Gas Transfer

Gas Transfer

Some important examples of gas transfer in water and wastewater treatment.

1. Oxygen transfer to biological processes.
2. Stripping of volatile toxic organics (solvents).
3. CO_2 exchange as it relates to pH control.
4. Ammonia removal by stripping.
5. Odor removal – volatile sulfur compounds
6. Chlorination, ozonation for disinfection and odor control.

The materials of interest are soluble in water and volatile (i.e. they exert a significant vapor pressure).

Equilibrium and Solubility:

For such materials there is an equilibrium established between the liquid phase and the gaseous phase if there is enough time allowed and if the environmental conditions are held constant. This equilibrium is usually modeled, for dilute solutions, as **Henry's Law**. There are various forms of Henry's law as shown in the table below. In general saturation goes up as T goes down and as TDS goes down.

Form of equation	H	Liquid phase conc.	Gas phase conc.
$P = H \cdot C$	$\frac{atm \cdot m^3}{mol}$	mol/m^3	atm
$C_g = H_c \cdot C_l$	unitless	mol/m^3	mol/m^3
$P = H_a \cdot X$	atm	mol/mol	atm

Some typical “H” values:

gas	H_a
O_2	4×10^4
He	12×10^4
CH_4	3.76×10^4
CO_2	0.14×10^4
H_2S	4.83×10^4

Volatile compound	H_c	H
Carbon tetrachloride	1.24	0.0304
Chloroform	0.15	0.00367
Vinyl chloride	1.14	0.0278

Henry's constants for various compounds are reported in a variety of forms so it's necessary to know how to convert between these forms. Here is a sample calculation to show how to convert between various forms of "H"

Look at conversion between H_c (dimensionless) and H(atm-m^3/mol)

$$P = H \cdot C_l$$

$$C_g = H_c \cdot C_l$$

$$P \cdot V = n \cdot R \cdot T \text{ (ideal gas law)}$$

R = 0.0821 atm-L/mol-^{o}K = 0.0821 x 10^{-3} atm-m^3/mol-^{o}K

@25^{o}C

T = 273 + 25 = 298^{o}K

$$C_g = \frac{n}{V} = H_c \cdot C_l \qquad C_l = \frac{p}{H}$$

$$\frac{n}{V} = \frac{H_c \cdot p}{H} \qquad \frac{H_c}{H} = \frac{n}{V \cdot p}$$

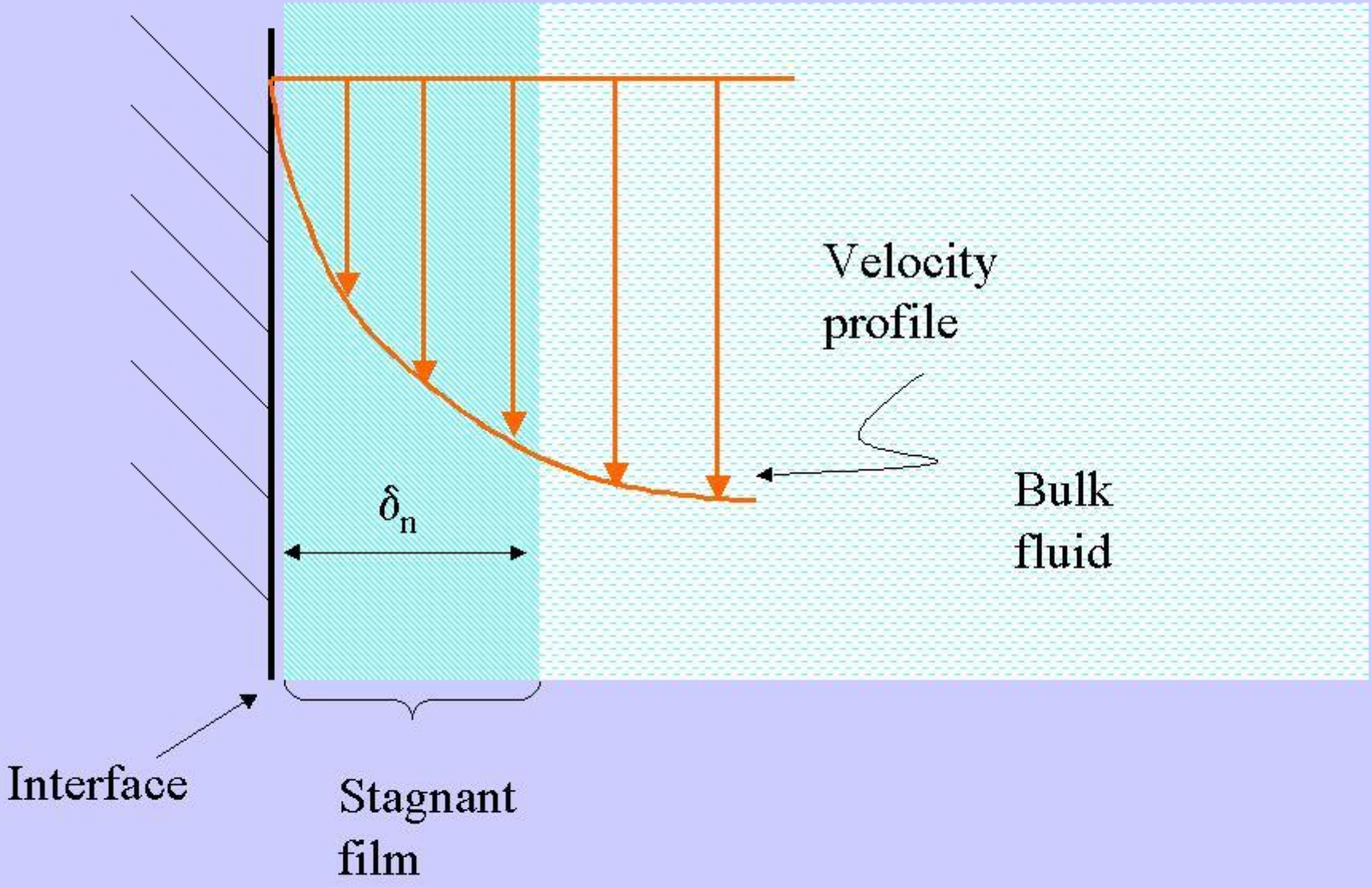
$$\frac{n}{V \cdot p} = \frac{1}{R \cdot T} = 40.87 \qquad \frac{H_c}{H} = 40.87$$

Gas transfer rates

If either phase concentration is not as predicted by Henry's law then there will be a transfer of mass across the interface until equilibrium is reached. The mechanisms and rate expressions for this transfer process have been conceptualized in a variety of ways so that quantitative descriptions are possible. Some of the common conceptualizations are discussed here.

