19.7. The following temperatures, salinities, and oxygen concentrations are measured in an estuary:

Distance from ocean, km	30	20	10
Temperature, °C	25	22	18
Salinity, ppt	5	10	20
Dissolved oxygen	5	6.5	7.5

Calculate the percent saturation of oxygen at the three locations.

19.8. What is the oxygen saturation concentration of a saline lake (mostly sodium chloride) that is located at an elevation of 1 km, and has a salinity of 10 ppt, and is at a temperature of 25°C?

LECTURE 20

Gas Transfer and Oxygen Reaeration

LECTURE OVERVIEW: I describe two theories of gas transfer, the two-film model and the surface renewal model, and show how they can be used to model oxygen transfer in natural waters. In addition I review formulas to predict reaeration in streams.

Suppose we fill an open bottle with oxygen-free distilled water. We know from the previous lecture that, given sufficient time, atmospheric oxygen will enter until the solution reaches the saturation level defined by Henry's law. Similarly if we had a bottle of water that was supersaturated, over time oxygen would leave the solution until the saturation value was reached.

The key question is, "How long will it take?" In other words we would like to assess the rate of the process. Now let's imagine an experiment to quantitatively answer this question.

We have our open bottle filled with oxygen-free distilled water. As depicted in Fig. 20.1, we place a mixing device in the bottle. This device keeps the volume well-mixed except in the bottle's narrow neck, where molecular diffusion governs transport.

To model this system, assume that the water at the air-water interface is at the saturation concentration. Under this assumption, a mass balance for the bottle can be written as

$$V\frac{do}{dt} = DA\frac{o_s - o}{\Delta H} \qquad (20.1)$$

where D = molecular diffusion coefficient of oxygen in water (m² d⁻¹)
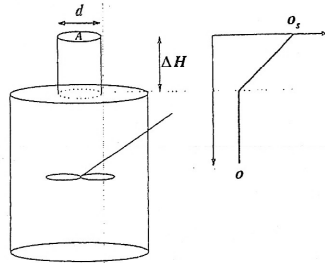A = cross-sectional area of the bottle neck (m²)

FIGURE 20.1
An open well-mixed bottle with a narrow neck in which molecular diffusion governs transport.

o_s = oxygen saturation concentration (mg L^{-1})
o = oxygen concentration in the bottle (mg L^{-1})
ΔH = length of the neck (m)

The model can also be expressed as

$$V\frac{do}{dt} = K_L A(o_s - o) \tag{20.2}$$

where K_L = oxygen mass-transfer velocity (m d^{-1}), which is equal to

$$K_L = \frac{D}{\Delta H} \tag{20.3}$$

Dividing both sides of Eq. 20.2 by the volume and rearranging yields

$$\frac{do}{dt} + k_a o = k_a o_s \tag{20.4}$$

where k_a = reaeration rate (d^{-1}), which is equal to $K_L A/V$. Together with the initial condition that $o = 0$ at $t = 0$, Eq. 20.4 can be solved for

$$o = o_s(1 - e^{-k_a t}) \tag{20.5}$$

EXAMPLE 20.1. OXYGEN TRANSFER FOR A BOTTLE. You fill the 300-mL bottle shown in Fig. 20.1 with oxygen-free water. Calculate the oxygen concentration as a function of time if $D = 2.09 \times 10^{-5}$ cm^2 s^{-1}, $d = 2$ cm, and $\Delta H = 2.6$ cm. Assume that the system is at a temperature of 20°C and the saturation concentration is 9.1 mg L^{-1}.

Solution: First, we must determine the mass-transfer velocity,

$$K_L = \frac{2.09 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}}{2.6 \text{ cm}} \left(\frac{1 \text{ m}}{100 \text{ cm}} \frac{86,400 \text{ s}}{d} \right) = 0.006945 \text{ m d}^{-1}$$

Next we can calculate the reaeration coefficient,

$$k_a = \frac{0.006945 \text{ m d}^{-1}[\pi(0.01)^2] \text{ m}^2}{300 \text{ mL}} \left(\frac{10^6 \text{ mL}}{\text{m}^3} \right) = 0.007273 \text{ d}^{-1}$$

The parameters can be substituted into Eq. 20.5,

$$c = 9.1(1 - e^{-0.007273 t})$$

which can be used to determined the following values as a function of time:

Time	0	80	160	240	320	400
Oxygen	0.00	4.01	6.25	7.50	8.21	8.60

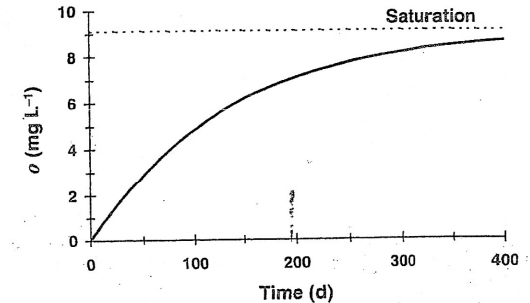A graph of the results can also be generated:

FIGURE E20.1.1

Over a long period of time the concentration approaches the saturation value. The time can be quantified by determining a 95% response time,

$$t_{95} = \frac{3}{0.007273} = 412 \text{ d}$$

Thus according to the model, it would take over 1 yr to reach 95% of saturation.

In the foregoing example we calculated that it would take over 1 yr for a bottle of water to reoxygenate. Although the situation in nature is not as slow, gas transfer in natural waters involves many of the principles we used to model the bottle.

20.1 GAS TRANSFER THEORIES

We will now describe two theories that are widely used to describe gas transfer in natural waters. Although both are used in streams, estuaries, and lakes, the stagnant-film theory is more widely used in standing waters such as lakes, whereas the surface-renewal model is more commonly used in flowing waters such as streams.

