Prediction of diffusivities

The diffusivity (D_{AB}) for the transfer of one component (A) in another component (B) can be calculated empirically:

1. Empirical correlation for calculation of gas diffusivity:

The diffusivity (D_{AB}) for the transfer of one gas in another is not known and experimental determination is not practicable. It is necessary to use one of the many predictive procedures. The equation developed by **Fuller et al. (1966)** is easy to apply and gives reliable estimates:

$$\mathbf{D_{AB}} = \frac{\mathbf{1.013 \times 10^{-7}\ T^{1.75}} \sqrt{\dfrac{\mathbf{1}}{\mathbf{M_A}} + \dfrac{\mathbf{1}}{\mathbf{M_B}}}}{\mathbf{P}\left[(\Sigma_a\ v_i)^{\frac{1}{3}} + (\Sigma_b\ v_i)^{\frac{1}{3}}\right]^2}$$

Where:

D_{AB}: is the diffusivity of (A) in (B), m^2/s.
T: is the temperature, K.
p is the total pressure, bar.
M_A, M_B are the molecular masses of component (A) and (B).
$\sum_a v_i$, $\sum_b v_i$: are the summation of the special diffusion volume coefficients for components a and b, given in Table 8.5.

Table 8.5. Special atomic diffusion volumes (*Fuller et al.*, 1966)

Atomic and structural diffusion volume increments

C	16.5	Cl	19.5*
H	1.98	S	17.0*
O	5.48	Aromatic or heterocyclic rings	−20.0
N	5.69*		

Diffusion volumes of simple molecules

H_2	7.07	CO	18.9
D_2	6.70	CO_2	26.9
He	2.88	N_2O	35.9
N_2	17.9	NH_3	14.9
O_2	16.6	H_2	12.7
Air	20.1	CCL_2F_2	114.8*
Ne	5.59	SF_6	69.7*
Ar	16.1	Cl_2	37.7*
Kr	22.8	Br_2	67.2*
Xe	37.9*	SO_2	41.1*

* Value based on only a few data points

Example: Estimate the diffusivity of methanol in air at atmospheric pressure and 25°C.

Solution:

Diffusion volumes from Table 8.5: methanol:

Element	v_i		No. of		
C	16.50	×	1	=	16.50
H	1.98	×	4	=	7.92
O	5.48	×	1	=	5.48
			$\sum_a v_i$		29.90

Diffusion volume for air = 20.1.
1 standard atmosphere = 1.013 bar.
molecular mass CH_3OH = 32, air = 29.

$$D_v = \frac{1.013 \times 10^{-7} \times 298^{1.75}(1/32 + 1/29)^{1/2}}{1.013[(29.90)^{1/3} + (20.1)^{1/3}]^2}$$

$$= \underline{\underline{16.2 \times 10^{-6} \text{m}^2/\text{s}}}$$

Experimental value, 15.9×10^{-6} m^2/s.

2. Empirical correlation for calculation of liquid diffusivity:

The equation developed by Wilke and Chang (1955), given below, can be used to predict liquid diffusivity diffusivities of dilute solutions of non-electrolytes. The Wilke-Chang equation gives satisfactory predictions for the diffusivity of organic compounds in water but not for water in organic solvents.

$$\mathbf{D_{AB}} = \frac{\mathbf{1.173 \times 10^{-16}\ (\emptyset_B\ M_B)^{0.5}\ T}}{\boldsymbol{\mu}\,\mathbf{V_A^{0.6}}}$$

Where:

D_{AB}: is the diffusivity of solute (A) in solvent (B), m^2/s.

T: is the absolute temperature, K.

M_B: is the molecular weight of the solvent.

μ: is viscosity of the solution, ($N\ s/m^2$).

V_A: is the molar volume of the solute at its boiling point, $m^3/kmol$. Values for simple molecules are given in Table 10.4. For more complex molecules, V_A is calculated by summation of the atomic volume and other contributions given in **Table 8.6**. It may be noted that for water a value of 0.0756 m^3/kmol should be used.

$\emptyset_B$: is the association factor for the solvent (2.26 for water, 1.9 for methanol, 1.5 for ethanol and 1.0 for unassociated solvents such as hydrocarbons and ethers).

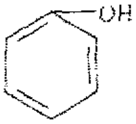
Table 8.6. Structural contributions to molar volumes, m^3/kmol (Gambill, 1958)

			Molecular volumes				
Air	0.0299	CO_2	0.0340	H_2S	0.0329	NO	0.0236
Br_2	0.0532	COS	0.0515	I_2	0.0715	N_2O	0.0364
Cl_2	0.0484	H_2	0.0143	N_2	0.0312	O_2	0.0256
CO	0.0307	H_2O	0.0189	NH_3	0.0258	SO_2	0.0448
			Atomic volumes				
As	0.0305	F	0.0087	P	0.0270	Sn	0.0423
Bi	0.0480	Ge	0.0345	Pb	0.0480	Ti	0.0357
Br	0.0270	H	0.0037	S	0.0256	V	0.0320
C	0.0148	Hg	0.0190	Sb	0.0342	Zn	0.0204
Cr	0.0274	I	0.037	Si	0.0320		

Cl, terminal, as in RCl	0.0216	in higher esters, ethers	0.0110
medial, as in R—CHCl—R	0.0246	in acids	0.0120
Nitrogen, double-bonded	0.0156	in union with S, P, N	0.0083
triply bonded, as in nitriles	0.0162	three-membered ring	−0.0060
in primary amines, RNH_2	0.0105	four-membered ring	−0.0085
in secondary amines, R_2NH	0.012	five-membered ring	−0.0115
in tertiary amines, R_3N	0.0108	six-membered ring as in benzene, cyclohexane, pyridine	−0.0150
Oxygen, except as noted below	0.0074		
in methyl esters	0.0091	Naphthalene ring	−0.0300
in methyl ethers	0.0099	Anthracene ring	−0.0475

Example: Estimate the diffusivity of phenol in ethanol at 20°C (293 K).

Solution:

Viscosity of ethanol at 20°C, 1.2 mNs/m^2.
Molecular mass, 46.
Molar volume of phenol 

from Table 8.6:

Atom	Vol.		No. of		
C	0.0148	×	6	=	0.0888
H	0.0037	×	6	=	0.0222
O	0.0074	×	1	=	0.0074
ring	−0.015	×	1	=	−0.015
					0.1034 m^3/k mol

$$D_L = \frac{1.173 \times 10^{-13}(1.5 \times 46)^{0.5} 293}{1.2 \times 0.1034^{0.6}} = \underline{\underline{9.28 \times 10^{-10}\ \mathrm{m^2/s}}}$$

Experimental value, 8×10^{-10} m^2/s

* The **Wilke-Chang correlation** is shown graphically in Figure 8.2. This figure can be used to determine the association constant for a solvent from experimental values for D_{AB} (D_L) in the solvent. The Wilke-Chang equation gives satisfactory predictions for the diffusivity of organic compounds in water but not for water in organic solvents.

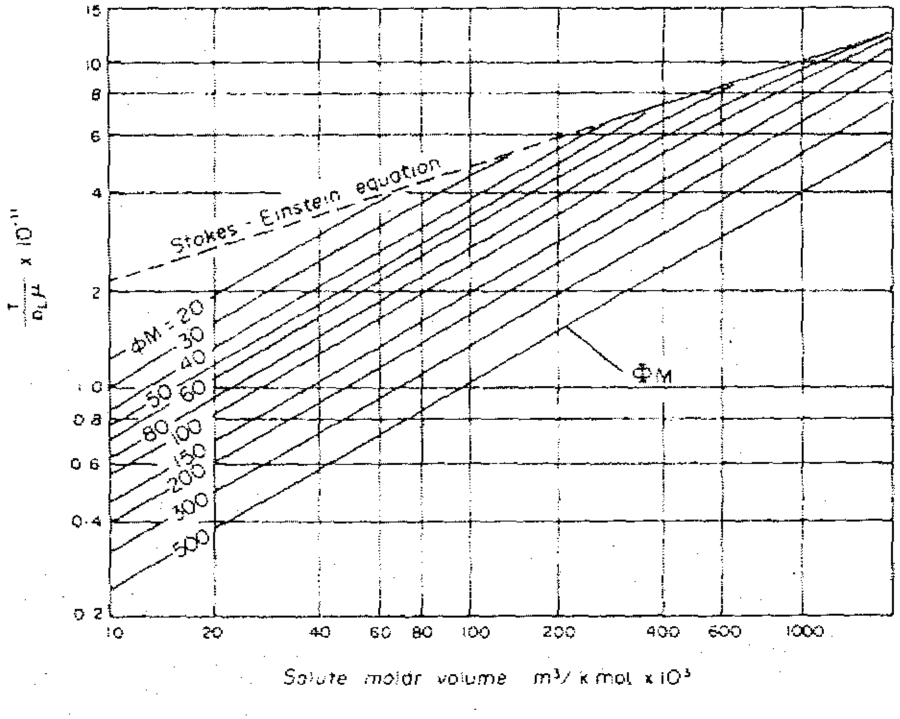


Figure 8.2. The Wilke-Chang correlation

It will be noted from the diffusivity equation is inversely proportional to the pressure and varies with the absolute temperature raised to the power of 1.5. In order to correct the diffusivity coefficient given in Table (10.2) we use the equation below:

$$\frac{D_{AB}(1)}{D_{AB}(2)}=\left(\frac{T_1}{T_2}\right)^{1.5}\left(\frac{P_2}{P_1}\right)$$

Where:

$D_{AB}(1)$ is the diffusivity at T_1 and P_1 given in Table (10.2) at 298 K and 101.3 kPa.

$D_{AB}(2)$ is the diffusivity at T_2 and P_2 .

Unsteady-state Diffusion

Considering an element of gas of cross-sectional area **A** and of thickness **δy** in the direction of mass transfer in which the concentrations C_A and C_B of the components **A** and **B** are a function of both position **y** and time **t** (See Figure below), then if the mass transfer flux is composed of two components, one attributable to diffusion according to Fick's Law and the other to a bulk flow velocity u_f, the fluxes of **A** and **B** at a distance **y** from the origin may be taken as N_A and N_B, respectively. These will increase to $N_A + (dN_A/dy)\,\delta y$ and $N_B + (dN_B/dy)\,\delta y$ at a distance $y + \delta y$ from the origin.

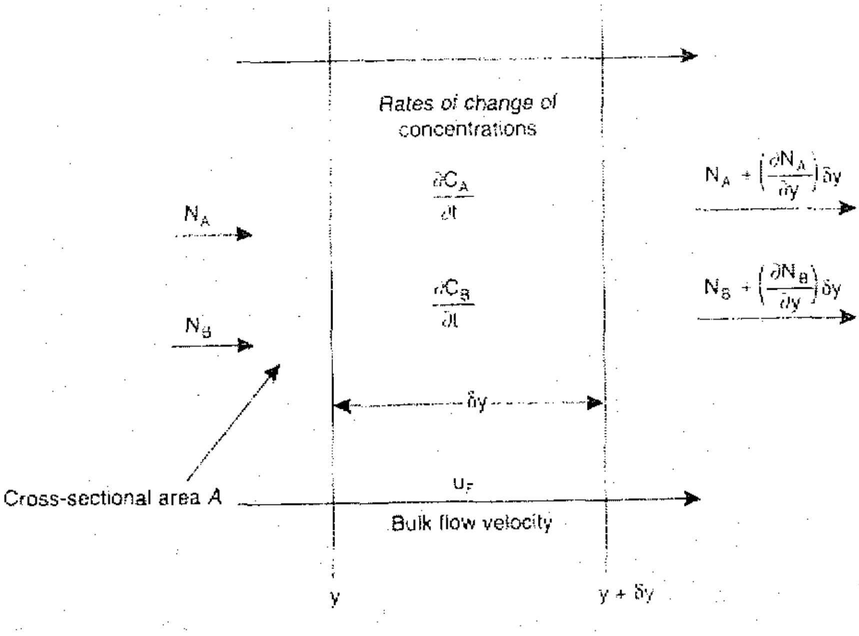


Figure 10.4: Unsteady state mass transfer

Thus, for **A**:

$$\overset{\substack{\textit{moles IN/unit time}\\ \text{(at } y)}}{\left\{-D\frac{\partial C_A}{\partial y}+u_F C_A\right\}A}-\overset{\substack{\text{moles OUT/unit time}\\ \text{(at } y+\partial y)}}{\left\{-D\frac{\partial C_A}{\partial y}+u_F C_A+\frac{\partial}{\partial y}\left[-D\frac{\partial C_A}{\partial y}+u_F C_A\right]\delta y\right\}A}=\overset{\substack{\text{= rate of change of concn.}\\ \times \text{ element volume}}}{\frac{\partial C_A}{\partial t}(\delta y.A)}$$