Film Theory

The simplest conceptualization of the gas-liquid transfer process is attributed to Nernst (1904). Nernst postulated that near the interface there exists a stagnant film . This stagnant film is hypothetical since we really don't know the details of the velocity profile near the interface.


Velocity
profile
Bulk
fluid
δ_n
Interface
Stagnant
film

In this film transport is governed essentially by molecular diffusion. Therefore, Fick's law describes flux through the film.

$$J = -D\frac{\partial C}{\partial X} \quad \left(\text{typical units } \frac{mg}{cm^2 \cdot sec}\right)$$

If the thickness of the stagnant film is given by δ_n then the gradient can be approximated by:

$$\frac{\partial C}{\partial X} \approx \frac{C_b - C_i}{\delta_n}$$

C_b and C_i are concentrations in the bulk and at the interface, respectively.

At steady-state if there are no reactions in the stagnant film there will be no accumulation in the film (Assume that D = constant) -- therefore the gradient must be linear and the approximation is appropriate.

And:

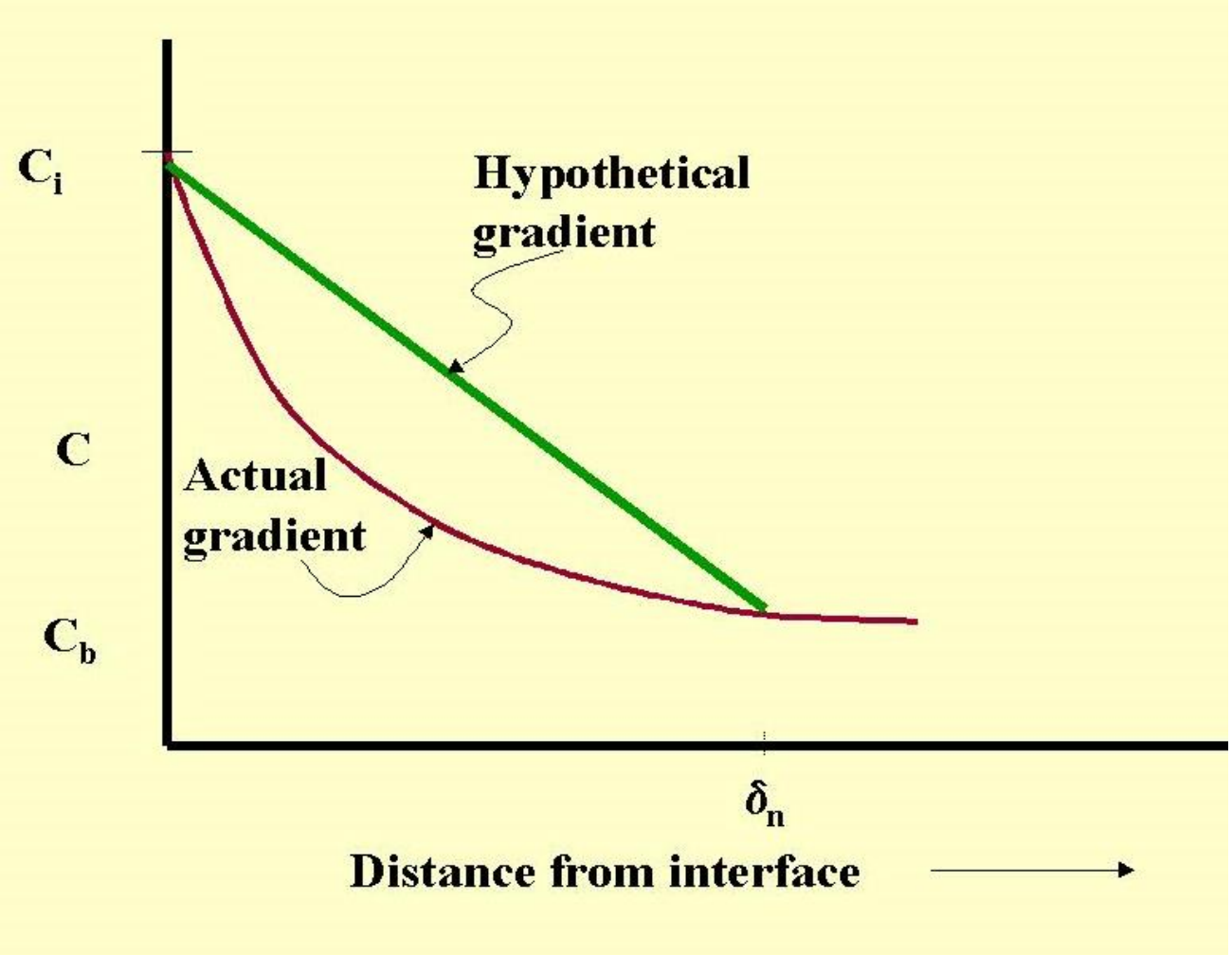
$$J = -D\frac{(C_b - C_i)}{\delta_n}$$

Calculation of C_i is done by assuming that equilibrium (Henry's Law) is attained instantly at the interface. (i.e., use Henry's law based on the bulk concentration of the other bulk phase.) Of course this assumes that the other phase doesn't have a "film". This problem will be addressed later. So for the moment:

$$C_i = \frac{C_g}{H_C}$$

(if the film side is liquid and the opposite side is the gas phase).