20.1.1 Whitman's Two-Film Theory

A simple model of gas exchange is provided by Whitman's two-film or two-resistance model (Whitman 1923, Lewis and Whitman 1924).
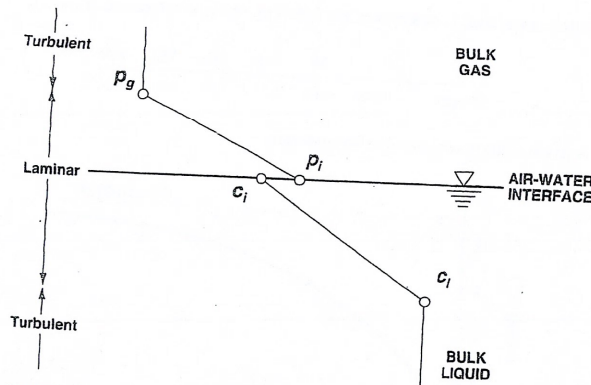
FIGURE 20.2
Schematic representation of Whitman's two-film theory of gas transfer. Liquid and gas concentration at the interface are assumed to be at an equilibrium as defined by Henry's law. Gradients in the films control the rate of gas transfer between the bulk fluids.

As depicted in Fig. 20.2, the bulk or main body of the gaseous and liquid phases are assumed to be turbulently well-mixed and homogeneous. The two-film theory assumes that a substance moving between the phases encounters maximum resistance in two laminar boundary layers where mass transfer is via molecular diffusion. The mass transfer through the individual films would be a function of a mass-transfer velocity and the gradient between the concentrations at the interface and in the bulk fluid. For example transfer through the liquid film can be represented by

$$J_l = K_l(c_i - c_l) \tag{20.6}$$

where J_l = mass flux from the bulk liquid to the interface (mole m^{-2} d^{-1})
K_l = mass-transfer velocity in the liquid laminar layer (m d^{-1})
c_i and c_l = liquid concentrations at the air-water interface and in the bulk liquid, respectively (mole m^{-3}).

Similarly transfer through the gaseous film can be represented by

$$J_g = \frac{K_g}{RT_a}(p_g - p_i) \tag{20.7}$$

where J_g = mass flux from the interface to the bulk gas (mole m^{-2} d^{-1}),
K_g = mass-transfer velocity in the gaseous laminar layer (m d^{-1})
p_g and p_i = the gas pressures in the bulk gas and at the air-water interface, respectively (atm)

Notice that for both Eqs. 20.6 and 20.7, a positive flux represents a gain to the water.

The transfer coefficients can be related to more fundamental parameters by

$$K_l = \frac{D_l}{z_l} \tag{20.8}$$

and

$$K_g = \frac{D_g}{z_g} \tag{20.9}$$

where D_l = liquid molecular diffusion coefficient (m^2 d^{-1})
D_g = gas molecular diffusion coefficient (m^2 d^{-1})
z_l = thickness of the liquid film (m)
z_g = thickness of the gas film (m)

A key assumption of the two-film theory is that an equilibrium exists at the air-water interface. In other words Henry's law (recall Eq. 19.29) holds:

$$p_i = H_e c_i \tag{20.10}$$

Equation 20.10 can be substituted into Eq. 20.6, which can be solved for

$$p_i = H_e\left(\frac{J_l}{K_l} + c_l\right) \tag{20.11}$$

Equation 20.7 can be solved for

$$p_i = p_g - \frac{RT_a J_g}{K_g} \tag{20.12}$$

Equations 20.11 and 20.12 can be equated and solved for flux,

$$J = v_v\left(\frac{p_g}{H_e} - c_l\right) \tag{20.13}$$

where v_v = net transfer velocity across the air-water interface (m d^{-1}), which can be computed by

$$\frac{1}{v_v} = \frac{1}{K_l} + \frac{RT_a}{H_e K_g} \tag{20.14}$$

Equation 20.13 now provides a means to compute mass transfer as a function of the gradient between the bulk levels in the gaseous and the liquid phases. In addition it yields a net transfer velocity (Eq. 20.14) that is a function of environmental characteristics K_l and K_g and the gas-specific parameter H_e. Note that Eq. 20.14 can be inverted to calculate the mass-transfer velocity directly,
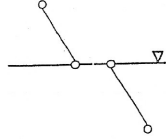
$$v_v = K_l \frac{H_e}{H_e + RT_a\left(K_l/K_g\right)} \tag{20.15}$$

Notice that I have modified the nomenclature slightly by using a "v" rather than a "K" for the net transfer velocity. I did this to make the coefficient's nomenclature consistent with its units—that is, a velocity. The subscript v is intended to signify that the coefficient is a volatilization mass-transfer velocity.
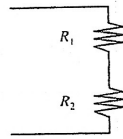
$$R = R_1 + R_2$$

$$\frac{1}{v_v} = \frac{1}{K_l} + \frac{RT_a}{H_e K_g}$$

(a) Two resistors in series   **(b) Two films in series**

FIGURE 20.3
The two-film theory of gas transfer is analogous to the formulation for two resistors in series in an electrical circuit.

FIGURE 20.4
Percent resistance to gas transfer in the liquid phase as a function of H_e, the Henry's constant for lakes. Values of H_e for some environmentally important gases and toxic substances are indicated (modified from Mackay 1977).

Also observe that Eq. 20.14 seems to be analogous to the formulation used to determine the effect of two resistors in parallel in an electrical circuit:

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} \tag{20.16}$$

Although Eq. 20.14 might superficially be in this format, it can be recognized that the resistance in each film is actually the reciprocal of its mass-transfer velocity. Consequently Eq. 20.14 is actually analogous to the formulation used to determine the effect of two resistors in series in an electrical circuit (Fig. 20.3).

