

Solubility of the gases

- The principal atmospheric gases that go into solution are **oxygen, nitrogen, carbon dioxide**.
- All water exposed to atmosphere will have these gases in solution.
- Other gases in solution are ammonia (NH₃), hydrogen sulphide (H₂S), and methane (CH₄), which are associated with microbial activity.
- The amount of particular gas dissolved in water depends upon:
 - Its solubility in water
 - Its partial pressure at the air/water interface
 - Temperature of water
 - Level of salts in the water

If water contains as much as specific gas that it can hold in the presence of an abundant supply, then the water is said to be saturated.

- E.g., saturation concentration of oxygen in water at 20 °C is 9.3 mg/L.
- If oxygen content is 7.5 mg/L at 20 °C, it is 80% saturated.
- When oxygen content exceeds 100%, it is said to be supersaturated.

Supersaturation occurs because of:

- High photosynthetic activity (in summer)
- When high temperature water is discharged to river, the rapid rise in water temperature causes O₂ supersaturation.

The solubility of gases in water is related to the partial pressure of the gas in the atmosphere above the water (by Henry's law).

$$P_g = K_h \cdot X_g$$

where, P_g = Partial pressure of gas, atm.

K_h = Henry's law constant, atm/mole

X_g = Equilibrium mole fraction of dissolved gas

X_g = Mole of gas (n_g) / {mole of gas (n_g) + mole of water (n_w)}

For example: As air contains nearly 21% O₂, the partial pressure of O₂ ≈ 0.21 atm

Henry's law constant for common gases soluble in water, K_h x 10⁻⁴ atm/mole

Temperature	N ₂	O ₂	CO ₂	H ₂ S	CH ₄
0	5.29	2.55	0.073	0.027	2.24
10	6.68	3.27	0.104	0.037	2.97
20	8.04	4.01	0.142	0.048	3.76
30	9.24	4.75	0.186	0.061	4.49

Example: Determine saturation concentration of O₂ in water at 10°C at 1 atm.

Solution:

O₂ is 21% in air (v/v), hence, P_g = 0.21 x 1 atm = 0.21 atm

Henry's law constant K_h = 3.27 x 10⁴ atm/mole at 10 °C.

Now P_g = K_h · X_g

Therefore X_g = P_g/K_h

X_g = 0.21/(3.27 x 10⁴) = 6.42 x 10⁻⁶ (equilibrium mole fraction)

Since, 1 mole of water is 18 g, hence mole/L for water (n_w) = 1000/18 = 55.6 mole/L

Now X_g = n_g / (n_g + n_w)

Solving for n_g, n_g = 3.57 x 10⁻⁴ mole/L

Saturation concentration of O₂:

C_s = n_g · M

Where, M = molecular wt. of oxygen

C_s = 3.57 x 10⁻⁴ mole/L x 32 g/mole x 10³ mg/g = 11.4 mg/L

Example: Determine saturation concentration of CO₂ in water at 20 °C at 1 atm.

Air contains 0.033% CO₂ (V/V), K_h = 0.142 x 10⁴ atm/mole.

Solution:

$$x_g = 0.00033 / (0.142 \times 10^4) = 0.233 \times 10^{-6}$$

$$x_g = n_g / (n_g + n_w)$$

Therefore, for $n_w = 55.6$; $n_g = 0.13 \times 10^{-4}$ mole/L

Saturation concentration

$$C_s = 0.13 \times 10^{-4} \times (12 + 32) \times 10^3 = 0.57 \text{ mg/L at } 20^\circ\text{C and } 1 \text{ atm.}$$

Example: Determine solubility of CH_4 in UASB reactor operated at 30°C at 1 atm
The partial pressure of methane inside the reactor would be 0.8 atm. $K_h = 4.49 \times 10^4$ atm/mole.

Solution

$$P_g = K_h \cdot X_g$$

$$\text{Therefore } X_g = P_g / K_h$$

$$X_g = 0.8 / (4.49 \times 10^4) = 1.78 \times 10^{-5} \text{ (equilibrium mole fraction)}$$

Since, 1 mole of water is 18 g, hence mole/L for water (n_w) = $1000/18 = 55.6$ mole/L

$$\text{Now } X_g = n_g / (n_g + n_w)$$

$$\text{Solving for } n_g, \quad n_g = 9.906 \times 10^{-4} \text{ mole/L}$$

Saturation concentration:

$$C_s = n_g \cdot M$$

Where, M = molecular wt. of CH_4

$$C_s = 9.906 \times 10^{-4} \text{ mole/L} \times 16 \text{ g/mole} \times 10^3 \text{ mg/g} = 15.85 \text{ mg of } \text{CH}_4/\text{L}$$

Aeration and Mass transfer

Aeration is used in wastewater treatment for:

- Transferring O₂ in biological treatment processes.
- For stripping solvents from wastewater.
- Removing volatile gases such as H₂S, NH₃

Aeration is gas-liquid mass transfer process in which interphase diffusion occurs.

