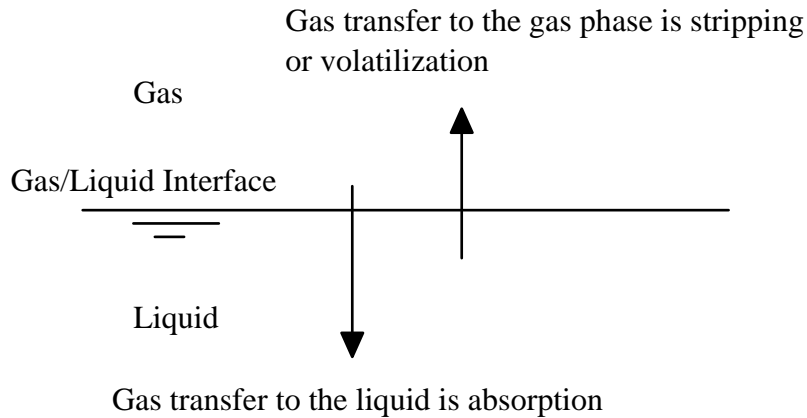


## 1.0 GAS TRANSFER

An important process used in water and wastewater treatment. Also very important when analyzing the impact of pollutants on the environment, such as discharging partially treated wastewaters to the stream.



A subtle distinction

- Volatilization - Stripping due to natural phenomenon.
- Stripping - Stripping due to a mechanical device - aeration.

## 2 APPLICATIONS

Stripping

1.  $H_2S$  Sour water in refineries, taste and odor removed in drinking water treatment, unwanted loss of  $H_2S$  in septic sewers causing pipe corrosion.
2.  $CO_2$  Stripping of some ground waters, industrial process waters.
3.  $O_2$  Stripping boiler fuel waters.
4. Trace organics Stripping of reclaimed wastewaters, groundwaters, etc.
5.  $NH_3$  stripping A proposed method of removing ammonia from wastewaters, actually practiced at the Tahoe Truckee plant.

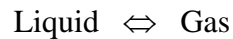
Absorption

1.  $O_2$  (In treatment plants - biological ~ 60% of the energy consumption)  
(water treatment - oxidation of  $Fe^{+2}$ ,  $Mn^{+2}$ ) - River aeration

2. SO<sub>2</sub> (Absorption for dechlorination)
3. Cl<sub>2</sub> (Absorption - chlorine disinfection)
4. O<sub>3</sub> (Absorption - ozone disinfection)

### 3 EQUILIBRIUM RELATIONSHIPS

A gas and a liquid will come to some equilibrium relationship



Henry's law: not really a law like the laws of thermodynamics.  
Pretty good rule for dilute solutions, sparingly soluble gases.

$$C_s H_e = P_i \quad (1)$$

where

C<sub>s</sub> = saturation concentration

H<sub>e</sub> = Henry's law coefficient

P<sub>i</sub> = partial pressure of the gas

Units - One always has to make some mistakes with Henry's law coefficient. Practice converting the units.

Frequently, H<sub>e</sub> is expressed in terms of atm·m<sup>3</sup>/mole then P is in terms of atm, and C<sub>s</sub> is in mole/m<sup>3</sup>.

Symbols for Henry's law coefficient.

H<sub>e</sub> - general - don't know the units or types.

H = atm·m<sup>3</sup>/mole or l<sup>2</sup>/t<sup>2</sup>

H<sub>c</sub> = dimensionless - often more convenient.

$$H_c = \frac{C_g^*(\text{mg/L})}{C_L(\text{mg/L})} = \frac{16.04 P M_W}{T S} \quad (2)$$

where

P = vapor pressure of pure solution in mm Hg

$M_W$  = molecular weight  
 $T$  = temperature K  
 $S$  = solubility of the solution in mg/L

$$H_c = \frac{H}{RT} \quad (3)$$

where

$R$  = gas constant  $\equiv 8.2 \times 10^{-5}$  [atm m<sup>3</sup>/mol-K].

The greater the Henry's law coefficient, the greater the volatility and the less solubility. It is valid for dilute solutions and non-reacting gases at near ambient pressure and temperature. Ionic strength increases the Henry's coefficient and decreases gas solubility.