As in Eq. 20.15 the total resistance to gas transfer is a function of the individual resistances in the liquid and the gaseous boundary layers. The liquid, the gas, or both layers can be the controlling or limiting factor depending on the values of the three coefficients K_l, K_g, and H_e. This can be quantified by using Eq. 20.15 to develop (Mackay 1977)

$$R_l = \frac{H_e}{H_e + RT_a(K_l/K_g)} \tag{20.17}$$

where R_l = ratio of the liquid-layer resistance to the total resistance. For lakes, K_g varies from approximately 100 to 12,000 m d^{-1} and K_l from 0.1 to 10 m d^{-1} (Liss 1975, Emerson 1975). The ratio of K_l to K_g generally ranges from 0.001 to 0.01, with the higher values in small lakes due primarily to lower K_g because of sheltering from wind. A plot of R_l versus H_e (Fig. 20.4) indicates where the liquid, gas, or both films govern transport for contaminants of differing solubility. In general the higher the Henry's constant, the more the control shifts to the liquid film. Also note that smaller lakes tend to be more gas-film controlled than larger lakes.

As mentioned previously the two-film theory usually represents a good approximation for standing waters such as lakes. Next we turn to another theory, one that extends the two-film theory to systems such as streams that have strong advective flow.
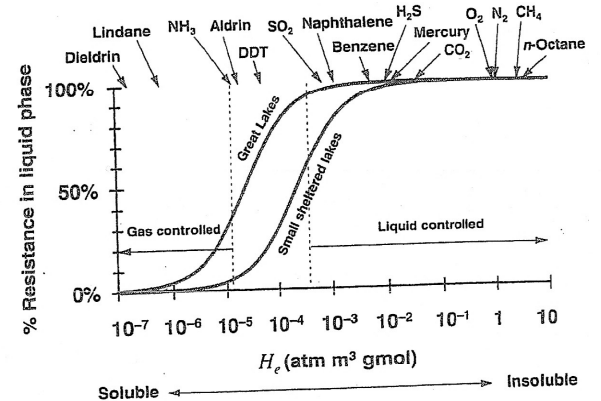
20.1.2 Surface Renewal Model

We now turn to a model that takes a different approach to gas transfer from the two-film theory described in the previous section. Rather than as a stagnant film, the system is conceptualized as consisting of parcels of water that are brought to the surface for a period of time. While at the surface, exchange takes place. Then the parcels are moved away from the surface and mixed with the bulk liquid (Fig. 20.5).

Higbie (1935) suggested that when the liquid and gas are first brought into contact, the liquid film will be at the concentration of the bulk liquid. Thus, prior to the situation envisioned by the two-film theory (Fig. 20.2), the dissolved gas must penetrate the film. Hence it was dubbed the *penetration theory*. The evolution of this penetration is depicted by the succession of dashed lines in Fig. 20.6. If the
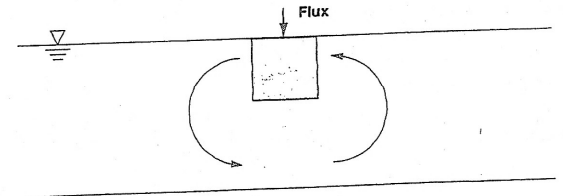

FIGURE 20.5
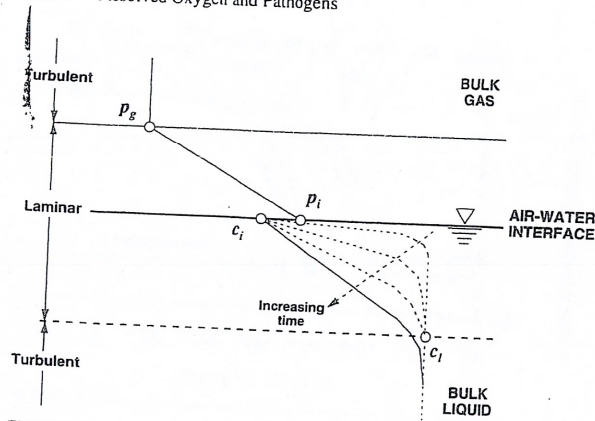Depiction of surface renewal model of gas exchange.

FIGURE 20.6
The temporal evolution of the liquid film immediately after it is brought into contact with the gas.

process is not interrupted, the Whitman two-film condition (the solid line) will be attained.

As described in Box 20.1, the penetration theory can be used to estimate the flux of gas across the air-water interface as

$$J = \sqrt{\frac{D_l}{\pi t^*}}(c_s - c_l) \qquad (20.18)$$

where D_l = liquid diffusion coefficient
$\quad c_s$ = concentration at the air-water interface
$\quad c_l$ = concentration in the bulk water
$\quad t^*$ = average contact time of the fluid parcel at the interface

This equation is of little value in itself because the average contact time at the interface is difficult to measure. However, Eq. 20.18 yields the valuable insight that if the penetration theory holds, the mass-transfer velocity is proportional to the square root of the gas's molecular diffusivity.

BOX 20.1.   Derivation of Penetration Theory

Suppose that a parcel of water moves to the air-water interface (Fig. 20.5). The parcel can be idealized as a one-dimensional semi-infinite medium described by the equation

$$\frac{\partial c}{\partial t} = D_l \frac{\partial^2 c}{\partial z^2} \qquad (20.19)$$

subject to the initial and boundary conditions

$$c(z, 0) = c_l \qquad \text{initial condition}$$

$$c(0, t) = c_s \qquad \text{boundary condition at air-water interface} \qquad (20.20)$$
$$c(\infty, t) = c_l \qquad \text{bottom boundary condition}$$

where D_l = liquid diffusion coefficient
$\quad c_s$ = concentration at the air-water interface
$\quad c_l$ = concentration in the bulk water

