

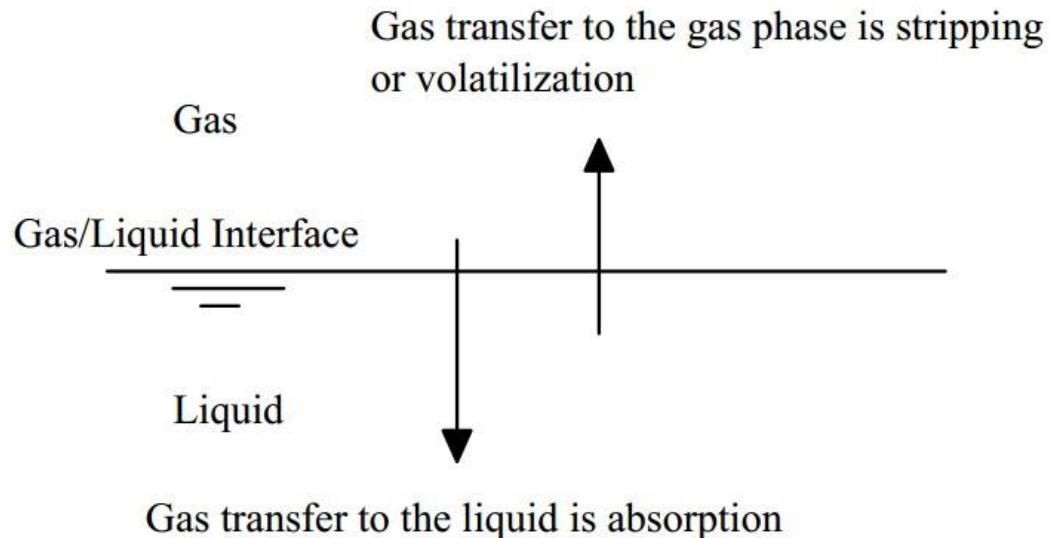
BAE 820 Physical Principles of Environmental Systems

Inter phase mass transfer

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Mass transfer between two phases

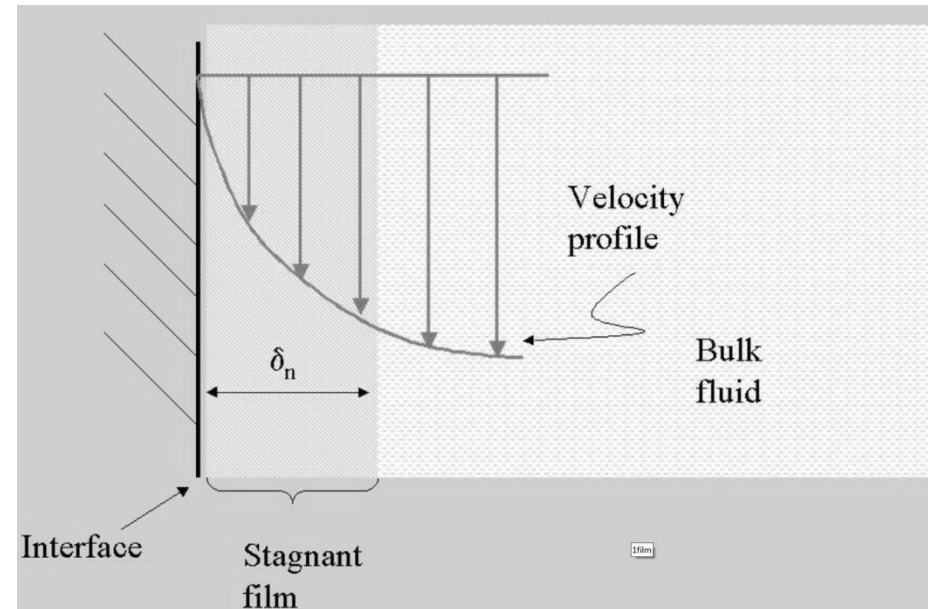
- For a two phase system not at equilibrium (concentrations in the two phases are not as predicted by Henry's law), mass transfer will occur to bring it to equilibrium. There must be concentration gradient in the direction of diffusion within each phase. E.g. diffusion of a soluble gas such as ammonia between air and water.