Other gas transfer – chlorine gas - for disinfection.

Description of gas transfer

- O₂ transfer in wastewater treatment is most common.
- For transferring sufficient O₂, additional surface than normal water surface should be brought in contact with air or O₂
- Either air or O₂ is introduced in liquid
- Or water droplets are exposed to air.

Commonly used aeration devices

Type	Description	Uses of application
Diffuse air		
Porous (fine bubble)	Ceramic, vitreous, porous plates with resin, domes, tubes	All types of ASP
Porous (medium bubble)	Perforated membrane or plastic tubes	”
Non porous (coarse bubble)	Bubbles generated from orifices, nozzles etc.	”
Jet	Compresses air injected into mixed liquor	”
Sparger turbine	Low- speed turbine and compressed injection system	”
Surface aerator		
Low speed turbine aerator	Large dia. turbine used to expose liquid droplets to atmosphere.	Conventional ASP. Aerated lagoon.

High –speed floating aerator

Small-dia. propeller used to expose liquid droplets to atmosphere

Aerated lagoons

Rotar –brush aerator

Blades mounted on central shaft are rotated through liquid. O₂ is introduced by splashing action of blades & liquid droplet formation

Oxidation ditch, Aerated lagoons

Cascade

Wastewater flows over cascade in sheet flow

Post aeration

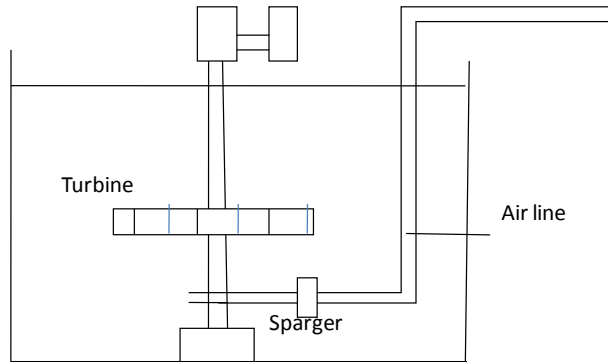
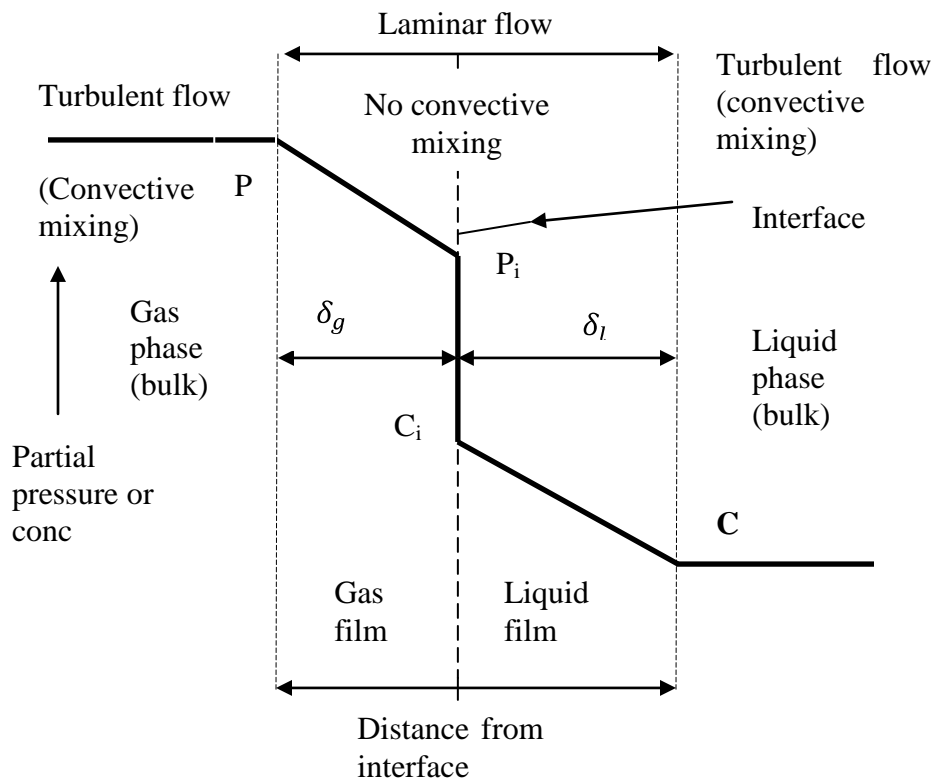