A problem with the model is that the effective diffusion coefficient is seldom constant since some turbulence does enter the film area. So the concentration profile in the film looks more like:



Penetration and Surface Renewal Models

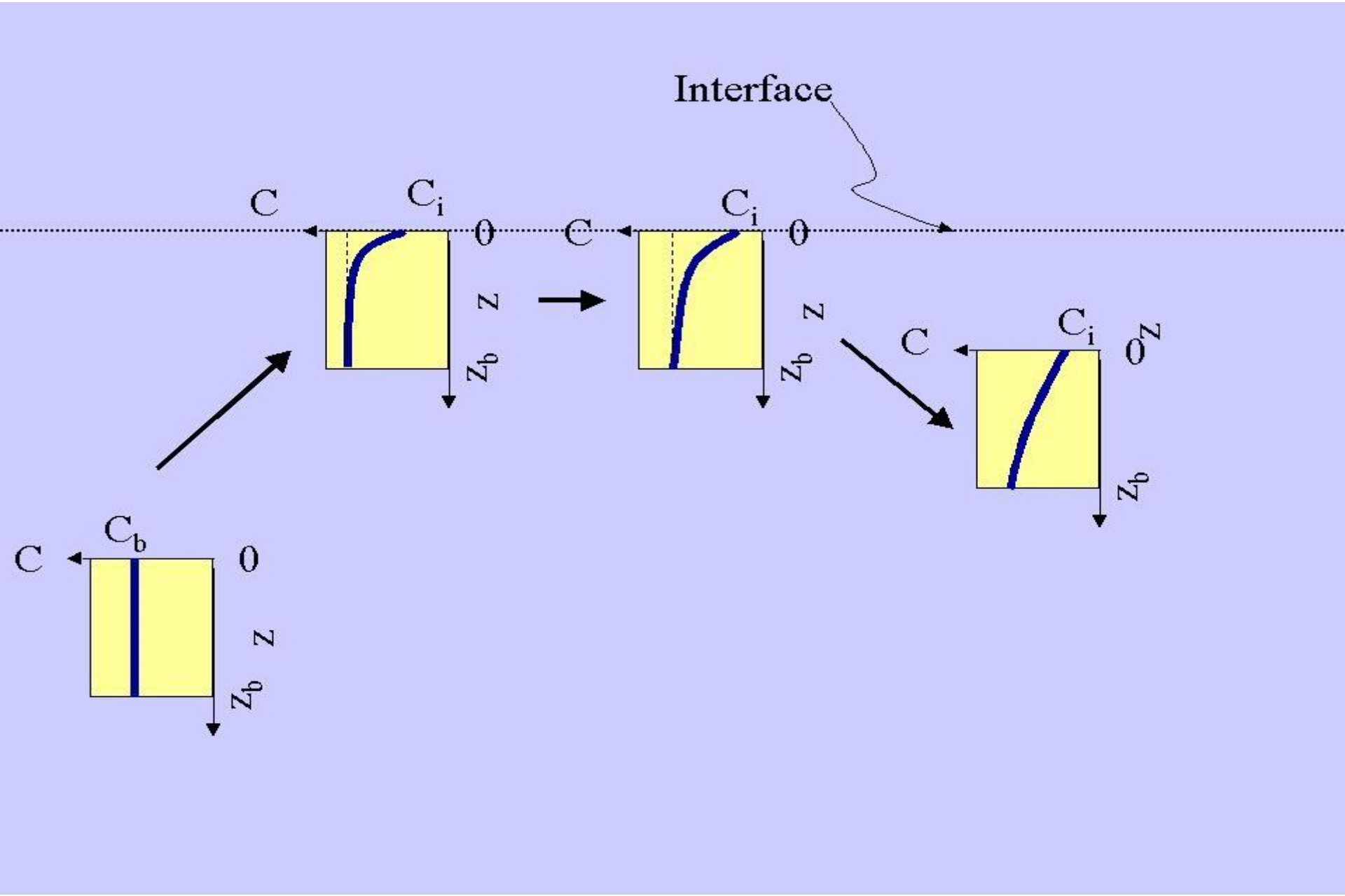
More realistic models of the process have been proposed by Higbie (1935, penetration model) and by Danckwerts (1951, surface renewal model).

In these models bulk fluid packets (eddies) work their way to the interface from the bulk solution. While at the interface they attempt to equilibrate with the other phase under non-steady state conditions. No film concepts need be invoked. The concentration profile in each eddy (packet) is determined by the molecular diffusion dominated advective-diffusion equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Assumption: no advection within the eddy

The solution to this governing equation depends, of course, on boundary conditions. In the Higbie penetration model it is assumed that the eddy does not remain at the surface long enough to affect concentration at the bottom of the eddy ($z = z_b$). In other words the eddy behaves as a semi-infinite slab. Where C (@ $z = z_b$) = C_b. Also C (@ $z = 0$) = C_i .


Interface
C
C_i
0
z
z_b
C
C_i
0
z
z_b
C
C_i
0
z
z_b
C
C_b
0
z
z_b

Solving the equation with these boundary conditions and then solving for the gradient at z = 0 to get the flux at z = 0 **and** then finding the average flux over the time the eddy spends on the surface yields the following:

$$J = 2\sqrt{\frac{D}{\pi\theta}} \cdot [C_i - C_b]$$

θ = average time at surface (a constant for a given mixing level).

Danckwerts modified the penetration model with the **surface renewal** model by allowing for the fluid packets to exist at the surface for varying lengths of time. (according to some probability distribution). The Dankwerts model is given by:

$$J = \left[C_i - C_b \right] \sqrt{D \cdot s}$$

s = surface renewal rate (again, a function of mixing level in bulk phase).

Comparison of the models:

Higbie and Danckwert's models both predict that J is proportional to $D^{0.5}$ where the Nernst film model predicts that J is proportional to D. Actual observations show that J is proportional to something in between, $D^{0.5\,-1}$. There are more complicated models which may fit the experimental data better, but we don't need to invoke them at this time.

Mass transfer coefficients

To simplify calculations we usually define a **mass transfer coefficient** for either the liquid or gas phase as k_l or k_g (dimensions = L/t).