Simplifying: $$\frac{\partial C_A}{\partial t}=D\frac{\partial^2 C_A}{\partial y^2}-\frac{\partial(u_F C_A)}{\partial y}$$

For component **B**: $$\frac{\partial C_B}{\partial t}=D\frac{\partial^2 C_B}{\partial y^2}-\frac{\partial(u_F C_B)}{\partial y}$$

and adding: $$\frac{\partial(C_A+C_B)}{\partial t}=D\frac{\partial^2(C_A+C_B)}{\partial y^2}-\frac{\partial}{\partial y}[(C_A+C_B)u_F]$$

Since, for an ideal gas, $C_A+C_B=C_T=\text{constant}$:

$$0=0-\frac{\partial}{\partial y}(u_F C_T)$$

and: $$\frac{\partial u_F}{\partial y}=0$$

where u_F is therefore independent of y.

$$\frac{\partial C_A}{\partial t}=D\frac{\partial^2 C_A}{\partial y^2}-u_F\frac{\partial C_A}{\partial y}$$

For equimolecular counterdiffusion, $u_F=0$:

$$\frac{\partial C_A}{\partial t}=D\frac{\partial^2 C_A}{\partial y^2}$$

Fick's second law for unsteady state diffusion in one direction

This equation can be solved for a number of important boundary conditions. For the more general three-dimensional case where concentration gradients are changing in the x, y and z directions, these changes must be added to give:

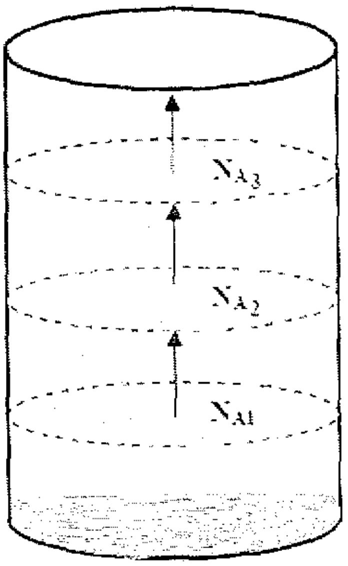
$$\frac{\partial C_A}{\partial t}=D\left[\frac{\partial^2 C_A}{\partial x^2}+\frac{\partial^2 C_A}{\partial y^2}+\frac{\partial^2 C_A}{\partial z^2}\right]$$

Fick's second law for unsteady state diffusion in three direction

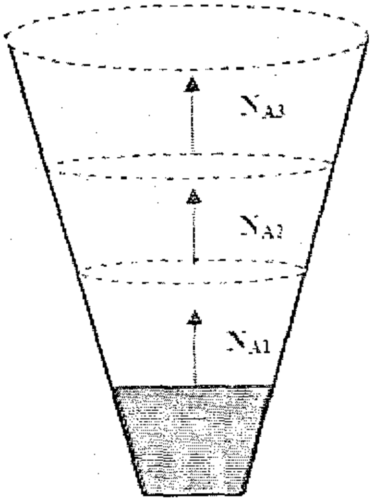
Diffusion through a varying cross-section area

The mole rate ($\bar{N}_A$, $\frac{\text{kmol}}{\text{s}}$) through a system of a varying cross section area is constant, while the mole flux (N_A, $\frac{kmol}{m^2.s}$) is variable. The mass transfer through a cone and sphere can be consider as a mass transfer through a system of varying cross section area. On the other hand, the transfer through a cylinder can be consider as a mass transfer through a system of constant cross section area.

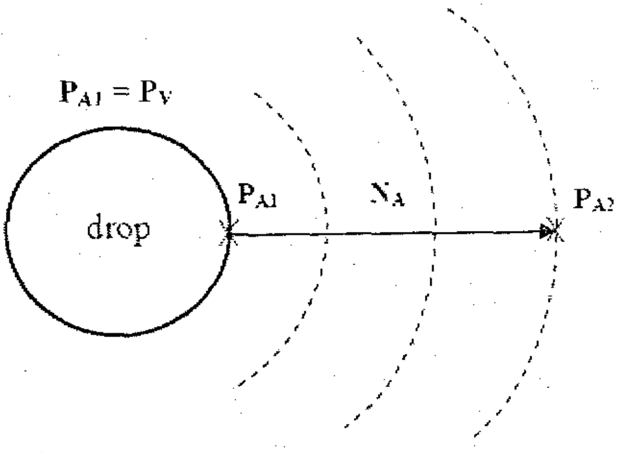
$$N_A = \frac{\text{mole rate}}{\text{surface area}} = \frac{\bar{N}_A}{A} = \frac{\frac{\text{kmol}}{\text{s}}}{\text{m}^2} = \frac{\text{kmol}}{\text{m}^2.\text{s}}$$



$N_{A1} = N_{A2} = N_{A3}$



$N_{A1} > N_{A2} > N_{A3}$



Diffusion through a spherical body

$$N_A = -D_{AB}\ \frac{dC_A}{dr} + \frac{C_A}{C_T}\,(N_A + N_B) \qquad \text{......................................(1)}$$

$$\frac{\bar{N}_A}{A} = -D_{AB}\ \frac{dC_A}{dr} + \frac{C_A}{C_T}\left(\frac{\bar{N}_A}{A} + \frac{\bar{N}_B}{A}\right) \qquad \text{......................................(2)}$$

$$\bar{N}_A = -D_{AB}\ A\ \frac{dC_A}{dr} + \frac{C_A}{C_T}\,(\bar{N}_A + \bar{N}_B) \qquad \text{......................................(3)}$$

But: The surface area of sphere = $A = 4\pi\, r^2$

$$\boxed{\bar{N}_A = -\ 4\pi\, r^2\ D_{AB}\ \frac{dC_A}{dr} + \frac{C_A}{C_T}\,(\bar{N}_A + \bar{N}_B) \qquad \text{......................................(4)}}$$

Case (I): Diffusion through a stagnant layer ($\bar{N}_B = 0$):

$$\bar{N}_A = -\ 4\pi\, r^2\ D_{AB}\ \frac{dC_A}{dr} + \frac{C_A}{C_T}\,(\bar{N}_A + 0)$$

$$\bar{N}_A(1 - C_A) = -\ 4\pi\, r^2\ D_{AB}\ C_T\ \frac{dC_A}{dr}$$

$$\bar{N}_A \int_{r_0}^{r_1} \frac{dr}{r^2} = 4\pi\ D_{AB}\ C_T \ln\left[\frac{C_T - C_{A_2}}{C_T - C_{A_1}}\right]$$

$$\boxed{\bar{N}_A = \frac{4\pi\ D_{AB}\ C_T}{\frac{1}{r_0} - \frac{1}{r_1}}\ \ln\left[\frac{C_T - C_{A_2}}{C_T - C_{A_1}}\right]} \qquad \text{......................................(1)}$$

The most important things is to calculate the mass transfer rate for the sphere surface where the surface area is constant ($4\pi\, r_0^2$):

$$N_A . A = \frac{4\pi\ D_{AB}\ C_T}{\frac{1}{r_0} - \frac{1}{r_1}}\ \ln\left[\frac{C_T - C_{A_2}}{C_T - C_{A_1}}\right]$$

$$N_A\,(4\pi r_0^2) = \frac{4\pi\ D_{AB}\ C_T}{\frac{1}{r_0} - \frac{1}{r_1}}\ \ln\left[\frac{C_T - C_{A_2}}{C_T - C_{A_1}}\right]$$

$$\boxed{N_A = \frac{D_{AB}\ C_T}{r_0^2\left(\frac{1}{r_0} - \frac{1}{r_1}\right)}\ \ln\left[\frac{C_T - C_{A_2}}{C_T - C_{A_1}}\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$\longrightarrow$ ***Mole flux from the sphere surface***

* When the mass transfer from surface to a large distance compare to the sphere surface (r_0):

$r_1 \to \infty$ and $C_{A_2} = 0$

$$N_A = \frac{D_{AB}\ C_T}{r_0^2\left(\frac{1}{r_0} - \frac{1}{\infty}\right)}\ \ln\left[\frac{C_T - C_{A_2}}{C_T - C_{A_1}}\right]$$

$$\boxed{N_A = \frac{D_{AB}\ C_T}{r_0}\ \ln\left[\frac{C_T - C_{A_2}}{C_T - C_{A_1}}\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

In partial pressure form:

$$\boxed{N_A = \frac{D_{AB}\ P_T}{r_0 . RT}\ \ln\left[\frac{P_T - P_{A_2}}{P_T - P_{A_1}}\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Example: A sphere of naphthalene having a radius of 2 mm is suspended in a large volume of still air at 318 K and 101.3 kPa. The surface temperature of naphthalene can be assumed to be 318 K and its vapour pressure at this temperature is 0.555 mmHg. The diffusivity of naphthalene in air at 318 K is $6.92 * 10^{-6}$ m^2/s. Calculate the rate of naphthalene evaporation from surface.

Solution:

The sphere is suspended in a large volume of still air means:

$r_1 \rightarrow \infty$ and $P_{A_2} = 0$

$$N_A = \frac{D_{AB}\ P_T}{r_0 . RT}\ \ln\left[\frac{P_T - P_{A_2}}{P_T - P_{A_1}}\right]$$

$$P_{A_1} = \left(\frac{0.555}{760}\right) * 101.3 = 0.07397\ \text{kPa}$$

$$r_0 = 2 * 10^{-3}$$

$$N_A = \frac{(6.92 * 10^{-6})\ (101.3)}{(2 * 10^{-3})(8.314)(318)}\ \ln\left[\frac{101.3 - 0}{101.3 - 0.07397}\right] = 9.68 * 10^{-8}\ \frac{\text{kmol}}{m^2.s}$$

Case (II): Equimolecular Counter Diffusion ($\bar{N}_B = -\bar{N}_A$):

$$N_A = -D_{AB}\,\frac{dC_A}{dr} + \frac{C_A}{C_T}\,(N_A + N_B) \qquad \text{.........} (1)$$

$$\frac{\bar{N}_A}{A} = -D_{AB}\,\frac{dC_A}{dr} + \frac{C_A}{C_T}\left(\frac{\bar{N}_A}{A} - \frac{\bar{N}_B}{A}\right) \qquad \text{.........} (2)$$

$$\bar{N}_A = -\,4\pi\, r^2\, D_{AB}\,\frac{dC_A}{dr} \qquad \text{.........} (3)$$

$$\bar{N}_A \int_{r_0}^{r_1} \frac{dr}{r^2} = -\,4\pi\, D_{AB} \int_{C_{A_1}}^{C_{A_2}} dC_A \qquad \text{.........} (4)$$

$$\bar{N}_A \left[\frac{1}{r_0} - \frac{1}{r_1}\right] = 4\pi\, D_{AB}\,\left(C_{A_1} - C_{A_2}\right) \qquad \text{.........} (5)$$

$$\boxed{\bar{N}_A = \frac{4\pi\, D_{AB}}{\left[\frac{1}{r_0} - \frac{1}{r_1}\right]}\,\left(C_{A_1} - C_{A_2}\right)}$$

For the mass transfer from surface ($A = 4\pi\, r_o^2$):

$$\boxed{N_A = \frac{D_{AB}}{r_0^2\left[\frac{1}{r_0} - \frac{1}{r_1}\right]}\,\left(C_{A_1} - C_{A_2}\right)}$$

In the case of r_1 is very large $\Longrightarrow \frac{1}{r_1} = 0$

$$\boxed{N_A = \frac{D_{AB}}{r_0}\,\left(C_{A_1} - C_{A_2}\right)}$$

In the form of partial pressure:

$$\boxed{N_A = \frac{D_{AB}}{r_0 .\ RT}\,\left(P_{A_1} - P_{A_2}\right)}$$

Case (III): Unequimolecular Counter Diffusion ($\bar{N}_B = -n\,\bar{N}_A$):

$$\boxed{N_A = \frac{D_{AB}}{RT}\,\frac{P_T}{r_0}\,\frac{1}{(1-n)}\,\ln\left[\frac{P_T-(1-n)\,P_{A_2}}{P_T-(1-n)\,P_{A_1}}\right]}$$

Example: Calculate the rate of burning of carbon particle 2.56 cm radius in an atmosphere of pure oxygen at 1000 K and 1 atm. Assuming a very large blanking layer of CO_2 has formed a round the particle. At the carbon surface $P_{CO_2} = 1$ atm and $P_{O_2} = 0$. At very large radius $P_{CO_2} = 0$ and $P_{O_2} = 1$ atm. Given the diffusivity of oxygen in carbon dioxide = 1.032 cm^2/s.