### 3.1 Methods to determine H or H<sub>c</sub>.

1. Calculate it from published vapor pressure and solution data
2. Measure it in a system at equilibrium
3. Strip the dissolved gas into an absorber and measure the amount stripped.
4. Measure it in an Equilibrium Partitioning in Closed System (EPICS).

The EPICS procedure (No. 4 above) is usually the easiest and most accurate method for measuring Henry's coefficients.

$$M = C_L V_L + C_G V_G \quad (4)$$

$$M = C_L V_L + (H_c C_L) V_G \quad (5)$$

$$M = C_L (C_L + H_c V_G) \quad (6)$$

where

$C_L$  = liquid phase concentration,

$V_L$  = liquid volume,

$C_G$  = gas phase concentration,

$V_G$  = gas volume,

$H_c$  = dimensionless Henry's law coefficient and

$M$  = mass of gas.

Now use two bottles, with different liquid volumes,  $V_{L1} \neq V_{L2}$  and apply the same equation, as follows:

$$M_1 = C_{L1}(V_{L1} + H_c V_{G1}) \quad (7)$$

$$M_2 = C_{L2}(V_{L2} + H_c V_{G2}) \quad (8)$$

After dividing equation 7 by  $M_1$  and 8 by  $M_2$ , the left hand sides become unity, so we can equate the two, as follows:

$$\frac{C_{L1}}{M_1}(V_{L1} + H_c V_{G1}) = \frac{C_{L2}}{M_2}(V_{L2} + H_c V_{G2}) \quad (9)$$

Solves for  $H_c$ , as follows:

$$H_c = \frac{V_{L2} - rV_{L1}}{rV_{G1} - V_{G2}} \quad (10)$$

where

$$r = \left[ \frac{C_{L1}}{C_{L2}} \right] \left[ \frac{M_2}{M_1} \right] \quad (11)$$

### Advantages

We do not need to measure  $M_2$  and  $M_1$  - we only need to measure their ratio. The ratio can be determined gravimetrically or through some other procedure.

Similarily, we only need the ratio of  $C_{L1}$  and  $C_{L2}$ , which can be measured as a ratio, as opposed to an absolute concentration (e.g., ratio of peak heights on the GC, as opposed to the actual concentration).

### 3.2 Temperature Effects

$$\frac{d(\ln H_c)}{d(1/T)} = \frac{\Delta H}{R} \quad (12)$$

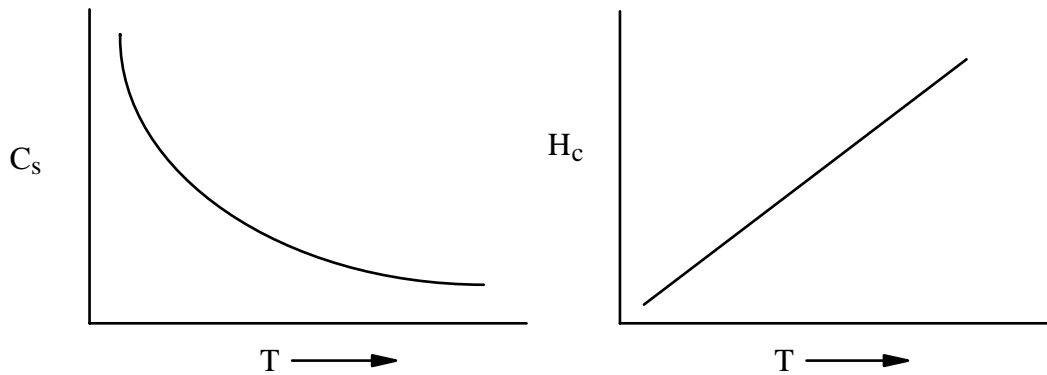
where

$H_c \equiv$  Henry's law coefficient

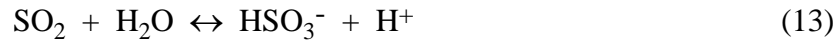
$R \equiv$  Universal gas constant

$\Delta H \equiv$  heat of absorption ( $< 0$ )