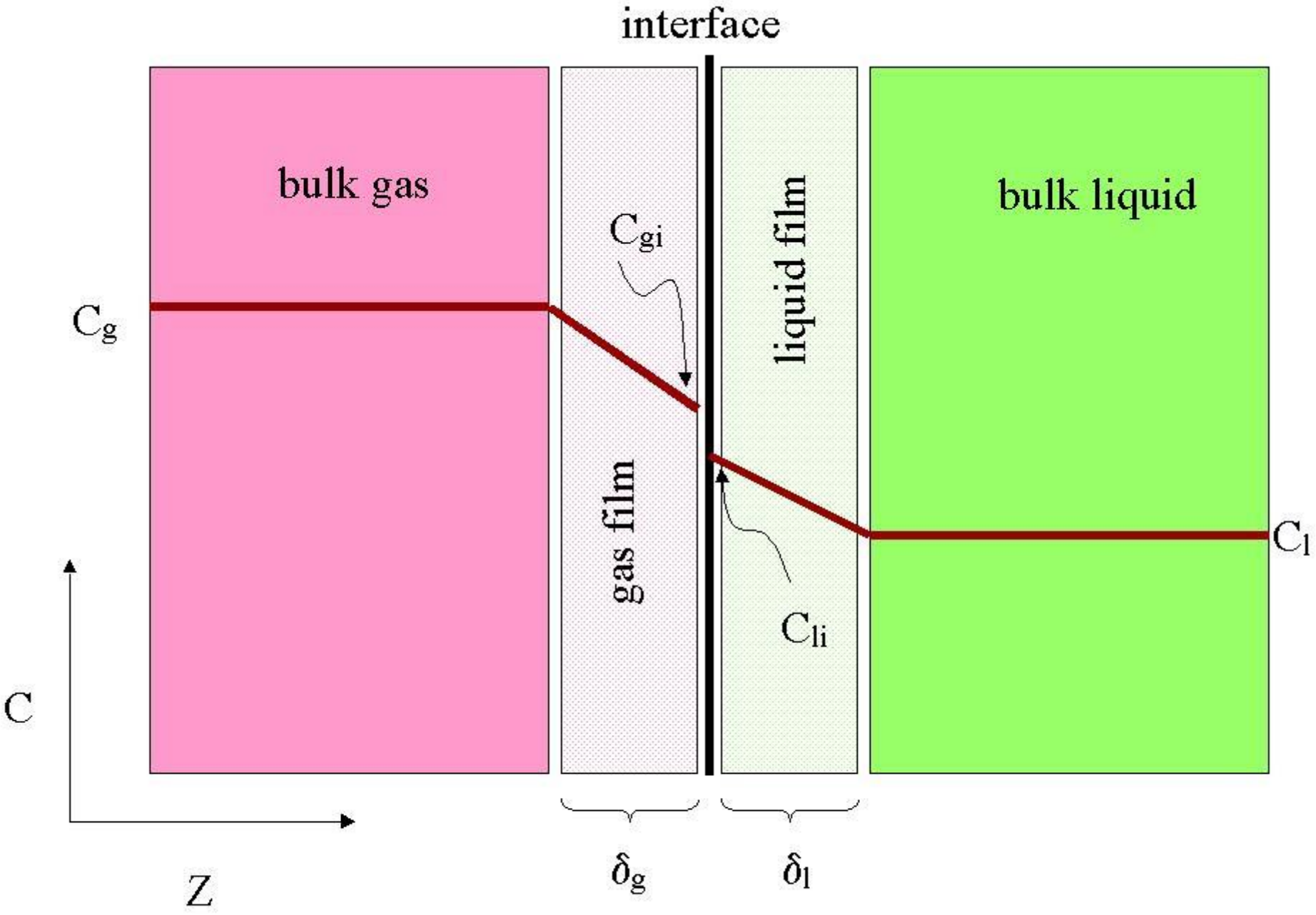
$$k_{l,g} = 2\sqrt{\frac{D}{\theta\pi}} \quad \text{(Higbie)}$$

$$k_{l,g} = \sqrt{D \cdot s} \quad \text{(Danckwerts)}$$

$$k_{l,g} = \frac{D}{\delta_n} \quad \text{(Nernst)}$$

Two film model

In many cases with gas-liquid transfer we have transfer considerations from both sides of the interface. For example, if we invoke the Nernst film model we get the Lewis-Whitman (1923) two-film model as described below.


interface
bulk gas
C_{gi}
liquid film
bulk liquid
C_g
gas film
C_l
C_{li}
C
Z
δ_g
δ_l

The same assumptions apply to the two films as apply in the single Nernst film model. The problem, of course, is that we will now have difficulty in finding interface concentrations, C_{gi} or C_{li}. We can assume that equilibrium will be attained at the interface (gas solubilization reactions occur rather fast), however, so that:

$$C_{li} = \frac{C_{gi}}{H_C}$$

A steady-state flux balance (okay for thin films) through each film can now be performed. The fluxes are given by:

$J = k_l(C_l - C_{li})$

and

$J = k_g(C_{gi} - C_g)$

If the Whitman film model is used:

$$k_{l,g} = \frac{D_{l,g}}{\delta_{l,g}} \quad \text{(m/sec)}$$

(Note the Higbie or Danckwerts models can be used without upsetting the conceptualization)

Unfortunately, concentrations at the interface cannot be measured so *overall* mass transfer coefficients are defined. These coefficients are based on the difference between the bulk concentration in one phase and the concentration that would be in equilibrium with the bulk concentration in the other phase.

Define:

$$J = K_l \left(C_l - C_l^* \right)$$

$$J = K_g \left(C_g^* - C_g \right)$$

K_l = *overall* mass transfer coefficient based on liquid-phase concentration.

K_g = *overall* mass transfer coefficient based on gas-phase concentration.

$K_{g,l}$ have dimensions of L/t.

C_l^* = liquid phase concentration that would be in equilibrium with the bulk gas concentration.

= C_g/H_c (typical dimensions are moles/m^3).

C_g^* = gas phase concentration that would be in equilibrium with the bulk liquid concentration.

= $H_c C_l$ (typical dimensions are moles/m^3).