Figure 13.1 Sparger turbine aerator

Analysis of gas transfer: The two film theory: (This is better than other theories with 95% cases accurate results).



P & P_i = Partial pressure of solute in bulk gas and at the interface, atm

C , C_i = solute concentration in bulk water and at interfaces, mg/L

Two films

- One liquid and one gas
- These two films provide resistance to the passage of gas molecules from gas phase to liquid phase.
- **Slightly soluble gas** encounters primary **resistance to transfer from liquid film**.
- **Very soluble gases** encounter primary **resistance from gaseous film**
- Intermediate solubility encounters significant resistance from both films.

Addition of gases

The rate of gas transfer is proportional to difference between existing concentration and equilibrium concentration of the gas in solution. (Saturation conc. & existing conc.)

$$r_m = k_g A (C_s - C)$$

where,

r_m = rate of mass transfer,

k_g = coefficient of diffusion for gas,

A = area through which gas is diffusing

C_s = saturation concentration of gas in solution

C = concentration of gas in solution

Under condition of mass transfer in field $r_m = \nabla \cdot \frac{dc}{dt}$ & $r_c = \frac{r_m}{\nabla}$

$$r_c = \frac{dc}{dt} = K_g \frac{A}{V} (C_s - C)$$

The term $K_g \left(\frac{A}{V}\right)$ is replaced by ' $K_L a$ ' a proportionality factor related to existing exposer conditions.

$$r_c = \frac{dc}{dt} = K_L a (C_s - C)$$

Where: r_c = rate of change in concentration, mg/L.s

$K_L a$ = overall mass transfer coefficient, s^{-1}

Integrating between the limits $C = C_0$ at $t = 0$ and $C = C_t$ at $t = t$

$$\int_{C_0}^{C_t} \frac{dc}{C_s - C} = K_L a \int_0^t dt$$

$$\frac{C_s - C_t}{C_s - C_0} = e^{-(K_L a).t}$$

$(C_s - C_t)$ and $(C_s - C_0)$ represents the final and initial oxygen saturation deficits.

For Removal of gases

Where a supersaturated solution is to be degassed then equation is modified as

$$\frac{C_t - C_s}{C_0 - C_s} = e^{-(K_L a).t}$$

Evaluation of O₂ - Transfer Coefficient

O₂ transfer in clean water:

- Remove DO from known volume of water by adding sodium sulphite.
- Carry out reoxygenation to near the saturation level.
- During reaeration **monitor DO concentration at several representative points** of the tank.
- The data obtained is analyzed by above equation to estimate K_La and equilibrium concentration C_x*. C_x* is obtained when aeration period approaches infinity. The term C_s is substituted by C_x.
- A nonlinear regression is employed to fit the equation to the DO profile measured at each determination point.
- In this way, estimate K_La & C_x* for each point.
- Adjust if it standard conditions and avg. it to get K_La (ASTM procedure).

Oxygen transfer in wastewater:

- In ASP, the K_La can be determined by considering the uptake of O₂ by microorganisms.
- Typical O₂ concentration is 1 to 3 mg/l in aeration tank, and it is used by microorganisms rapidly

$$\frac{dc}{dt} = K_L a (C_s - C) - r_m$$

Where, r_m = rate of O₂ used by the microorganism. (typical value 2 to 7g/d.g MLVSS)

If DO level is constant r_m = K_La (C_s - C)

Value of r_m can be determined in laboratory (by Wargburg apparatus or respirometer).

$$\text{Then } K_L a = \frac{r_m}{C_s - C}$$

Factors Affecting oxygen Transfer

1) Effect of temperature

The effect of temperature is similar as that in BOD rate coefficient. Using van't Hoff-Arrhenius relationship

$$K_L a_{(T)} = K_{La(20^\circ C)} \theta^{(T-20)}$$

Where, $K_{La(T)}$ = Oxygen mass-transfer coefficient at temp T, S^{-1} .

