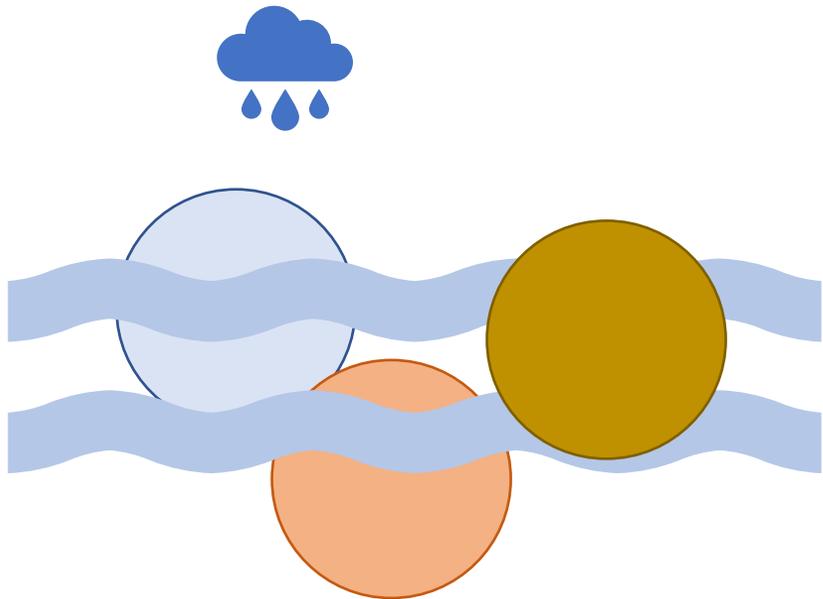


# Gas Transfer & Oxygen Reaeration



# Gas Transfer Theories

Whitman's Two-Film Theory

Surface Renewal Model

Oxygen Reaeration

Reaeration Formulas

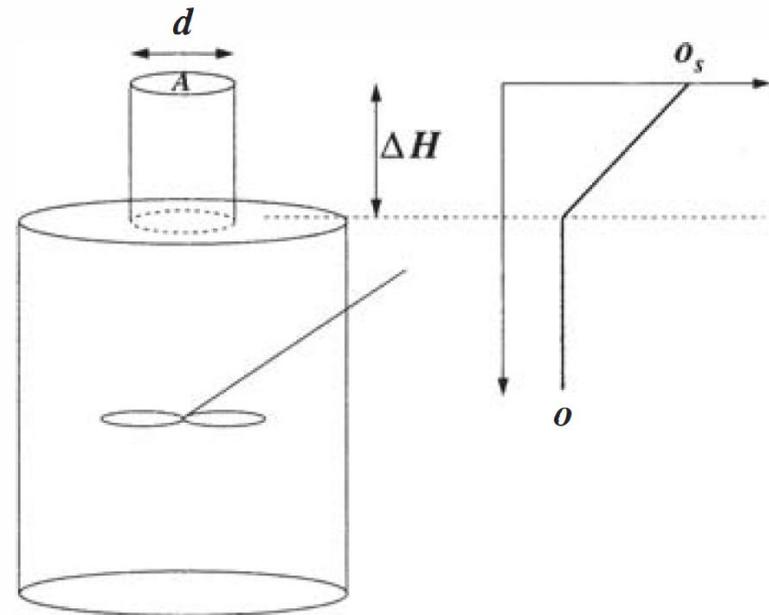
Rivers and Streams

Waterfalls and Dams

Standing Waters and Estuaries

Extrapolating Reaeration to Other Gases

Measurement of Reaeration with Tracers



**FIGURE 20.1**

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

# Gas Transfer & Oxygen Reaeration

A mass balance for the bottle can be written as:

$$V \frac{do}{dt} = DA \frac{o_s - o}{\Delta H}$$

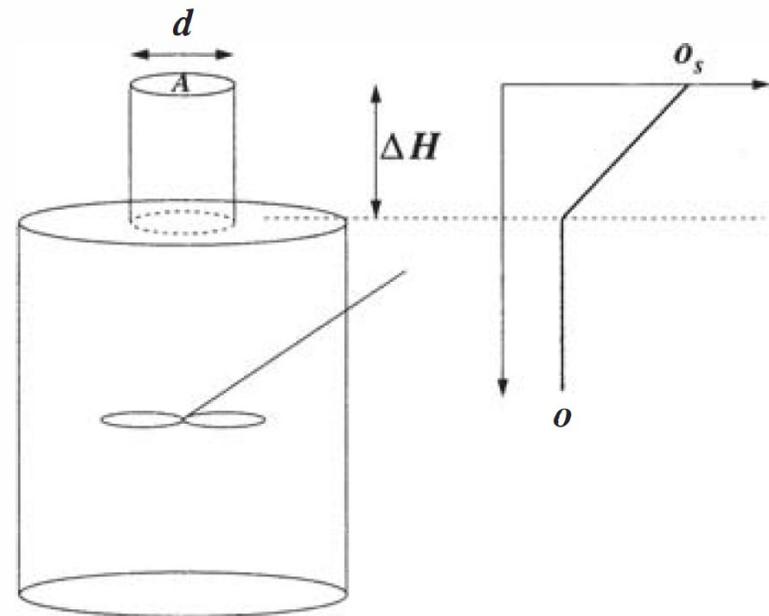
where  $D$  = molecular diffusion coefficient ( $\text{m}^2 \text{d}^{-1}$ )

