By : iman hussein

MASS TRANSFER

Introduction:-

Mass transfer is a transport of components under a chemical potential gradient. The component moves to the direction of reducing concentration gradient. The transport occurs from a region of higher concentration to lower concentration. Equilibrium is reached when the gradient is zero. The transport or migration of one constituent from a region of higher concentration to that of a lower concentration is known as mass transfer.

Mass transfer operations depend on molecules diffusing from one distinct phase to another and are based upon differences in the physicochemical properties of the molecules, such as vapour pressure or solubility. For interphase mass transfer, there is a concentration gradient between bulk and interface, however under steady state, at interface equilibrium is assumed. Mass transfer operation plays an important role in many industrial processes. A group of operations for separating the components of mixtures is based on the transfer of material from one homogeneous phase to another. These methods is covered by the term mass transfer operations which include techniques like gas absorption and stripping,liquid-liquid extraction, leaching, distillation, humidification, drying, crystallization and number of other separation techniques.

Mass transfer and diffusion :-

When mass is being transferred from one distinct phase to another or through a single phase, the basic mechanism are the same whether the phase is gas, liquid or solid.

$$\text{Rate of transfer process} = \frac{Driving\ force}{Resistance}$$

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The transfer of molecules from a higher concentration to lower concentration is often called diffusion. The rate of molecular diffusion is connected with concentration and fluxes.

Concentration and Flux

1.Concentration:

The concentration of particular species is expressed in variety of ways. In mass transfer operation, the concentration gradient is the driving force when other driving forces (temperature, pressure gradients, etc.) are kept constant. The actual driving force for mass transfer to occur is to create gradient of chemical potential (between two points) which is a function of all external forces. The concentration gradients are generally expressed in terms of mass concentration of component, molar concentration of component and mass or mole fraction of species.

Mass concentration

The mass concentration of species i is expressed as ρ_i. It is defined as the mass of i per unit volume of a multi-component mixture; that is:

$$\rho_i = \frac{m_i}{V} \qquad (1.1)$$

It has the same unit as density. Total mass concentration within a mixture is equal to overall density which can be expressed as

$$\rho = \sum_{i=1}^{n} \rho_i \qquad (1.2)$$

where n is the number of species in the mixture.

Mass fraction

The mass fraction of species i is defined by the ratio of mass concentration of species i to the total mass density. It can be expressed as:

$$w_i = \frac{\rho_i}{\sum\limits_{i}^{n} \rho_i} = \frac{\rho_i}{\rho} \qquad (1.3)$$

From Equations (1.2) and (1.3), it is shown that

$$\sum_{i=1}^{n} w_i = \sum_{i=1}^{n} \frac{\rho_i}{\rho} = 1 \qquad (1.4)$$

Molar Concentration:-

The molar concentration of component is denoted by C_i. It is defined as moles of the component per unit volume of mixture. The total concentration in the system can be obtained by sum up all molar concentrations for all species which can be represented as:-

$$C = \sum_{i=1}^{n} C_i \qquad (1.5)$$

Sometimes it is required to convert from mass to molar concentration. This can be accomplished by dividing the mass concentration of species i by the molar weight of that species. For an ideal gas mixture the molar concentration of species i can be obtained from the ideal gas law (PV = nRT) as

$$C_i = \frac{p_i}{RT} \qquad (1.6)$$

where p_i is the partial pressure of species i in the mixture, T is the absolute temperature and R is the universal gas constant. So total concentration in the gaseous system can be represented by

$$C = \frac{1}{RT} \sum_{i=1}^{n} p_i = \frac{P_t}{RT} \qquad (1.7)$$

where P_t is the total pressure of the system which is sum of partial pressures of all components.

Mole fraction

The mole fraction of species i is found by dividing the molar concentration of species i by total concentration in the system which is expressed as

$$x_i = \frac{C_i}{C} \quad \text{for liquid and solid} \qquad (1.8)$$

and

$$y_i = \frac{p_i}{P_t} \quad \text{for gases} \qquad (1.9)$$

If it is summed over all species, then one can get $\sum_i x_i = 1$ and $\sum_i y_i = 1$.