$K_{La(20^{\circ}C)}$ = Oxygen mass transfer coefficient at 20° , S^{-1}

θ = varies with test conditions. (Range 1.015 - 1.040).

$\theta = 1.024$ - Typical value used for diffused and mechanical aeration device.

2) Effect of mixing intensity and Tank Geometry

- Difficult to estimate on theoretical basis.
- Aeration devices are selected based on efficiency of O_2 transfer.
- Efficiency is strongly related to K_{La} value associated with given aeration unit.
- In most cases aeration devices are rated with range of operating conditions using tap water i.e. (low TDS water).
- Hence correction factor (α) is used to estimate K_{La} for actual system

$$\alpha = \frac{K_{La}(\text{wastewater})}{K_{La}(\text{tap water})}$$

α - Value varies with type of aeration device, basin geometry, degree of mixing, & wastewater characteristics.

$\alpha = 0.3$ to 1.2 in general range

= 0.4 to 0.8 for diffused aeration

= 0.6 to 1.2 for mechanical aeration

3) **Effect of wastewater characteristics:** Due to difference in saturation concentration

- A correction factor ' β ' is used to correct the test result for differences in O_2 solubility due to constituent such as salts, particulate and surface active substances.

$$\beta = \frac{C_s(\text{wastewater})}{C_s(\text{tap water})}$$

$\beta = 0.7$ to 0.98 - value 0.95 is commonly used for wastewater.

Application of correction factors

The correction factors are applied to predict field oxygen transfer rates based on the measurements made in experimental test facilities (for mechanical surface aerator).

$$OTR_f = SOTR \frac{(\beta C_s - C_w)}{C_{s20}} \theta^{(T-20)} (\alpha)$$

Where, OTR_f = actual O_2 transfer rate under test conditions, kg O_2 /k.W.h

SOTR = standardized O_2 –transfer rate under test conditions, at 20°C and zero DO, kg O_2 /k.W.h

C_s = O_2 saturation concentration for tap water at field –operating conditions, mg/L

C_w = Operating oxygen concentration in wastewater, mg/L

C_{s20} = O_2 saturation concentration for tap water at 20°C, mg/L

For diffused air aeration system, the C_s values must be corrected to account for higher than atmospheric O_2 saturation concentration achieved due to application of air at the reactor bottom.

The C_s is taken as average DO attained at infinit time.

(Refer.Ex 6-11 Metcalf page-285 for problem on determination of $K_L a$)

$$\text{Or, } N = N_0 \frac{(\beta C_s - C_w)}{C_{s20}} \alpha \cdot \theta^{(T-20)} \quad (\text{As per Eckenfelder})$$

Where, N_0 = SORT = $K_L a \cdot V \cdot C_s$

Example: A step aeration activated sludge process is being designed using the diffused- aeration system. The design criteria for the period of critical oxygen demand in the aeration basin are as follows.

BOD loading = 1.268 kg BOD/ m³.d

Oxygen transfer requirement= 1kg of O_2 /kg of BOD applied.

Temp. of mixed liquor = 14°C

Min. allowable DO = 2.0 mg/l

$\alpha = 0.70$; $\beta = 0.90$

Oxygen transfer coefficient $(K_L a)_{20} = 12 \text{ hr}^{-1}$

O_2 transfer efficiency = 6.0%

Pressure at mid depth of diffusers = 810 mm of Hg

Compare the rate of oxygen transfer dc/dt to the rate of O_2 utilization 'r' and calculate the volume of standard air required per kg of BOD applied.

Consider C_s at 810 mm Hg and 14°C as = 11.1 mg/L

Solution:

Correcting $(K_L a)_{20}$ for 14°C

$$K_L a \text{ at } 14^\circ\text{C} = (K_L a)_{20} (1.024)^{14-20} = 10.4 \text{ hr}^{-1}$$

$$\text{Now } dc/dt = \alpha K_L a (\beta C_s - C_t)$$

$$= 0.70 \times 10.4 (0.90 \times 11.1 - 2.0) = 58.17 \text{ mg/L. hr}$$

Considering 1 kg of oxygen utilized per kg of BOD applied, then the rate of dissolved oxygen utilization is (*This will change if actual cell production and BOD ultimate is considered*)

$$r = 1.268 \frac{\text{kg BOD}}{\text{m}^3 \cdot \text{d}} = 1.268 \frac{\text{mg BOD}}{\text{L}} \times \frac{1}{24} \times 10^3 = 52.8 \frac{\text{mg}}{\text{L} \cdot \text{hr}}$$

The O_2 transfer rate of the aeration system is adequate, since higher than utilization rate (Since dc/dt exceeds 'r'). This oxygen resource limits the loading rate on aerobic reactor.