Expand the liquid-phase overall flux equation to include the interface liquid concentration.

$$J = K_l \cdot \left(\left[C_l - C_{li} \right] + \left[C_{li} - C_l^* \right] \right)$$

Then substitute

$$C_{li} = \frac{C_{gi}}{H_c} \quad \text{and} \quad C_l^* = \frac{C_g}{H_c}$$

to get:

$$J = K_l \left\{ \left(C_l - C_{li} \right) + \left(C_{gi} - Cg \right) / H_c \right\}$$

In the steady-state, fluxes through all films must be equal. Let all these fluxes be equal to J.

On an individual film basis:

$$\left(C_l - C_{li}\right) = \frac{J}{k_l}$$

and

$$\left(C_{gi} - C_g\right) = \frac{J}{k_g}$$

Since all J's are equal:

$$J = K_l \left(\frac{J}{k_l} + \frac{J}{H_C \cdot k_g} \right)$$

This can be arranged to give:

$$\frac{1}{K_l} = \frac{1}{k_l} + \frac{1}{H_c \cdot k_g}$$

A similar manipulation starting with the overall flux equation based on gas phase concentration will give:

$$\frac{1}{K_g} = \frac{H_c}{k_l} + \frac{1}{k_g}$$

These last two equations can be viewed as "resistance" expressions where $1/K_g$ or $1/K_l$ represent total resistance to mass transfer based on gas or liquid phase concentration, respectively.

In fact, the total resistance to transfer is made up of three series resistances: liquid film, interface and gas film. But we assume instant equilibrium at the interface so there is no transfer limitation here. It should be noted that model selection (penetration, surface renewal or film) does not influence the outcome of this analysis.

Single film control

It is possible that one of the films exhibits relatively high resistance and therefore dominates the overall resistance to transfer. This, of course, depends on the relative magnitudes of k_l, k_g and H_c. So the solubility of the gas and the hydrodynamic conditions which establish the film thickness or renewal rate (in either phase) determine if a film controls.

In general, highly soluble gases (low H_c) have transfer rates controlled by gas film (or renewal rate) and vice versa. For example, oxygen (slightly soluble) transfer is usually controlled by liquid film. Ammonia (highly soluble) transfer is usually controlled by gas phase film.

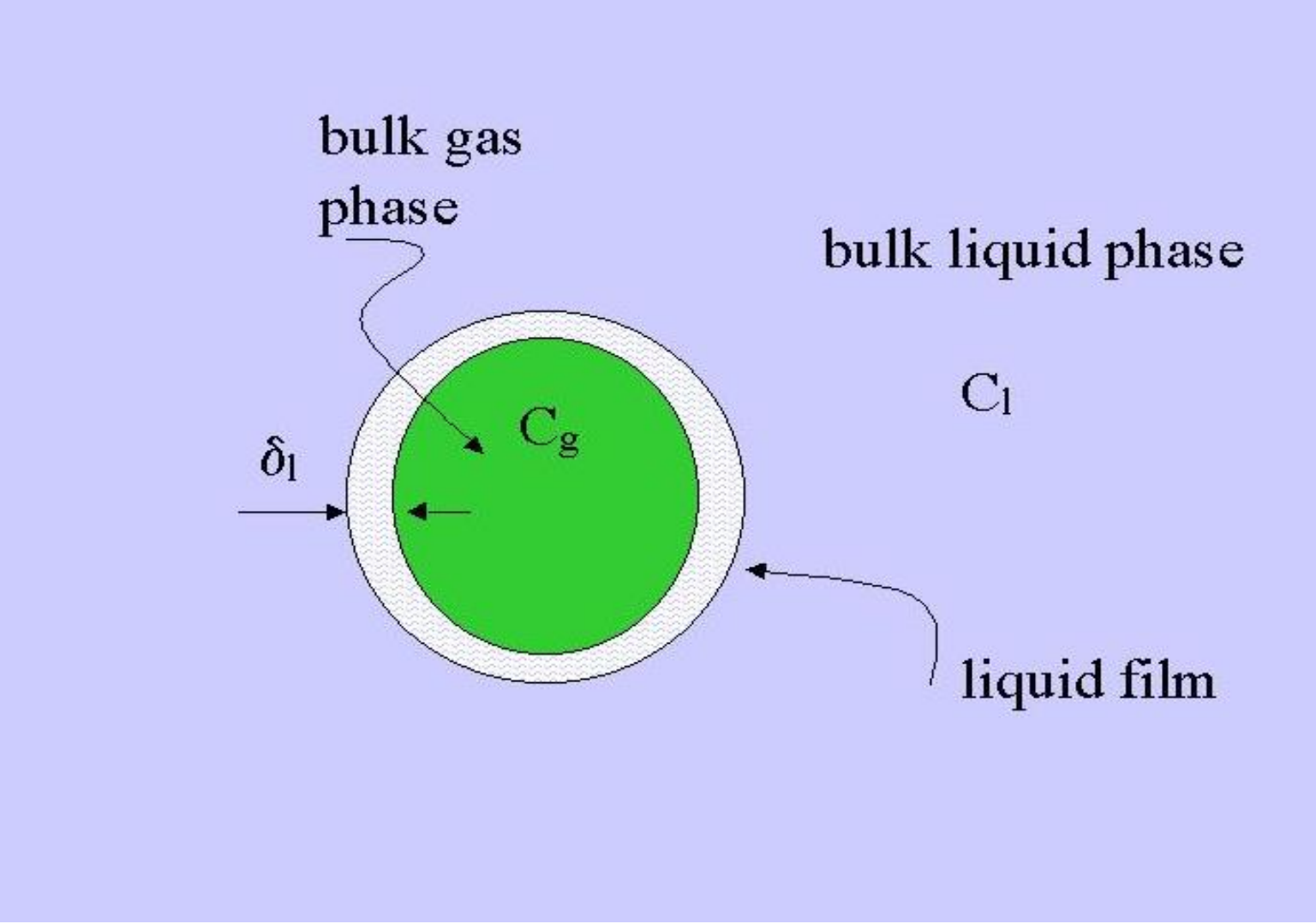
APPLICATIONS

Transfer of gas across a gas-liquid interface can be accomplished by bubbles or by creating large surfaces (interfaces). The following are some common applications of gas transfer in treatment process.