Film Theory

- A simple conceptualization of the gas-liquid transfer process developed by Nernst (1904).
- Near the interface, there exists a hypothetical stagnant film.
- In this film, bulk liquid is not moving. Therefore, transport is governed essentially by molecular diffusion. Fick's law describes flux through the film.
- If the thickness of the stagnant film is given by δ_n then the diffusion flux can be approximated by

$$J = -D \frac{\partial C}{\partial x} \approx -D \frac{(C_b - C_i)}{\delta_n}$$



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

Two film theory

Developed by Lewis-Whitman (1924).

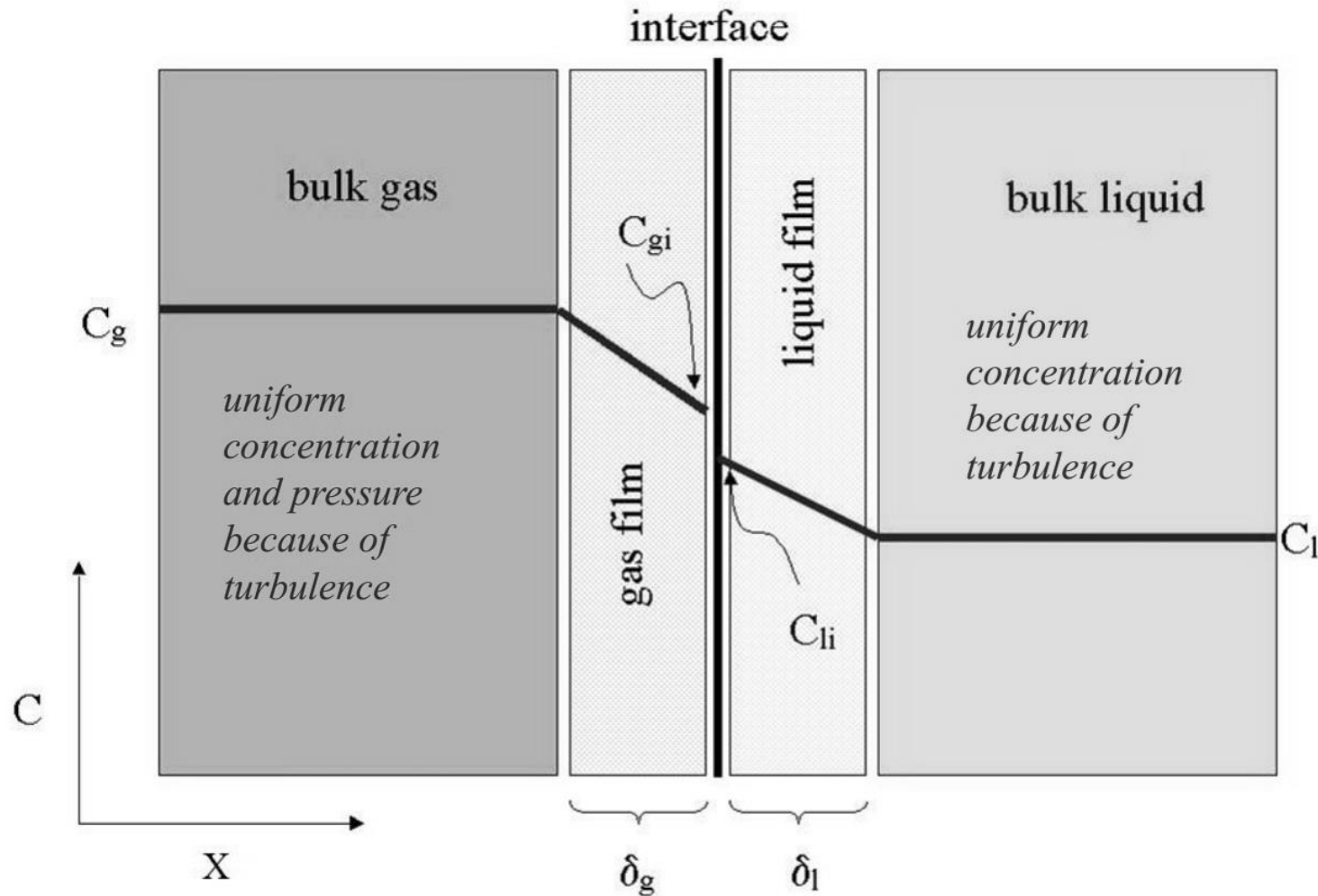
Assuming that

