# ENVE 301 <br> Environmental Engineering Unit Operations 

## CHAPTER: 4

## Gas transfer

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## Removal of constituents

Chemical and/or biological conversion reactions

Transfer of material from one homogenous phase to another

Mass transfer

Principal applicationss of mass transfer operations in env. eng.:
Addition of gases to water (Absorption) (gas $\longrightarrow$ liquid)
Removal of organics w/activated carbon (Adsorption) ( liquid $\longrightarrow$ solid) ( gas $\longrightarrow$ solid)

Removal of gases (gas stripping, desorption) ( liquid $\longrightarrow$ gas ) (e.g., $\mathrm{CO}_{2}, \mathrm{O}_{2}, \mathrm{H}_{2} \mathrm{~S}, \mathrm{NH}_{3}, \mathrm{VOC}$ )

Selective removal of chemical constituents (ion exchange) (liquid $\longrightarrow$ solid)

## GAS TRANSFER



Gas transfer $\longrightarrow$ process by which gas is transferred from one phase to another.
from gas phase $\longrightarrow$ to liquid phase (Absorption) from liquid phase $\longrightarrow$ to gas phase (Desorption)

## Applications in environmental engineering:

$\rightarrow$ Oxygen supply in aerobic process
$\rightarrow$ Transfer of chlorine (in the gas form) into the liquid for disinfection purposes.
$\rightarrow$ Transfer of ozone into the water.
$\rightarrow$ Removal of gases dissolved in water $\left(\mathrm{H}_{2} \mathrm{~S}, \mathrm{CH}_{4}, \mathrm{NH}_{3}\right)$


If the liquid is initially pure with respect to the gas;
$\rightarrow$ Gas molecules will migrate across the gas-liquid interface and become dissolved in the liquid (ABSORPTION)

Although some molecules of gas will begin leaving the liquid and returning the gas phase, the net reaction will be toward the liquid until a state of equilibrium is reached.
@ equilibrium:
the number of molecules
leaving the liquid
the number of molecules
$=\quad$ entering the liquid again

Important characteristic of this process:

1. SOLUBILITY of gas in water
2. TRANSFER RATE (rate at which absorption or desorption occur)

## Solubility of Gas

The solubility of a gas in equilibrium with a liquid is quantified by HENRY's LAW
Solubility of a gas at constant temp. $\alpha$ Partial pressure of gas in contact with liquid

## Dalton's law of partial pressure:

When a container is filled with a mixture of $N$ gases, each gas exerts the some pressure as it would if it were the only gas in the vessel. The pressure of each component of the gas mixture (partial pressure) will depend solely on the number of moles of that gas present.

$$
\begin{aligned}
& P_{\text {total }}=P_{1}+P_{2}+P_{3}+\ldots+P_{N} \\
& \therefore \underbrace{\text { Partial pressure of a gas }\left(\mathrm{P}_{1}\right)}_{\text {Total pressure }\left(P_{T}\right)}
\end{aligned}=\frac{n_{1}}{n_{1}+n_{2}+\ldots n_{N}} .
$$

Mole fraction of gas

## HENRY'S LAW

mole fraction of gas in the liquid (mol gas/mol water)

Henry's constant $\longrightarrow$ the unit of this parameter is variable ( $\mathrm{atm}^{-1}$; atm/mole fraction; , mg/l/atm ...)
$\longrightarrow$ highly variable with temperature

## EXAMPLE 1:

Calculate the solubility of $\mathrm{CO}_{2}$ (in air) in water at $25^{\circ} \mathrm{C}$ and 1atm pressure. $\left(\mathrm{CO}_{2}\right.$ in air $\left.=0,03 \% \mathrm{H}=6.11 \cdot 10^{-4} \mathrm{~atm}^{-1}\right)$

## EXAMPLE 2:

Calculate the solubility of nitrogen (in air) in water at $0^{\circ} \mathrm{C}$ and 1 atm pressure. ( $\mathrm{N}_{2}$ in air $=79 \% \mathrm{H}=5.29 .10^{4} \frac{\mathrm{~atm}}{\text { mole fraction }}$ )

## EXAMPLE 3:

Calculate the solubility of $\mathrm{O}_{2}$ (in air) in water at $20^{\circ} \mathrm{C}$, 1atm pressure.
( $\mathrm{O}_{2}$ in air $21 \% \mathrm{H}=43,3 \mathrm{mg} / \mathrm{L} / \mathrm{atm}$ )

## GAS TRANSFER RATE

The rate at which a gas transfer into solution can be described by Fick's first law;


$$
\frac{\mathrm{dc}}{\mathrm{dt}}=\mathrm{K}_{\mathrm{L}}\left(\mathrm{C}_{\mathrm{s}}-\mathrm{C}\right)
$$

Value of $\left(\mathrm{C}_{\mathrm{s}}-\mathrm{C}\right) \longrightarrow$ represents a concentration gradient.
As $C$ approaches to $\mathrm{Cs} \longrightarrow$ transfer rate decreases.


