TWO FILM THEORY

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Gas transfer rates

If either phase concentration can not be 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.

One common conceptualization method is the **film theory**.
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.
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 \text{(typical units \( \frac{\text{mg}}{\text{cm}^2 \cdot \text{sec}} \))} \]
If the thickness of the stagnant film is given by \( \delta_n \) 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 $D = \text{constant}$) -- therefore the gradient must be linear and the approximation is appropriate.

And:

\[ J = -D \frac{(C_b - C_i)}{\delta_n} \]
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).

\[ k_{l,g} = \frac{D}{\delta_n} \]
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).
Two film model

In many cases with gas-liquid transfer we have transfer considerations from both sides of the interface. Therefore, we use the Lewis-Whitman (1923) two-film model as described below.
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

\[ J = k_g(C_{gi} - C_g) \]

assuming that the flux is in the X direction, in other words from bulk gas phase to bulk liquid phase.
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:

\[ J = K_1 (C_1 - C_1^*) \]

\[ J = K_g (C_g^* - C_g) \]

\( K_1 \) = *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 $L/t$.

$C_{l}^* = \text{liquid phase concentration that would be in equilibrium with the bulk gas concentration.}$

$= \frac{C_g}{H_c}$ (typical dimensions are moles/m$^3$).

$C_{g}^* = \text{gas phase concentration that would be in equilibrium with the bulk liquid concentration.}$

$= H_cC_l$ (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:

$$J = K_{l} \left\{ (C_{l} - C_{li}) + \left( \frac{C_{gi} - C_{g}}{H_c} \right) \right\}$$
In the steady-state, fluxes through all films must be equal. Let all these fluxes be equal to $J$.

On an individual film basis:

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

and

$$(C_{gi} - C_g) = \frac{J}{k_g}$$
Since all J’s are equal:

\[ J = K_1 \left( \frac{J}{k_1} + \frac{J}{H_c \cdot k_g} \right) \]
This can be arranged to give:

\[
\frac{1}{K_1} = \frac{1}{k_1} + \frac{1}{H_c \cdot k_g}
\]

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

\[
\frac{1}{K_g} = \frac{H_c}{k_1} + \frac{1}{k_g}
\]
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.
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.