$T \equiv$  absolute temperature



Henry's is only good for gaseous part of the dissolved gas. For example, consider sulfur dioxide, which is equilibrium with sulfurous acid, as follows:



$$K_a = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{SO}_2]} = 1.7 \times 10^{-2} \quad (14)$$

$$[\text{H}^+][\text{HSO}_3^-] = 1.7 \times 10^{-2} [\text{SO}_2]$$

$$[\text{H}^+] = 1.7 \times 10^{-2} \frac{[\text{SO}_2]}{[\text{HSO}_3^-]}$$

If the total concentration is:

$$[\text{SO}_2] + [\text{HSO}_3^-] = 1.8 \text{ gmole/L} \quad (15)$$

$$[\text{H}^+] = \frac{1.7 \times 10^{-2} [\text{SO}_2]}{(1.8 - [\text{SO}_2])}$$

Henry's law coefficient calculates 1.63 for the  $[\text{SO}_2]$ .

*Example* Find  $\text{O}_2$  solubility at  $20^\circ\text{C}$ , in air with 20.95 %  $\text{O}_2$  at 1 atm.

$H = 4.01 \times 10^4$  gmole solute/gmole solvent (Perry's Chemical Engineers' Handbook)

$$C_s = \frac{0.2095}{4.01 \times 10^4} = 4.98 \times 10^{-6} \frac{\text{gmole O}_2}{\text{gmole H}_2\text{O}}$$

$$C_s = 4.98 \times 10^{-6} \times \frac{32 \text{ g O}_2 / \text{gmole O}_2}{18 \text{ g H}_2\text{O} / \text{gmole H}_2\text{O}} = 8.86 \times 10^{-6} \frac{\text{g}}{\text{g}}$$

$$= 8.86 \text{ ppm} \text{ or } \sim 8.86 \text{ mg/L}$$

#### 4 MASS TRANSFER MODELS

Three "famous" theories for Gas Transfer

W.K. Lewis & W.G. Whitman (1924) "Principles of Gas Transfer Absorption," *Industrial and Engineering Chemistry*, Vol. 16, No. 12, pp. 1215-1237.

Higbie (1935) "The Rate of Absorption of a Pure Gas into a Still Liquid During Short Periods of Exposure," *American Institute of Chemical Engineers*, Vol.

31, pp. 365-389.

P.V.Dankwertz (1951) "Significance of Liquid-Film Coefficients in Gas Absorption," *Industrial and Engineering Chemistry*, Vol. 43, No. 6, pp. 1460.

#### 4.1 Theories

We can derive the three theories, but the overall difference and conclusions will relate to the impact of  $D$  upon  $k_L$ , as follows,

*Two Film:*

$$k_L \approx D \quad (\text{molecular diffusivity})$$

*Penetration:*

$$k_L = 2\sqrt{\frac{D}{t_c}} \quad (20)$$

where  $t_c$  = contact time

Note that transfer is greatest for the shortest contact time.  $k_L$  tends to zero for long contact times.

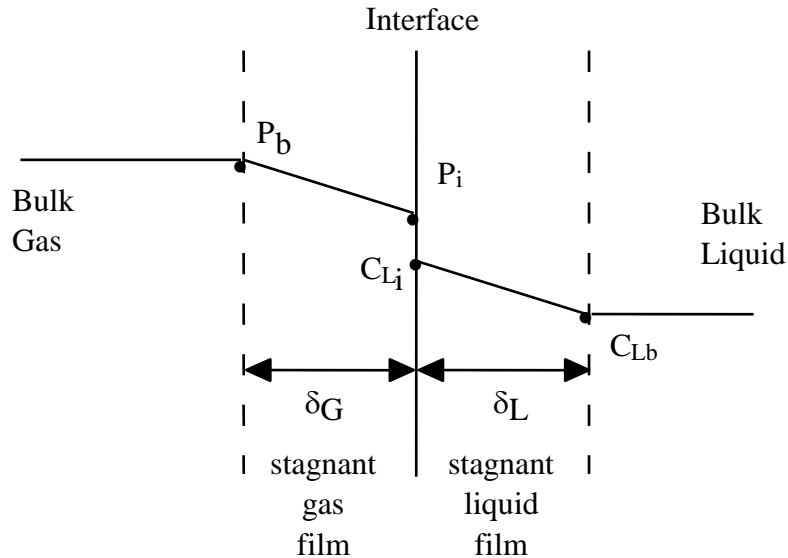
*Surface Renewal*

$$k_L \approx \sqrt{D r_c} \quad (21)$$

where  $r_c$  is a surface renewal rate, related to the rate of production of fresh surface.