Solution:

$C + O_2 \rightarrow CO_2$

The diffusion is equimolecular counter diffusion:

$$N_A = \frac{D_{AB}}{RT\,.\,r_0^2\left[\frac{1}{r_0}-\frac{1}{r_1}\right]}\left(P_{A_1}-P_{A_2}\right)$$

In the case of r_1 is very large $(r_1 \rightarrow \infty)$ $\Longrightarrow \frac{1}{r_1} = 0$

$$N_A = \frac{D_{AB}}{RT\,.\,r_0}\left(P_{A_1}-P_{A_2}\right) = \frac{1.032 * 10^{-4}}{(8.314)(1000)(2.56 * 10^{-2})}(101.3-0)$$

$$N_A = 4.95 * 10^{-5}\,\frac{kmol}{m^2.\,s}$$

Mass transfer theories

1. The Two-Film Theory

The two-film theory of ***Whitman (1923)*** was the first serious attempt to represent conditions occurring when material is transferred in ***a steady state process*** from one fluid stream to another. In this approach, it is assumed that a laminar layer exists in each of the two fluids. Outside the laminar layer, turbulent eddies supplement the action caused by the random movement of the molecules, and the resistance to transfer becomes progressively smaller as shown in Figure below. The thicknesses of the two films are z_1 and z_2. Equilibrium is assumed to exist at the interface and therefore the relative positions of the points C and D are determined by the equilibrium relation between the phases.

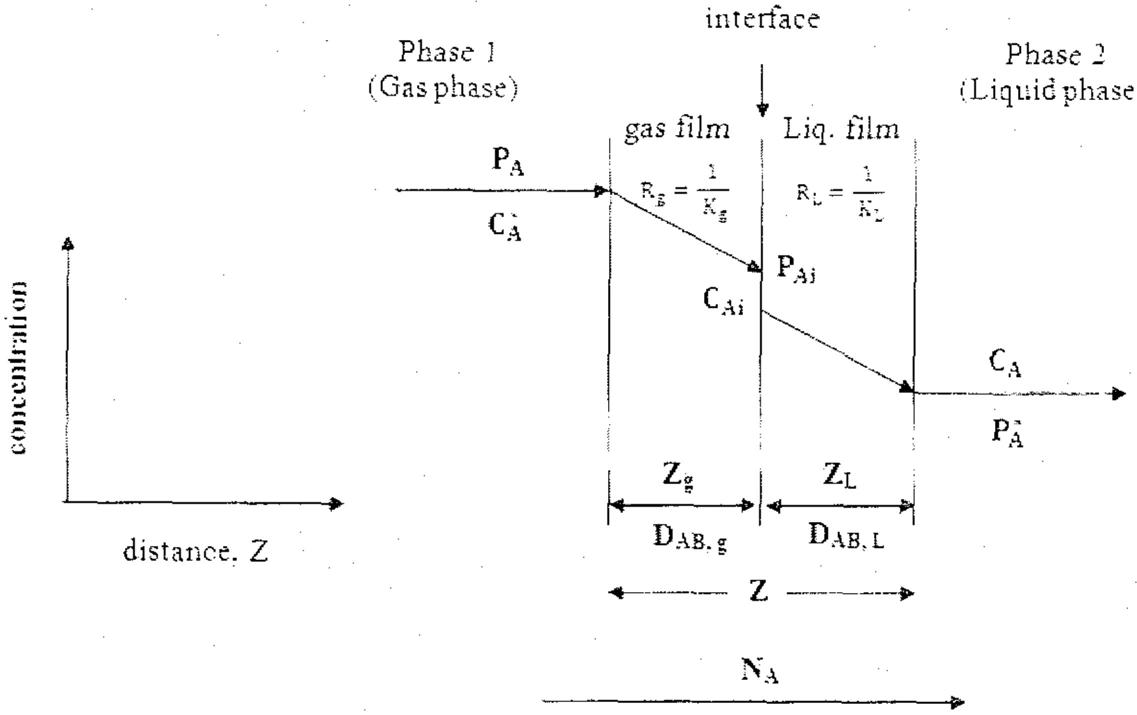


Figure 1: Two - Film Theory

The rate of mass transfer per unit area in terms of the two-film theory for equimolecular counterdiffusion is given for the first phase as:

$$N_A = -D_{AB}\frac{dC_A}{dz}$$

$$N_A = D_{AB}\frac{(C_A^* - C_A)}{z}$$

In the form of partial pressure:

$$N_A = \frac{\text{[redacted]}\,D_{AB}}{RT}\,\frac{(P_A - P_A^*)}{Z}$$

$$N_A = \text{[redacted]}\,D_{AB}\,\frac{(C_A^* - C_A)}{Z} = \frac{-D_{AB}}{RT}\,\frac{(P_A - P_A^*)}{Z}$$

Where: $Z = Z_g + Z_L$

The rate of mass transfer per unit area from the gas film:

$$N_{A_g} = \frac{\text{[redacted]}(D_{AB})_g}{Z_g\,.\,RT}\,(P_A - P_{A_i})$$

The rate of mass transfer per unit area from the liquid film:

$$N_{A_L} = \frac{\text{[redacted]}(D_{AB})_L}{Z_L}\,(C_{A_i} - C_A\text{[redacted]})$$

The relation between the partial pressur (P_A) and concentration (C_A):

Rault's law:

$$P_A = P_A^o\ X_A$$

$$\frac{P_A}{P_T} = \frac{P_A^o}{P_T}\ X_A$$

$$\boxed{y_A = K\ X_A}$$

Henry's law:

$$\boxed{P_A = H\ C_A}$$

Where: H is the Henry's constant.

$P_A^* = H\ C_A$	or	$y_A^* = H\ x_A$
$C_A = H\ P_A^*$	or	$y_A = H\ x_A^*$
$P_{A_i} = H\ C_{A_i}$	or	$y_{A_i} = H\ x_{A_i}$

2. The Penetration Theory

The penetration theory was suggested in ***1935 by Higbie*** who was investigating whether or not a resistance to transfer existed at the interface when a pure gas was absorbed in a liquid. In his experiments, a slug-like bubble of carbon dioxide was allowed rise through a vertical column of water in a 3 mm diameter glass tube. As the bubble rose, the displaced liquid ran back as a thin film between the bubble and the tube, ***Higbie assumed that each element of surface in this liquid was exposed to the gas for the time taken for the gas bubble to pass it; that is for the time given by the quotient of the bubble length and its velocity***. It was further supposed that during this short period, which varied between 0.01 and 0.1 s in the experiments, absorption took place as the result of ***unsteady state molecular diffusion*** into the liquid, and, for the purposes of calculation, the liquid was regarded as infinite in depth because the time of exposure was so short.

The way in which the concentration gradient builds up as a result of exposing a liquid - initially pure - to the action of a soluble gas is shown in Figure 10.6. The percentage saturation of the liquid is plotted agains the distance from the surface for a number of exposure times in arbitrary units. Initially only the surface layer contains solute and the concentration changes abruptly from 100 percent to 0 percent at the surface. For progressively longer exposure times the concentration profile develops as shown, until after an infinite time the whole of the liquid becomes saturated. The shape of the profiles is such that at any time the effective depth of liquid which contains an appreciable concentration of solute can be specified.If this depth of penetration is less than the total depth of liquid, no significant error is introduced by assuming that the total depth is infinite.

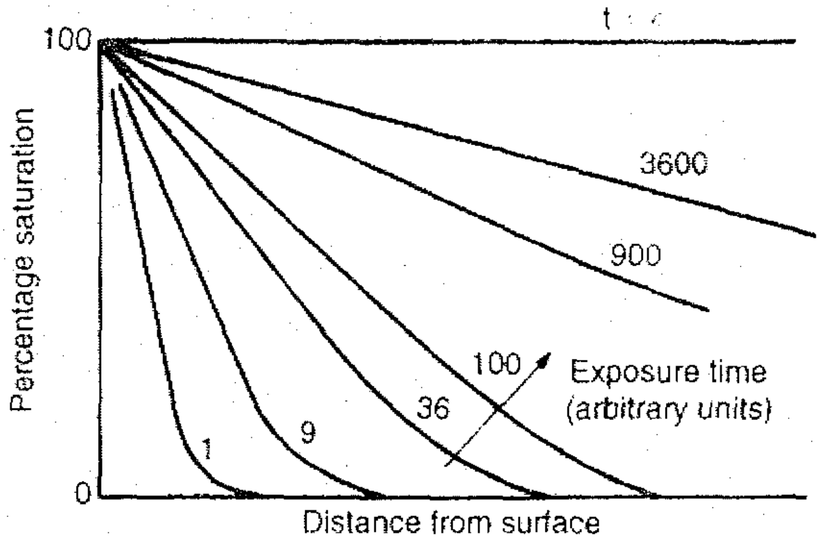


Figure 10.6. Penetration of solute into a solvent

The work of Higbie laid the basis of the penetration theory in which it is assumed that the eddies in the fluid bring an element of fluid to the interface where it is exposed to the second phase for a definite interval of time, after which the surface element is mixed with the bulk again. Thus, fluid whose initial composition corresponds with that of the bulk fluid remote from the interface is suddenly exposed to the second phase. It is assumed that equilibrium is immediately attained by the surface layers, that a process of unsteady state molecular diffusion then occurs and that the element is remixed after a fixed interval of time. In the calculation, the depth of the liquid element is assumed to be infinite and this is justifiable if the time of exposure is sufficiently short for penetration to be confined to the surface layers. Throughout, the existence of velocity gradients within the fluids is ignored and the fluid at all depths is assumed to be moving at the same rate as the interface.

The diffusion of solute **A** away from the interface (**y-direction**) is thus given by:

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{\partial y^2}$$

The following boundary conditions apply for the pentration theory:

$$\begin{array}{lll} t = 0 & 0 < y < \infty & C_A = C_{Ao} \\ t > 0 & y = 0 & C_A = C_{Ai} \\ t > 0 & y = \infty & C_A = C_{Ao} \end{array}$$

The mass transfer rate per unit area of surface is then given by:

$$(N_A)_{t,y=0} = -D\left(\frac{\partial C_A}{\partial y}\right)_{y=0}$$

$$\boxed{(N_A)_{t,y=0} = (C_{Ai} - C_{Ao})\sqrt{\frac{D}{\pi t}}}$$

Note:

$N_A \ \alpha \ D_{AB}$ **film theory**

$N_A \ \alpha \ \sqrt{D_{AB}}$ **pertration theory**

3. The Random Surface Renewal Theory

Danckwerts (1951) suggested that each element of surface would not be exposed for the same time, but that a random distribution of ages would exist. It was assumed that the probability of any element of surface becoming destroyed and mixed with the bulk of the fluid was independent of the age of the element.

Thus, the overall rate of mass transfer per unit area when the surface is renewed in a random manner is:

$$\boxed{N_A = (C_{Ai} - C_{Ao})\sqrt{Ds}}$$

Where:

S is the rate of production of fresh surface per unit total area of surface.

4. The Film - Penetration Theory

A theory which incorporates some of the principles of both the two-film theory and the penetration theory has been proposed by ***Toor and Marchello (1958)*** . The whole of the resistance to transfer is regarded as lying within a laminar film at the interface, as in the two-film theory, but the mass transfer is regarded as an unsteady state process. It is assumed that fresh surface is formed at intervals from fluid which is brought from the bulk of the fluid to the interface by the action of the eddy currents mass transfer then takes place as in the penetration theory, except that the resistance is confined to the finite film, and material which traverses the film is immediately completely mixed with the bulk of the fluid. For short times of exposure, when none of the diffusing material has reached the far side of the layer, the process is identica to that postulated in the penetration theory. For prolonged periods of exposure when a steady concentration gradient has developed, conditions are similar to those considered in the two-film theory.

