# ENVE 301 <br> Environmental Engineering Unit Operations 

Lecture 4<br>Gas Transfer - I

SPRING 2014<br>Assist. Prof. A. Evren Tugtas

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## Gas Transfer

## Lecture notes from

- Reynolds, T. D., and P. A. Richards. Unit Operations and Processes in Environmental Engineering. 2nd ed. Boston, MA: PWS Publishing Company, 1996. (Textbook)
- American Water Works Association. Water Quality and Treatment: A handbook of community water supplies. 5th ed. McGraw Hill, 1999 ISBN: 0-0070016593


## Gas Transfer

Gas is transferred from one phase to another. Gas phase $\rightarrow$ Liquid phase Absorption
Liquid phase $\rightarrow$ Gas phase Desorption


Fig:http://www.spartanwatertreatment.com /ozone-fine-bubble-diffusers.html


Ömerli wtp, Courtesy of Prof. Dr. A. M. Saatc1

## Gas Transfer in Water Treatment

Systems involving gas transfer are used for variety of water treatment applications;

1. Absorption of reactive gases for water stabilization or disinfection

- Aeration or bubble systems are used for the absorption of reactive gases $\left(\mathrm{O}_{2}, \mathrm{O}_{3}, \mathrm{Cl}_{2}\right)$
- Ozone is used for disinfection and oxidation of total organic carbon (TOC)
- Chlorine is used for disinfection and sometimes preoxidant for the oxidation of Fe and Mg


## Gas Transfer in Water Treatment

## 2. Precipitation of inorganic contaminants

- Oxygen is used for the oxidation/precipitation of iron and manganese

3. Air stripping of volatile organic compounds, $\mathrm{NH}_{3}, \mathrm{CO}_{2}$, $\mathrm{H}_{2} \mathrm{~S}, \mathrm{O}_{2}$

- Diffused-aeration systems are used for the stripping of odor causing chemicals and VOCs
- Surface aerators primarily used for VOC removal
- Packed-tower or spray nozzle systems are used for the removal of $\mathrm{NH}_{3}, \mathrm{CO}_{2}, \mathrm{H}_{2} \mathrm{~S}$, VOCs


Ref:
http://markduehmig.photoshelter.com/image/ I0000gcq5vE3gUHk


## Theory of Gas Transfer

To design and operate aeration/air stripping devices understanding of;

- Equilibrium partitioning of chemicals between air and water
- Mass transfer rate across the air-water interface is required
Both equilibrium and mass transfer equations are incorporated into mass balance equations


## Theory of Gas Transfer



## If the system is at equilibrium;

$\underset{\text { leaving the system }}{\text { Number of molecules } \uparrow} \uparrow=\downarrow \begin{gathered}\text { Number of molecules } \\ \text { entering the system }\end{gathered}$

## Dalton's Law of Partial Pressures

- The total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone.

$$
\begin{aligned}
P_{\text {total }} & =P_{1}+P_{2}+P_{3}+\ldots \\
P_{i} & =n_{i}\left(\frac{R T}{V}\right)
\end{aligned}
$$

## Dalton's Law of Partial Pressures



## Henry's Law

- Equilibrium partitioning of a gas or organic contaminant between air and water is described by Henry's Law

| Component A Water Vapor Air | A(air) |
| :---: | :---: |
| Component A Water | $A(a q)$ |

A closed system
If component A is in equilibrium with both phases at constant pressure, equilibrium can be described by;
$\mathrm{K}_{\text {eq }}=$ Equilibrium constant

$$
K_{e q}=\frac{\{A\}_{a i r}}{\{A\}_{a q}} \quad \begin{aligned}
& \{\mathrm{A}\}_{\text {air }}=\text { activity of component in } \\
& \text { the gas phase } \\
& \{\mathrm{A}\}_{\text {aq }}=\text { activity of component in } \\
& \text { the aqueous phase }
\end{aligned}
$$

## Henry's Law

At a pressure of 1 atm , the gas behaves ideally, so the equation becomes,

$$
H=K_{e q}=\frac{P_{A}}{\gamma[A]} \quad \begin{aligned}
& \text { H: Henry's law constant (atm-L/mol) } \\
& \begin{array}{l}
\gamma: \text { the activity of } \mathrm{A} \text { in the aq. Phase } \\
{[\mathrm{A}]: \text { Molar concentration of } \mathrm{A}(\mathrm{~mol} / \mathrm{L})} \\
\text { PA: Pressure A exerts in the gas phase (atm) }
\end{array}
\end{aligned}
$$