We can derive the theories as follows, beginning with two film and progressing with increasing complexity.

## 4.2 Two Film Theory



Assumptions:

1. Linear concentration profile through stagnant film
2. Steady state conditions
3. Instantaneous equilibrium
4. Transport by bulk diffusion is not limiting
5. Dilute solutions, therefore apply Henry's Law

Let  $N_o$  ( $\frac{\text{mass}}{\text{time}}$ ) represent the mass transfer of oxygen at steady state conditions:

$$N_{oG} = N_{oL} \quad (\text{no accumulation in gas or liquid films}) \quad (22)$$

Invoking Fick's 1st Law, we obtain:

$$N_{oG} = k_G a \left( \frac{P_b M_w}{RT} - \frac{P_i M_w}{RT} \right) \quad (23)$$

$$N_{oL} = k_L a (C_{Li} - C_{Lb}) \quad (24)$$

where

$$k_L = \text{liquid film mass transfer coefficient} = \frac{D_{O_2L}}{\delta_L}, \quad \frac{[\text{length}]}{[\text{time}]}$$

$$k_G = \text{gas film mass transfer coefficient} = \frac{D_{O_2G}}{\delta_G}, \quad \frac{[\text{length}]}{[\text{time}]}$$

$D_{O_2L}$  = diffusion coefficient of oxygen in liquid film,  $\frac{[\text{length}]^2}{[\text{time}]}$

$D_{O_2G}$  = diffusion coefficient of oxygen in gas film,  $\frac{[\text{length}]^2}{[\text{time}]}$

$\delta_L$  = liquid film (boundary layer) thickness, [length]

$\delta_G$  = gas film (boundary layer) thickness, [length]

$a$  = interfacial area, [length]<sup>2</sup>

$C_{Li}$  = concentration of oxygen in liquid film at interface,  $\frac{[\text{mass}]}{[\text{length}]^3}$

$C_{Lb}$  = concentration of oxygen in bulk liquid,  $\frac{[\text{mass}]}{[\text{length}]^3}$

$P_i$  = partial pressure of oxygen in gas film at interface,  $\frac{[\text{mass}]}{[\text{length}][\text{time}]^2}$

$P_b$  = partial pressure of oxygen in bulk gas,  $\frac{[\text{mass}]}{[\text{length}][\text{time}]^2}$

$M_w$  = molecular weight.

Setting (23) and (24) equal to each other, we obtain:

$$k_G a \left( \frac{P_b M_w}{RT} - \frac{P_i M_w}{RT} \right) = k_L a (C_{Li} - C_{Lb}) \quad (25)$$

To eliminate partial pressure, invoke Henry's Law:

$$P_b = H C_{\infty}^* \quad (26)$$

$$P_i = H C_{Li} \quad (27)$$

where

$H$  = Henry's coefficient for O<sub>2</sub> in water,  $\frac{[\text{length}]^2}{[\text{time}]^2}$

$C_{\infty}^*$  = Concentration of oxygen in water in equilibrium with bulk gas partial pressure,  $\frac{[\text{mass}]}{[\text{length}]^2}$

The goal is to solve for interfacial concentration,  $C_{Li}$ , because this quantity is essentially impossible to determine. Substitute (26) and (27) [eliminate  $a$ ] into (25) and let

$$H = \text{dimensionless Henry's coefficient} = H \cdot \left( \frac{M_w}{RT} \right), \quad [ - ]$$

we get

$$k_G (H C_{\infty}^* - H C_{Li}) = k_L (C_{Li} - C_{Lb}) \quad (28)$$



Solve for  $C_{Li}$

$$C_{Li}(k_L + k_G H_c) = k_G H_c C_\infty^* + k_L C_{Lb} \quad (29)$$

$$C_{Li} = \frac{k_G H_c C_\infty^* + k_L C_{Lb}}{k_L + k_G H_c} \quad (30)$$

Substitute (30) into (24), obtain

$$N_o = k_L \left( \frac{k_G H_c C_\infty^* + k_L C_{Lb}}{k_L + k_G H_c} - C_{Lb} \right) \quad (31)$$