$A$  = cross-sectional area of the bottle neck ( $\text{m}^2$ )

$o_s$  = oxygen saturation concentration ( $\text{mg L}^{-1}$ )

$o$  = oxygen concentration in bottle ( $\text{mg L}^{-1}$ )

$\Delta H$  = length of the neck (m)



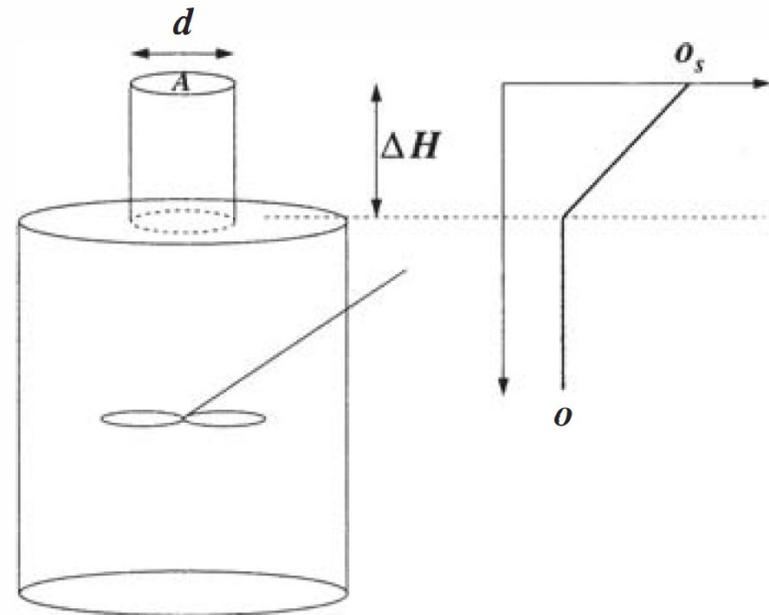
# Gas Transfer & Oxygen Reaeration

The model can be expressed as:

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

where  $K_L$  = oxygen mass-transfer velocity ( $\text{m d}^{-1}$ ), equal to:

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



**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  $D = 2.09 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ,  $d = 2 \text{ cm}$ , and  $\Delta H = 2.6 \text{ cm}$ . Assume that the system is at a temperature of  $20^\circ\text{C}$  and the saturation concentration is  $9.1 \text{ mg L}^{-1}$ .

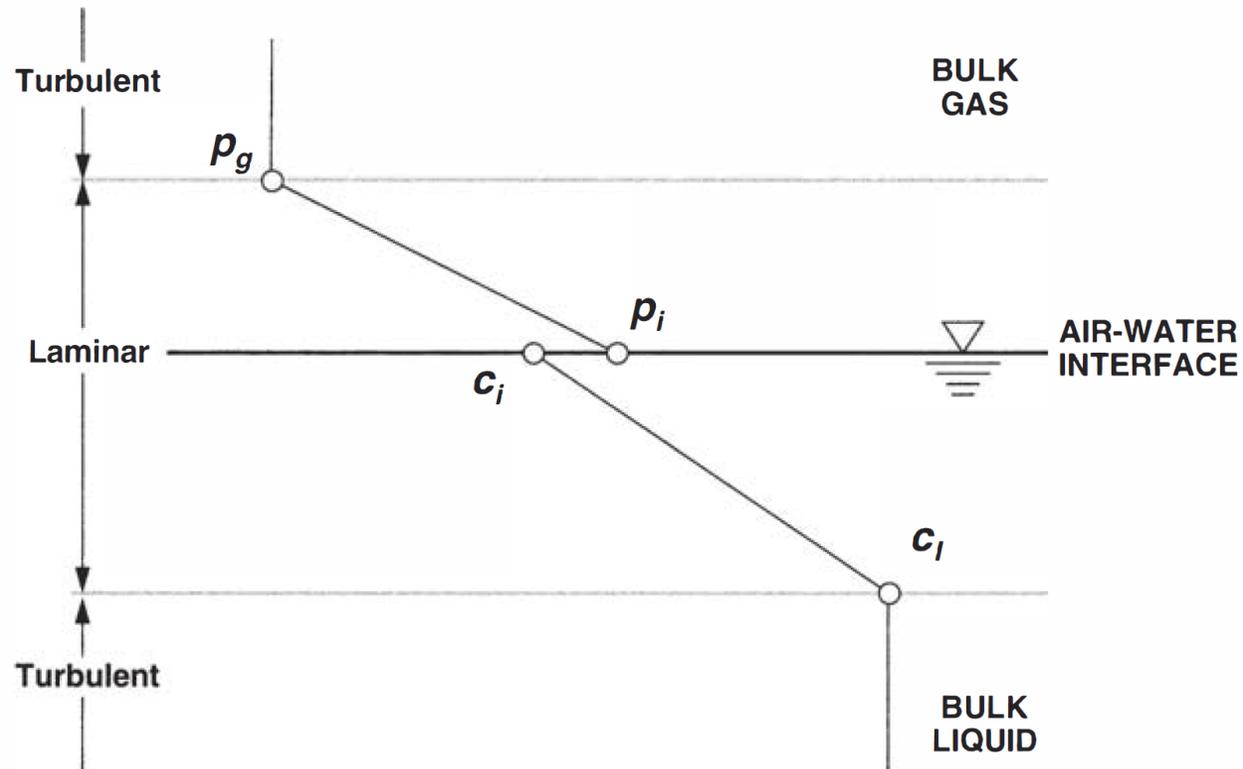
# Gas Transfer Theories

We will describe the two theories:

Stagnant film theory- widely used in standing water (lakes)

Surface-renewal model- flowing waters (streams)

# Whitman's Two-Film Theory



**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.

# Whitman's Two-Film Theory

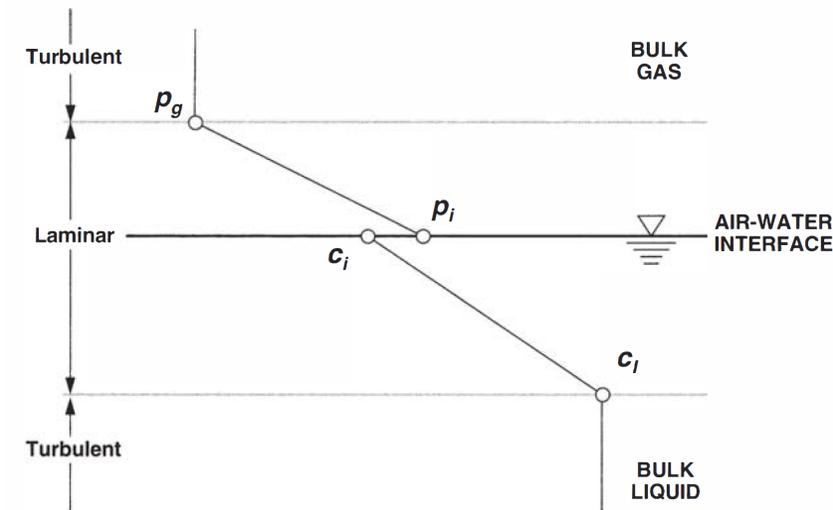
The two-film theory assumes that a substance moving between the phases encounters maximum resistance in two laminar boundary layers where mass transfer is via molecular diffusion.

$$J_l = K_l(c_i - c_l)$$

where  $J_l$  = mass flux (mole  $\text{m}^{-2} \text{d}^{-1}$ )

$K_l$  = mass-transfer velocity in liquid ( $\text{m d}^{-1}$ )

$c_i$  and  $c_l$  = liquid concentration in bulk and interface (mole  $\text{m}^{-3}$ )



**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.

# Whitman's Two-Film Theory

Transfer through the gaseous film can be represented by:

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

where  $J_g$  = mass flux (mole m<sup>-2</sup> d<sup>-1</sup>)

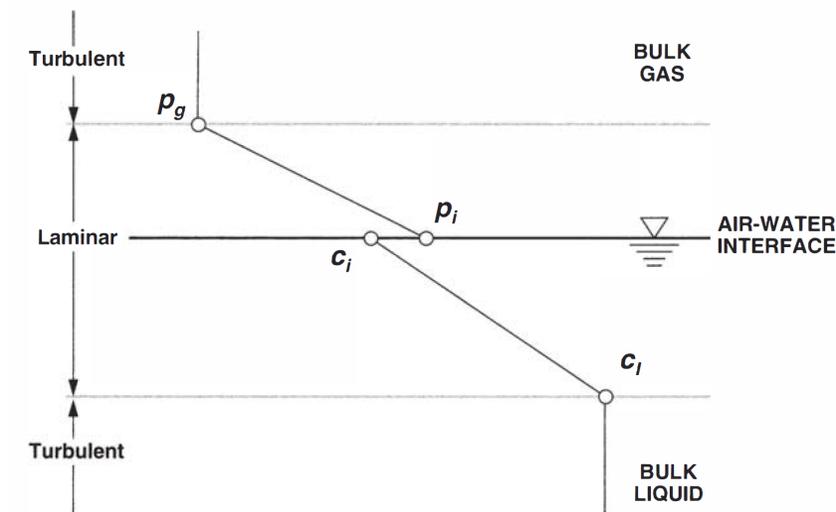
$K_g$  = mass-transfer velocity in gas (m d<sup>-1</sup>)

$p_g$  and  $p_i$  = gas pressure in bulk and interface  
(mole m<sup>-3</sup>)

Transfer coefficients can be related to:

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

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



**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.

# Whitman's Two-Film Theory

Transfer coefficients can be related to:

$$K_l = \frac{D_l}{z_l}$$
$$K_g = \frac{D_g}{z_g}$$

where  $D_l$  = liquid molecular diffusion coefficient ( $\text{m}^2\text{d}^{-1}$ )

$D_g$  = gas molecular diffusion coefficient ( $\text{m}^2\text{d}^{-1}$ )

$z_l$  = thickness of liquid film (m)

$z_g$  = thickness of gas film (m)