Overall liquid mass transfer coeff.
(L/T)
(1/T)
unique for each situation.
numerical values of $\mathrm{K}_{\mathrm{La}}$ are usually determined experimentally.

$$
\begin{aligned}
& \frac{\mathrm{dc}}{\mathrm{dt}}=\mathrm{K}_{\mathrm{La}}\left(\mathrm{C}_{\mathrm{s}}-\mathrm{C}\right) \\
& \int_{\mathrm{C}_{0}}^{\mathrm{C}} \frac{\mathrm{dc}}{\mathrm{C}_{\mathrm{s}}-\mathrm{C}}=\mathrm{K}_{\mathrm{La}} \int_{0}^{\mathrm{t}} \mathrm{dt} \\
& \left\{\int \frac{1}{\mathrm{ax}+\mathrm{b}} \mathrm{dx}=\frac{1}{\mathrm{a}} \cdot \operatorname{Ln}|\mathrm{ax}+\mathrm{b}|\right\} \\
& -\left.\operatorname{Ln}\left(\mathrm{C}_{\mathrm{s}}-\mathrm{C}\right)\right|_{\mathrm{C}_{0}} ^{\mathrm{C}}=\mathrm{K}_{\mathrm{La}}{ }^{\mathrm{t}} \\
& -\operatorname{Ln}\left(\mathrm{C}_{\mathrm{s}}-\mathrm{C}_{\mathrm{t}}\right)+\operatorname{Ln}\left(\mathrm{C}_{\mathrm{S}}-\mathrm{C}_{0}\right)=\mathrm{K}_{\mathrm{La}}{ }^{\mathrm{t}} \\
& \operatorname{Ln}\left(\mathrm{C}_{\mathrm{s}}-\mathrm{C}_{\mathrm{t}}\right)-\operatorname{Ln}\left(\mathrm{C}_{\mathrm{s}}-\mathrm{C}_{0}\right)=-\mathrm{K}_{\mathrm{La}}{ }^{\mathrm{t}} \\
& \operatorname{Ln} \frac{\mathrm{C}_{\mathrm{s}}-\mathrm{C}_{\mathrm{t}}}{\mathrm{C}_{\mathrm{S}}-\mathrm{C}_{0}}=-\mathrm{K}_{\mathrm{La}} \cdot \mathrm{t} \\
& \frac{\mathrm{C}_{\mathrm{s}}-\mathrm{C}_{\mathrm{t}}}{\mathrm{C}_{\mathrm{s}}-\mathrm{C}_{0}}=\mathrm{e}^{-\mathrm{K}_{\mathrm{La}} \cdot \mathrm{t}} \\
& \text { (It only takes place when } \mathrm{C}<\mathrm{Cs} \text { ) }
\end{aligned}
$$

## EXAMPLE 4 :

Dechlorinated secondary effluent is placed in a storage basin until needed for reuse. If the initial DO conc. is $1,5 \mathrm{mg} /$ L estimate the time required for the DO conc. to increase to $8,5 \mathrm{mg} / \mathrm{L}$ due to surface re-aeration assuming the water in storage basin is circulated and not stagnant. Assume the $K_{L}$ value for oxygen is equal to $0,03 \mathrm{~m} / \mathrm{h}$. The surface area of the storage basin is $400 \mathrm{~m}^{2}$ and the depth is $0,025 \mathrm{~m} . \mathrm{T}=20^{\circ} \mathrm{C}$

## DESORPTION OF GAS INTO A SOLUTION

## If $\mathrm{C}>\mathrm{Cs} \longrightarrow$ DESORPTION OF GAS OCCURS

$\longrightarrow \frac{\mathrm{dc}}{\mathrm{dt}} \cdot \underbrace{\mathrm{A}_{\mathrm{s}}}_{\forall} \cdot \mathrm{h}=0-0-\mathrm{rA}_{\mathrm{s}}$
$\longrightarrow \quad \frac{\mathrm{dc}}{\mathrm{dt}} \cdot \mathrm{A} . \mathrm{s} \cdot \mathrm{h}=-\mathrm{K}\left(\mathrm{C}-\mathrm{C}_{\mathrm{s}}\right) \mathrm{A}$

$\longrightarrow \quad \frac{\mathrm{dc}}{\mathrm{dt}}=-\frac{\mathrm{K}}{\mathrm{h}}\left(\mathrm{C}-\mathrm{C}_{\mathrm{S}}\right)$
$\longrightarrow \quad \int_{\mathrm{C}_{0}}^{\mathrm{C}} \frac{\mathrm{dc}}{\mathrm{C}-\mathrm{C}_{\mathrm{s}}}=-\frac{\mathrm{K}}{\mathrm{h}} \int_{0}^{\mathrm{t}} \mathrm{t}$

$$
\frac{\mathrm{C}_{\mathrm{t}}-\mathrm{C}_{\mathrm{s}}}{\mathrm{C}_{0}-\mathrm{C}_{\mathrm{s}}}=\mathrm{e}^{-(\mathrm{K} / \mathrm{h}) . \mathrm{t}}
$$

DESORPTION OF GAS FROM A SOLUTION (If the conc. of specific volatile chemical is not common to atmosphere $\mathrm{C}_{\mathrm{s}} \cong 0$

## EXAMPLE:

A quantity of benzene was spilled accidently into a treated wastewater storage basin having depth of 2 m . Estimate the time required for the concentration of benzene to drop out $50 \%$ from the initial concentration due to volatilization.
$\mathrm{K}_{\mathrm{L}}$ for benzene $=0,144 \mathrm{~m} / \mathrm{hr}$

## TWO FILM THEORY (Lewis - Whitman)

The resistance to movement between the phases can be explained by TWO-FILM THEORY (Lewis-Whitman)

Acc. to this theory, transfer of a gas must occur across the two films that are assumed to exist at the gas-liquid interface.


(b)

Figure 3-2 Two-film model of the interface between gas and liquid: (a) absorption mode and $(b)$ desorption mode.

Gases that are highly soluble in water $\longrightarrow$ Encounter more resistance in passing (e.g. Ammonia) through the gas film. GAS-FILM CONTROLLED.

Gases that are slightly soluble in water $\longrightarrow$ Encounter more resistance in passing (e.g. Oxygen, Nitrogen) through liquid film. LIQUID-FILM CONTROLLED.

Gases of intermediate solubility
$\longrightarrow$ Encounter approximately equal resistance through the films. (MIXED FILM CONTROLLED)