- There are two stagnant layers of film at the interface.
- The mass transfer across the films is by molecular diffusion.
- The bulks of gas and liquid are homogeneous with respect to solute.

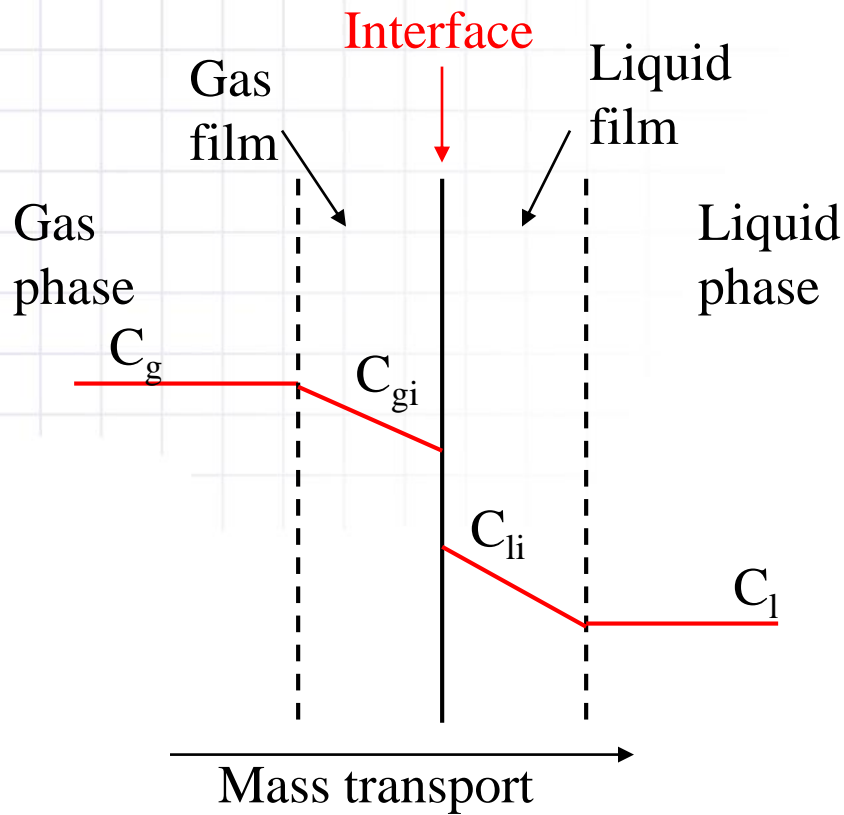
When the mass transfer is in the X direction (from gas phase to liquid phase), there must be a concentration gradient in the direction of mass-transfer within each phase.

- The bulk gas concentration C_g falls to C_{gi} at the interface.
- In the liquid phase, the concentration falls from C_{li} at the interface to C_l in the main body of liquid.
- C_{gi} and C_{li} are at equilibrium.
- C_g and C_l are clearly not the equilibrium values since otherwise the mass transfer would not occur.