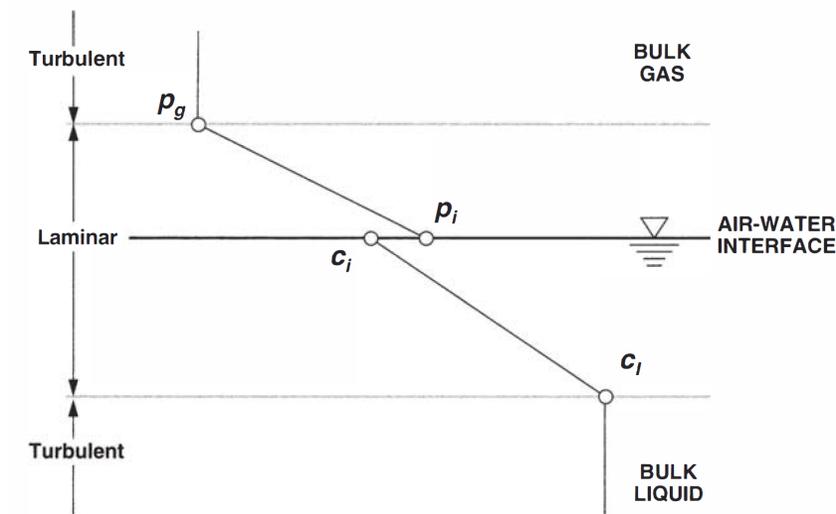


FIGURE 20.2

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.

# Whitman's Two-Film Theory

A key assumption is that equilibrium exists:

$$p_i = H_e c_i$$

Equation above can be substituted into ( $J_l = K_l(c_i - c_l)$ ):

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

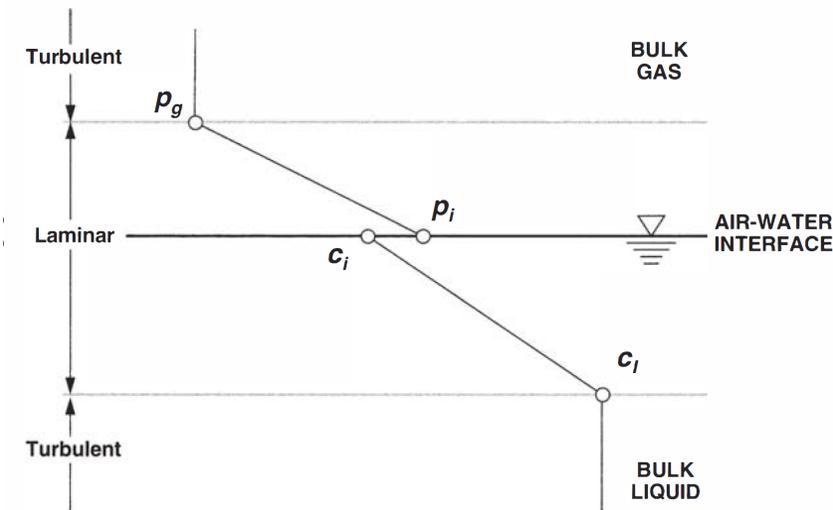
The gaseous film equation ( $J_g = \frac{K_g}{RT_a} (p_g - p_i)$ ) can be solved for:

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

Solve for flux and equated:

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

where  $v_v$  = net transfer velocity across air-water interface ( $\text{m d}^{-1}$ )



**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.

# Whitman's Two-Film Theory

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

where  $v_v$  = net transfer velocity across air-water interface ( $\text{m d}^{-1}$ ), this can be computed by:

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

Inverted this results to:

$$v_v = K_l \frac{H_e}{H_e + RT_a (K_l / K_g)}$$

“ $v$ ” is the coefficient since it is a velocity.

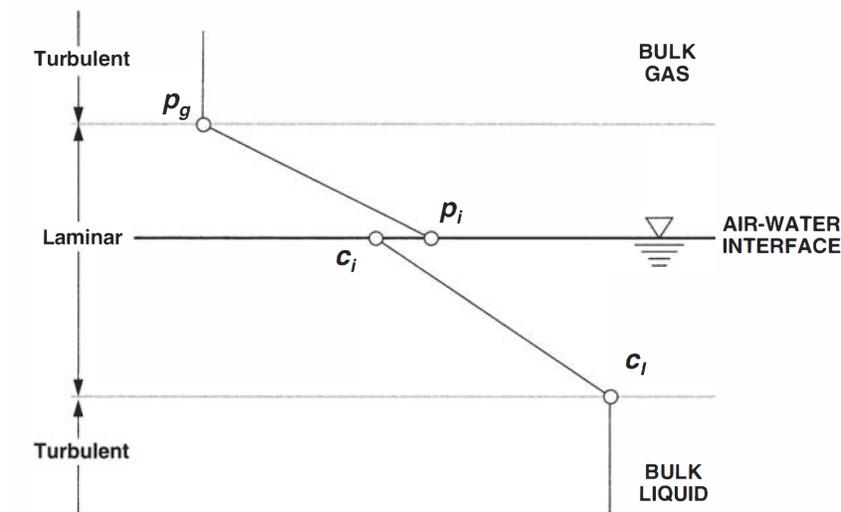


FIGURE 20.2

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.