1.2.2 Fluxes

The flux is defined as the rate of transport of species i per unit area in a direction normal to the transport. The flux is calculated with respect to a fixed reference frame. The molar flux of species i can be represented as

$$N_{i-mol} = C_i u_i \qquad (1.10)$$

Here $N_{i-molar}$ is the molar flux of species i and u_i is the velocity of i with respect to a fixed reference frame. In the same fashion, a mass flux, N_{i-mass} can be represented as

$$N_{i-mass} = \rho_i u_i \qquad (1.11)$$

The units of the molar and mass fluxes are moles/m^2.s and mass/m^2.s. Sometimes it is convenient to interpret the total flux of species i with respect to an arbitrary reference frame rather than a fixed set of reference frame. The molar flux of species i based on arbitrary reference velocity u_0 is denoted by J_{i-mol} which can be defined as

$$J_{i-mol} = C_i (u_i - u_0) \qquad (1.12)$$

Similarly mass flux of species i based on arbitrary reference velocity u_0 is denoted by J_{i-mass} which can be expressed as

$$J_{i-mass} = \rho_i (u_i - u_0) \qquad (1.13)$$

In a system, since several molecular species move with different average velocities, a frame of moving reference must be chosen. The important moving references are mass average, molar average and volume average velocities.

Mass-average velocity

The mass average velocity can be defined in terms of the mass concentration and the velocity of species i based on fixed axis. It is expressed as

$$U_{mass} = \frac{\sum_{i=1}^{n} \rho_i u_i}{\sum_{i=1}^{n} \rho_i} \qquad (1.14)$$

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Molar average velocity

The molar average velocity can be expressed by the expression analogous to the mass average velocity. It can be represented by replacing mass concentration of species i, ρ_i with molar concentration of species i, C_i :

$$U_{mol} = \frac{\sum\limits_{i-1}^{n} C_i u_i}{\sum\limits_{i-1}^{n} C_i} \qquad (1.15)$$

Volume average velocity

For experimental analysis the volume average velocity is important due to a fixed system of constant volume. The volume average velocity can be expressed by

$$U_{vol} = \sum\limits_{i-1}^{n} \bar{v}_i C_i u_i \qquad (1.16)$$

where $\bar{v}_i$ is the partial molar volume of species i.

Relation between fluxes

One can obtained the molar flux of i expressed in Equation (1.12) with respect to the molar average velocity as

$$J_{i-mol} = C_i \left(u_i - U_{mol} \right) \qquad (1.17)$$

Substituting the Equation (1.10) into the Equation (1.17) and rearranging gibes

$$N_{i-mol} = J_{i-mol} + C_i U_{mol} \qquad (1.18)$$

Again substituting the definition of molar average velocity defined in Equation (1.15) into the Equation (1.18) we get

$$N_{i-mol} = J_{i-mol} + C_i \frac{\sum\limits_{i-1}^{n} C_i u_i}{\sum\limits_{i-1}^{n} C_i} \qquad (1.19)$$

Or

$$N_{i-mol} = J_{i-mol} + x_i \sum\limits_{i-1}^{n} N_{i-mol} \qquad (1.20)$$

For binary system of component A and B, $\sum_{i-1} N_{i-mol} = N_A + N_B = N$. Therefore the Equation (1.20) can be written for binary system as

$$N_{A-mol} = J_{A-mol} + x_A N \qquad (1.21)$$

Example 1:- A gas mixture ($N_2 = 5\%$, $H_2 = 15\%$, $NH_3 = 76\%$ and Ar $= 4\%$) flows through a pipe 25.4 mm in diameter at 4.05 bar total pressure. If the velocities of the respective components are 0.03 m/s , 0.035 m/s , 0.03 m/s and 0.02 m/s. Calculate mass average velocity and molar average velocity of the mixture?