$$= k_L \left( \frac{k_G H_c C_\infty^* + k_L C_{Lb} - k_L C_{Lb} - k_G H_c C_{Lb}}{k_L + k_G H_c} \right) \quad (32)$$

$$= k_L \left( \frac{k_G H_c C_\infty^* - k_G H_c C_{Lb}}{k_L + k_G H_c} \right) \quad (33)$$

$$= \frac{k_L k_G H_c}{k_L + k_G H_c} (C_\infty^* - C_{Lb}) \quad (34)$$

$$= \frac{k_L}{\frac{k_L}{k_G H_c} + 1} (C_\infty^* - C_{Lb}) \quad (35)$$

Now let

$$\frac{k_L}{\frac{k_L}{k_G H_c} + 1} = K_L \quad (36)$$

where

$$K_L = \text{overall mass transfer coefficient, } \frac{[\text{mass}]}{[\text{time}]}$$

we get

$$N_o = K_L (C_\infty^* - C_{Lb}) \quad (37)$$

Applying the same relationship to the gas film, we would obtain

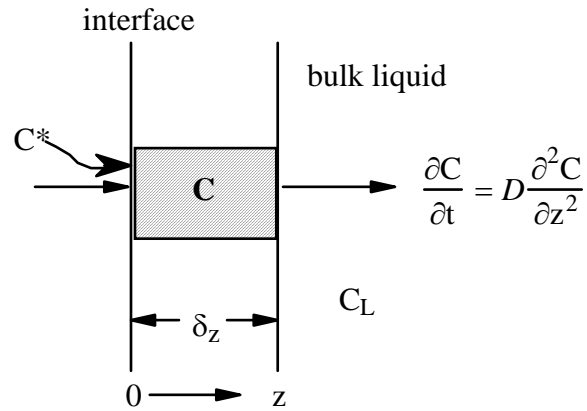
$$N_o = K_G (P_b - P_\infty^*) \quad (38)$$

where

$$P_\infty^* = \text{Partial pressure of oxygen in gas in equilibrium with bulk liquid concentration, } \frac{[\text{mass}]}{[\text{length}][\text{time}]^2} \left\{ P_\infty^* = H C_{Lb} \right\}$$

### 4.3 Penetration Theory

We assume a non-steady-state film, which at the moment of film formation, curtains the bulk concentrations in both the gas and liquid phases.



We know that (from CE 253)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad (39)$$

initial and boundary conditions

$$\begin{aligned} t = 0, \quad z > 0, \quad C &= C_L \\ t > 0, \quad z = 0, \quad C &= C^* \\ t > 0, \quad z = \infty, \quad C &= C_L \end{aligned}$$

Analytical solution of equation (39) is easier if we assume  $C' = C - C_L$ .  
(normalizes!)

$$\frac{\partial C'}{\partial t} = D \frac{\partial^2 C'}{\partial z^2} \quad (40)$$

Use Laplace transform as follows:

$$L\{C'\} = \int_0^\infty C' e^{-st} dt = \bar{C}' \quad (41)$$

then

$$L\left[\frac{\partial C'}{\partial t}\right] = s\bar{C}' \quad (42)$$

$$L\left[\frac{\partial^2 C'}{\partial z^2}\right] = D \frac{\partial^2 \bar{C}'}{\partial z^2} \quad (43)$$

so

$$s\bar{C} = D \frac{\partial^2 \bar{C}}{\partial Z^2} \quad (44)$$

Solution in

$$\bar{C} = B_1 e^{Z\sqrt{s/D}} + B_2 e^{-Z\sqrt{s/D}} \quad (45)$$

at boundary,  $z = 0$

$$\begin{aligned} C &= C^* - C_L \\ \bar{C}_0' &= \int_0^\infty C_0' e^{-st} dt = \frac{C_0'}{s} \end{aligned} \quad (46)$$