The diffusion of solute **A** away from the interface (**y-direction**) is thus given by:

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{\partial y^2}$$

The following boundary conditions apply for the pentration theory:

$$t = 0 \quad \rightarrow \quad C_A = C_{A_0}$$

$$y = 0 \quad \rightarrow \quad C_A = C_A^*$$

$$y = L \quad \rightarrow \quad C_A = C_{A_0}$$

The mass transfer rate across the interface per unit area is therefore given by:

$$\boxed{(N_A)_t = (C_A^* - C_{Ao})\frac{D}{L}\left(1 + 2\sum_{n=1}^{n=\infty} e^{-(n^2\pi^2 Dt)/L^2}\right)}$$

When:

$\frac{Dt}{L^2}$ is small the pentration theory applicable.

$\frac{Dt}{L^2}$ is large the two film theory applicable.

The concentration profiles near an interface on the basis of:

(a) the film theory (steady-state)

(b) the penetration-theory (unsteady-state)

(c) the film-penetration theory (unsteady-state)

are shown in Figure 10.7.

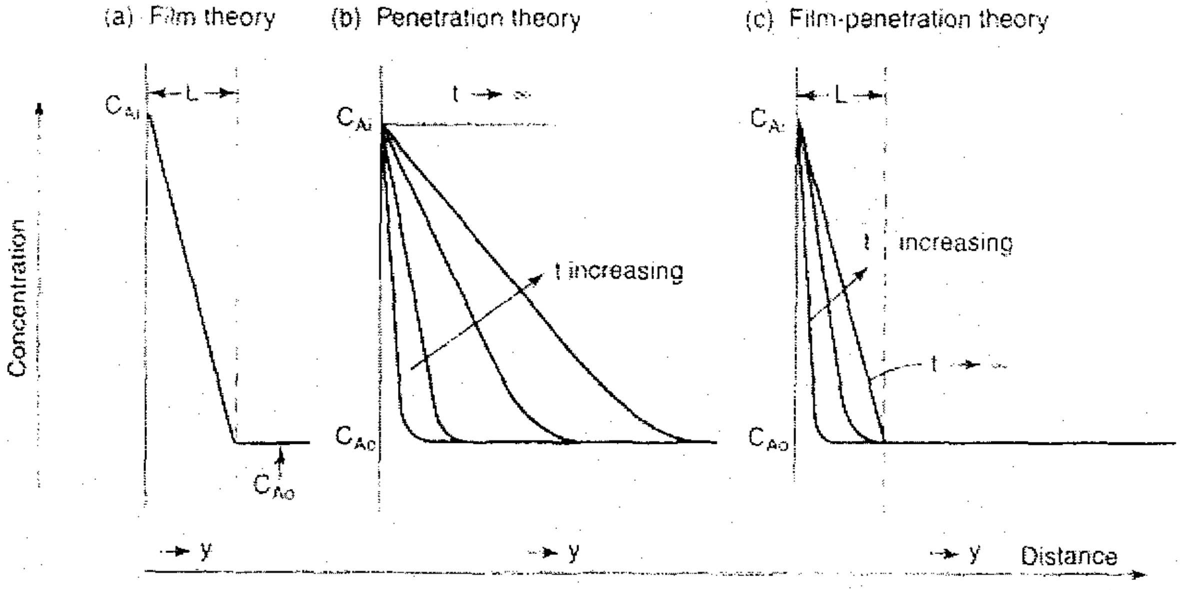


Figure 10.7. Concentration profiles near an interface

Mass transfer coefficients

Consider the two-film theory as shown in Figure (1):

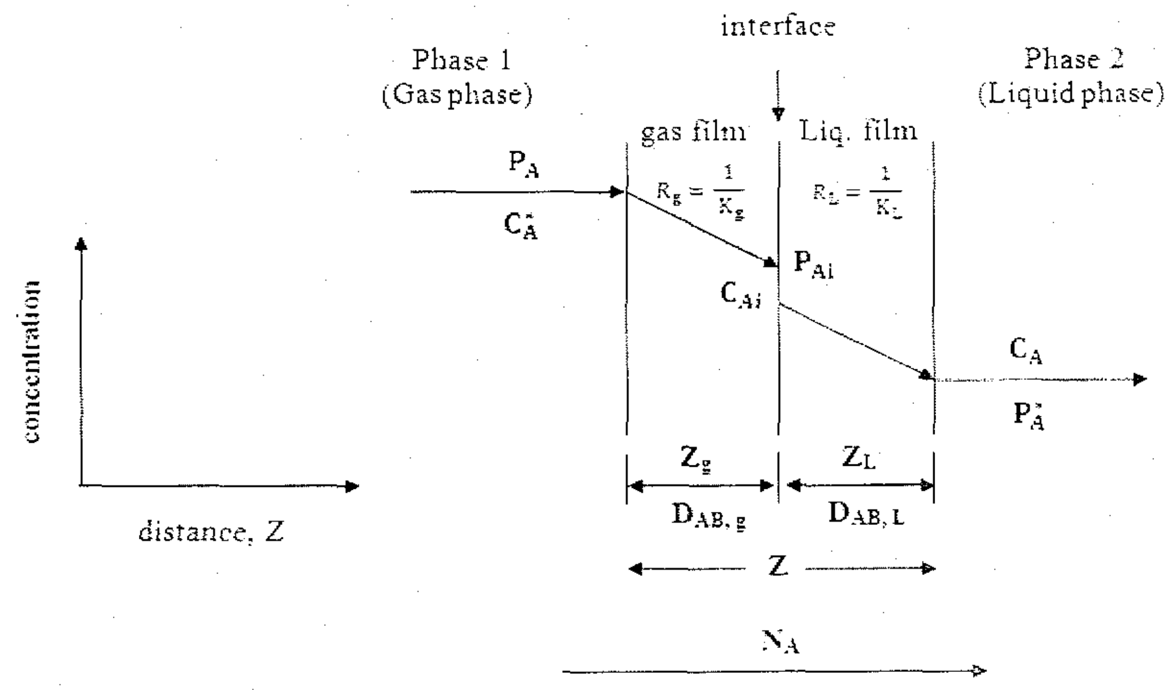


Figure 1: Two - Film Theory

The rate of mass transfer per unit area from the gas film:

$$N_{A_g} = \frac{(D_{AB})_g}{Z_g \, . \, RT} \quad (P_A - P_{A_i})$$

The rate of mass transfer per unit area from the liquid film:

$$N_{A_L} = \frac{(D_{AB})_L}{Z_L} \quad (C_{A_i} - C_A^*)$$

Where:

$(D_{AB})_g = (D_{AB})_L$

$N_{A_g} = N_{A_L} =$

Since the film thickness $\mathbf{Z_g}$ and $\mathbf{Z_L}$ are difficult to define or estimate, then we rewrite the above egyations as follow:

$$\mathbf{N_A = k_g \ (P_A - P_{A_i})}$$

$$\mathbf{N_A = k_L \ (C_{A_i} - C_A)}$$

But $\mathbf{P_{A_i}}$ and $\mathbf{C_{A_i}}$ are difficult to measure, therefore we define the overall mass transfer coefficient:

$$\mathbf{N_A = K_{OG} \ (P_A - P_A^*)}$$

$$\mathbf{N_A = K_{OL} \ (C_A^* - C_A)}$$

Where:

$\mathbf{k_L}$ is the individual liquid film mass transfer coeficient.

$\mathbf{k_g}$ is the individual gas film mass transfer coeficient.

$\mathbf{K_{OL}}$ is the overall mass transfer coeficient based on liquid phase.

$\mathbf{K_{OG}}$ is the overall mass transfer coeficient based on gas phase.

$\mathbf{P_{A_i}}$ is the partial pressure of the gas (A) at the interface.

$\mathbf{C_{A_i}}$ is the concentration of the liquid (A) at the interface.

$\mathbf{P_A^*}$ is the partial pressure of the gas phase which is in equilibrium with the liquid phase $\mathbf{C_A}$.

$\mathbf{C_A^*}$ is the concentration of the liquid phase which is in equilibrium with the gas phase $\mathbf{P_A}$.

The Relationships between the various mass transfer coefficients

$$\mathbf{N_A = k_g \ \left(P_A - P_{A_i}\right)} \quad \dots\dots\dots\dots (1)$$

$$\mathbf{N_A = k_L \ \left(C_{A_i} - C_A\right)} \quad \dots\dots\dots\dots (2)$$

$$\mathbf{N_A = K_{OG} \ (P_A - P_A^*)} \quad \dots\dots\dots\dots (3)$$

$$\mathbf{N_A = K_{OL} \ (C_A^* - C_A)} \quad \dots\dots\dots\dots (4)$$

$$\mathbf{\frac{1}{K_{OG}} = \frac{1}{k_g} + \frac{H}{k_L}} \quad \dots\dots\dots\dots (5)$$

$$\mathbf{\frac{1}{K_{OL}} = \frac{1}{H\,k_g} + \frac{1}{k_L}} \quad \dots\dots\dots\dots (6)$$

Q: Prove that $\frac{1}{K_{OG}} = \frac{1}{k_g} + \frac{H}{k_L}$

From Eq.(3) above:

$$\frac{1}{K_{OG}} = \frac{P_A - P_A^*}{N_A}$$

$$\frac{1}{K_{OG}} = \frac{P_A - P_A^* + P_{A_i} - P_{A_i}}{N_A}$$

$$\frac{1}{K_{OG}} = \frac{P_A - P_{A_i}}{N_A} + \frac{P_{A_i} - P_A^*}{N_A}$$

$$\frac{1}{K_{OG}} = \frac{P_A - P_{A_i}}{N_A} + \frac{H\,C_{A_i} - H\,C_A}{N_A}$$

$$\frac{1}{K_{OG}} = \frac{P_A - P_{A_i}}{N_A} + \frac{H\,(C_{A_i} - C_A)}{N_A}$$

$$\frac{1}{K_{OG}} = \frac{1}{k_g} + \frac{H}{k_L}$$

Q: Prove that $\frac{1}{K_{OL}} = \frac{1}{H\,k_g} + \frac{1}{k_L}$

From Eq.(4) above:

$$\frac{1}{K_{OL}} = \frac{C_A^* - C_A}{N_A}$$

$$\frac{1}{K_{OL}} = \frac{C_A^* - C_A + C_{A_i} - C_{A_i}}{N_A}$$

$$\frac{1}{K_{OL}} = \frac{C_A^* - C_{A_i}}{N_A} + \frac{C_{A_i} - C_A}{N_A}$$

$$\frac{1}{K_{OL}} = \frac{\frac{P_A}{H} - \frac{P_{A_i}}{H}}{N_A} + \frac{C_{A_i} - C_A}{N_A}$$

$$\frac{1}{K_{OL}} = \frac{1}{H}\left(\frac{P_A - P_{A_i}}{N_A} + \frac{C_{A_i} - C_A}{N_A}\right)$$

$$\frac{1}{K_{OL}} = \frac{1}{H\,k_g} + \frac{1}{k_L}$$

Notes:

1. The inverse to mass transfer coefficient $\left(\frac{1}{K}\right)$ is termed as a resistance to mass transfer.
2. The term (gas film control) refers to the resistance lie in the gas film.

Thus: $$\frac{1}{K_{OG}} = \frac{1}{k_g} + \cancelto{0}{\frac{H}{k_L}}$$ [when the solute is very soluble in liquid solvent]

Ro =

3. The term (liquid film control) refers to the resistance lie in the liquid film.

Thus: $$\frac{1}{K_{OL}} = \cancelto{0}{\frac{1}{H\,k_g}} + \frac{1}{k_L}$$

4. The units of mass transfer coeficients are as follows:

$$N_A = k_L\left(C_{A_1} - C_{A_2}\right) \quad \rightarrow \quad k_L = \frac{m}{s}$$

$$N_A = \bar{k}_g\left(P_{A_1} - P_{A_2}\right) \quad \rightarrow \quad \bar{k}_g = \frac{kmol}{m^2.\,s.\,kPa}$$

$$N_A = \bar{\bar{k}}_g\left(X_{A_1} - X_{A_2}\right) \quad \rightarrow \quad \bar{\bar{k}}_g = \frac{kmol}{m^2.\,s.}$$

$$k_L * \frac{1}{RT} = \bar{k}_g$$

$$k_L * \frac{P_T}{RT} = \bar{\bar{k}}_g$$

$$\bar{k}_g * P_T = \bar{\bar{k}}_g$$

$$kJ = kN.m = kg.\frac{m^2}{s^2} \quad , \quad kPa = \frac{kN}{m^2}$$

$$\frac{m}{s} * \frac{1}{\frac{kJ}{kmol.K} * K} = \frac{m}{s} * \frac{kmol}{kJ} = \frac{m}{s} * \frac{kmol}{kN.m} = \frac{kmol}{S.kN} = \frac{kmol}{S.\ \frac{kN}{m^2} * m^2}$$
$$= \frac{kmol}{m^2.kPa.S} = \bar{k}_g$$

$$\frac{m}{s} * \frac{kPa}{\frac{kJ}{kmol.K} * K} = \frac{m}{s} * \frac{kPa.kmol}{kJ} = \frac{m}{s} * \frac{kN}{m^2} * \frac{kmol}{kN.m} = \frac{kmol}{m^2.s}$$
$$= \bar{\bar{k}}_g$$

Example: For a system in which component (A) is transfering from the liquid to the gas phase, the equilibrium is given by $y_A^* = 0.75\, x_A$. At one point in the appartus the liquid contain 90 mol% of (A) and gas contain 45 mol% of (A). The individual gas film mass transfer coefficient at this point in the appartus of 0.02716 kmol/m^2.s , and 70% of the overall resistance to mass transfer is known to be encountered in the gas film: determine:

1. The molar flux of (A).
2. The interficial concentration of (A).
3. The overall mass transfer coefficient for liquid and gas phases.