M.wt for : $N_2 = 28$ $NH_3 = 17$ $Ar = 40$

Solution:-

1) To find mass average velocity:-

$$U = \frac{1}{\rho}(\rho_1 u_1 + \rho_2 u_2 + \rho_3 u_3 + \rho_4 u_4)$$

$$\rho_i = P_i . M_i / R. T$$

$$\rho_T = P_T . M_T / R. T$$

$$U = \frac{R.T}{P.M} (\frac{P.M}{R.T}u_1 + \frac{P.M}{R.T}u_2 + \frac{P.M}{R.T}u_3 + \frac{P.M}{R.T}u_4)$$

$$U = \frac{1}{M_T} (\frac{P_1}{P_T} M_1 u_1 + \frac{P_2}{P_T} M_2 u_2 + \frac{P_3}{P_T} M_3 u_3 + \frac{P_4}{P_T} M_4 u_4)$$

$$y_i = \frac{P_i}{P_T}$$

therefor $U = \frac{1}{M_T} (y_1 M_1 u_1 + y_2 M_2 u_2 + y_3 M_3 u_3 + y_4 M_4 u_4)$

$$M_T = y_1 M_1 + y_2 M_2 + y_3 M_3 + y_4 M_4$$

$$M_T = 0.05 * 28 + 0.15 * 2 + 0.76 * 17 + 0.04 * 40$$

$$= 16.22$$

$$U = \frac{1}{16.22} (0.05 * 28 * 0.03 + 0.15 * 2 * 0.035 + 0.76 * 17 * 0.03 + 0.04 * 40 * 0.02)$$

$$U = 0.029 \text{ m/s}$$

2) To find molar average velocity:-

$$U_{mol.} = \frac{1}{C_T} (C_1 u_1 + C_2 u_2 + C_3 u_3 + C_4 u_4)$$

$y_i = \frac{C_i}{C_T}$ for vapor and gas

$U_{mol.} = 0.05 * 0.03 + 0.15 * 0.035 + 0.76 * 0.03 + 0.04 * 0.02$

$\qquad = 0.0303$ m/s

molar average velocity $=$ mass average velocity (for gases)

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DIFFUSION

STEADY-STATE ORDINARY MOLECULAR DIFFUSION:-

Suppose a cylindrical glass vessel is partly filled with water containing a soluble red dye. Clear water is carefully added on top so that the dyed solution on the bottom is undisturbed. At first, a sharp boundary exists between the two layers, but after a time the upper layer becomes colored, while the layer below becomes less colored. The upper layer is more colored near the original interface between the two layers and less colored in the region near the top of the upper layer. During this color change, the motion of each dye molecule is random, undergoing collisions mainly with water molecules and sometimes with other dye molecules, moving first in one direction and then in another, with no one direction preferred. This type of motion is sometimes referred to as a random-walk process, which yields a mean-square distance of travel for a given interval of time, but not a direction of travel. Thus, at a given horizontal plane through the solution in the cylinder, it is not possible to determine whether, in a given time interval, a given molecule will cross the plane or not. However, on the average, a fraction of the molecules in the solution below the plane will cross over into the region above and the same fraction will cross over in the opposite direction. Therefore, if the concentration of dye molecules in the lower region is greater than in the upper region, a net rate of mass transfer of dye molecules will take place from the lower to the upper region. After a long period of time, the concentration of dye will be uniform throughout the solution. Based on these observations, it is clear that:

1. Mass transfer by ordinary molecular diffusion occurs because of a concentration difference or gradient; that is, a species diffuses in the direction of decreasing concentration.

2. The mass transfer rate is proportional to the area normal to the direction of masstransfer and not to the volume of the mixture. Thus, the rate can be expressed as a flux.

3. Mass transfer stops when the concentration is uniform.

FICK'S LAW OF DIFFUSION:-

1.1 First law of diffusion :-

Adolf Fick (1955) first described the molecular diffusion in an isothermal, isobaric binary system of components A and B. According to his idea of molecular diffusion, the molar flux of a species relative to an observer moving with molar average velocity is proportional to the concentration gradient in a certain direction.

$$J_A \propto \frac{dC_A}{dZ} \tag{2.1}$$

Or

$$J_A = -D_{AB} \frac{dC_A}{dZ} \tag{2.2}$$

Where, J_A is the molar flux of component A in the Z direction. C_A is the concentration of A and Z is the distance of diffusion. The proportionality constant, D_{AB} is the diffusion coefficient of the molecule A in B. This is valid only at steady state condition of diffusion. The Equation (2.2) is called Fick"s first law of diffusion.

$$JA = -D_{AB} \frac{dC_A}{dZ} = C_A (u_A - u)$$

$$-D_{AB} \frac{dC_A}{dZ} = C_A u_A - C_A u = N_A - C_A \frac{1}{C} (C_A u_A + C_B u_B)$$