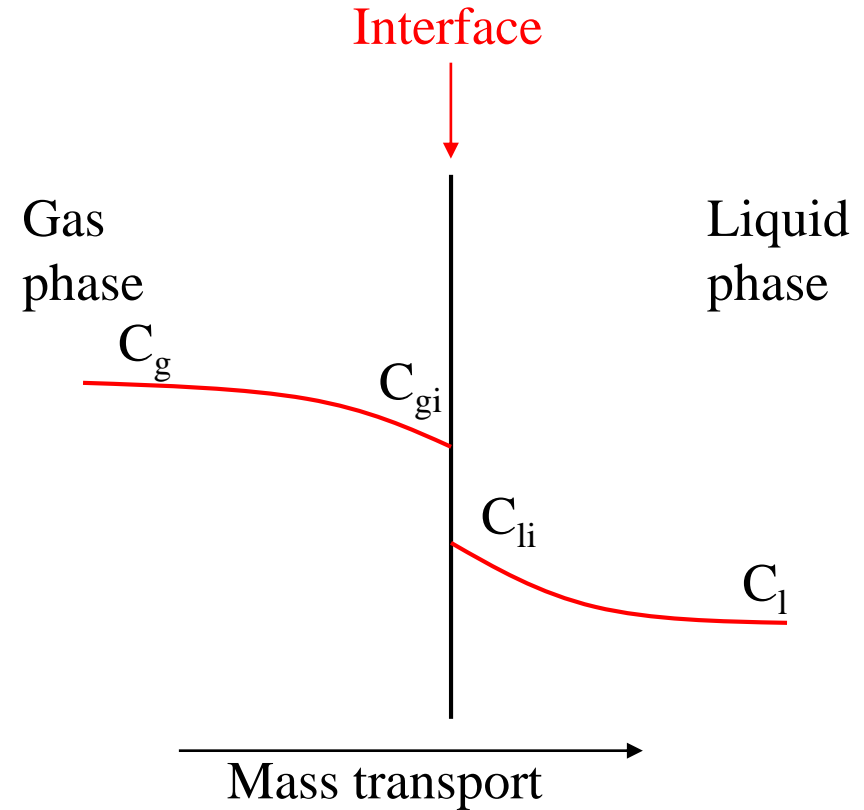
The two film theory



Concentration gradients for the film theory



More realistic concentration gradients



The flux equations

Gas phase transport

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

Liquid phase transport

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

Where

- k_l or k_g = mass transfer coefficient for either the liquid or gas phase. $k_l = D_l / \delta_l$, $k_g = D_g / \delta_g$

$$C_{gi} = H_c C_{li}$$

At steady state,

$$J = J_g = J_l$$

The difficulty is finding interface concentrations, C_{gi} or C_{li} , which cannot be measured directly. We want to be able to relate flux to bulk air and water concentrations. Therefore, overall mass transfer coefficients are defined.