Aeration

Aeration or transfer of air or oxygen to water is a very common process in treatment systems. Bubble injection is a common method to accomplish this transfer. For the case of oxygen transfer to water consider each bubble to consist of completely mixed bulk gas phase (inside the bubble) plus a stagnant liquid film. (the stagnant air film may exist but for oxygen transfer control is usually in the liquid film).

For a single bubble:



Invoking the film model for gas transfer.

$$J = \frac{D_l}{\delta_l}\left(C_l^* - C_l\right)$$

$$C_l^* = \frac{C_g}{H_c}$$

For the case of many bubbles with total surface area = A (in a unit volume of liquid in which they are suspended), total flux per unit volume of liquid is given by:

$$J_{total} = A \cdot K_l \left(C_l^* - C_l \right)$$

If the liquid film is controlling:

$$k_l = \frac{D_l}{\delta} \approx K_l$$

If the liquid bulk phase concentration is not at steady-state, then:

$$\frac{dC_l}{dt} = \frac{A}{V} \cdot J = \frac{A}{V} \cdot K_l \left\{ C_l^* - C_l \right\}$$

V is the volume of the liquid phase.

Of course, if we are not at steady-state in the bulk phase the assumption of steady-state in the film boundary needs further analysis. Justification for assuming steady-state in the film lies in the fact that the film is extremely thin and the bulk volume is many magnitudes larger. The bulk phase will then take much longer to reach steady-state relative to the film. This is not a problem if the surface-renewal or penetration model are invoked since there is no requirement of steady-state for these models.

Further, we can then define:

$$K_l a = \frac{A}{V} K_l$$

$K_l a$ is a lumped parameter which takes into account bubble size, temperature (through its effect on diffusion), turbulence (through its effect on film thickness or surface renewal rate). It's a handy engineering coefficient. Note $K_l a$ has units 1/time.

Temperature corrections for $K_l a$ are generally made using the expression:

$$K_l a_T = K_l a_{20^oC} \theta^{(T-20^oC)}$$

$$\theta = 1.024$$

Turbulence levels affects the bubble size and the liquid film thickness. As turbulence increases film thickness decreases and bubble size decreases. Both result in increases in $K_l a$. As bubble size decreases $K_l a$ increases up to a certain point where the bubble rise velocity increases with bubble size. As the rise velocity increases the film thickness decreases and $K_l a$ again increases. With all these factors taken into account, it turns out that the optimum bubble size is about $r = 1.5$ mm.

Another important factor affecting $K_l a$ is the concentration of surfactants in the liquid phase. This is of particular concern when we deal with wastewaters. Surfactant effects are often taken into account by defining :

$$\alpha = \frac{K_l a(\text{wastewater})}{K_l a(\text{clean water})}$$

$$0.2 < \alpha < 1$$

In addition, since the solubility of gases in wastewater is affected by the TDS, the following term is also defined to adjust for solubility.

$$\beta = \frac{C_l^*(\text{wastewater})}{C_l^*(\text{clean water})}$$

$$0.85<\beta<1$$

Determination of $K_l a$:

$K_l a$ is usually determined by experimental techniques such as the non-steady state procedure described here.

The time rate of change of gas concentration in the liquid phase is given by:

$$\frac{dC_l}{dt} = K_l a \left(C_l^* - C_l \right)$$

Integration yields:

$$K_l a(t) = \ln \frac{\left(C_l^* - C_0\right)}{\left(C_l^* - C_l\right)}$$

C_0 is the initial liquid bulk concentration at t = 0.

$$D = \left(C_l^* - C_l \right)$$

and:

$$D_0 = \left(C_l^* - C_0 \right)$$

then:

$$\ln \frac{D}{D_0} = -K_l a(t)$$

A plot of $\ln D/D_0$ versus time should yield a straight line with slope equal to $-K_l a$.