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$$= N_A - \frac{C_A}{C} (N_A + N_B)$$

$$N_A = \frac{C_A}{C} (N_A + N_B) - D_{AB} \frac{dC_A}{dZ}$$

For gas mixture : $P = C. R. T$

$$C = \frac{P}{RT} \quad , \quad C_A = \frac{P_A}{RT}$$

$$dp = R T d C \quad , \quad dC = \frac{dp}{RT} \quad , \quad dC_A = \frac{dP_A}{RT}$$

$$N_A = \frac{P_A}{P_T} (N_A + N_B) - D_{AB} \frac{dP_A}{RT. \, dZ}$$

To convert (N_A) in terms of mole fraction (y_A)

$$y_A = \frac{P_A}{P_T} \quad , \quad P_A = y_A \, PT \quad , \quad dp_A = P_T \, dy_A$$

$$N_A = (N_A + N_B) \, y_A - \frac{D_{AB}}{RT} . P_T \frac{dy_A}{dz}$$

Not : All the above equations for component (A) is derived in same way for species (B) .

Then the total flux will be :-

$$N_T = N_A + N_B$$

Diffusion in Gases

The most important cases to be studied are:-
1. Equimolar counter diffusion (EMD).
2. Diffusion of species (A) through stagnant non-diffusing (B).
3. Diffusion of gas (A) and (B) plus-convection.
4. Diffusion through a varying :-
    a. Path – length (time dependent).
    b. Cross-sectional area.

Equimolar counter diffusion :-

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In equimolar counter diffusion (EMD), the molar fluxes of A and B are equal, but opposite in direction

$N = N_A + N_B = 0$

Areal life example for this case is :-

a. Particle of carbon burning in air :- the particle is surrounded by an air-film , through which the molecules of oxygen diffuse and reach the surface the particle to sustain combustion .
If (O_2) molecule diffuses to the surface, a molecule of CO_2 is formed which diffuses out through the air-film. So (O_2 and CO_2) undergo (EMD).

$C + O_2 \qquad CO_2$

b. Vapour rising in the distillation column remain in contact with the down-flowing liquid.

$N_A = - N_B$

$N_A = \dfrac{P_A}{P_T} \ (N_A + N_B) - \dfrac{D_{AB}}{RT} \dfrac{d \ P_A}{d \ z}$

For stationary bulk flow

$N_A = - \dfrac{D_{AB}}{RT} \dfrac{d \ P_A}{d \ z}$

$N_A . dz = - \dfrac{D_{AB}}{RT} \ d \ p_A$

By integration:-

$N_A = \dfrac{D_{AB}}{RT} . \dfrac{P_{A1} - P_{A2}}{Z}$ ……….. for EMD

- In this case , total pressure (P_T) must be constant , therefore the moles of (A) diffusing to the right must equal moles of (B) diffusing to the left .
- $N_A = - N_B$
  H.W :
  Prove $\quad D_{AB} = D_{BA} = D$

The distribution of the partial of (A) and (B) along the diffusion path in this case are linear.

Example :

A uniform tube (0.1) m long and (0.01) m di , containing N_2 gas (A) diffusing through the pipe. At point (1) , $P_{A1} = 1.013 * 10^4$ Pas, and at point (2) $P_{A2} = 0.507 * 10^4$ Pas. The total pressure is $1.013 * 10^5$ Pas. And the diffusivity $D_{AB} = 0.23 * 10^{-4}$ cm^3 / sec. calculate :-

1. Fluxes of (A) and (B), at temp. = 298 k

2. The rate of M.T for species (A) and (B).

Solution :-

1. closed system with constant pressure and temp. , then the diffusion flow is EMD :-

$$N_A = \frac{D_{AB}}{RT} \cdot \frac{P_{A1} - P_{A2}}{Z_1 - Z_2}$$

$$= \frac{0.23 * 10^{-4}}{8.314 * 298} \cdot \frac{1.013 * 10^4 - 0.507 * 10^4}{0.1 - 0.0}$$