Solution:

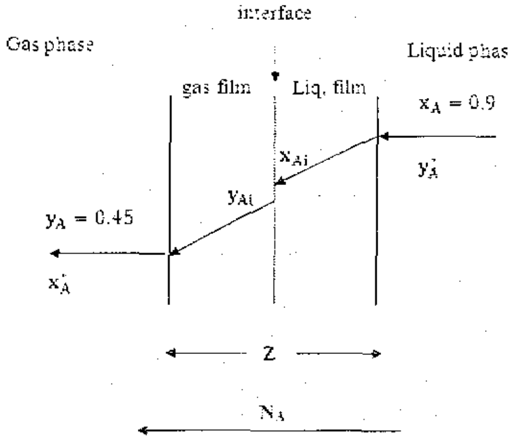
$$\frac{1}{k_g} = 0.7\left(\frac{1}{K_{OG}}\right)$$

$$\frac{1}{0.02716} = 0.7\left(\frac{1}{K_{OG}}\right)$$

$$K_{OG} = 0.019 \quad \frac{\text{kmol}}{\text{m}^2.\,\text{s}}$$

$$N_A = K_{OG}\left(y_A^* - y_A\right)$$

$$y_A^* = 0.75\, x_A = (0.75)(0.9) = 0.675$$



1. $N_A = (0.019)\,(0.675 - 0.45) = 4.274 * 10^{-3} \ \frac{\text{kmol}}{\text{m}^2.\text{s}}$

2. $N_A = k_g\left(y_{A_i} - y_A\right)$

$$4.274 * 10^{-3} = (0.02716)(y_{A_i} - 0.45)$$

$$y_{A_i} = 0.607$$

3. $\frac{1}{K_{OG}} = \frac{1}{k_g} + \frac{H}{k_L}$

$$\frac{1}{0.019} = \frac{1}{0.02716} + \frac{0.75}{k_L}$$

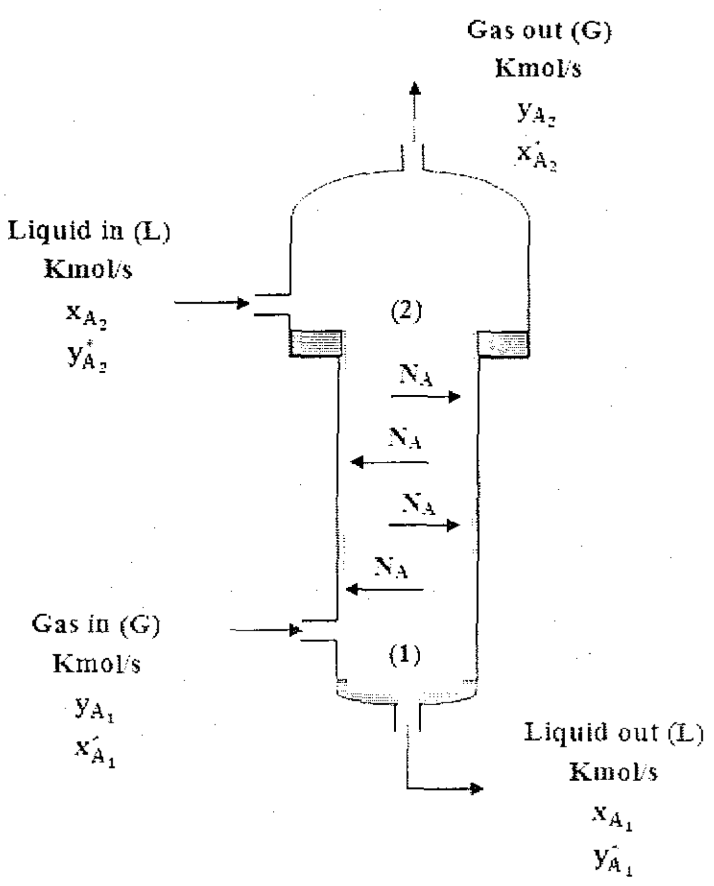
$$k_L = 0.0476$$

$$\frac{1}{K_{OL}} = \frac{1}{H\,k_g} + \frac{1}{k_L}$$

$$\frac{1}{K_{OL}} = \frac{1}{(0.75)(0.02716)} + \frac{1}{0.0476} \quad \rightarrow \quad K_{OL} = 0.0142 \ \frac{\text{kmol}}{\text{m}^2.\,\text{s}}$$

The wetted wall column

The wetted wall column is a small experimental device used to determine the average mass transfer coefficient (K_{OG}). Usually it is (1 - 1.5 inch) in diameter and one meter long.



Let the mass transfer being from gas phase to liquid phase:

$$\bar{W}_A = G\left(y_{A_1} - y_{A_2}\right) = L\left(x_{A_1} - x_{A_2}\right)$$

Where:

$\bar{W}_A$ is the total mole rate diffusion along the column.

At one point in the apparatus the diffusion is as follows:

$$\bar{N}_A = K_{OG} \cdot A \cdot (P_A - P_A^*) \qquad \text{or} \qquad \bar{N}_A = K_{OG} \cdot A \cdot (y_A - y_A^*)$$

$$\sum \bar{N}_{A_i} = \bar{W}_A = \sum K_{OG_i} \cdot A \cdot (\Delta y_A)_i$$

$$\bar{W}_A = K_{OG} \cdot A \cdot \Delta P_{Am} \quad \ldots\ldots\ldots\ldots\ldots \quad \text{(kmol/s)}$$

$$W_A = K_{OG} \cdot \Delta P_{Am} \quad \ldots\ldots\ldots\ldots\ldots \quad \text{(kmol/m}^2\text{.s)}$$

Where:

A is the transfer area (πdL) in (m^2).
ΔP_{Am} is the logarithmic mean of partial pressure.

$$\boxed{\bar{W}_A = K_{OG} \cdot A \cdot \Delta P_{Am}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Now to calculate (K_{OG}) from Eq.(1) we must calculate ($\bar{W}_A$) and (ΔP_{Am}):

1. $$\Delta P_{Am} = \frac{\Delta P_1 - \Delta P_2}{\ln\left[\frac{\Delta P_1}{\Delta P_2}\right]}$$

Where:

$\Delta P_1 = P_{A_1} - P^*_{A_1}$, $P^*_{A_1} = H\,C_{A_1}$

$\Delta P_2 = P_{A_2} - P^*_{A_2}$, $P^*_{A_2} = H\,C_{A_2}$

2. From overall material balance:

$$\bar{W}_A = G\left(y_{A_1} - y_{A_2}\right) = L\left(x_{A_1} - x_{A_2}\right)$$

Where:

y_A and x_A are the mole fraction of component (A) in gas and liquid phase, respectively.

G is the mole flow rate of gas (kmol/s).

L is the mole flow rate of liquid (kmol/s).

We can rewrite the Eq.(1) in the mole fraction form instead of partial pressure as follows:

$$\boxed{\bar{W}_A = K_{OG} \cdot A \cdot \Delta y_{Am}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where:

$$\Delta y_{Am} = \frac{\Delta y_1 - \Delta y_2}{\ln\left[\frac{\Delta y_1}{\Delta y_2}\right]}$$

$\Delta y_1 = y_{A_1} - y^*_{A_1}$ and $y^*_{A_1} = Hx_{A_1}$

$\Delta y_2 = y_{A_2} - y^*_{A_2}$ and $y^*_{A_2} = Hx_{A_2}$

Example: A wetted wall column is used to absorbed NH_3 by water from 6 vol.% in air. The gas flow rate is 1.2 kmol/min at 1 atm and 20°C. Calculate the overall mass transfer coefficient. The data given are:

- The water flow rate to gas flow rate ratio is 1.4.
- The outlet gas concentration is 1.5 vol.%.
- The column height is 100 cm.
- The column diameter is 2 cm.
- Henry's constant is 1.3.

Solution:

$$\bar{W}_A = G\left(y_{A_1} - y_{A_2}\right) = 1.2\,(0.06 - 0.015) = 0.054\ \frac{\text{kmol}}{\text{min}}$$

$$\bar{W}_A = 9 * 10^{-4}\ \frac{\text{kmol}}{\text{s}}$$

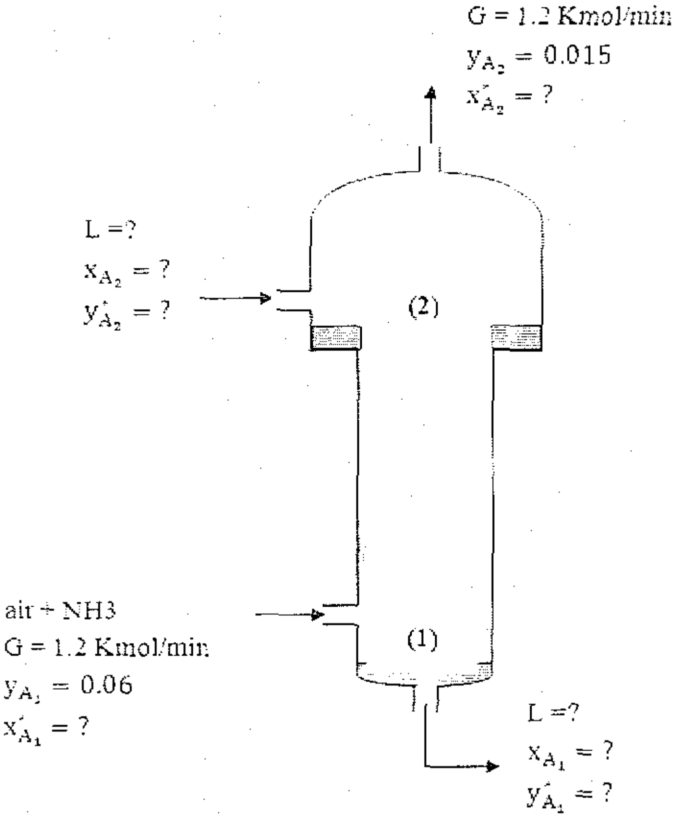
$$A = \pi dL = (3.14)\,(2*10^{-2})\,(1)$$

$$A = 0.06283\ \text{m}^2$$

$$\Delta y_{Am} = \frac{\Delta y_1 - \Delta y_2}{\ln\left[\frac{\Delta y_1}{\Delta y_2}\right]}$$

$$\Delta y_1 = y_{A_1} - y^*_{A_1}$$

$$\Delta y_2 = y_{A_2} - y^*_{A_2}$$



To find (x_{A_1})

$$G\left(y_{A_1} - y_{A_2}\right) = L\left(x_{A_1} - x_{A_2}\right)$$

$$x_{A_1} = \frac{G}{L}\left(y_{A_1} - y_{A_2}\right) + x_{A_2}$$

$$x_{A_1} = \frac{1}{1.4}(0.06 - 0.015) + 0$$

$$x_{A_1} = 0.321$$

$$y^*_{A_1} = Hx_{A_1} = 1.3 * 0.0321 = 0.04173$$

$$y^*_{A_2} = Hx_{A_2} = 1.3 * 0 = 0$$

$\Delta y_1 = y_{A_1} - y^*_{A_1} = 0.06 - 0.04173 = 0.01827$

$\Delta y_2 = y_{A_2} - y^*_{A_2} = 0.015 - 0 = 0.015$

$$\Delta y_{Am} = \frac{0.01827 - 0.015}{\ln\left[\frac{0.01827}{0.015}\right]} = 0.0165$$

$\bar{W}_A = K_{OG} \, . A \, . \, \Delta y_{Am}$

$$K_{OG} = \frac{\bar{W}_A}{A \, . \, \Delta y_{Am}} = \frac{9 * 10^{-4}}{(0.06283)(0.0165)} = 0.868 \; \frac{\text{kmol}}{\text{m}^2 . \text{s}}$$

Mass Transfer Coefficient From Empirical Correlation

Several workers have measured the rate of transfer from a liquid flowing down the inside wall of a tube to a gas passing counter currently upwards. GILLILAND and SHERWOOD vaporized a number of liquids including water, toluene, aniline and propyl, amyl and butyl alcohols into an air stream flowing up the tube in order to measure the individual mass transfer coefficient (k_g). *GILLILAND and SHERWOOD used the empirical* relation below to measure the individual mass transfer coefficient (k_g) and this relation in forms of dimensionless groups:

$$\mathbf{Sh = a\,.(Re)^b.(Sc)^c}$$

Where:

Sh: Sherwood number , $Sh = \frac{k_g\, d}{D}$

Re: Renold's number , $Re = \frac{\rho\, u\, d}{\mu}$

Sc: Schmidt number , $Sc = \frac{\mu}{\rho D}$

k_g individual mass transfer coefficient (m/s).

d: diameter (m).