The **efficiency of oxygen transfer** is proportional to the rate of oxygen transfer.

$$E_{\text{actual}} = 6.0 \frac{\alpha \cdot K_L a \cdot (\beta C_s - C_t)}{(K_L a)_{20} (C_s)_{20}} \quad (\text{For } (K_L a)_{20} \text{ efficiency is 6\% hence for actual?})$$
$$= \frac{6.0 \times 0.7 \times 10.4 (0.9 \times 11.1 - 2.0)}{12.0 \times 9.8}$$
$$= 2.96\%$$

The volume of standard air required at an actual oxygen transfer efficiency of 2.96% per kg of BOD load, (considering 1 kg O_2 utilised per kg of BOD applied) is

$$\frac{1.0 \text{ kg of } O_2}{0.0296 \times 0.279 \text{ kg of } O_2/\text{m}^3} = 121 \text{ m}^3/\text{kg of BOD applied}$$

Considering one cubic meter of air at temperature and pressure of 14°C and 760 mm contains 0.279 kg O₂/m³.

Example:

If the saturation concentration of O₂ in water is 9.2 mg/L and initial concentration C₀ is 2.1 mg/L, determine the time it takes for the concentration C_t to become 7.5 mg/L if K_La is 0.25/day. What is the time required for C_t to be 5.0, 6.0, 7.0, 8.0 and 9.0 mg/L?

Solution:

$$\log \frac{C_s - C_0}{C_s - C_t} = (K_L a) \cdot t$$

$$t = \frac{1}{K_L a} \log_e \frac{(C_s - C_0)}{(C_s - C_t)}$$

For C_t = 7.5 mg/L, $t = \frac{1}{0.25} \log_e \frac{(9.2 - 2.1)}{(9.2 - 7.5)} = 5.7 \text{ days}$

Similarly

C _t	Time t(days)	
5	2.1	If left molecular diffusion alone, several days are required for reoxygenation to occur. However, in most rivers, there is some turbulent diffusion in addition to molecular diffusion; therefore, in reality the reaeration time is significantly less.
6	3.2	
7	4.8	
7.5	5.7	
8	7.1	
8.5	9.3	
9	14.3	

Volatilization and Gas stripping (of volatile organic compounds)

VOC – such as trichloroethylene (TCE); 1,2-dibromo-3-chloropropane (DBCP), etc.

Emission of VOCs

The principal mechanisms governing the release of VOCs in wastewater collection and treatment facilities are (i) volatilization and (2) gas stripping.

Volatilization

- Release of VOCs from wastewater surface to the atmosphere.
- These compounds are released because they partition between the gas and water phase until equilibrium is reached.
- Mass transfer between two phases is function of concentration in each phase relative to equilibrium concentration.
 - Thus, transfer is greatest when the concentration in one of the phases is far from equilibrium.
 - Since, VOC in atmosphere is extremely low, transfer of VOC usually occurs from wastewater to atmosphere.

Gas Stripping:

- When air is introduced in water, stripping of VOCs occurs.
- When gas is introduced into wastewater, VOCs are transferred from the wastewater to the gas by the principal explained above.
- In wastewater treatment, air stripping occurs in aerated grit chambers, aerated biological treatment and aerated transfer channels.

Mass-Transfer rates of VOCs

Mass transfer can be modeled using following equation

$$r_{\text{VOC}} = -K_{L\text{aVOC}} (C - C_s)$$

where, r_{VOC} = rate of VOC transfer, $\mu\text{g}/\text{m}^3 \cdot \text{h}$

$K_{L\text{aVOC}}$ = Overall VOC mass transfer coefficient, h^{-1}

C = Concentration of VOC in liquid, $\mu\text{g}/\text{m}^3$

C_s = Saturation concentration of VOC in liquid, $\mu\text{g}/\text{m}^3$

The mass transfer coefficient of VOC, is proportional to the mass transfer coefficient for oxygen

$$K_{LaVOC} = \psi (K_{LaO_2})$$

ψ = Coefficient of proportionality and K_{LaO_2} is overall oxygen mass transfer coefficient.