$N_A = 4.7 * 10^{-7}$ kg mol./ m^2 . s

For species (B) , $P_{B2} = P_T - P_{A1}$, $P_{B1} = P_T - P_{A1}$

$N_B = - 4.7 * 10^{-7}$ kg mol./ m^2 . s

2. Mass transfer rate (n_A)

$N_A = \frac{n_A}{Area}$, $n_A = N_A * A$

$A = d_i^2 = (0.01)^2 = 7.8 * 10^{-5}$ m^2

$n_A = 4.7 * 10^{-7} * 7.8 * 10^{-5}$

$= 36.66 * 10^{-12}$ kg mol/sec

$n_B = - 36.66 * 10^{-12}$ kg mol/sec

Example :- Tow large vessels are connected as shown in fig. vessel (1) contains 80% N_2 and 20% O_2 (B) , vessel (2) contains 20% N_2 and 80% O_2. The temp. ($20^{o}c$) a(2 atm). Calculate :-

1. The flux and rate of transport of N_2 from vessel 1 to 2, and same for O_2 .

2. The partial pressure of N_2 and its gradient in the tube (0.05 m) from vessel 1 .

3. The net mass flux (n_T).

Given that diffusivity of $N_2 - O_2$ pair is $1.01 * 10^{-5}$ m^2 / s at $20^{o}c$ and 2 atm.

Solution :-

1. $N_A = \dfrac{+D_{AB}}{RT} \cdot \dfrac{P_{A1}-P_{A2}}{Z_2-Z_1}$

$D_{AB} = 1.01 * 10^{-5}$ (m^2 / s) , R = 0.0821 , T = 293 k

$Z = Z_2 - Z_1 = 0.15$ m , to find P_{A1} , P_{A2}

$P_{A1} = y_{A1} \cdot P_T$

$= 0.8 * 2$

$= 1.6$ atm. $= 1.62 * 10^5$ N/m^2

$P_{A2} = y_{A2} . P_T$

$= 0.2 * 2$

$= 0.4$ atm. $= 0.406 * 10^5$ N/m^2

$N_A = 3.3 * 10^{-1}$ kmol. / m^2 . sec.

Rate of transport $= n_A = N_A$. Area

Area $= (0.05)^2$

$n_A = 6.6 * 10^{-9}$ kmol. /sec.

$N_B = -N_A = -3.36 * 10^{-6}$ kmol./m^2.s.

$n_A = - n_B = - 6.6 * 10^{-9}$ kmol. /sec.

2. Partial pressure changes linearly with diffusion path.

$\frac{dP}{dZ} = \frac{P_{A2} - P_{A1}}{Z} = \frac{(0.4 - 1.6)}{0.15} = -8$ atm / m

At point 0.05

$P_A = P_T + (\frac{dP_A}{d_Z})$. dz

$= 1.6 + (- 8) * 0.05$

$P_A = 1.2$ atm.

3. $n_T = N_A . Mwt_A + N_B . Mwt_B$

$= (3.36 * 10^{-6} * 28) - (3.36 * 10^{-6} * 32)$

$= - 1.344 * 10^{-5}$ kmol. / m^2 .s

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For a Non-Equimolar Counter Diffusion (NEMD):-

When the mass transfer rates of the two components are unequal and opposite, the process is said to be the unequimolecular diffusion, such a process occurs in a chemical reaction.

Producing (CO_2) from (O_2) and hot-char-particle

$1/2\ O_2 + CO \qquad\qquad CO_2$

$N_A = 1/2\ N_B$

$N_A = (N_A + N_B) \cdot \dfrac{P_A}{P_T} + \left(\dfrac{-D_{AB}}{R\,T}\right)\dfrac{dP_A}{dz}$

Now substitute $N_B = 2N_A$ and then integrate.

$N_A = (N_A + N_B) \cdot \dfrac{P_A}{P_T} + \left(\dfrac{-D_{AB}}{R\,T}\right)\dfrac{dP_A}{dz}$

Since unequimolecular counter diffusion: $N_B = -\,n\ N_A$

$N_A = (N_A - n\ N_A) \cdot \dfrac{P_A}{P_T} + \left(\dfrac{-D_{AB}}{R\,T}\right)\dfrac{dP_A}{dz}$

$N_A \left(1 - \left[\dfrac{P_A}{P_T}\right](1 - n)\right) = \left(\dfrac{-D_{AB}}{R\,T}\right)\dfrac{dP_A}{dz}$