# Whitman's Two-Film Theory

Also by analogy:

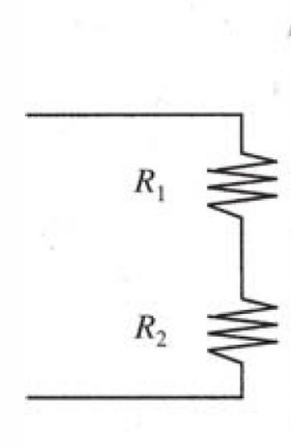
$$\frac{1}{v_v} = \frac{1}{K_l} + \frac{RT_a}{H_e K_g}$$

is similar to two resistors in parallel in electrical current

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

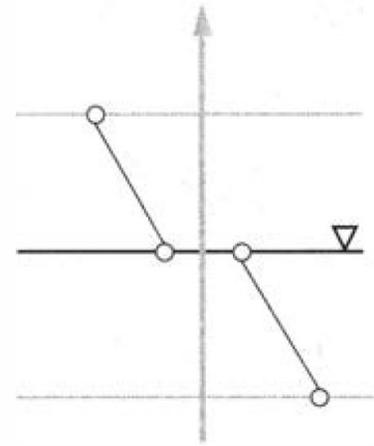
Individual resistance on the liquid and gaseous boundary layer can be quantified as”:

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



$$R = R_1 + R_2$$

(a) Two resistors in series



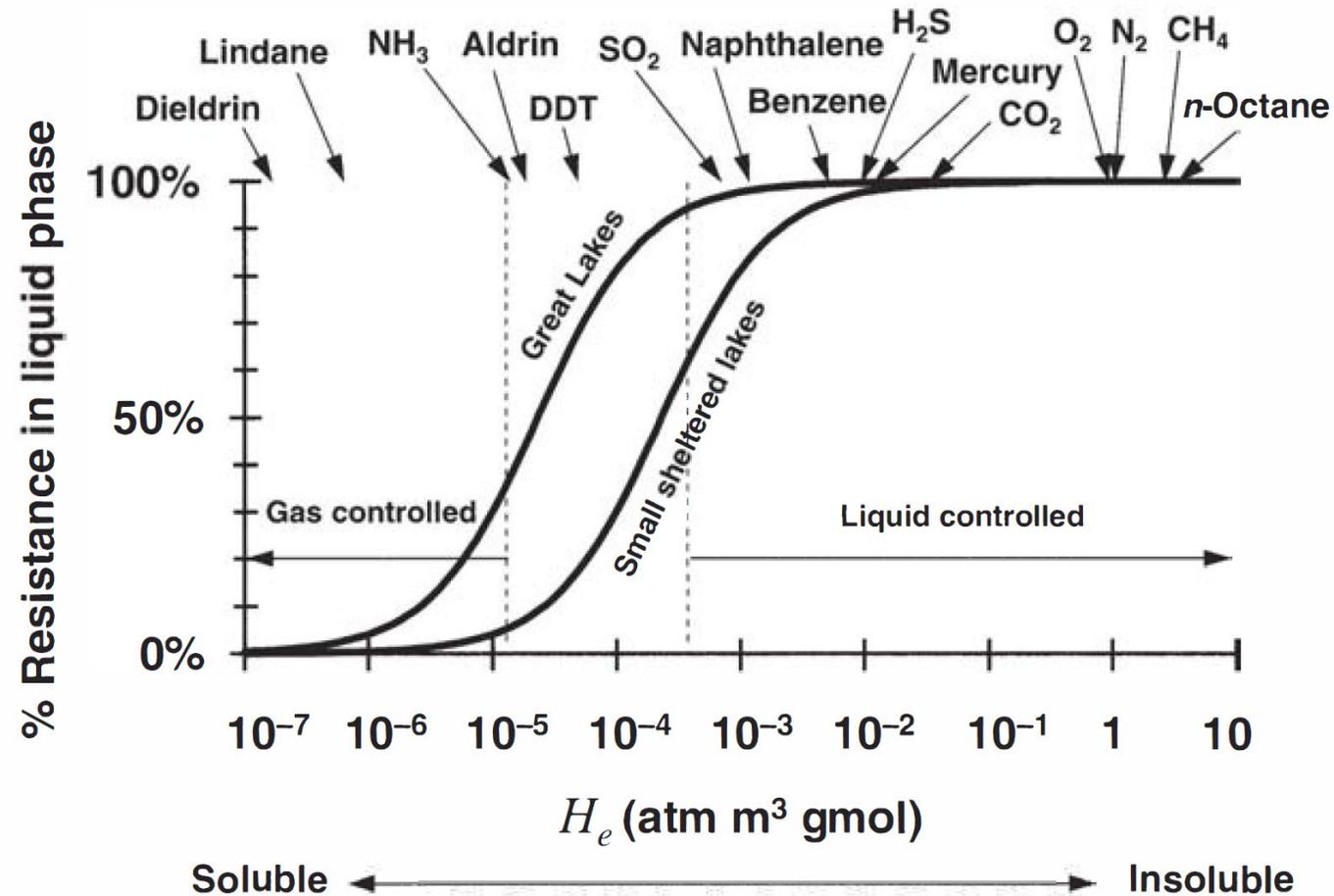
$$\frac{1}{v_v} = \frac{1}{K_l} + \frac{RT_a}{H_e K_g}$$

(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.