The range of values for coefficient of proportionality ψ is 0.55 to 0.65 and it is **necessarily same for clear water as for wastewater.**

The saturation concentration of VOC in wastewater is function of partial pressure of VOC in atmosphere in contact with wastewater. This is given by Henry's Law as

$$C_g/C_s = H_c$$

Where, C_g = concentration of VOC in gas phase ($\mu\text{g}/\text{m}^3$)

C_s = Saturation concentration of VOC in liquid phase ($\mu\text{g}/\text{m}^3$)

H_c = Henry's law constant, unitless (values available in books for different gases)

Following relation can be used to convert unitless constant values to Henry's law

$$H_c = K_H/R.T$$

K_H = Henry's law constant, atm/g-mole

R = Universal gas constant, 0.000082057 atm/g-mole. $^{\circ}\text{K}$

T = Temperature, $^{\circ}\text{K} = 273 + ^{\circ}\text{C}$

Mass Transfer of VOCs from Surface Aeration

Material balance for the stripping of VOC from CSTR is as follows

Accumulation = inflow – outflow + generation

$$V(dc/dt) = Q_L \cdot C_{L,i} - Q_L \cdot C_{L,e} + r_{VOC} \cdot V$$

Where, V = Volume of completely mixed reactor, m^3

dc/dt = rate of change of VOC concentration in reactor, $\mu\text{g}/\text{m}^3 \cdot \text{h}$

Q_L = Liquid flow rate (m^3/s)

$C_{L,i}$ = Concentration of VOC in influent, $\mu\text{g}/\text{m}^3$

$C_{L,e}$ = Concentration of VOC in effluent, $\mu\text{g}/\text{m}^3$

r_{VOC} = rate of VOC mass transfer, $\mu\text{g}/\text{m}^3 \cdot \text{h}$

Now,

$$r_{\text{VOC}} = -K_L a_{\text{VOC}} (C_{L,e} - C_s)$$

Hence,

$$dc/dt = (1/\theta)(C_{L,i} - C_{L,e}) - K_L a_{\text{VOC}} (C_{L,e} - C_s)$$

Where $\theta = V/Q$

Assuming steady state condition, hence $dc/dt = \text{zero}$ and C_s is assumed to be zero

$$0 = (C_{L,i} - C_{L,e}) - K_L a_{\text{VOC}} (C_{L,e} - C_s) \theta$$

$$= C_{L,i} - C_{L,e} [1 + K_L a_{\text{VOC}} \cdot \theta]$$

Then amount of VOC that can be removed by surface aeration (fraction)

$$1 - (C_{L,e} / C_{L,i}) = 1 - [1 + K_L a_{\text{VOC}} \cdot \theta]^{-1}$$

If significant amount of the VOC is adsorbed or biodegraded, then results obtained with the above equation will be over estimated.

For completely mixed reactor with diffused aeration the equation is

$$1 - (C_{L,e} / C_{L,i}) = 1 - [1 + (Q_g/Q_L)(Hc)(1-e^{-\Phi})]^{-1}$$

Where, Q_g = gas flow rate, m^3/sec ;

Q_L = Liquid flow rate, m^3/sec ; and

$$\Phi = \text{saturation parameter} = K_L a_{\text{VOC}} \cdot V / (Hc \cdot Q_g)$$

Example: Determine amount of benzene that can be stripped in a completely mixed reactor equipped with diffused air aeration system. Assume following conditions:

1. Wastewaterflow rate = 1.0 MG/day
2. Aeration tank volume = 0.25 MG
3. Depth of aeration tank = 20 ft.

4. Air flow rate = 1750 ft³/min at std. condition
5. Oxygen transfer rate = 6.2 per hr
6. Influent concentration of benzene = 100 μg/ft³
7. $H_c = 5.49 \times 10^{-3} \text{ m}^3 \cdot \text{atm}/\text{mol}$
8. $\Psi = 0.6$
9. Temperature = 20 °C

Solution:

Questions

1. Describe in short commonly used aeration devices used in aerobic wastewater treatment.
2. Explain in short the two-film theory of gas transfer in liquid, derive the expression for gas transfer rate in liquid and gas release from the liquid.
3. Explain in short how to evaluate O₂- transfer coefficient in water and wastewater.
- 4.