Applying these conditions, we can solve Eq. 20.19 for

$$c(z, t) = (c_s - c_l)\, \text{erfc}\left(\frac{z}{2\sqrt{D_l t}}\right) \qquad (20.21)$$

where erfc is the error function complement, equal to $1 - \text{erf}$; where erf is the error function (recall Sec. 10.3.2 and App. G),

$$\text{erf}\,\phi = \frac{2}{\sqrt{\pi}}\int_0^{\phi} e^{-\xi^2}\, d\xi \qquad (20.22)$$

The flux across the air-water interface can be computed by applying Fick's first law at the interface ($z = 0$),

$$J(0, t) = -D_l \frac{\partial c(0, t)}{\partial z} \qquad (20.23)$$

and the average flux is determined by

$$J = \frac{\int_0^{t^*} J(0, t)\, dt}{t^*} \qquad (20.24)$$

where t^* = average contact time of the fluid parcel at the interface. Equation 20.21 can be differentiated and substituted into Eqs. 20.23 and 20.24 and solved for

$$J = \sqrt{\frac{D_l}{\pi t^*}}(c_s - c_l) \qquad (20.25)$$

One of Higbie's underlying assumptions was that all packets of water have the same contact time at the interface. Danckwerts (1951) modified the approach by assuming that the fluid elements reach and leave the interface randomly. That is, their exposure is described by a statistical distribution. This approach, which is called the *surface renewal theory*, was used to derive

$$J = \sqrt{D_l r_l}(c_s - c_l) \qquad (20.26)$$

where r_l = liquid surface renewal rate, which has units of T^{-1}.

The surface renewal theory can also be applied to the gaseous side of the interface by assuming that packets of gas are brought into contact with the air-water interface in a random fashion. The transfer velocities for the liquid and gaseous phases can thus be written as

$$K_l = \sqrt{r_l D_l} \qquad (20.27)$$

and

$$K_g = \sqrt{r_g D_g} \qquad (20.28)$$

These relationships can be substituted into either Eqs. 20.14 or 20.15 to estimate a total transfer velocity for the interface.

We can now see that a major difference between two-film and the surface renewal theories relates to how the liquid and gas-film exchange velocities are formulated. In particular for the two-film theory, the velocities are proportional to D (Eqs. 20.8 and 20.9), whereas for the surface renewal theory they are proportional to the square root of D (Eqs. 20.27 and 20.28).

We return to the topic of gas transfer when we cover toxic substances later in this text. At that time, I provide additional information on Henry's constant and exchange coefficients for organic toxicants. For the time being let's narrow our focus and concentrate on the problem at hand: oxygen transfer.

20.2 OXYGEN REAERATION

At this point we have a general equation for the flux of any gas (Eq. 20.13),

$$J = v_v\left(\frac{p_g}{H_e} - c_l\right) \tag{20.29}$$

Now let's apply it to oxygen reaeration. Because of its high Henry's constant (≈ 0.8 atm m^3 mole^{-1}), oxygen is overwhelmingly liquid-film controlled. Consequently $v_v = K_l$ and Eq. 20.29 becomes

$$J = K_l\left(\frac{p_g}{H_e} - o\right) \tag{20.30}$$

where o = oxygen concentration in the water. Further, because oxygen is so abundant in the atmosphere, the partial pressure is constant and therefore

$$J = K_l(o_s - o) \tag{20.31}$$

where o_s = saturation concentration of oxygen.

Next the mole flux can be converted to a mass flux, and the liquid concentrations can be reexpressed in mass rather than mole units by multiplying both sides of Eq. 20.31 by the molecular weight of oxygen (32 g mole^{-1}). The equation can also be transformed from a flux to units of mass per time by multiplying it by the surface area of the liquid exposed to the atmosphere. Thus for a well-mixed open batch reactor, a mass balance for oxygen can be written as

$$V\frac{do}{dt} = K_l A_s(o_s - o) \tag{20.32}$$

where A_s = surface area of the water body.

Finally there are many cases (especially streams and rivers) where the transfer velocity is expressed as a first-order rate. In cases where the air-water interface is not constricted (as was not the case for the bottle from Fig. 20.1), the volume is

$$V = A_s H \tag{20.33}$$

where H = mean depth. If this is true Eq. 20.32 can be expressed as

$$V\frac{do}{dt} = k_a V(o_s - o) \tag{20.34}$$

where k_a = reaeration rate, which is equivalent to

$$k_a = \frac{K_l}{H} \tag{20.35}$$

Regardless of how the oxygen transfer rate is parameterized, Eq. 20.32 or 20.34 provides insight into how the mechanism of oxygen reaeration operates. The direction and magnitude of the mass transfer depends partially on the difference between the saturation value and the actual value in the water. If the water is undersaturated ($o < o_s$), then transfer will be positive (a gain) as oxygen moves from the atmosphere into the water to try to bring the water back to the equilibrium state of saturation. Conversely if the water is supersaturated ($o > o_s$), then transfer will be negative (a loss) as oxygen is purged from the system.

Oxygen reaeration rates can be extrapolated to other temperatures by

$$k_{a,T} = k_{a,20}\theta^{T-20} \tag{20.36}$$

where $\theta \cong 1.024$.

20.3 REAERATION FORMULAS

Many investigators have developed formulas for predicting reaeration in streams and rivers. Comprehensive reviews can be found elsewhere (Bowie et al. 1985). In this section we describe some of the more commonly used formulas that have been developed for natural waters.

20.3.1 Rivers and Streams

Numerous formulas have been proposed to model stream reaeration. Among these, three are very commonly used: the O'Connor-Dobbins, Churchill, and Owens-Gibbs formulas.