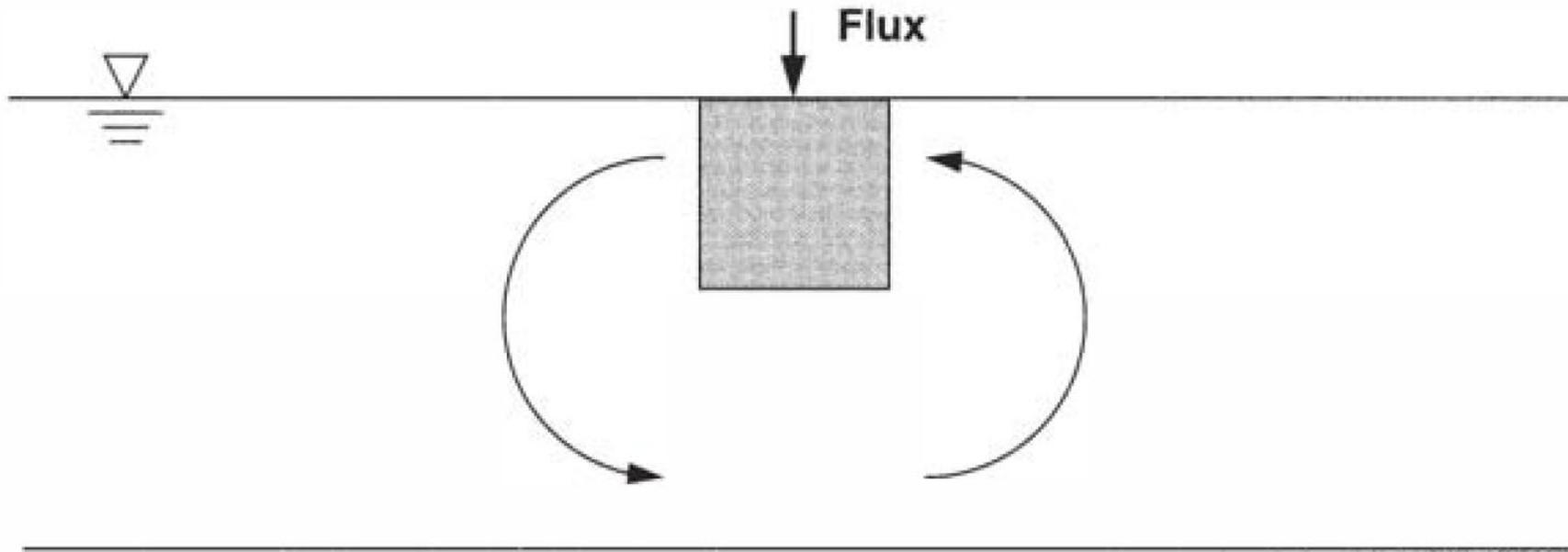
# Whitman's Two-Film Theory



**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).

# Surface Renewal Model



**FIGURE 20.5**

Depiction of surface renewal model of gas exchange.

# Surface Renewal Model

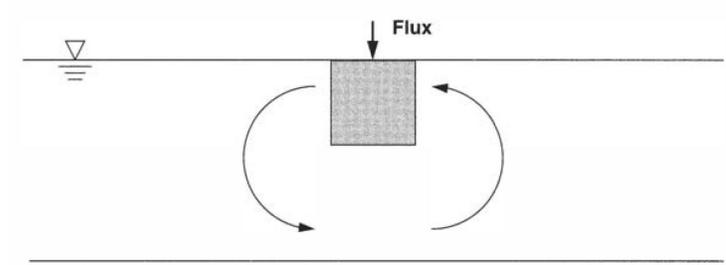


FIGURE 20.5  
Depiction of surface renewal model of gas exchange.

Penetration theory is what is envisioned by two-film theory

To estimate the flux of gas across the air-water interface:

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

where  $D_l$  = liquid diffusion coefficient

$c_s$  = concentration at the air-water interface

$c_l$  = concentration in the bulk water

$t^*$  = average contact time of the fluid parcel at the interface.

# Surface Renewal Model

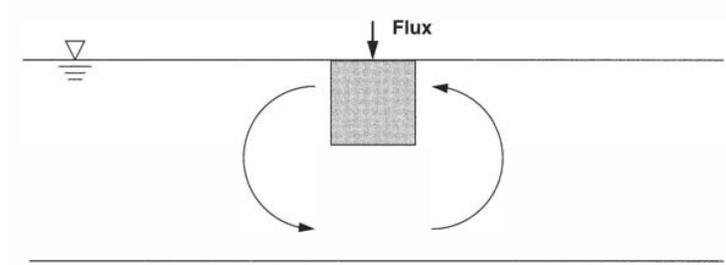


FIGURE 20.5  
Depiction of surface renewal model of gas exchange.

Danckwerts (1951) modified the approach by assuming that the fluid elements reach and leave the interface randomly. This statistical approach is called surface renewal theory

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

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

The transfer velocities for the liquid and gaseous phases can be written:

$$K_l = \sqrt{r_l D_l}$$
$$K_g = \sqrt{r_g D_g}$$

# Oxygen Reaeration

At this point we have a general equation for the flux of any gas:

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

Since oxygen is liquid controlled, then  $v_v = K_l$ :

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

where  $o$  = the concentration in water. Because oxygen is so abundant in the atmosphere, the partial pressure is constant and therefore:

$$J = K_l(o_s - o)$$

# Oxygen Reaeration

For a well-mixed open batch reactor, a mass balance for oxygen can be written as :

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

where  $A_s$  = surface area of the water body.

$$V = A_s H$$

In cases where the air-water interface is not constricted, the volume is:

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

where  $k_a$  = reaeration rate, equivalent to

$$k_{a,T} = k_{a,20} \theta^{T-20}, \quad k_a = \frac{K_l}{H} \quad \text{where } \theta \cong 1.024$$

# Reaeration Formulas

This section describes some of the commonly used formulas that have been developed for predicting reaeration in streams and rivers.