The overall mass transfer coefficients

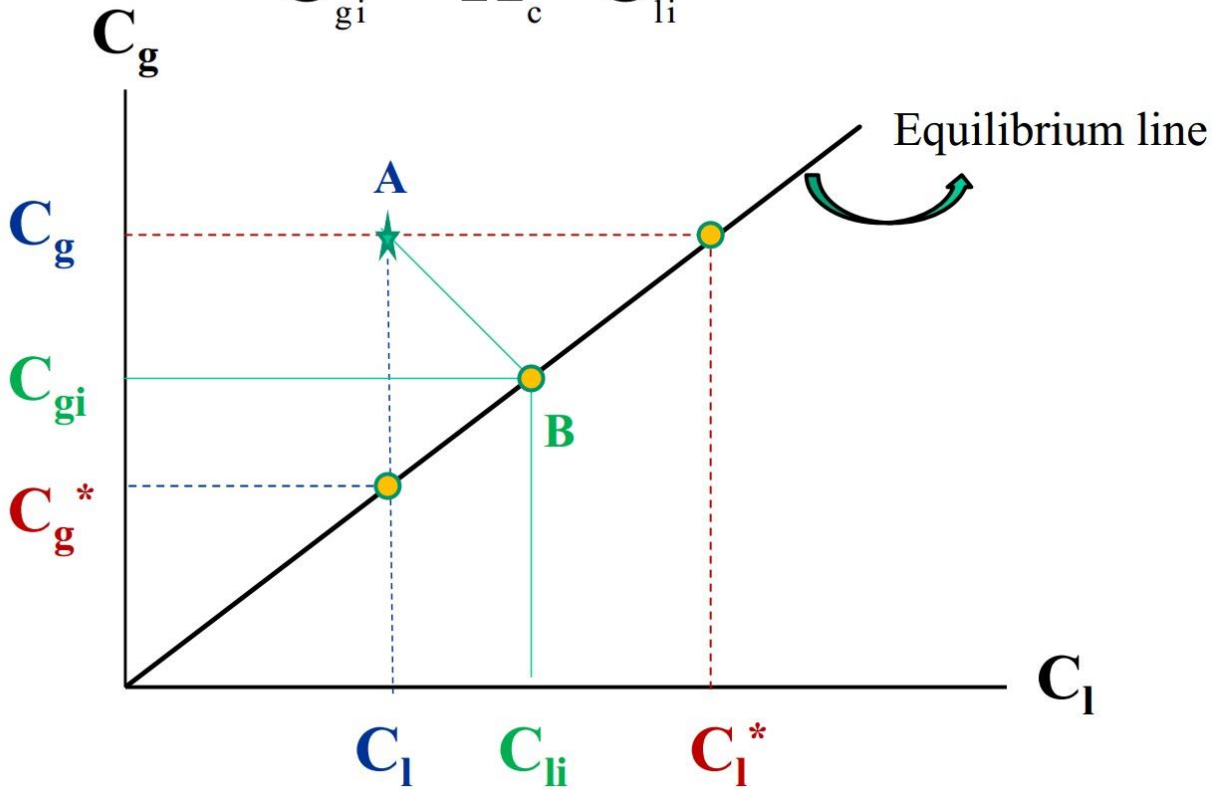
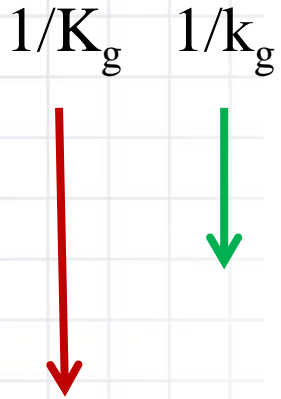
Define

$$J = K_g (C_g - C_g^*) = K_l (C_1^* - C_1)$$

Where

- K_g is overall mass transfer coefficient based on gas-phase concentration,
- K_l is overall mass transfer coefficient based on liquid-phase concentration.
- C_g^* is gas phase concentration that would be in equilibrium with the bulk liquid concentration. $C_g^* = H_c C_1$.
- C_1^* is liquid phase concentration that would be in equilibrium with the bulk gas concentration. $C_1^* = C_g / H_c$.

$$C_{gi} = H_c \cdot C_{li}$$



Expand the liquid-phase overall flux equation

$$\begin{aligned} J &= K_l (C_1 - C_1^*) = K_l [(C_1 - C_{li}) + (C_{li} - C_1^*)] \\ &= K_l [(C_1 - C_{li}) + (C_{gi} - C_g)/H_c] \\ &= K_l [J/k_l + J/(k_g H_c)] \end{aligned}$$

Therefore,

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

In which, $\frac{1}{K_l}$ represent the overall resistance to mass transfer based on liquid phase concentration, and it is the sum of liquid film resistance ($\frac{1}{k_l}$) and gas film resistance ($\frac{1}{H_c k_g}$).

Similarly,

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

- It is possible that one of the films exhibits relatively high resistance and therefore dominates the overall resistance to transfer. This depends on the relative magnitudes of k_l , k_g and H_c .
- For highly soluble gases such as NH_3 and SO_2 (H_c is low), mass transfer is controlled by gas film resistance.

$$\frac{1}{k_l} \ll \frac{1}{H_c k_g} \quad \text{So,} \quad K_l \approx H_c k_g$$

- For less soluble gases such as N_2 and O_2 (H_c is high), mass transfer is controlled by liquid film resistance.