O'Connor-Dobbins. In Sec. 20.1.2 we developed the surface renewal model. For oxygen this model can be used to formulate the transfer velocity as

$$K_l = \sqrt{r_l D_l} \tag{20.37}$$

O'Connor and Dobbins (1956) hypothesized that the surface renewal rate could be approximated by the ratio of the average stream velocity to depth,

$$r_l = \frac{U}{H} \tag{20.38}$$

This hypothesis was backed up by experimental measurements. Substituting this value into Eq. 20.37 yields

$$K_l = \sqrt{\frac{D_l U}{H}} \tag{20.39}$$

The relationship is usually expressed as a reaeration rate,

$$k_a = \sqrt{D_l}\frac{U^{0.5}}{H^{1.5}} \tag{20.40}$$

The diffusivity of oxygen in natural waters is approximately 2.09×10^{-5} cm^2 s^{-1}. Therefore the *O'Connor-Dobbins formula* can be expressed as

Metric:

$$k_a = 3.93\frac{U^{0.5}}{H^{1.5}}$$

Units: $k_a(d^{-1})$, U(mps), H(m)

English:

$$k_a = 12.9\frac{U^{0.5}}{H^{1.5}} \tag{20.41}$$

Units: $k_a(d^{-1})$, U(fps), H(ft)

Churchill. Churchill et al. (1962) used a more empirical approach than that used by O'Connor and Dobbins. They exploited the fact that the water leaving some of the reservoirs in the Tennessee River valley were undersaturated with oxygen. They therefore measured oxygen levels in the stretches below these dams and calculated associated reaeration rates. They then correlated their results with depth and velocity to obtain

Metric:

$$k_a = 5.026\frac{U}{H^{1.67}}$$

English:

$$k_a = 11.6\frac{U}{H^{1.67}} \tag{20.42}$$

Same units as Eq. 20.41.

Owens and Gibbs. Owens et al. (1964) also used an empirical approach, but they induced oxygen depletion by adding sulfite to several streams in Great Britain. They combined their results with the data from the Tennessee River and fit the following formulas:

Metric:

$$k_a = 5.32\frac{U^{0.67}}{H^{1.85}}$$

English:

$$k_a = 21.6\frac{U^{0.67}}{H^{1.85}} \tag{20.43}$$

Same units as Eq. 20.41.

Comparison among formulas. As summarized in Table 20.1, the O'Connor-Dobbins, Churchill, and Owens-Gibbs formulas were developed for different types of streams. Covar (1976) found that they could be used jointly to predict reaeration for ranges of depths and velocity combinations (Zison et al. 1978). According to Fig. 20.7, O'Connor-Dobbins has the widest applicability being appropriate for moderate to deep streams with moderate to low velocities. The Churchill formula applies for similar depths but for faster streams. Finally the Owens-Gibbs relationship is used for shallower systems.

TABLE 20.1
Ranges of depth and velocity used to develop the O'Connor-Dobbins, Churchill, and Owens-Gibbs formulas for stream reaeration

Parameter	O'Connor-Dobbins	Churchill	Owens-Gibbs
Depth, m	0.30–9.14	0.61–3.35	0.12–0.73
ft	1–30	2–11	0.4–2.4
Velocity, mps	0.15–0.49	0.55–1.52	0.03–0.55
fps	0.5–1.6	1.8–5	0.1–1.8

Notice that the O'Connor-Dobbins formula generally gives lower values than the Churchill and Owens-Gibbs formulas. One possible explanation is that the slower, deeper channels for which O'Connor-Dobbins performs best are more idealized (i.e., more like a flume) than faster, shallower streams where drop structures and riffles may enhance reaeration.
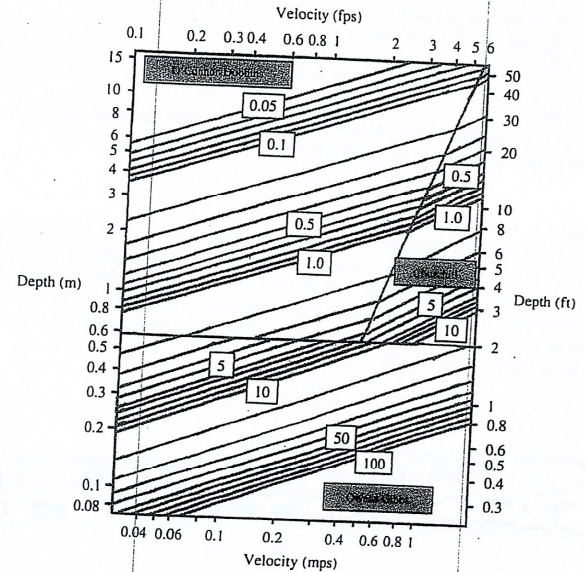

FIGURE 20.7
Reaeration rate (d^{-1}) versus velocity and depth (Covar 1976 and Zison et al. 1978).

Other formulas. There are many other reaeration equations beyond the O'Connor-Dobbins, Churchill, and Owens-Gibbs formulas. Bowie et al. (1985) provide an extensive compilation of many formulas along with references to major critiques and intercomparisons that have been performed.

In addition, along with allowing the user to specify reaeration values directly, software packages such as EPA's QUAL2E model also provide the option to automatically compute reaeration rates according to formulas. I will present these formulas when I describe the QUAL2E model in Lec. 26.

20.3.2 Waterfalls and Dams

Oxygen transfer in streams can be significantly influenced by the presence of waterfalls and dams. Butts and Evans (1983) have reviewed efforts to characterize this transfer and have suggested the following formula:

$$r = 1 + 0.38abH(1 - 0.11H)(1 + 0.046T) \qquad (20.44)$$

where r = ratio of the deficit above and below the dam
H = difference in water elevation (m)
T = water temperature (°C)
a and b = coefficients that correct for water quality and dam type

Values of a and b are summarized in Table 20.2.