Therefore

$$B_2 = \frac{C_0'}{s}$$

at the exit boundary

$$C_\infty' = 0$$

we get

$$\bar{C} = \frac{C_0'}{s} e^{-Z\sqrt{\frac{s}{D}}} \quad (47)$$

Taking inverse transform, we get

$$C = C_0' \operatorname{erfc} \frac{Z}{2\sqrt{Dt}} \quad (48)$$

definition of Erfc is

$$\operatorname{erfc} \alpha = \frac{2}{\sqrt{\pi}} \int_\alpha^\infty e^{-Z^2} dZ \quad (49)$$

so we get 
$$\frac{C}{C_0'} = \frac{C - C_L}{C^* - C_L} = \frac{2}{\sqrt{\pi}} \int_{Z/2\sqrt{Dt}}^\infty e^{-Z^2} d\frac{Z}{2\sqrt{Dt}} \quad (50)$$

Integrate and differentiate at  $z = 0$ , we get

$$N_0 = -\sqrt{\frac{s}{\pi t}} (C^* - C_L) \quad (51)$$

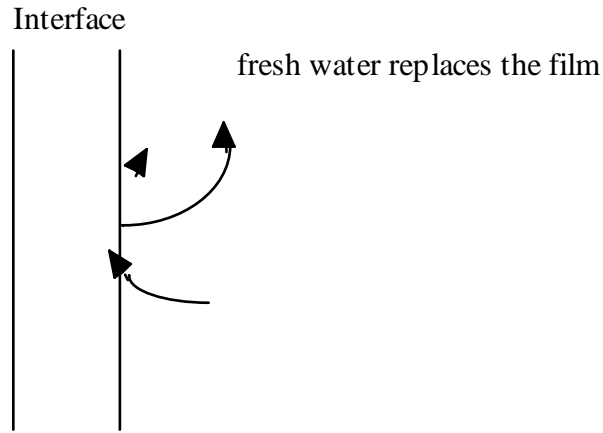
at  $t = 0$

To find the average flux over a period of time, we get

$$\bar{N}_0 = -(C^* - C_L) \sqrt{\frac{D}{\pi}} \frac{1}{t_c} \int_0^{t_c} \frac{dt}{t^{1/2}} \quad (52)$$

$$= -2\sqrt{\frac{D}{t_c}} (C^* - C_L) \quad (53)$$

#### 4.4 Surface Renewal



We no longer have a laminar film.

$$A(t)\Delta t = A(t - \Delta t)\Delta t - [A(t - \Delta t)\Delta t]r_s\Delta t \quad (54)$$

where  $\Delta t$  = renewal time  
 $A(t)\Delta t$  = old surface area (area x length of contact)  
 $r_s$  = rate of production of fresh surface area.

A change in surface area becomes:

$$\frac{dA(t)}{dt} = -r_s A(t) \quad (55)$$

$$Ke^{-r_s t} = A(t) \quad (56)$$

By definition

$$1 = \int_0^{\infty} A(t)dt = 1 \quad (57)$$

$$= \int_0^{\infty} Ke^{-r_s t} dt \quad (58)$$

$$A(t) = r_s e^{-r_s t} \quad (59)$$

substitute into equation (51)

$$N_o = -(C^* - C_L) \int_0^{\infty} \sqrt{\frac{D}{\pi t}} r_s e^{-r_s t} dt \quad (60)$$

$$N_o = 2(C^* - C_L) r_s^{1/2} \left[ \frac{D}{\pi} \right]^{1/2} \int_0^{\infty} e^{-\beta^2} d\beta \quad (61)$$

where  $\beta = r_s t$

$$N_o = 2(C^* - C_L) \left[ \frac{r_s D}{\pi} \right]^{1/2} \frac{\pi^{1/2}}{2} \quad (62)$$

$$= 2(C^* - C_L)\sqrt{Dr_s} \quad (63)$$

The three theories produce similar results in that they envision two resistances, gas and liquid, and the proportion of the total resistance is dependent upon the Henry's law coefficient. High coefficients mean high liquid phase resistance and low gas phase resistance.

