the sphere (e.g., bubble) diameter. The density difference between the phases is an important and unique term in Equation I.16. For the case of spheres above 2.5 mm in diameter, the bubbles rise exclusively under gravitational forces, and the density difference between the liquid and gas phase becomes important:

$$
\begin{equation*}
\mathrm{Sh}=0.42\left[\frac{\left(\rho_{L}-\rho_{G}\right) \rho_{L} g d_{B}^{3}}{\mu_{L}^{2}}\right]^{1 / 3} \mathrm{Sc}^{1 / 2} \tag{I. 17}
\end{equation*}
$$

In Equations I. 16 and I.17, the term in brackets is referred to as the Grasshof Number, and it is the ratio of buoyancy forces to viscous forces in systems of free convection.

Many situations arise in which the total surface area across which transport occurs is not calculable.

For example, in a stirred solution containing numerous dissolving air bubbles, the total surface area for the transport of oxygen is not known. In such situations the total volume of the system is often incalculable as well. In these cases it is convenient to define a surface area to volume ratio, $a=A / V$. Thus, some correlations are used to estimate the product of the mass transfer coefficient and the surface area to volume ratio: $\mathrm{k}_{\mathrm{L}} \mathrm{a}$. For example, a simple correlation for non-coalescing dispersions is:

$$
\begin{equation*}
k_{L} a=0.0020\left[\frac{P}{V}\right]^{0.7} v_{s}^{0.2} \tag{I. 18}
\end{equation*}
$$

where $(\mathrm{P} / \mathrm{V})$ is in units of watts $/ \mathrm{m}^{3}$ and $\mathrm{v}_{\mathrm{S}}$ is the superficial gas velocity $(\mathrm{m} / \mathrm{s})$. The units of $\mathrm{k}_{\mathrm{L}} \mathrm{a}$ in Equation I. 18 are s $^{-1}$. The range of power input for which Equation I. 18 is valid lies between 500 and 10000 watts $/ \mathrm{m}^{3}$.

It is important to remember that dozens of correlations for $\mathrm{k}_{\mathrm{L}}$ and for $\mathrm{k}_{\mathrm{L}} \mathrm{a}$ are available depending on the system. It is often quite difficult to distinguish between the correlations, and it is not uncommon for a correlation to yield a value in error of reality by more than $50 \%$.

Question 3: Air bubbles having a diameters of 3.0 mm are stirred in a vessel containing water at $37^{\circ} \mathrm{C}$. The diffusion coefficient of oxygen in water is $3.3 \times 10^{-5} \mathrm{~cm}^{2} / \mathrm{s}$.
a) Estimate the mass transfer coefficient.
b) If the solubility of oxygen at $37^{\circ} \mathrm{C}$ is $2.26 \times 10^{-7} \mathrm{~mol} / \mathrm{cm}^{3}$, calculate the maximum flux of oxygen into the fermentor.
c) If the bubbles are 0.3 mm in diameter, calculate the mass transfer coefficient.

## Solution:

a) For the case of large bubbles, an estimate of the mass transfer coefficient may be found from Equation 5.17:

$$
\operatorname{Sh}=0.42\left[\frac{\left(\rho_{L}-\rho_{G}\right) \rho_{L} g d_{B}^{3}}{\mu_{L}^{2}}\right]^{1 / 3} \mathrm{Sc}^{1 / 2}
$$