D: diffusivity (m^2/s).

ρ : density (kg/m^3).

μ : viscosity ($N.s/m^2$).

- When the constant (a), (b) and (c) in the above equation are unknown, then we can take them as below:

$$\mathbf{Sh = 0.023\ (Re)^{0.83}\,(Sc)^{0.44}}$$

Example: Calculate the gas film coefficient for the absorption of sulpher dioxide from a dilute mixture with air in a wetted wall column using Gilliland and Sherwood correlation for wetted wall column for the following data:

- Gas velocity = 2.5 m/s.
- Gas temperature = 293 K.
- Gas viscosity = $1.78 * 10^{-5}$ N.s/m^2.
- Gas density = 1.22 kg/m^3.
- Gas diffusivity = $1.22 * 10^{-5}$ m^2/s.
- Inside column diameter = 25 mm.

Solution:

$$\mathrm{Sh} = 0.023\ (\mathrm{Re})^{0.83}\ (\mathrm{Sc})^{0.44}$$

$$\mathrm{Sh} = \frac{\mathbf{k_g\,d}}{\mathrm{D}} = \mathrm{k_g}\left(\frac{25 * 10^{-3}}{1.2 * 10^{-5}}\right) = 2049\ \mathrm{k_g}$$

$$\mathrm{Re} = \frac{\rho\,\mathrm{u}\,\mathrm{d}}{\mu} = \frac{(1.22)(2.2)(25 * 10^{-3})}{1.78 * 10^{-5}} = 3370$$

$$\mathrm{Sc} = \frac{\mu}{\rho \mathrm{D}} = \frac{1.78 * 10^{-5}}{(1.22)(1.2 * 10^{-5})} = 1.1959$$

$$2049\ \mathrm{k_g} = 0.023\ (3370)^{0.83}\ (1.1959)^{0.44}$$

$$\mathrm{k_g} = 0.01129\ \ \frac{\mathrm{m}}{\mathrm{s}}$$

Chapter (12) in Volume (2)
Absorption of Gases
((Gas – Liquid Separation))

In absorption (also called gas absorption, gas scrubbing, and gas washing), a gas mixture is contacted with a liquid (the absorbent or solvent) to selectively dissolve one or more components by mass transfer from the gas to the liquid. The components transferred to the liquid are referred to as solute or absorbate.

Absorption is used to separate gas mixture; remove impurities, contaminants, pollutants, or catalyst poisons from gas; or recovery valuable chemicals. Thus, the species of interest in the gas mixture may be all components, only the component(s) not transferred, or only the component(s) transferred. The opposite of absorption is ***stripping*** (also called ***desorption***), wherein a liquid mixture is contacted with gas to selectively remove components by mass transfer from the liquid to the gas phase.

There are two types of absorption processes:

1. Physical process (e.g. absorption of acetone from acetone – air mixture by water.
2. Chemical process, sometimes called chemi-sorption (e.g. absorption of nitrogen oxides by water to produce nitric acid.

Equipment:

Absorption and stripping are conducted in tray towers (plate column), packed column, spray tower, bubble column, and centrifugal contactors. The first two types of these equipment will be considered in our course for this year.

1. Tray tower:

A tray tower is a vertical, cylindrical pressure vessel in which gas and liquid, which flow counter currently, are contacted on a series of metal trays or plates. Liquid flows across any tray over an outlet weir, and into a down comer, which takes the liquid by gravity to the tray below. The gas flows upward through opening in each tray, bubbling through the liquid on the other tray. A schematic diagram for the flow patterns inside the tray column is shown below.

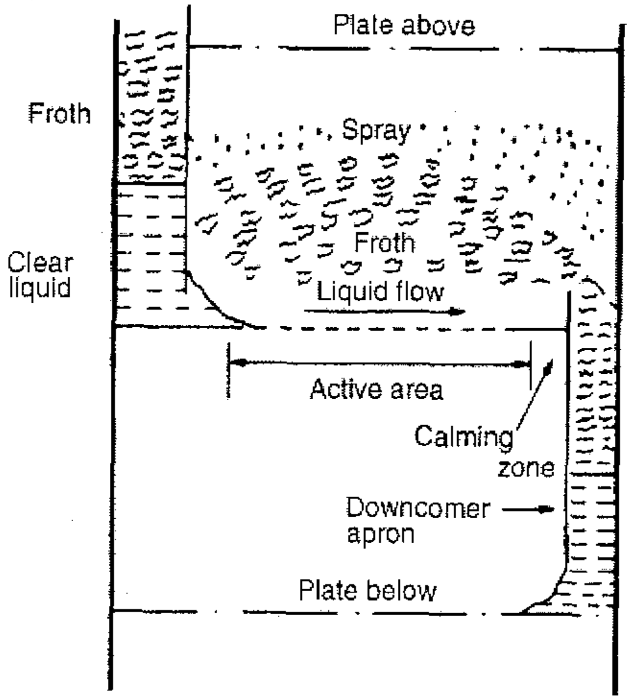


Figure : Typical cross-flow plate (sieve)

2. Packed tower:

The packed column is a vertical, cylindrical pressure vessel containing one or more section of packing material over who's the liquid flows down wards by gravity as a film or as droplets between packing elements. Gas flows upwards through the wetted packing contacting the liquid. The sections of packing are contained between a lower gas – injection support plate, which holds the packing, and an upper grid or mish hold – down plate, which prevent packing movement. A liquid distributor, placed above the hold – down plate, ensures uniform distribution of liquid as it enters the packing section.

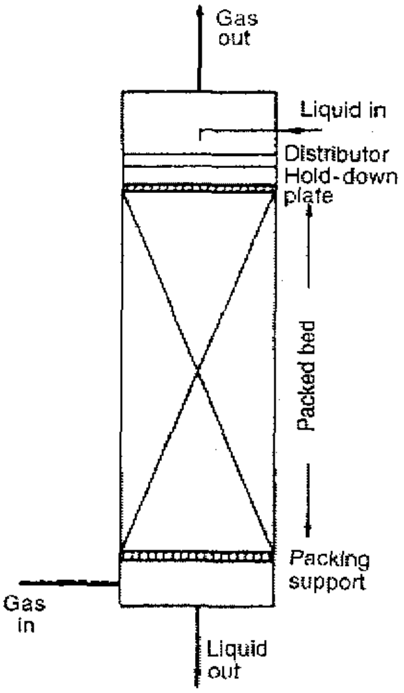


Figure: Packing absorber column.

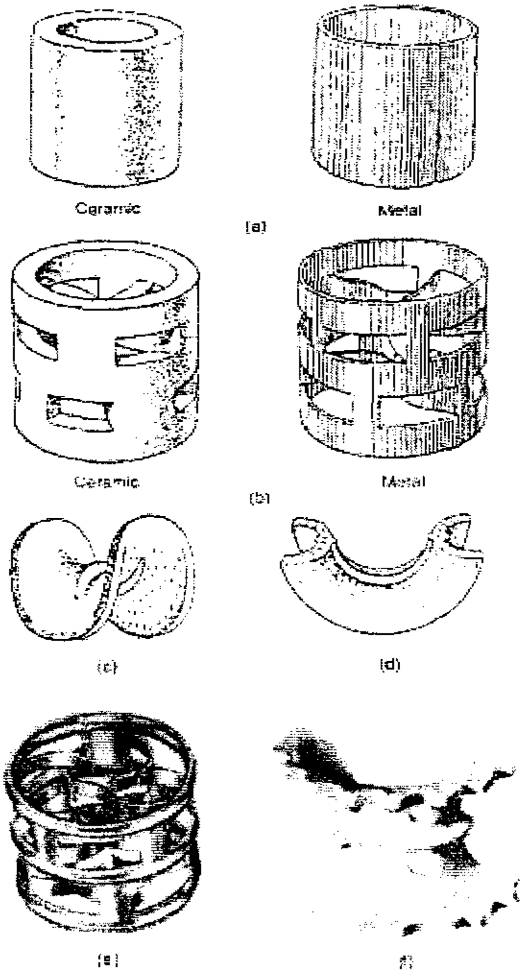


Figure: Types of packing (a) Raschig rings (b) Pall rings (c) Berl saddle ceramic (d) Intalox saddle ceramic (e) Metal Hypac (f) Ceramic, super Intalox.

General Design Consideration:

Design or analysis of an absorber (or stripper) requires consideration of a number of factors, including:

1. Entering gas (liquid) flow rate, composition, temperature, and pressure.
2. Design degree of recovery (R) of one or more solutes.
3. Choice absorbent (solvent) agent.
4. Operating pressure and temperature and allowable pressure drop.
5. Minimum absorbent (solvent) agent flow rate and actual solvent flow rate as a multiple of the minimum rate needed to make the separation.
6. Number of equilibrium stages.
7. Heat effects and need for cooling (heating).
8. Type of absorber (stripper) equipment.
9. Height of absorber (stripper) column.
10. Diameter of absorber (stripper) column.

The ideal absorbent (solvent) should have:

a. High solubility for the solute(s) to minimize the need for absorbent (solvent).
b. A low volatility to reduce the loss of absorbent (solvent) and facilitate separation of absorbent (solvent) from solute(s). 84
c. Be stable to maximize absorbent (solvent) life and reduce absorbent makeup requirement.
d. Be non – corrosive to permit use of common material of construction.
e. Have a low viscosity to provide low pressure drop and high mass and heat transfer rates.
f. Be non – foaming when contacted with gas so as to make it unnecessary.
g. Be non – toxic and non – flammable to facilitate its safe use.
h. Be available, if possible.

The most widely absorbent (solvent) used are water, hydrocarbon oils, and aqueous solutions of acids and bases. While the most common stripping agents used are water vapor, air, inert gases, and hydrocarbon gases.

Equilibrium Relations Between Gas and Liquid Phases:

The equilibrium of any gas-liquid system can be expressed as:

Non-ideal system (Henry's law):

$P_A = H\,x_A$ divided by (P_T)

$$\frac{P_A}{P_T} = \frac{H}{P_T}\,x_A$$

$$\mathbf{y_A = m\,x_A}$$

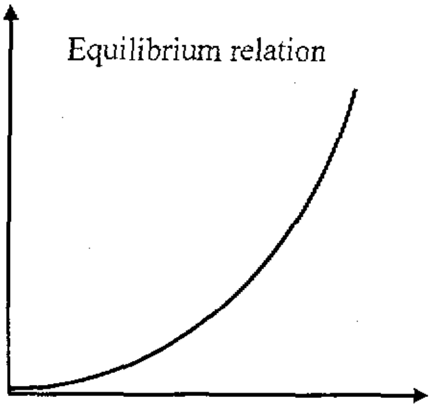
Ideal system (Raoult's law):

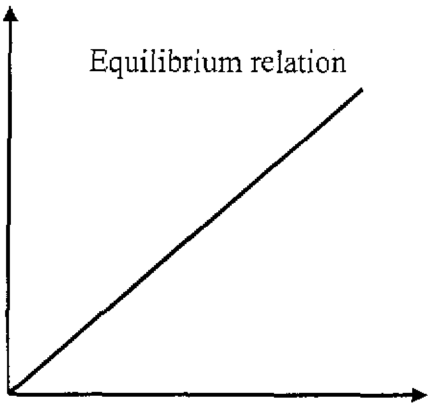
$P_A = P_A^0\,x_A$ divided by (P_T)

$$\frac{P_A}{P_T} = \frac{P_A^0}{P_T}\,x_A$$

$$\mathbf{y_A = m\,x_A}$$

* في عمليات الامتصاص من المهم جدا معرفة طبيعة علاقة التعادل (وهي العلاقة بين تركيز المذاب (A) في الغاز ($\mathbf{Y_A}$) مع تركيز المذاب (A) في السائل ($\mathbf{X_A}$)) . فقد تكون علاقة التعادل بين ($\mathbf{X_A}$) و ($\mathbf{Y_A}$) علاقة خطية أو علاقة غير خطية اعتمادا على طبيعة المواد وتركيز المذاب.