$$\frac{1}{k_l} \gg \frac{1}{H_c k_g} \quad \text{So,} \quad K_l \approx k_l$$

Other theoretical models for interphase mass transfer

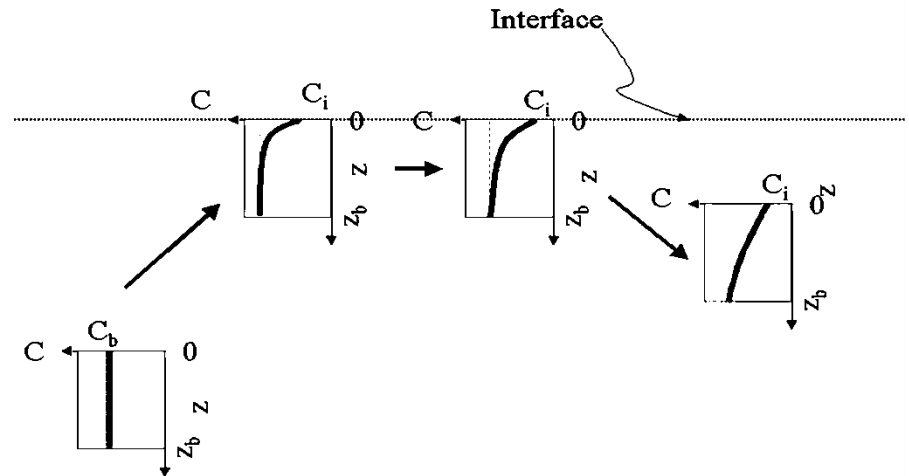
- Interphase mass transfer (gas/liquid interface or liquid/liquid interface) are of great interest in separation processes, such as absorption, distillation, extraction, stripping, etc.
- Theoretical models for interphase mass transfer
 - Film theory (Nernst, 1904)
 - Penetration theory (Higbie, 1935)
 - Surface renewal theory (Dankwerts, 1951)
 - Film-penetration theory
 - Boundary layer theory

Penetration theory (Higbie, 1935)

- Eddies move from the bulk to the interface and then leave the interface to mix with the bulk stream. They stay at the interface for a short, fixed period of time during which they remain static so that molecular diffusion takes place. the penetration theory is most useful when mass transfer involves bubbles or droplets or flow over random packing.
- Mass transfer flux is given by

$$J = 2 \sqrt{\frac{D}{\pi t_c}} (C_i - C_b)$$

Where t_c is the average contact time of the static eddy at the interface during one cycle (a constant for a given mixing level)



Surface renewal theory (Dankwerts, 1951)

- Danckwerts suggested an improvement to the penetration theory that involves the replacement of the constant eddy contact time with the assumption of a residence-time distribution.
- Mass transfer flux is given by

$$J = \sqrt{Ds}(C_i - C_b)$$

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

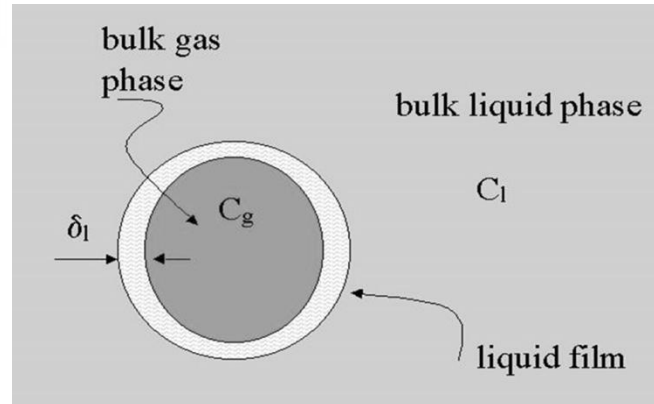
Comparison of the three theories

Film theory	$k = \frac{D}{\delta_n}$
Penetration theory	$k = 2 \sqrt{\frac{D}{\pi t_c}}$
Surface renewal theory	$k = \sqrt{Ds}$
Boundary layer theory	$k \sim D^{2/3}$

- In the film theory, k is proportional to D . In penetration theory and surface renewal theory, k is proportional to $D^{0.5}$. Most experimental observations show that k is proportional to something in between. The power of D are between 0.5 and 1.0, with higher turbulence being closer to 0.5. In boundary layer theory, the power = 2/3.

Aeration

- Transfer of gas across a gas-liquid interface can be accomplished by bubbles or by creating large surfaces (interfaces).
- 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).