The values necessary for this equation are:
$\mathrm{d}_{\mathrm{B}}=0.30 \mathrm{~cm}$
$\rho_{\mathrm{L}}=0.994 \mathrm{~g} / \mathrm{cm}^{3}$
$\rho_{\mathrm{G}}=0.00113 \mathrm{~g} / \mathrm{cm}^{3}$
$\mathrm{g}=981 \mathrm{~cm} / \mathrm{s}^{2}$
$\mu=6.95 \times 10^{-3} \mathrm{~g} / \mathrm{cms}$
$\mathrm{Sc}=\left(6.95 \times 10^{-3} \mathrm{~g} / \mathrm{cms}\right) /\left(0.994 \mathrm{~g} / \mathrm{cm}^{3}\right)\left(3.3 \times 10^{-5} \mathrm{~cm}^{2} / \mathrm{s}\right)=212$
$\mathrm{Sh}=0.42(0.994-0.001)^{1 / 3}(0.994)^{1 / 3}(981)^{1 / 3}(0.30)\left(6.95 \times 10^{-3}\right)^{-2 / 3}(212)^{1 / 2}=498$
So, $\mathrm{k}_{\mathrm{L}}=\operatorname{Sh} \mathrm{D}_{\mathrm{AB}} / \mathrm{d}_{\mathrm{B}}=(498)\left(3.3 \times 10^{-5} \mathrm{~cm}^{2} / \mathrm{s}\right) /(0.30 \mathrm{~cm})=\underline{0.055 \mathrm{~cm} / \mathrm{s}}$
b) The flux may be found by Equation I.4:

$$
N_{O_{2}}=k_{L}\left(c_{O_{2}}^{i}-c_{O_{2}}^{l}\right)
$$

The value of $\mathrm{k}_{\mathrm{L}}$ has been found in part a). The maximum flux occurs when the concentration difference is as great as possible. This condition occurs when the interface concentration $\mathrm{c}^{\mathrm{i}}{ }_{\mathrm{O} 2}$ is equal to the saturation concentration, and $\mathrm{c}_{\mathrm{O} 2}^{1}$ is equal to zero. Thus the maximum flux is:
$\mathrm{N}_{\mathrm{O} 2}=(0.055 \mathrm{~cm} / \mathrm{s})\left(2.26 \times 10^{-7} \mathrm{~mol} / \mathrm{cm}^{3}-0\right)=\underline{\left.\underline{1.24} \times 10^{-\underline{8}} \underline{\underline{\mathrm{~mol} \mathrm{O}}} \underline{\underline{2}} \underline{\underline{\mathrm{~cm}^{2}}} \underline{\underline{\mathrm{2}}} \underline{\underline{s}}\right]}$
c) For the case of small bubbles, Equation I. 16 may be used:

$$
\mathrm{Sh}=2+0.31\left[\frac{\left(\rho_{L}-\rho_{G}\right) \rho g d_{B}^{3}}{\mu^{2}}\right]^{1 / 3} \mathrm{Sc}^{1 / 3}
$$

All the necessary values have been calculated in part a). We find:

$$
\begin{aligned}
& \mathrm{Sh}=2+0.31(0.994-0.001)^{1 / 3}(0.994)^{1 / 3}(981)^{1 / 3}(0.03)\left(6.95 \times 10^{-3}\right)^{-2 / 3}(212)^{1 / 2}=17.1 \\
& \mathrm{k}_{\mathrm{L}}=\operatorname{Sh} \mathrm{D}_{\mathrm{AB}} / \mathrm{d}_{\mathrm{B}}=(17.1)\left(3.3 \times 10^{-5} \mathrm{~cm}^{2} / \mathrm{s}\right) /(0.03 \mathrm{~cm})=\underline{\underline{0.019} \mathrm{~cm} / \mathrm{s}}
\end{aligned}
$$

## Problems:

1. Liquid bromine is poured into a large vessel of water. The water is stirred sufficiently to produce a mass transfer coefficient $\mathrm{k}_{\mathrm{L}}$ a of $3.82 \times 10^{-3} \mathrm{~s}^{-1}$. How long will be required for bromine to reach a concentration in the water equal to one-half the saturation concentration?
2. Jasmone is a valuable chemical in the perfume industry used in soaps and cosmetics. The compound is recovered by suspending jasmine flowers in water (the continuous phase) and extracting with benzene. The mass transfer coefficient in benzene drops is $3.0 \times 10^{-4} \mathrm{~cm} / \mathrm{s}$, while the mass transfer coefficient in the water phase is $2.4 \times 10^{-3} \mathrm{~cm} / \mathrm{s}$. Jasmone is 170 times more soluble in benzene than it is in water. Is the mass transfer controlled by the water phase or the benzene phase?