Where:

$\mathbf{X_A}$: is the mole ratio of solute in liquid phase (A/C).

$\mathbf{Y_A}$: is the mole ratio of solute in gas phase (A/B).

Notes:

The equilibrium relation is the ratio between the *mole ratio* of solute in gas phase (Y_A) and the *mole ratio* of solute in liquid phase (X_A). The equilibrium relation may be linear or no linear.

* إذا كانت علاقة التعادل خطية فتعطى بالشكل التالي ($Y_A = m X_A$).

* أما إذا أعطيت علاقة التعادل بشكل بيانات كما في أدناه:

X_A	-	-	-	-	-	-
Y_A	-	-	-	-	-	-

ففي هذه الحالة لمعرفة طبيعة علاقة التعادل فيتم رسم البيانات أولا فإذا كان الرسم بين X_A و Y_A هو خط مستقيم عند ذاك سوف يتم اخذ الميل من الرسم فقط وتكوين علاقة التعادل ($Y_A = m X_A$).

أما إذا كان الرسم الناتج بين X_A و Y_A بشكل منحني فعند ذاك سيكون الحل بالرسم.

* في بعض الأحيان تعطى علاقة التعادل بين الضغط الجزيئي (P_A) والنسبة المولية (x_A) كما في علاقة راؤول أو هنري ففي هذه الحالة يجب تحويلها الى علاقة بين (X_A , Y_A).

The relation between the mole fraction and mole ratio:

$$\boxed{Y_A = \frac{y_A}{1 - y_A}} \quad \textit{and} \quad \boxed{X_A = \frac{x_A}{1 - x_A}}$$

Where:

x_A and y_A : are the mole fractions of solute (A) in liquid and gas phases, respectively.

X_A and Y_A : are the mole ratio of solute (A) in liquid and gas phases, respectively.

The relation between the mole fraction and weight fraction:

$$\boxed{\mathbf{wt.\,\% = \frac{(mol\%) * (M.wt)}{\sum[(mol\%) * (M.wt)]}}}$$

$$\boxed{\mathbf{mol\% = \frac{(wt.\,\%)\,/(M.wt)}{\sum[(wt.\,\%)/(M.wt)]}}}$$

Where:

wt. % : is the weight fraction.

mol% : is the mole fraction.

M. wt : is the molecular weight.

Symbols used in the absorption processes:

A solute (A) in a mixture (A, B) shall be absorbed in Liquid (C), the inert gas (B) is insoluble in solvent (C). The following symbols will be used:

$\mathbf{G}$: is the mole rate of the gas mixture (A + B), kmol/s.

$\mathbf{G_s}$: is the mole rate of the inert (insoluble) gas (B), kmol/s.

$\mathbf{\bar{G}}$: is the mole flux of the gas mixture (A + B), kmol/m^2.s.

$\mathbf{\bar{G}_s}$: is the mole flux of the inert (insoluble) gas (B), kmol/m^2.s.

$\mathbf{L}$: is the mole rate of the liquid mixture (A + C), kmol/s.

$\mathbf{L_s}$: is the mole rate of the liquid solvent only (C), kmol/s.

$\mathbf{\bar{L}}$: is the mole flux of the liquid mixture (A + C), kmol/m^2.s.

$\mathbf{\bar{L}_s}$: is the mole flux of the liquid solvent only (C), kmol/m^2.s.

$\mathbf{x_A}$: is the mole fraction of solute (A) in liquid, (A /A+C).

$\mathbf{y_A}$: is the mole fraction of solute (A) in gas, (A /A+B).

$\mathbf{X_A}$: is the mole ratio of solute (A) in liquid, (A / C).

$\mathbf{Y_A}$: is the mole ratio of solute (A) in gas, (A / B).

Calculation of Tower Height

The physical absorption process can be carried out in countercurrent flow process, which may be carried out in packed or tray column:

Packed Tower

Z = HOG * NOG

Where:

HOG: is the height of transfer unit (HTU) based on gas phase, and it can be calculated from the equation below:

$$HOG = \frac{\bar{G}_s}{KoG.\,a} \quad \text{, in (meter)}$$

NOG: is the number of transfer unit (NTU) based on gas phase, and it can be calculated based on equilibrium data:

- If the equilibrium data are ***linear***, then **NOG** will be calculated using a suitable equation.
- If the equilibrium data are ***non-linear***, then **NOG** will be calculated graphical method.

Tray Tower

Z = H * N

Where:

H : is the distance between two trays, and it is given (0.3 - 0.7 m)

N : is the number of trays, and it can be calculated based on equilibrium data:

- If the equilibrium data are ***linear***, then **N** will be calculated using a suitable equation.
- If the equilibrium data are ***non-linear***, then **N** will be calculated graphical method.

1. Packed tower:

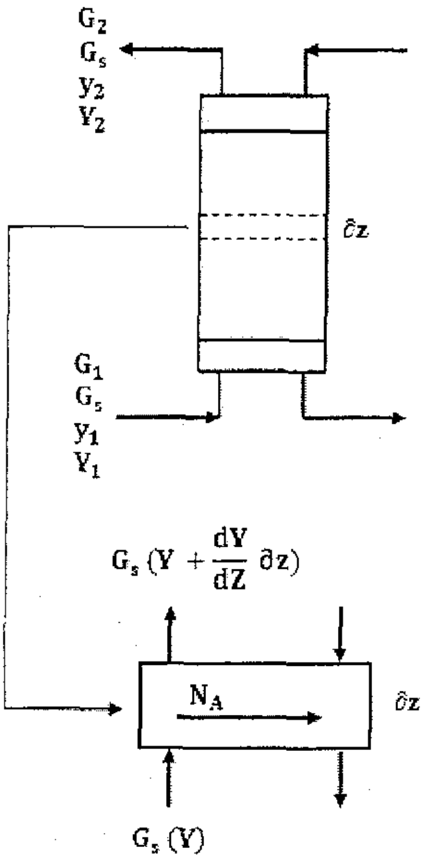
Absorption and stripping are frequently conducted in packed columns, particularly when:

(1) the required column diameter is less than 0.6 m.
(2) the pressure drop must be low, as for a vacuum service.
(3) corrosion consideration favor the use of ceramic or polymeric material.
(4) low liquid holdup is desirable.

The gas liquid contact in a packed bed column is continuous, not stage-wise, as in a plate column. The liquid flows down the column over the packing surface and the gas or vapour, counter-currently, up the column. In some gas-absorption columns co-current flow is used. The performance of a packed column is very dependent on the maintenance of good liquid and gas distribution throughout the packed bed, and this is an important consideration in packed-column design.

Calculations of the packing height:

Overall material balance on the solute (A) over an element (∂z) based on gas phase:



$$\mathbf{G_S.\ A\,.\,dY = L_S.\ A\,.\,dX = N_A}$$

$$\mathbf{N_A = G_s Y - \ G_s \left(Y + \frac{dY}{dZ}\,\partial z\right) = (KoG)(a\ \ S\ \partial z)(Y - Y^*)}$$

Where:

The interficial area for transfer = a dV = a S ∂z

S: is the cross-sectional area of column (m^2).

a: is the surface area of interface per unit volume of column (m^2/m^3).

$$\mathbf{-\,G_s \left(Y + \frac{dY}{dZ}\,\partial z\right) = (KoG.a)(S\,.\,\partial z)(Y - Y^*)}$$

$$G_s \frac{dY}{dZ} = -(KoG.a)(S\,.\,\partial z)(Y - Y^*)$$

$$\int_0^Z dZ = \frac{-G_s}{(KoG.a).S} \int_{Y_1}^{Y_2} \frac{dY}{(Y - Y^*)}$$

$$Z = \frac{(G_s/S)}{KoG.a} \int_{Y_1}^{Y_1} \frac{dY}{(Y - Y^*)}$$

$$\boxed{Z = \frac{\overline{G}_s}{KoG.a} \int_{Y_1}^{Y_1} \frac{dY}{(Y - Y^*)}}$$

$$\boxed{Z = HOG * NOG = HTU * NTU}$$

Where:

$HOG = \dfrac{\overline{G}_s}{KoG.a}$: heiht of transfer unit (HTU) based on gas phase, with the units of (m).

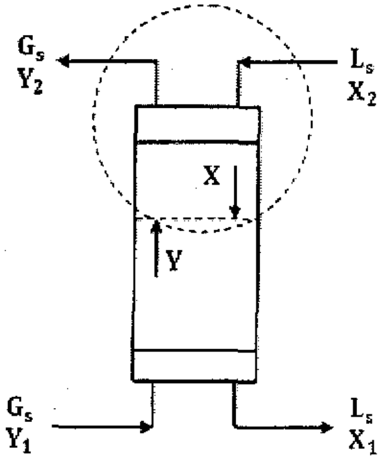
$NOG = \displaystyle\int_{Y_1}^{Y_1} \frac{dY}{(Y - Y^*)}$: number of transfer unit (NTU) based on gas phase, without units.

Equation of the operating line:

Solute material balance between one end of the column and any point will give:

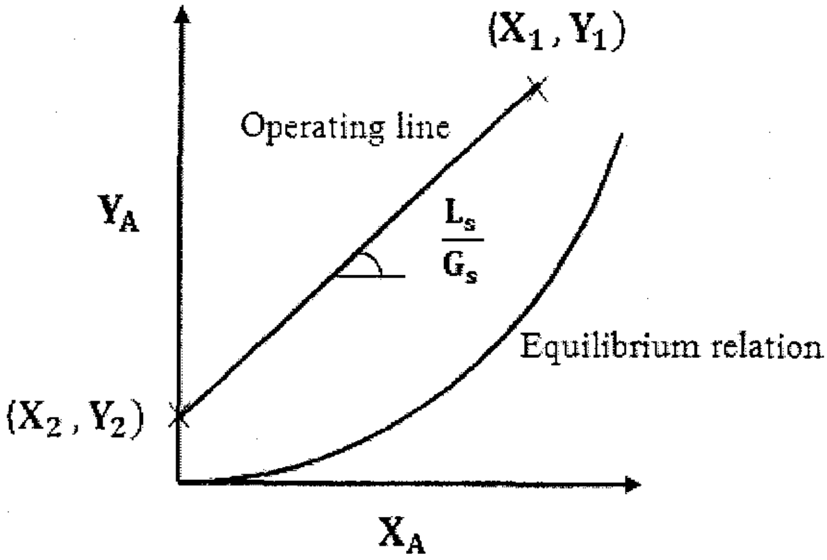
$$G_s\,(Y - Y_2) = L_s\,(X - X_2)$$

$$\boxed{Y = \frac{L_s}{G_s}(X - X_2) + Y_2}$$



* The equation of operating line is a relation between mole ratio of solute in gas phase (Y) and the mole ratio of solute in liquid phase.

* The operating line can be draw from two points **(X_1, Y_1)** and **(X_2, Y_2)**, or from its slope ($\frac{L_s}{G_s}$) and one of the two points.