# Rivers and Streams

O' Conner-Dobbins, Churchill, and Owens-Gibbs

O' Conner-Dobbins. To formulate the transfer velocity:

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

O'Conner and Dobbins hypothesized that the surface renewal rate could be approximated by the ratio of the average stream velocity to depth.

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

Substituting into the above equation:

$$K_l = \sqrt{\frac{D_l U}{H}}, \quad \text{usually expressed as} \quad k_a = \sqrt{D_l} \frac{U^{0.5}}{H^{1.5}}$$

# Rivers and Streams

Since the diffusivity is approximately  $2.09 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . Therefore:

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

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

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

$k_a$  ( $\text{d}^{-1}$ ),  $U$  (fps),  $H$  (ft)

Churchill (Tennessee River Valley)

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

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

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

$k_a$  ( $\text{d}^{-1}$ ),  $U$  (fps),  $H$  (ft)

# Rivers and Streams

Owen and Gibbs (Sulfite)

Metric

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

Units:  $k_a$  (d<sup>-1</sup>),  $U$  (mps),  $H$  (m)

English

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

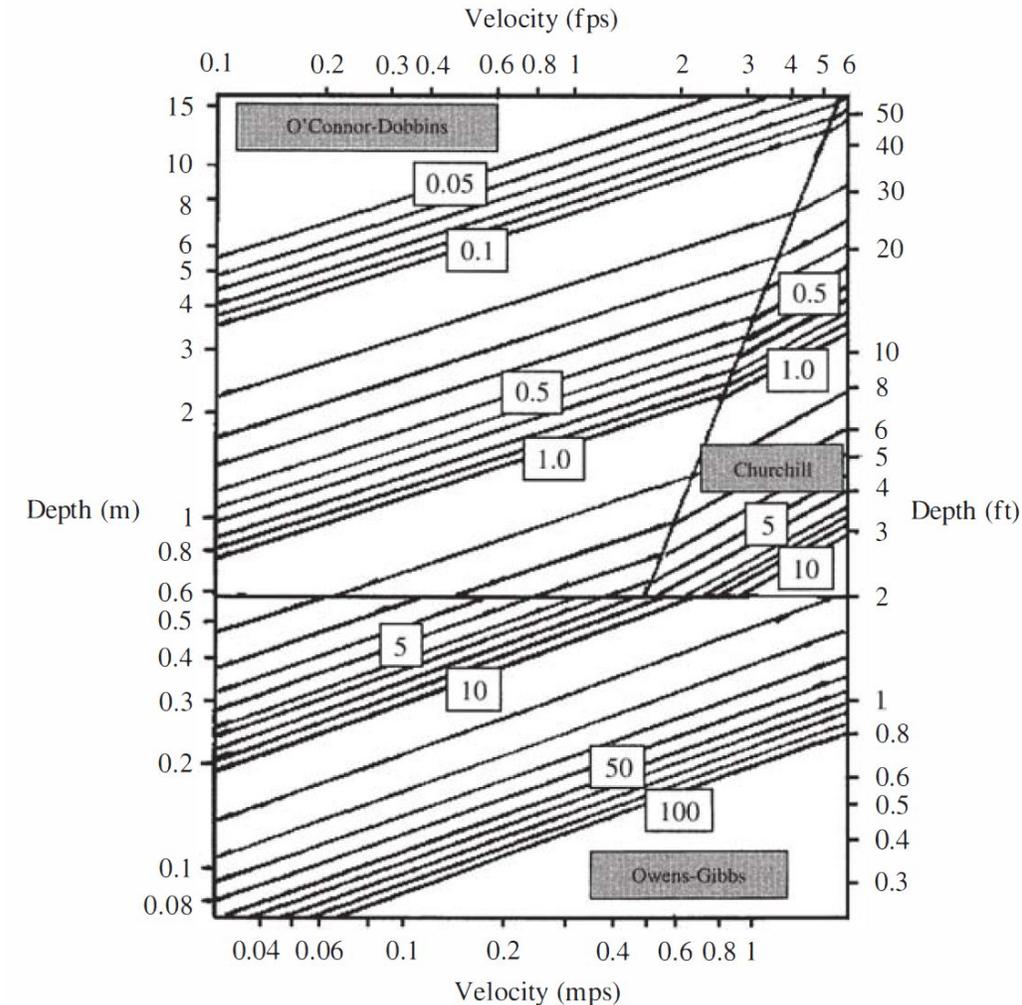
$k_a$  (d<sup>-1</sup>),  $U$  (fps),  $H$  (ft)

# Rivers and Streams

Comparison among formulas: O' Connor-Dobbins, Churchill, and Owens-Gibbs formulas were developed for different streams

**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



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

# Rivers and Streams

Other formulas: beyond these three there is also Bowie (1985). Software packages such as EPA QUAL2E model provide the option to automatically compute reaeration rates according to formulas.