The rate of change of gas concentration in the liquid phase

$$\frac{dC_L}{dt} = \frac{AJ}{V} = \frac{A}{V} K_L (C_L^* - C_L) = K_L a (C_L^* - C_L)$$

Where, A is the total surface area of the bubbles, V is the volume of the liquid phase.

Define $K_L a = \frac{A}{V} K_L$, is a handy engineering coefficient. It is a lumped parameter takes into account bubble size, temperature (through its effect on diffusion), turbulence (through its effect on film thickness or surface renewal rate).

Integration yields

$$-K_L a = \frac{\ln(C_L^* - C_{t_1}) - \ln(C_L^* - C_{t_2})}{t_1 - t_2}$$

$K_L a$ can be determined from experiment data though a plot of $\ln(C_L^* - C_t)$ vs time, which will yield a straight line with slop equal to $-K_L a$.

Factors that may affect $K_L a$

- Factors that affect $K_L a$
 - 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

$$K_L a (\text{wastewater}) = \alpha K_L a (\text{clean water}) \quad 0.2 < \alpha < 1$$

- Temperature

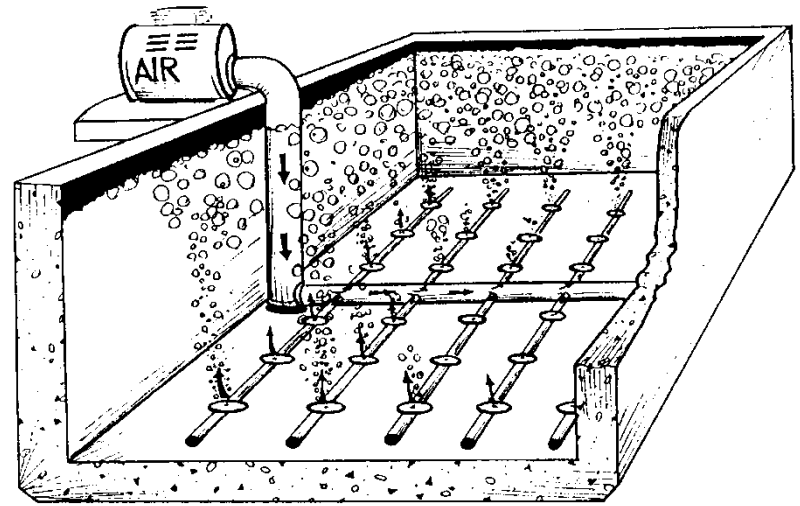
$$(K_L a)_T = (K_L a)_{20^\circ\text{C}} \times 1.024^{(T-20)}$$

- Factors that affect C_L^*
 - The solubility of gases in wastewater is affected by solid content.

$$C_L^* (\text{wastewater}) = \beta C_L^* (\text{clean water}) \quad 0.85 < \beta < 1$$