For dilute solutions (eg. Environmental eng applications conc $<0.1 \mathrm{gmol} / \mathrm{L}$ ),

$$
P_{A}=H[A]
$$

Unit of Henry's law constant is variable
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## Henry's Law

## Factors affecting the equilibrium partitioning

 between air and water;

## Pressure

Surfactants

## Henry's Law

- H tends to increase with increasing temperature
- Aqueous solubility of components decrease as the temperature increase
- The change in H with temperature can be calculated using Van't Hoff Equation

$$
H_{2}=H_{1} \times \exp \left[\frac{-\Delta H^{0}}{R}\left(\frac{1}{T_{2}}-\frac{1}{T_{1}}\right)\right]
$$

$\Delta \mathrm{H}^{\circ}=$ Standard enthaphy change in water due to dissolution of component (kcal/kmol)
$\mathrm{R}=$ Universal gas constant

## Henry's Law

- pH does not directly affect Henry' Law constant, however, it does affect the distribution of species between ionized and unionized forms
- Only unionized species are volatile
- Therefore, pH affects the overall gas-liquid distribution


## Henry's Law

- Surfactants lower volatility of compounds by several mechanism
- Most important mechanism is that, surfactants tend to collect at the air-water interface
- In untreated water, solubility of oxygen can be lowered $30-50 \%$ due to the presence of surfactants


## Mass Transfer

## 

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The driving force for mass transfer from one phase to another derives from the displacement of the system from equilibrium

Ref: American Water Works Association. Water Quality and Treatment: A handbook of community water supplies. 5th ed. McGraw Hill, 1999, page 499

## Mass Transfer


$\mathrm{P}_{\mathrm{G}}$ : Partial pressure of the solute gas in the bulk
$\mathrm{P}_{\mathrm{GI}}$ : Partial pressure of the solute gas at the gas interface
$\mathrm{C}_{\mathrm{L}}$ : Concentration of the solute gas in the bulk liquid $\mathrm{C}_{\mathrm{Li}}$ : Concentration of the solute gas at the liquid interface

## Mass Transfer <br> Two Film Theory

The transfer of a solute gas from a gas mixture into a liquid that is in contact with the mixture can be described by the two-film theory of Lewis and Whitman.

- For gases that are very soluble in water/liquid, the rate limiting step is the diffusion of the solute gas through the gas film (GASFILM CONTROLLED)
- Ammonia
- For gases that are slightly soluble in water $\left(\mathrm{O}_{2}\right.$ in water $)$, the rate limiting step is the diffusion of solute gas through the liquid film (LIQUID FILM CONTROLLED)
- For gases with intermediate solubility, equal resistance from both films (MIXED FILM CONTROLLED)


## Mass Transfer



$$
\frac{d C}{d t}=K_{L} a\left(C_{s}-C_{L}\right)
$$

$\mathbf{d C} / \mathrm{dt}$ : rate of oxygen transfer, mass/volume.time $\mathbf{K}_{\mathrm{L}}$ : diffusion transfer coefficient
a: interfecial bubble area per unit volume of water
$\mathbf{K}_{\mathrm{L}} \mathbf{a}$ : overall liquid mass transfer coefficient, time ${ }^{-1}$
Cs: Saturation dissolved oxygen concentration, mass/volume
$\mathbf{C}_{\mathbf{L}}$ : dissolved oxygen concentration in the liquid, mass/volume

$$
K_{L}=\frac{D}{\delta_{l}}
$$

D: Diffusivity coefficient of oxygen in water $\delta_{1}$ : Film thickness

## Absorption of Gas

## Unsteady state gas transfer

$$
\begin{gathered}
\frac{d C}{d t}=K_{L} a\left(C_{s}-C_{L}\right) \\
\int_{C_{o}}^{C_{t}} \frac{-d C}{C_{s}-C}=K_{L} a \int_{0}^{t}-d t
\end{gathered}
$$

$$
\ln \left(C_{s}-C_{t}\right)=\ln \left(C_{s}-C_{o}\right)-K_{L} a t
$$

Absorption of gas into a solution $\mathrm{C}<\mathrm{Cs}$

## Desorption of Gas

## Unsteady state gas transfer

$$
\begin{gathered}
\frac{d C}{d t} h=-K_{L}\left(C-C_{S}\right) \\
\int_{C_{o}}^{C_{t}} \frac{d C}{C-C_{s}}=\frac{K_{L}}{h} \int_{0}^{t}-d t \\
\ln \left(C_{t}-C_{s}\right)=\ln \left(C_{0}-C_{s}\right)-\frac{K_{L}}{h} t
\end{gathered}
$$

Desorption of gas out of a solution $\mathrm{C}>\mathrm{Cs}$