TABLE 20.2
Coefficient values for use in Eq. 20.44 to predict the effect of dams on stream reaeration

Water-quality coefficient	
Polluted state	a
Gross	0.65
Moderate	1.0
Slight	1.6
Clean	1.8
Dam-type coefficient	
Dam type	b
Flat broad-crested regular step	0.70
Flat broad-crested irregular step	0.80
Flat broad-crested vertical face	0.60
Flat broad-crested straight-slope face	0.75
Flat broad-crested curved face	0.45
Round broad-crested curved face	0.75
Sharp-crested straight-slope face	1.00
Sharp-crested vertical face	0.80
Sluice gates	0.05

20.3.3 Standing Waters and Estuaries

For standing waters, such as lakes, impoundments, and wide estuaries, wind becomes the predominant factor in causing reaeration.

Lakes. The oxygen-transfer coefficient itself can be estimated as a function of wind speed by a number of formulas. Some, such as the following relationship developed by Broecker et al. (1978), indicate a linear dependence,

$$K_l = 0.864U_w \qquad (20.45)$$

where K_l = oxygen mass-transfer coefficient (m d^{-1}) and U_w = wind speed measured 10 m above the water surface (m s^{-1}).

Others use various wind dependencies to attempt to characterize the different turbulence regimes that result at the air-water interface as wind velocity increases. For example the following is a widely used formula of this type (Banks 1975, Banks and Herrera 1977):

$$K_l = 0.728U_w^{0.5} - 0.317U_w + 0.0372U_w^2 \qquad (20.46)$$

Thus at high wind velocities, the relationship becomes dominated by the second-order term, as shown in Fig. 20.8.

As with stream reaeration formulas, lake oxygen-transfer formulas have both empirical and theoretical bases. For example Wanninkhof et al. (1991) used gas tracer experiments in lakes to develop the following formula:

$$K_l = 0.108U_w^{1.64}\left(\frac{Sc}{600}\right)^{0.5} \qquad (20.47)$$

where Sc = Schmidt number, which for oxygen in water is approximately 500. If this value is adopted the Wanninkhof formula reduces to $K_l = 0.0986U_w^{1.64}$.
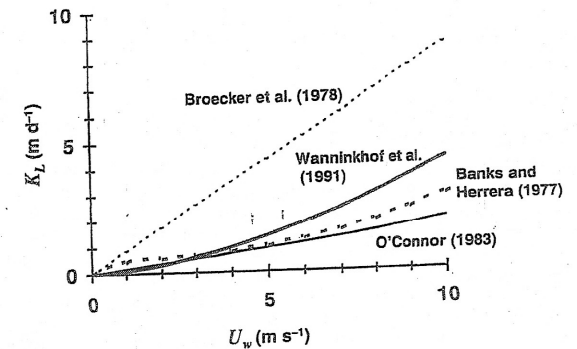

FIGURE 20.8
Comparison of wind-dependent reaeration formulas.

Finally O'Connor (1983) has developed a theoretically based set of formulas to compute transfer for low-solubility gases as a function of wind. His scheme can be applied to oxygen (Fig. 20.8).

It should be noted that there are many more formulas for calculating oxygen transfer as a function of wind. Many of these are summarized in general references such as Bowie et al. (1985). As evident from Fig. 20.8 these formulas yield a wide range of predictions. Consequently it is advisable to obtain system-specific measurements to check the validity of the formulas before using them in model calculations. As was the case for Wanninkhof et al. (1991) this can be done with artificial tracers (see Sec. 20.4). In addition natural oxygen-depletion events can sometimes be exploited to obtain direct measurements (Box 20.2).

BOX 20.2.   Direct Measurement of Reaeration in Lakes

Many lakes in temperate regions are thermally stratified in the summer, consisting of an upper layer (epilimnion) and a lower layer (hypolimnion). In general the surface layer has dissolved oxygen concentration near saturation. If it is productive (that is, has high plant growth), settling plant matter can collect in the hypolimnion. The decomposition of this matter can then lead to severe oxygen depletion in the bottom waters. When turnover (that is, vertical mixing due to dropping temperature and increasing winds) occurs in the fall, the mixing of the two layers sometimes results in the lake's having an oxygen concentration well below saturation.

In certain cases the lake can be assumed to act as an open batch reactor: that is, we can ignore inflows and outflows of oxygen, except gas transfer across the lake's surface. If any additional sources and sinks of oxygen (such as sediment oxygen demand) are negligible, a mass balance for oxygen can be written for the lake in the period following overturn as

$$V\frac{do}{dt} = k_a(o_s - o) \tag{20.48}$$

If the saturation value is constant over the ensuing period, this equation can be solved for (with $o = o_i$ at $t = 0$)

$$o = o_i e^{-k_a t} + o_s(1 - e^{-k_a t}) \tag{20.49}$$

Thus if the oxygen concentrations are measured as a function of time, this model provides a means to estimate the reaeration rate.

Gelda et al. (1996) applied such an approach to Onondaga Lake in Syracuse, New York. Figure B20.2 shows oxygen concentrations that occurred in the lake following fall overturn in 1990, along with a curve fit with Eq. 20.49 using a reaeration rate of approximately 0.055 d^{-1}. In addition the plot also shows a simulation using a wind-dependent reaeration rate. The superior fit obtained with variable winds illustrates how important accurate wind estimates are for simulating gas transfer in lakes.

The approach of Gelda et al. (1996) is particularly appealing because it is nonobtrusive; that is, it does not depend on the introduction of tracers and dyes to the environment. It is also attractive because it directly measures oxygen concentration on a whole-lake basis. Wherever possible such direct measurements are preferable to indirect formula estimation.
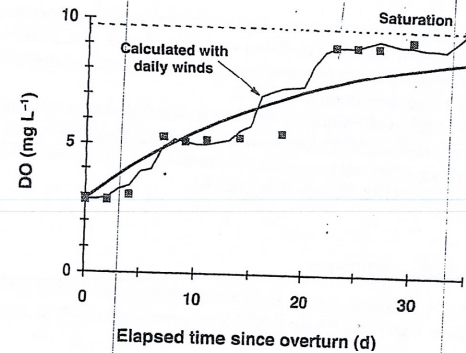

FIGURE B20.2

Estuaries. Because estuary gas transfer can be affected by both water and wind velocity, efforts to determine reaeration in estuaries combines elements of current and wind-driven approaches.