# Waterfalls and Dams

Oxygen transfer in streams can be significantly influenced by the presence of waterfalls and dams. Butts and Evans (1983) suggest the following formula:

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

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

# Waterfalls and Dams

Oxygen transfer in streams can be significantly influenced by the presence of waterfalls and dams. Butts and Evans (1983) suggest the following formula:

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

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

**TABLE 20.2**

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

Water-quality coefficient	
<b>Polluted state</b>	<i>a</i>
Gross	0.65
Moderate	1.0
Slight	1.6
Clean	1.8
Dam-type coefficient	
<b>Dam type</b>	<i>b</i>
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

# Standing Waters and Estuaries

For standing waters (lakes, impoundments, wide estuaries), wind becomes the predominant factor causing reaeration.

Lakes: The oxygen-transfer coefficient can be estimated by wind speed.

$$K_l = 0.864U_w \quad (\text{Broecker})$$

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

A widely used formula for turbulence regimes is:

$$K_l = 0.728U_w^{0.5} - 0.317U_w + 0.0372U_w^2 \quad (\text{Banks})$$

At high wind velocities, the relationship becomes dominated by the second term.

# Standing Waters and Estuaries

The gas tracer experiments in lakes can be used to develop the following formula:

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

where the  $S_c$  = Schmidt number, which for oxygen is approximately 500. If this value is adopted, the Wanninkhof formula reduces to:

$$K_l = 0.1183U_w^{1.64}$$

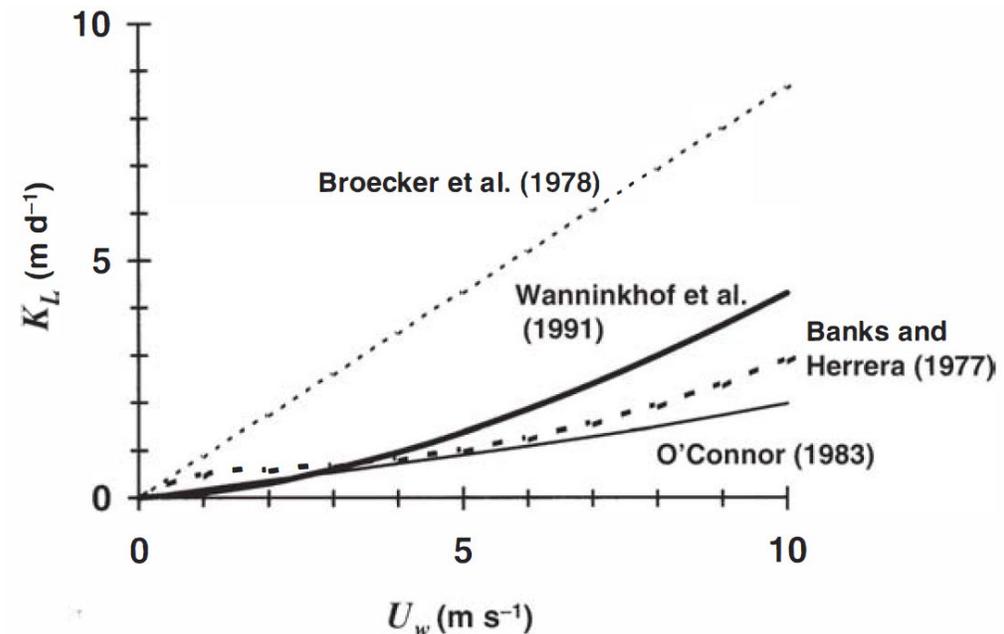


FIGURE 20.8  
Comparison of wind-dependent reaeration formulas.

# Estuaries

Estuary gas transfer can be affected by both water and wind velocity. The water velocity effects are typically computed with the O' Connor-Dobbins formula:

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

The wind effects can be computed

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

Two approaches for estuaries affect by both tidal velocities and wind:

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

# Extrapolating Reaeration to Other Gases

Beyond toxics there are a few other common gases that are of interest in environmental engineering. The most important is carbon dioxide and ammonia gas. The former is important for pH, the latter for ammonia toxicity.

Liquid film-exchange coefficient for gas can be determined:

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

where  $K_l$  and  $D_l$  = exchange coefficients and diffusivity, respectively. Subscript O<sub>2</sub> designates the value for oxygen. The gas-film exchange coefficient can be scaled to that of water vapor by:

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

# Extrapolating Reaeration to Other Gases

The gas-film coefficient for water can be approximated by:

$$K_{g,H_2O} = 168 U_w$$

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

The correlated diffusion coefficients with molecular weight. For a temperature of 25 °C. The resulting equations:

$$D_l = \frac{2.7 \times 10^{-4}}{M^{0.71}}$$

$$D_g = \frac{1.55}{M^{0.65}}$$

# Extrapolating Reaeration to Other Gases

Some investigators have combined relationships to directly calculate the exchange coefficients as a function of molecular weight.

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

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

# Measurement of Reaeration with Tracers

First order gas-transfer rate:

$$k = \frac{1}{\bar{t}_2 - \bar{t}_1} \ln \frac{M_1}{M_2}$$

Assuming constant flow:

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

The developers of tracer methods have directly estimated the scaling as represented by:

$$k_a = Rk$$

where R = scale factor to relate the tracer exchange rate to reaeration.

# Measurement of Reaeration with Tracers

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	Wilcock (1984 <i>a, b</i> )
Sulfur hexafluoride	1.38	Canale et al. (1995)
Krypton	1.2	Tsivoglou and Wallace (1972)