$N_A = \dfrac{-D_{AB}}{R\,T}\dfrac{dP_A}{dz} \cdot \dfrac{1}{\left(1 - \left[\frac{P_A}{P_T}\right](1 - n)\right)}$

$N_A = \dfrac{-D_{AB}}{R\,T}\dfrac{1}{\Delta Z} \cdot \dfrac{dP_A}{\left(1 - \left[\frac{P_A}{P_T}\right](1 - n)\right)}$

$N_A = \dfrac{-D_{AB}}{R\,T}\dfrac{P_T}{\Delta Z} \cdot \dfrac{1}{(1 - n)} \cdot \ln\left[\dfrac{P_T - (1 - n)\,P_{A_2}}{P_T - (1 - n)\,P_{A_1}}\right]$

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Example: Species A in a gaseous mixture diffuses through a (3 mm) thick film and reaches a catalyst surface where the reaction A → 3B takes place. If the partial pressure of A in the bulk of the gas is 8.5 kN/m² and the diffusivity of A is $2*10^{-5}$ m²/s. Find the mole flux of A, given the pressure and temperature of the system are 101.3 kPa and 297 K, respectively.

Solution:

A → 3B
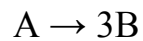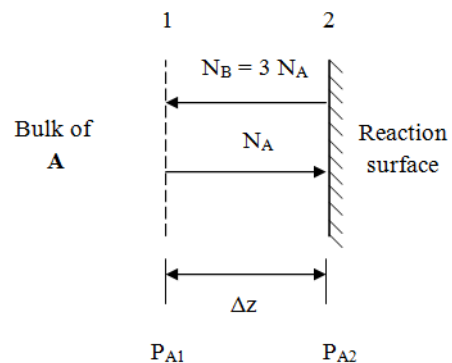
$$n = \frac{N_A}{N_B} = \frac{3}{1} = 3$$

Given:

$D_{AB}=2*10-5$ m²/s ,
P_T=101.3 kPa
T=297 K , P_{A1}=8.5 kPa
P_{A2}=0

$$N_A = \frac{-D_{AB}}{R\,T}\frac{P_T}{\Delta Z} \cdot \frac{1}{(1-n)} .\ln \left[\frac{P_T-(1-n)\,P_{A2}}{P_T-(1-n)\,P_{A1}}\right]$$

$$N_A = \frac{2*10^{-5}}{8.314*297}\frac{101.3}{3*10^{-3}} \cdot \frac{1}{(1-3)} .\ln \left[\frac{101.3+2\,(\,0\,)}{101.3+2\,(\,8.5\,)}\right]$$

$$= 2.12*10^{-5} \text{ kmol } / \text{ m}^2 . \text{ s}$$

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Diffusion of (A) through non-diffusing (B) :-

In this case one boundary at the end of the diffusion path is impermeable to other species, so it cannot pass through.
A real life example: Dry air in sulfuric acid plant.We need dry air for the purpose of burning sulfur in a sulfuric acid production plant, so the wet air passes through the sulfuric acid in the packed towers. Humidity will be applied through a layer of air and reach the surface of the acid and then suck. But the air does not dissolve in the acid and therefore cannot penetrate.

Another example (NH_3 in air) removal. NH_3 diffuses easily a cross air film to water ,but (Air) is in soluble.

$$N_A = (N_A + N_B) \cdot \frac{P_A}{P_T} + \left(\frac{-D_{AB}}{R T} \right) \frac{dP_A}{dz}$$
$$N_B = 0$$

$$N_A = N_A \cdot \frac{P_A}{P_T} - \left(\frac{D_{AB}}{R T} \right) \frac{dP_A}{dz}$$

$$N_A * dz = - \frac{D_{AB} P_T}{R T (P_T - P_A)} * dP_A$$

Integrating

$$N_A = \frac{D_{AB}}{R T} \frac{P_T}{\Delta Z} \ln \left[\frac{P_T - P_{A2}}{P_T - P_{A1}} \right]$$

$$N_A = \frac{D_{AB}}{R T} \frac{P_T}{Z} \cdot \left[\frac{P_{A1} - P_{A2}}{P_{BM}} \right]$$

$$P_{BM} = \frac{P_{B2} - P_{B1}}{\ln \frac{P_{B2}}{P_{B1}}}$$

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