Diffused aeration

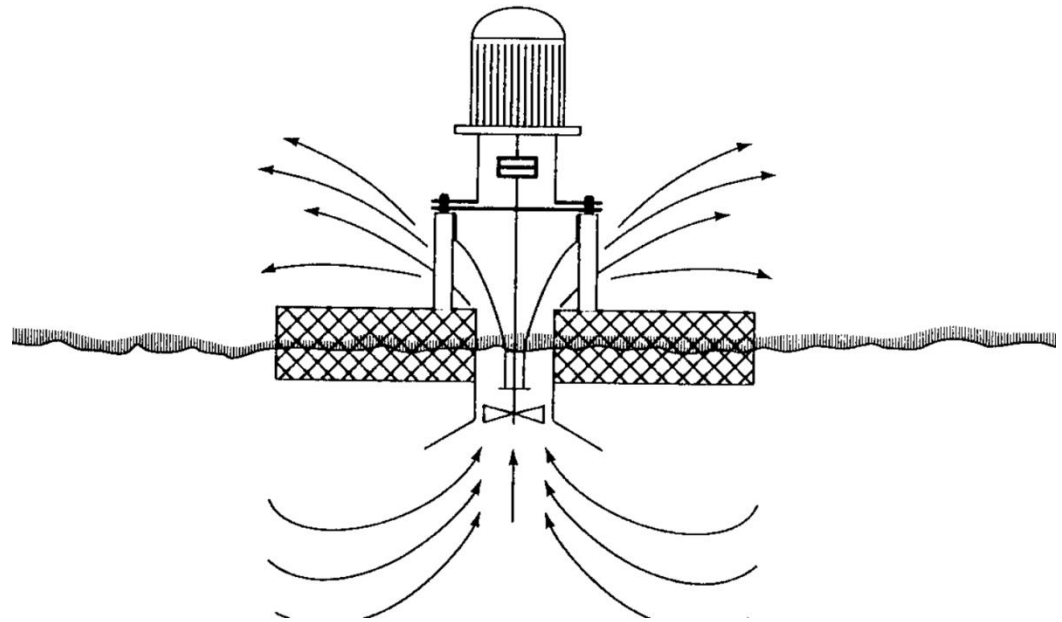
In diffused aeration systems air is pumped through some sort of diffuser to generate small bubbles. These diffusers are porous ceramics, cloth or plastic. Usually gas (air or oxygen) is injected into the bottom of the aeration tank and is allowed to rise to the surface in an open tank.



Activated Sludge Aeration Basin

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 .



Problem solving #6-1

- Estimate the overall liquid-side mass transfer coefficient at 25°C for oxygen from water into air. For oxygen in air, the diffusion coefficient is 0.23 cm²/sec; for oxygen in water, the diffusion coefficient is 2.1 x 10⁻⁵ cm²/sec. The Henry's law constant is 769 L·atm/mol. Use the two film theory, and assume that the film thickness is 0.01cm for both gas and liquid phase. Which phase has more resistance for the overall mass transfer?

Problem solving #6-2

- Carbon dioxide is being scrubbed out of a gas using water flowing through a packed bed of 1 cm Berl saddles. The carbon dioxide is absorbed at a rate of 2.3×10^{-6} mol/cm² sec. The carbon dioxide is present at a partial pressure of 25 atm, the Henry's law coefficient is 29 L·atm/mol, and the diffusion coefficient of carbon dioxide in water is 1.9×10^{-5} cm²/sec. Assuming mass transfer is controlled by liquid film resistance, find the film thickness.

Problem solving #6-3

- The value of K_1a for a certain industrial waste is 2.46 per hour at 20°C. What is the value of K_1a at 25°C?

Problem solution #6-1

- $\delta_n = 0.01 \text{ cm}$

- $k_l = \frac{D_l}{\delta_n} = \frac{2.1 \times 10^{-5}}{0.01} = 2.1 \times 10^{-3} \text{ cm/s}$

- $k_g = \frac{D_g}{\delta_n} = \frac{0.23}{0.01} = 23 \text{ cm/s}$

- $K_l = \frac{1}{\frac{1}{k_l} + \frac{1}{H_c k_g}} = \frac{1}{\frac{1}{2.1 \times 10^{-3}} + \frac{1}{23 \times 769 / 24.4}} = 2.1 \times 10^{-3} \text{ cm/s}$

- $K_l \approx k_l$ Mass transfer is controlled by liquid film resistance

Problem solution #6-2

- $C_1^* = p / H_c = 25/29 = 0.86 \text{ mol/L} = 0.00086 \text{ mol/cm}^3$
- $k_1 \approx K_1 = \frac{J}{C_1^* - C_l} \approx \frac{2.3 \times 10^{-6}}{0.00086 - 0} = 2.7 \times 10^{-3} \text{ cm/s}$
- $\delta_n = \frac{D_1}{k_1} = \frac{1.9 \times 10^{-5}}{2.7 \times 10^{-3}} = 0.007 \text{ cm}$

Problem solution #6-3

- $(K_{1a})_{25^{\circ}\text{C}} = (K_{1a})_{20^{\circ}\text{C}} \times 1.024^{(T-20)}$
 $= 2.46 \times 1.024^{(25-20)}$
 $= 2.77 \text{ h}^{-1}$