Calculation of Number of Transfer Unit (NOG):

A. **For Linear Equilibrium Relationship** ($Y^* = m\,X$):

$$NOG = \int_{Y_1}^{Y_1} \frac{dY}{(Y - Y^*)} \qquad \text{………………………………(1)}$$

$$Y^* = m\,X \qquad \text{………………………………(2)}$$

$$G_s\,(Y - Y_2) = L_s\,(X - X_2) \qquad \text{………………………………(3)}$$

$$\Longrightarrow \quad X = \frac{G_s}{L_s}(Y - X_2) + X_2$$

For pure liquid solvent used then, $X_2 = 0$

$$X = \frac{G_s}{L_s}(Y - Y_2) \qquad \text{………………………………(4)}$$

Substitution Eq.(4) into Eq.(2) to get:

$$Y^* = \frac{m\,G_s}{L_s}(Y - Y_2) \qquad \text{………………………………(5)}$$

Substitution Eq.(5) into Eq.(1) to get:

$$\mathbf{NOG} = \int_{Y_1}^{Y_1} \frac{\mathbf{dY}}{(Y - \frac{m\,G_s}{L_s}(Y - Y_2))}$$

Let: $\frac{m\,G_s}{L_s} = \phi = \frac{\textbf{Slope of equilibrium line}}{\textbf{Slope of operating line}} = \frac{m}{L_s/G_s} < 1.0$

$$\mathbf{NOG} = \int_{Y_1}^{Y_1} \frac{\mathbf{dY}}{Y - \phi Y + \phi Y_2}$$

$$\mathbf{NOG} = \int_{Y_1}^{Y_1} \frac{\mathbf{dY}}{(1 - \phi)Y + \phi Y_2}$$

$$\mathbf{NOG} = \frac{1}{(1 - \phi)} \ln\left[\frac{(1 - \phi)Y_1 + \phi Y_2}{(1 - \phi)Y_2 + \phi Y_2}\right]$$

NOG =

NOG =

B. For Non-linear Equilibrium Relationship:

In this case the integration [$\mathrm{NOG} = \int_{Y_1}^{Y_1} \frac{dY}{(Y-Y^*)}$] will be solved using graphical method or numerical method (Simpson rule) following steps below:

1. Draw the given equilibrium data.
2. Draw the operating line, from two points (X_1, Y_1) and (X_2, Y_2) or one point and slope of $(\frac{L_s}{G_s})$.
3. Create the table below by calculated (Y^*) from the plot as below:

Y Assume points between (Y_1 - Y_2)	Y* Calculated from plot	$\frac{1}{(Y-Y^*)}$
Y_1	- calculated	$\surd = f_0$
- (assumed)	- calculated	$\surd = f_1$
- (assumed)	- calculated	$\surd = f_2$
- (assumed)	- calculated	$\surd = f_3$
Y_2	- calculated	$\surd = f_n$

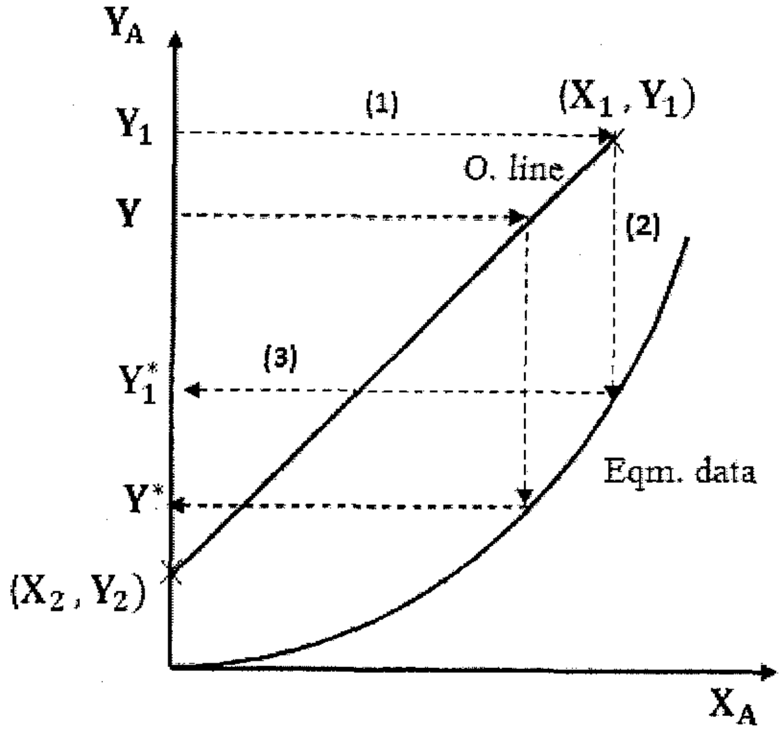
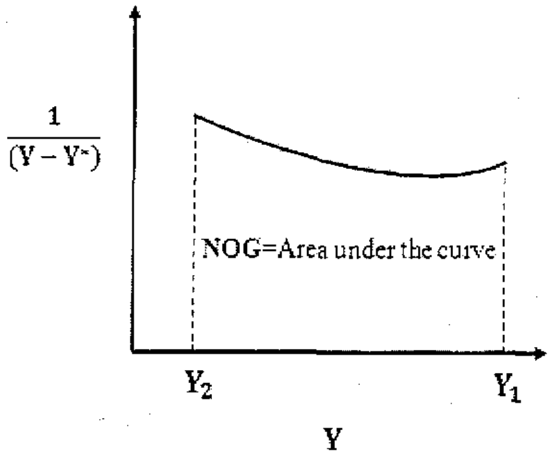


Figure: Calculation of (Y*) for packed column.

4. To calculate **NOG** we draw $[\frac{1}{(Y-Y^*)}]$ Vs. [Y] to find the area under the curve:

Where:

NOG = Area under the curve



Simpson rule for calculation of NOG:

NOG = Area under the curve

$$\boxed{\mathrm{NOG} = \frac{h}{3}\left[f_0 + f_n + 2\sum f_{even} + 4\sum f_{odd}\right]}$$

Where:

$$h = \frac{Y_1 - Y_2}{n} \qquad , \qquad n = 2, 4, 6, 8, \dots\dots \text{etc.}$$

Notes:

* If the entering solute concentration is dilute (Y < 5%), then:

$$Y_A = y_A \quad , \quad X_A = x_A \quad , \quad G_s = G \quad , \quad L_s = L$$

* If the tower type is not mention in the problem we can take it as a packed tower.

Example (1):

Ammonia is to be removed from a 10 percent ammonia–air mixture by countercurrent scrubbing with water in a packed tower at 293 K so that 99 percent of the ammonia is removed when working at a total pressure of 101.3 kN/m^2. If the gas rate is 0.95 kg/m^2.s of tower cross-section and the liquid rate is 0.65 kg/m^2. s, find the necessary height of the tower if the absorption coefficient KoG.a = 0.008 kmol/m^3.s. kPa., The equilibrium data are: $Y^* = m X$.

Solution:

$$Y_2 = (1 - recovery)\, Y_1 = (1 - 0.99)(0.1) = 0.001$$

Convert mole fraction to mole ratio:

$$Y_1 = \frac{y_1}{1 - y_1} = \frac{0.1}{1 - 0.1} = 0.11$$

$$Y_2 = \frac{y_2}{1 - y_2} = \frac{0.001}{1 - 0.001} = 0.001$$

We can see that at low conc. (mole ratio = mole fraction):

$$\text{The gas mole flux, } \bar{\mathbf{G}} = \frac{\text{gas mass flux}}{\text{average gas molecular weight}}$$

$$= \frac{0.95}{[(0.1)(17) + (0.9)(29)]} = 0.0341 \ \frac{\text{kmol}}{\text{m}^2.\text{s}}$$

$$\text{The liquid mole flux, } \bar{\mathbf{L}} = \frac{\text{liquid mass flux}}{\text{average liquid molecular weight}}$$

$$= \frac{0.65}{(18)} = 0.0361 \ \frac{\text{kmol}}{\text{m}^2.\text{s}}$$

the mole flux of the inert gas , $\bar{\mathbf{G}}_s = \bar{\mathbf{G}}(\mathbf{1} - \mathbf{y_1}) = (0.0341)(1 - 0.1) = 0.0307 \ \frac{\text{kmol}}{\text{m}^2.\text{s}}$

the mole flux of the inert liquid , $\bar{\mathbf{L}}_s = \bar{\mathbf{L}}(\mathbf{1} - \mathbf{x_1}) = (0.0361)(1 - 0) = 0.0361 \ \frac{\text{kmol}}{\text{m}^2.\text{s}}$

Therefore, for pure solvent: $\bar{\mathbf{L}}_s = \bar{\mathbf{L}}$

$$\text{HOG} = \frac{\bar{G}_s}{\text{KoG. a. P}_T} = \frac{0.0307}{(0.0008)(101.3)} = 0.38 \ \text{m}$$

Since the equilibrium is linear:

NOG = -

$$\phi = \frac{m\,\bar{G}_s}{\bar{L}_s} = \frac{(0.8)(0.0307)}{(0.0361)} = 0.68$$

NOG = -

Z = HOG * NOG = (0.38) (11.19) = 4.25 m

Example (2):

Ammonia is to be removed from a 10 percent ammonia–air mixture by countercurrent absorption with water in a packed tower at 293 K. The outlet gas concentration from the top of the tower is 0.1%. The absorption tower is working at a total pressure of 101.3 kN/m^2. If the inlet gas is 0.034 kmol/m^2.s and the liquid rate is 0.036 kmol/m^2. s, find the necessary height of the tower if the absorption coefficient KoG.a = 0.081 kmol/m^3.s. The equilibrium data is given by the following data:

kmol NH_3/kmol water:	0.021	0.031	0.042	0.053	0.079	0.106	0.159
Partial pressure NH_3 in gas phase (kN/m^2):	1.6	2.4	3.3	4.2	6.7	9.3	15.2

Solution:

First of all we have to convert the equilibrium data to mole ratio:

$$\mathit{mole\ fraction\ of\ NH_3\ in\ gas\ phase}\ , y_{NH_3} = \frac{P_A}{P_T} = \frac{\mathbf{1.6}}{101.3} = \mathbf{0.0158}$$

$$\mathit{mole\ ratio\ of\ NH_3\ in\ gas\ phase}\ , Y_{NH_3} = \frac{y_{NH_3}}{1 - y_{NH_3}} = \frac{0.0158}{1 - 0.0158} = \mathbf{0.0160}$$

The equilibrium data becomes:

$\mathbf{X_{NH_3}}$	0.021	0.031	0.042	0.053	0.079	0.106	0.159
$\mathbf{Y_{NH_3}}$	**0.0160**	0.0243	0.337	0.0433	0.0708	0.1011	0.1765

$$\mathrm{HOG} = \frac{\overline{G}_S}{\mathrm{KoG.a}} = \frac{0.034}{0.081} = 0.419\ \mathrm{m}$$

$$\mathbf{NOG} = \int_{Y_1}^{Y_1} \frac{\mathbf{dY}}{(\mathbf{Y} - \mathbf{Y}^*)}$$

The equilibrium data may be not linear relation, so that the integration should be solved by plotting or by Simpson's rule as follows:

1. Draw the equilibrium data:
2. Draw the operating line from two points:
   (X_1, Y_1) and (X_2, Y_2)

$$Y_1 = \frac{y_1}{1-y_1} = \frac{0.1}{1-0.1} = 0.11$$

$$Y_2 = \frac{y_2}{1-y_2} = \frac{0.001}{1-0.001} = 0.001$$

Overall ammonia material balance:

$$\bar{G}_s (Y_1 - Y_2) = \bar{L}_s (X_1 - X_2)$$

$$X_1 = \frac{\bar{G}_s}{\bar{L}_s}(Y_1 - Y_2) + X_2 = \frac{0.034}{0.036}(0.11 - 0.001) + 0$$

$$X_1 = 0.0935$$

Operating line:

$(X_1, Y_1) = (0.0935, 0.11) = (9.35*10^{-2}, 10*10^{-2})$

$(X_2, Y_2) = (0, 0.001) = (0, 0.1*10^{-2})$

We will solve the integration by Simpson's rule:

$$h = \frac{Y_1 - Y_2}{n} \quad , \quad We\ choose\ \ n = 4$$

$$h = \frac{0.11 - 0.001}{4} = 0.02725$$

Calculate Y^* from the plot as follows:

Y Assume points between (Y_1 - Y_2)	Y^* Calculated from plot	$\frac{1}{(Y - Y^*)}$
0.11	0.088	$45.45 = f_0$
0.08275	0.061	$45.98 = f_1$
0.05550	0.0375	$55.56 = f_2$
0.02825	0.0175	$93.02 = f_3$
0.001	0.00	$1000 = f_n$

$$\mathbf{NOG} = \frac{\mathbf{h}}{3}\left[\mathbf{f_0} + \mathbf{f_n} + 2\sum \mathbf{f_{even}} + 4\sum \mathbf{f_{odd}}\right]$$

$$\mathbf{NOG} = \frac{0.02725}{3}\;[45.45 + 1000 + 2(55.56) + 4[(45.98) + (93.02)]]$$

$$\mathbf{NOG} = 15.56$$

$$\mathbf{Z} = \mathbf{HOG} * \mathbf{NOG} = (0.419)(15.56) = 6.52\ \mathrm{m}$$