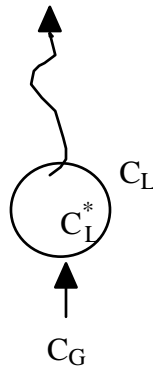
There are important differences in the implications of the theories when one must consider the impact of contaminants (surfactants) on gas transfer and when one tries to predict the transfer rate of one gas (e.g., a VOC like benzene) from the transfer rate of another gas (e.g., oxygen). This is related to the molecular diffusivity,  $D$  or  $D^{1/2}$ . Most experimental observations for the power of  $D$  are between 0.5 and 1.0, with higher turbulence being closer to 1/2.

## 5. VOC TRANSFER IN AERATION SYSTEM

Volatile Organic Compounds transfer is the new concern for wastewater treatment plants. Such compounds include:

- Benzene
- Toluene
- TCE
- TCA

Consider a mass balance on a single rising bubble.



$$V_b = \frac{dC_g}{dt} = K_L a(A_b) * (C_L - C_L^*) \quad (64)$$

where  $V_b$  = single bubble volume ( $l^3$ )  
 $A_b$  = area of a single bubble ( $l^2$ )  
 $C_L$  = liquid VOC concentration  
 $C_L^*$  = equilibrium VOC liquid concentration  
=  $C_G/H_c$

$$V_b \frac{d(C_L^* H_c)}{dt} = K_L (A_b) (C_L - C_L^*) \quad (65)$$

$$\frac{dC_L^*}{C_L - C_L^*} = \frac{K_L A_b}{H_c V_b} dt \quad (66)$$

now, we let

$$t_r = \frac{V_G}{Q_G} = \text{gas retention time} \quad (67)$$

$$v_b = \frac{Z_s - Z}{t_r} = \text{bubble velocity} \quad (68)$$

where  $Z_s$  = maximum diffuses submergence  
 $Z$  = diffuses submergence

$$\frac{A_b}{V_b} = \frac{A_B}{V_B} = \frac{nA_b}{V_L} \cdot \frac{V_L}{nV_b} = \frac{A_B}{V_L} \cdot \frac{V_L}{V_G} = a \frac{V_L}{V_G} \quad (69)$$

where  $A_B$  = total bubble area  
=  $nA_b$   
 $n$  = total number of bubbles  
 $V_L$  = liquid volume  
 $V_G$  = total gas volume  
 $a$  =  $\frac{A_B}{V_L}$   
= specific interface surface area (area per unit volume)

Substitute into equations (67) and (69) into (66) to obtain

$$\frac{dC_L^*}{C_L - C_L^*} = \frac{K_L a V_L}{H_c V_G} dt = \frac{K_L a V_L}{H_c Q_G t_r} dt \quad (70)$$

$$\ln|C_L - C_L^*| = -\frac{K_L a V_L}{Q_G H_c} \frac{t}{t_r} + K \quad (71)$$

where  $K$  = integration coefficient.

at  $t = 0$

$$\ln|C_L - C_L^*|_{t=0} = C \quad (72)$$

at  $t = 0$ , the gas entering the liquid is air, which is clean. Therefore,  $C_L^* = 0$ , then  $C = \ln C_L$ .

$$\ln\left|\frac{C_L - C_L^*}{C_L}\right| = \frac{-K_L a V_L}{Q_G H_c} \frac{t}{t_r} \quad (73)$$

$$1 - \frac{C_L^*}{C_L} = e^{-\frac{K_L a V_L}{Q_G H_c} \frac{t}{t_r}} \quad (74)$$

$$\frac{C_L^*}{C_L} = 1 - e^{-\frac{K_L a V_L}{Q_G H_c} \frac{t}{t_r}} \quad (75)$$

Remember that

$$C_L^* = \frac{C_G}{H_c} \quad \text{and} \quad C_L = \frac{C_G^*}{H_c}$$

$$\frac{C_L^*}{C_L} = \frac{C_G}{H_c C_L} = \frac{C_G}{H_c} \frac{H_c}{C_G^*} \quad (76)$$

$$\frac{C_G}{C_G^*} = 1 - e^{-\frac{K_L a V_L}{Q_G H_c} \frac{t}{t_r}} \quad (77)$$

Define  $S_d = \frac{C_G}{C_G^*}$  = saturation factor. We are only interested in  $t = t_r$  (bubbles existing in the liquid), so  $t/t_r = 1$ .