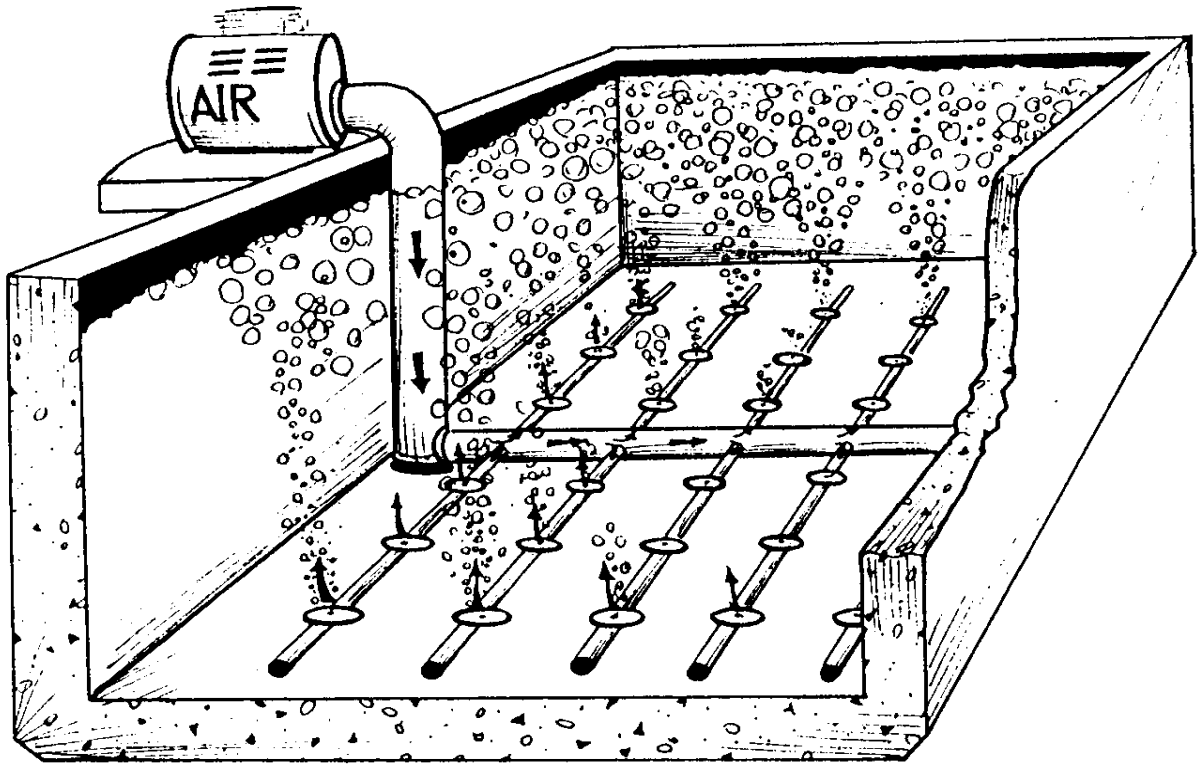
Aeration Systems

Diffused Air:

Focus for the moment on oxygen transfer since it is a common and important process in wastewater treatment. A common way to aerate water is via diffused air. In these systems air is pumped through some sort of diffuser to generate small bubbles. These diffusers are porous ceramics, cloth or plastic.

Usually gas (air or oxygen) is injected into the bottom of the aeration tank and is allowed to rise to the surface in an open tank. Oxygen transfer from the bubble varies as the bubble changes size, velocity, oxygen content and hydrostatic pressure (depth changes). These factors have to be considered in calculating overall transfer rate of oxygen to water.

Typical diffused aeration system looks like:



Activated Sludge Aeration Basin

There are a large variety of diffuser types. For example ceramic plates such as:

These plates are arranged on manifolds at the bottom of aeration tanks as shown here.

Other types of diffusers include coarse aerators:

Again, these diffusers would be arranged by a manifold on the bottom of an aeration tank.

To determine the oxygen transfer rate in these diffused aeration systems, first define the pressure difference from top to bottom of the tank.

At the surface:

$$P_{surface} = 14.7(1 - 0.032 \cdot Alt)$$

Alt = altitude in thousands feet above sea level

$P_{surface}$ has units of psi

$$P_{bottom} = P_{surface} + \frac{62.4 \cdot H}{144} \text{ (psi)}$$

H = depth of tank (depth of discharge point) in feet.

Oxygen transfer rate can then be modeled using the following:

$$\frac{dC_l}{dt} = K_l a \left(C^*_{l,m} - C_l \right)$$

$C^*_{l,m}$ is the saturation value for oxygen at mid-depth for the wastewater at an operating temperature T and altitude (Alt) as defined by:

$$C^*_{l,m} = \beta \cdot C^*_l \left\{ \frac{P_{bot}}{2 \cdot (14.7)} + \frac{O_t \cdot P_{surface}}{(0.21) \cdot (2) \cdot (14.7)} \right\}$$

O_t = mole fraction of oxygen in the bubbles reaching the top of the aeration tank. This value will depend on the efficiency of transfer as defined by:

$$E = \frac{O_2 \text{ transferred}}{O_2 \text{ supplied}}$$

Then:

$$O_t \approx \frac{(1-E)(0.21)}{1-E(0.21)}$$

For diffused air systems E is usually in the 0.1 to 0.2 range.

To calculate the actual amount of oxygen that a system will transfer the manufacturer generally gives some formula such as the one proposed by Eckenfelder and Ford (1968) in Reynolds/Richards (page 500). A formula of this type is necessary because manufacturer's conditions and the actual users conditions are generally different. (Typical manufacturer's condition are $20^{o}C$, clean water, at H = 15 ft).

$$N = C \cdot G_a^{1-n} H^{0.67} (C^*_{l,m} - C_l) \cdot 1.02^{(T-20)} \cdot \alpha$$

N = rate of oxygen transfer, lb/hr (depending on the units for C)

C, n are constants

G_a air flow (standard cubic feet per minute) at 20^{o}C and 1 atm.

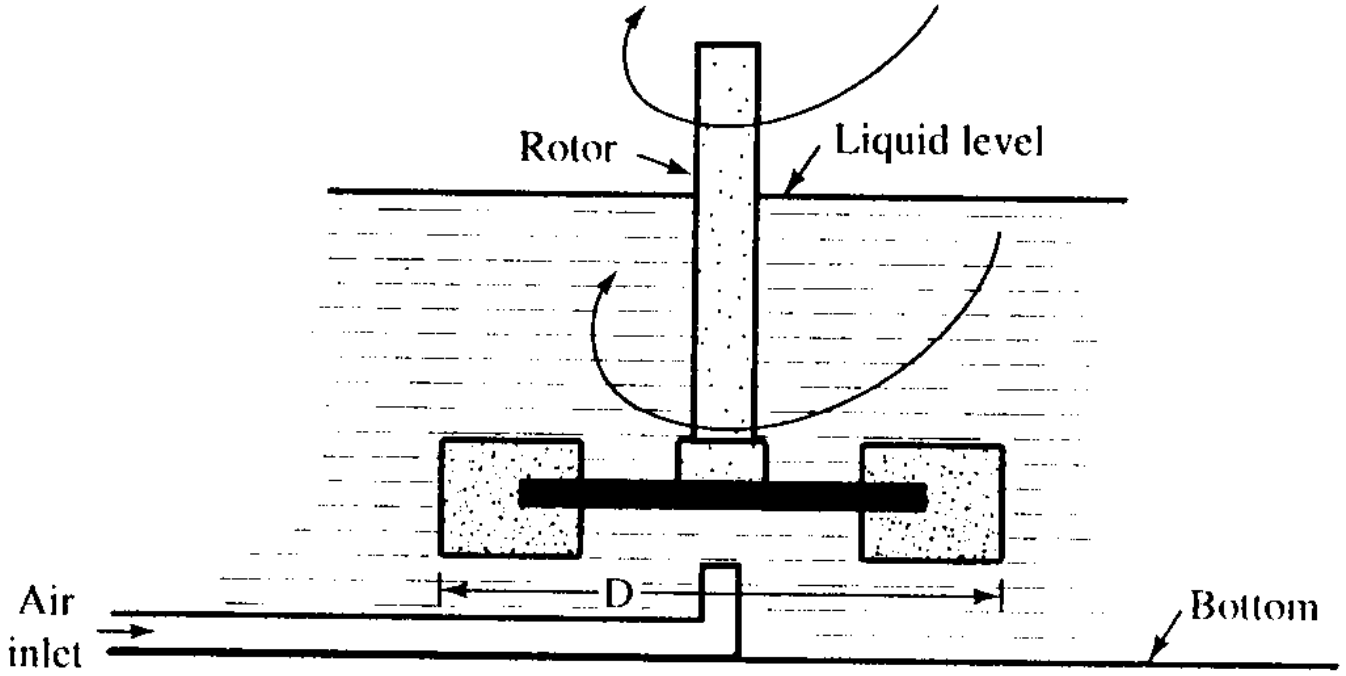
Note that $C^*_{l,m}$ is usually calculated with an assumed efficiency of about 5 – 10 %.