The water velocity effects are typically computed with the O'Connor-Dobbins formula (Eq. 20.40),

$$k_a = \frac{\sqrt{D_l U_o}}{H^{3/2}} \tag{20.50}$$

where U_o = mean tidal velocity over a complete tidal cycle.

The wind effects can be computed with any of the formulas developed for standing waters in the previous paragraphs. For example Eq. 20.46 can be expressed as a reaeration rate, as in

$$k_a = \frac{0.728U_w^{0.5} - 0.317U_w + 0.0372U_w^2}{H} \tag{20.51}$$

Thomann and Fitzpatrick (1982) have combined the two approaches for estuaries affected by both tidal velocities and wind,

$$k_a = 3.93\frac{\sqrt{U_o}}{H^{3/2}} + \frac{0.728U_w^{0.5} - 0.317U_w + 0.0372U_w^2}{H} \tag{20.52}$$

20.3.4 Extrapolating Reaeration to Other Gases

As stated earlier, we are going to return to the topic of gas transfer when we model toxic organics later in this text. However, beyond toxics there are a few other common gases that are of interest in environmental engineering.

The most important of these are carbon dioxide and ammonia gas. The former is important in pH calculations, whereas the latter relates to the problem of ammonia toxicity.

Mackay and Yeun (1983) have provided a way to extrapolate from commonly studied gases (such as oxygen and water vapor) to these other gases. For example the liquid-film exchange coefficient for a gas can be determined by

$$K_l = K_{l,O_2} \left(\frac{D_l}{D_{l,O_2}} \right)^{0.5} \qquad (20.53)$$

where K_l and D_l = exchange coefficient and diffusivity, respectively, and the subscript O_2 designates the values for oxygen. Similarly the gas-film exchange coefficient can be scaled to that of water vapor by

$$K_g = K_{g,H_2O} \left(\frac{D_g}{D_{g,H_2O}} \right)^{0.67} \qquad (20.54)$$

where it has been suggested (Mills et al. 1982) that the gas-film coefficient for water can be approximated by

$$K_{g,H_2O} = 168 U_w \qquad (20.55)$$

where K_{g,H_2O} has units of m d^{-1} and U_w = wind speed (m s^{-1}).

Schwarzenbach et al. (1993) have correlated diffusion coefficients with molecular weight. For a temperature of 25°C, the resulting equations are

$$D_l = \frac{2.7 \times 10^{-4}}{M^{0.71}} \qquad (20.56)$$

and

$$D_g = \frac{1.55}{M^{0.65}} \qquad (20.57)$$

Finally some investigators have combined relationships such as Eqs. 20.53 to 20.56 to directly calculate the exchange coefficients as a function of molecular weight. Using this approach Mills et al. (1982) have come up with

$$K_l = K_{l,O_2} \left(\frac{32}{M} \right)^{0.25} \qquad (20.58)$$

and

$$K_g = K_{g,H_2O} \left(\frac{18}{M} \right)^{0.25} \qquad (20.59)$$

20.4 MEASUREMENT OF REAERATION WITH TRACERS

Aside from formulas, reaeration can be measured directly in the field. Four methods are commonly used. The first three consist of techniques that back-calculate reaeration based on a mass balance model and field measurements of oxygen. These are:

- *Steady-state oxygen balance.* If all the other factors governing an oxygen sag (that is, deoxygenation rate, sediment oxygen demand, etc.) can be determined independently, the only unknown governing the sag will be the reaeration coefficient.

Unfortunately, because the other factors are difficult to measure accurately, estimates obtained in this fashion are usually highly uncertain. However, as in Churchill's studies on the Tennessee River (recall discussion of Eq. 20.42), there are certain problem settings where the approach works nicely. Box 20.2 outlines such a case that sometimes occurs in lakes.

- *Deoxygenation with sodium sulfite.* As in Owens' studies of British streams, oxygen levels can be artificially lowered by adding sodium sulfite to the stream. This method would be particularly attractive for relatively clean systems, where other effects would be negligible.
- *Diurnal oxygen swings.* In some streams, plant growth can induce diurnal swings in oxygen level. Chapra and Di Toro (1991) have illustrated how such data can be used to obtain reaeration estimates. I will describe this approach when I discuss the impact of photosynthesis on oxygen in Lec. 24.

The fourth method for measuring reaeration in the field takes a decidedly different tack. Rather than oxygen, a different volatile substance is injected into the system. Such substances are chosen because (1) they volatilize in an analogous fashion to oxygen, (2) they do not react, and (3) their concentrations can be measured at a relatively reasonable cost. Most commonly, radioactive (e.g., krypton-85), hydrocarbon (e.g., ethylene, propane, methyl chloride, etc.), and inorganic tracers (e.g., sulfur hexafluoride) are used. These tracers are usually discharged together with a conservative, nonvolatile tracer (tritium, lithium) to determine dispersion (recall Sec. 10.4).

Either continuous or pulse experiments are normally conducted. For the continuous case the tracers are injected at a constant rate until steady concentration levels are attained at two downstream locations. The first-order gas-transfer rate can then be estimated by Eq. 10.36,

$$k = \frac{l}{\bar{t}_2 - \bar{t}_1} \ln \frac{M_1}{M_2} \qquad (20.60)$$

where the subscripts 1 and 2 represent the upstream and the downstream locations, the $\bar{t}$'s are the average travel times to the two locations, and the M's are the masses of the tracer. Because the experiment is continuous, the masses should be equal to the flow times concentration at each point. Therefore the equation can be expressed as (assuming constant flow)

$$k = \frac{1}{\bar{t}_2 - \bar{t}_1} \ln \frac{c_1}{c_2} \qquad (20.61)$$

A similar approach can be used for the pulse experiment, except that the masses in Eq. 20.60 would be determined by integration as described previously in Lec. 10.