Let 
$$\frac{K_L a V_L}{Q_G \cdot H_c} = \phi(Z_s) \quad (78)$$

$Z_s$  denotes that  $\phi$  is a function of depth.  $K_L a$  will be a function of depth, bubble size, temperature, and other system parameters.  $\phi$  will be a constant for a given system at steady state conditions.

Now we perform a balance on the entire reactor, liquid phase.

$$V_L \frac{dC_L}{dt} = Q_G C_{GI} - Q_G C_{GE} \quad (79)$$

assume  $C_{GI} = 0$

$$V_L \frac{dC_L}{dt} = -Q_G C_L H_c \quad (80)$$

if the gas is in equilibrium with the liquid; however, we know the value of  $C_{GE}$ , from equations (78) and (79).

$$\frac{V_L dC_L}{dt} = -Q_G [C_L \cdot H_c [1 - e^{-\phi(Z_s)}]] \quad (81)$$

$1 - e^{-\phi(Z_s)}$  represents the degree of saturation,  $S_d$

integrating

$$\ln \left| \frac{C_L}{C_{Lo}} \right| = \frac{-Q_G H_c}{V_L} S_d (t - t_o) \quad (82)$$

$t_o$  = start time,  $C_{Lo}$  = start concentration

Plot  $\ln \left| \frac{C_L}{C_{Lo}} \right|$  vs.  $t$

$$\text{Slope} = \frac{-Q_G H_c}{V_L} S_d \quad (83)$$

Estimating  $K_L a$  from  $O_2$  and diffusion coefficients.

$$K_L = \frac{D}{\delta} \quad \text{for two film} \quad (84)$$

$$K_L = \sqrt{D/t_c} \quad \text{for penetration} \quad (85)$$

$$K_L = \sqrt{D r_c} \quad \text{for surface renewal} \quad (86)$$

$a$  is the same for all of them.

We can estimate VOC transfer from oxygen transfer, as follows:

$$K_L a_{VOC} = \frac{D_{VOC}}{D_{O_2}} \cdot K_L a_{O_2} \quad (\text{Two film})$$

or 
$$K_L a_{VOC} = \left\{ \frac{D_{VOC}}{D_{O_2}} \right\}^{1/2} K_L a_{O_2} \quad (\text{Penetration or surface renewal}) \quad (87)$$

let 
$$\psi = \left\{ \frac{D_{VOC}}{D_{O_2}} \right\}^n \quad (88)$$

where  $0.5 \leq n \leq 1.0$

Experimental observations of  $n$  show that the model ranges between surface renewal and two-film (1.0). We define two resistance theories as the two-film theory with  $n$  variable from 0.5 to 1.0, as required to fit the experimental conditions.

Generally for surface aeration



$$\frac{dC_{\text{VOC}}}{dt} = K_L a_{\text{VOC}} (C_L - C_L^*) \quad (89)$$

$$K_L a_{\text{VOC}} = \left[ \frac{D_{\text{VOC}}}{D_{\text{O}_2}} \right]^{0.6} K_L a_{\text{O}_2} \quad \text{where } H_c > 1$$

For subsurface systems recall the two resistance theory

$$K_L a = \frac{k_L a}{1 + \frac{k_L a}{k_G a H_c}} \quad (90)$$

if  $H_c$  or  $k_G a$  very large

$$K_L a = k_L a \quad (91)$$

where  $H_c$  is small, e.g., semi-volatile compounds, or when  $k_G a$  is small (subsurface aeration), then

$$K_L a \neq k_L a \quad (92)$$

Under these cases use the ratio of

$$\begin{aligned} \frac{R_L}{R_T} &= \frac{R_L}{R_L + R_G} \\ &= \frac{1}{1 + \frac{R_G}{R_L}} = \frac{1}{1 + \frac{1}{H_c \frac{k_G}{k_L}}} \end{aligned} \quad (93)$$

Use

$$\psi_m = \frac{R_L}{R_T} \left[ \frac{D_{\text{VOC}}}{D_{\text{O}_2}} \right]^n \quad (94)$$

with  $0.5 \leq n \leq 1.0$