Mechanical Aeration

Basically there are two types of mechanical aeration.

Turbine Aeration:

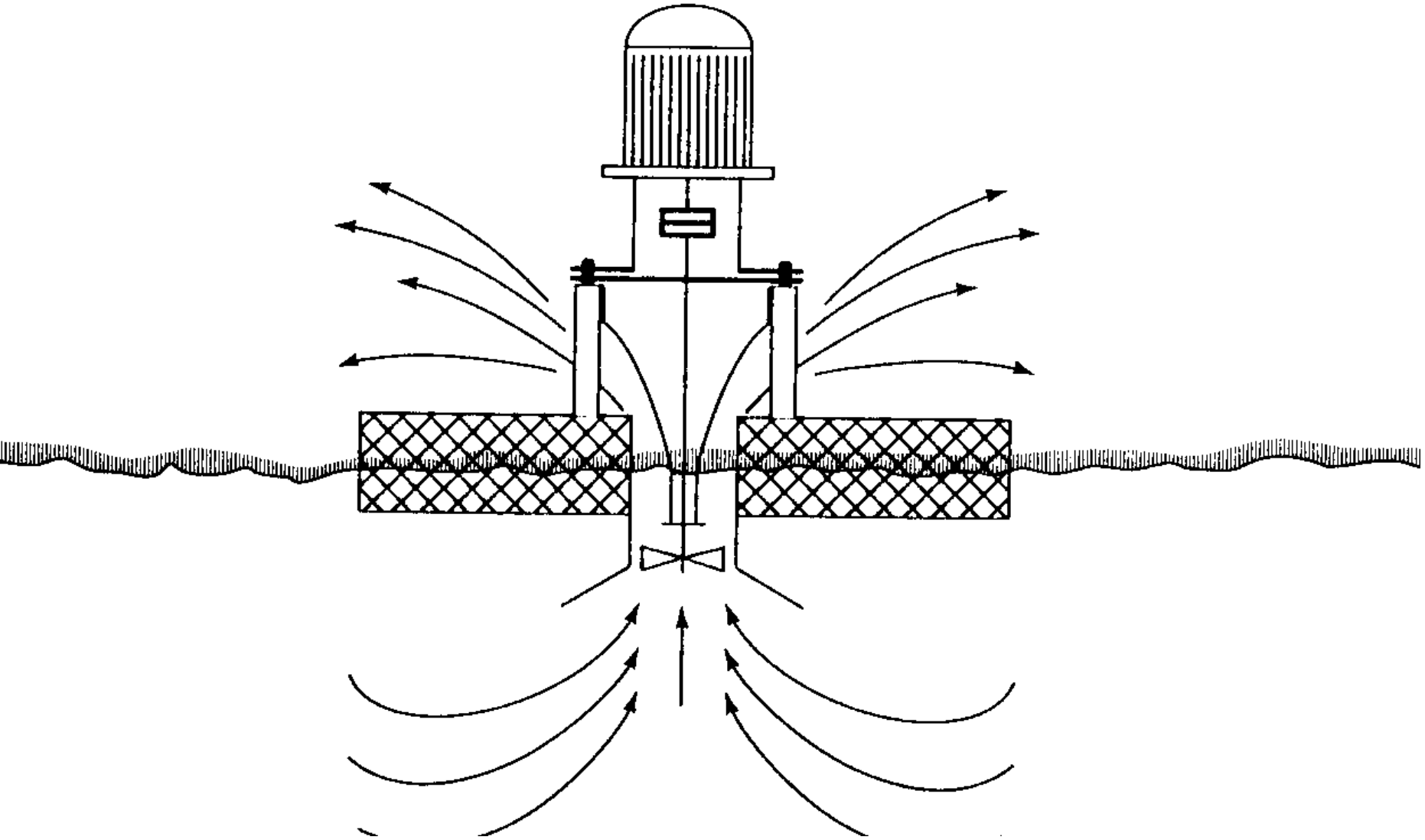
In this system coarse bubbles are injected into the bottom of the tank and then a turbine shears the bubbles for better oxygen transfer.



efficiency of turbine aerators is generally higher than diffused aeration. E is normally in the range of 0.2 to 0.25. Power required is about 2 – 4 lbs O_2 transferred per hp-hr.

Surface Aeration:

In this case a mixing device is used to agitate the surface so that there is increased interfacial area between liquid and air. There are many different proprietary types of surface aerators . A schematic and picture of a common surface aerator are shown below.



An actual surface aerator:

Design consideration for mechanical aerators is usually based on another Eckenfelder and Ford type of equation.

$$N = N_0 \left(\frac{C_w - C_l}{9.17} \right) \cdot (1.02)^{(T-20)} \cdot \alpha$$

Notice that there is no depth consideration for mechanical aeration.

N = actual transfer rate (lb-O_2/hr)

N_0 = manufacturer specified transfer rate (lb/hr) for clean water, 20^{o}C, zero DO.

C_w = saturation value for oxygen for wastewater under operating conditions.

9.17 = saturation DO for clean water, 20^{o}C.

C_l = the design oxygen concentration in the aeration basin.