Once the first-order gas-transfer rate is estimated, the result must be extrapolated to oxygen. One way to do this would be by using the empirically derived correlations such as Eqs. 20.58. Although this can be done, the developers of tracer methods have directly estimated the scaling as represented by

$$k_a = Rk \qquad (20.62)$$

where R = scale factor to relate the tracer exchange rate to reaeration (Table 20.3).

TABLE 20.3
Factors for scaling gas-tracer exchange rates to oxygen reaeration rates

Tracer	R	Reference
Ethylene	1.15	Rathbun et al. (1978)
Propane	1.39	Rathbun et al. (1978)
Methyl chloride	1.4	Wilcox (1984a, b)
Sulfur hexafluoride	1.38	Canale et al. (1995)
Krypton	1.2	Tsivoglou and Wallace (1972)

PROBLEMS

20.1. A tanker truck careens off the road and dumps 30,000 L of glucose syrup into a small mountain lake. The concentration of the syrup is 100 g-glucose L^{-1}. The lake has the following characteristics in the period immediately following the spill: residence time = 30 d, depth = 5 m, area = 5×10^4 m^2, altitude = 11,000 ft, wind speed = 2.235 m s^{-1}, and temperature = 10°C. Note that the lake is assumed to be completely mixed, and has zero BOD and is at saturation prior to the spill. Also recognize that the inflow river is at saturation.

  (a) Compute the grams of CBOD spilled.
  (b) Compute how the CBOD and oxygen in the lake change after the spill.
  (c) Determine the time of the worst oxygen level in the system.

20.2. A lake in the United States has a surface area of 5×10^5 m^2, a mean depth of 5 m, and a residence time of 1 wk. How large a community could discharge to the system during the summer (wind speed = 0.89 mps, temperature = 30°C, and elevation = 1 km) if the BOD decay rate is 0.1 d^{-1} and the desired oxygen level is 6 mg L^{-1}? Assume that the sewage has zero dissolved oxygen concentration and does not settle. Also express your result as an equivalent inflow concentration.

20.3. Suppose that the 300-mL bottle described in Example 20.1 had an open top as illustrated in Fig P20.3. Repeat the example for this case. As with the bottle neck, assume that transfer through the thin liquid film takes place by molecular diffusion.
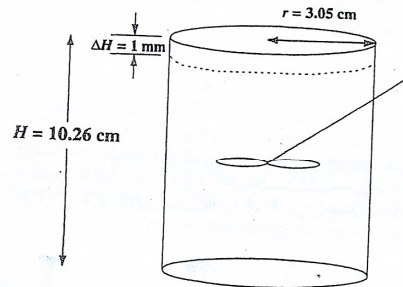

r = 3.05 cm
ΔH = 1 mm
H = 10.26 cm

FIGURE P20.3

20.4. A flat broad-crested regular step dam with a drop of 2 m is situated on a grossly polluted stretch of river below a sewage outfall plant. The river is located at an elevation of 2 km. Determine the oxygen concentration below the dam if the water upstream has a concentration of 2 mg L^{-1} and a temperature of 26°C.

20.5. Derive a relationship of the form of Eq. 20.58 by combining Eq. 20.56 with Eq. 20.53.

20.6. A dye study yields the following data for time and concentration of ethylene:

Station 1 (6 km)

t (min)	0	10	20	30	40	50	60	70	80	90	100
c (μg L^{-1})	0	9	69	81	78	74	71	80	80	80	0

Station 2 (13.5 km)

t (min)	9	9.5	10	10.5	11	11.5	12	12.5
c (μg L^{-1})	0.0	0.0	1.4	2.9	3.4	4.6	3.4	3.0
t (min)	13	13.5	14	14.5	15	15.5		
c (μg L^{-1})	2.9	2.3	2.1	1.1	1.1	0.6		

An accompanying tracer study using rhodamine dye and lithium has yielded estimates of 0.5 d and 8.3×10^4 cm^2 s^{-1} for travel time and dispersion, respectively. The river has the following characteristics: Q = 3.7 cms, B = 46 m, and T = 21°C.
  (a) Estimate the reaeration and compare your results with appropriate reaeration formulas.
  (b) Use Eq. 10.24 to compute the continuous distribution of ethylene at the second station. Plot the data on the same graph for comparison.

20.7. You continuously discharge sulfur hexafluoride into a stream having constant hydrogeometric characteristics. You measure concentrations of 400 and 150 pptr at locations 0.5 and 4 km downstream from the injection point, respectively. Use this data to estimate the reaeration rate if the velocity over the stretch is 0.2 m s^{-1}.

20.8. The following data are measured for a polluted lake with a mean depth of 12 m following overturn:

Time (d)	0	4	8	12	16	20	24	28	32
DO (mg L^{-1})	5	6.4	6.8	7.8	8	8.5	8.5	8.5	8.8

Determine the reaeration rate and the oxygen mass-transfer coefficient if the saturation during the sampling period was 9 mg L^{-1}.

20.9. A stream has a velocity of 0.4 mps, a depth of 0.3 m, and a temperature of 23°C. Estimate (a) the reaeration rate and (b) the comparable rate for carbon dioxide.

20.10. A stream with a rectangular channel has the following characteristics: S = 0.001, B = 20 m, n = 0.03, Q = 1 cms, and T = 10°C. Determine the reaeration rate following the introduction of a new point source that will discharge an additional 0.5 cms (T = 25°C) to the channel.