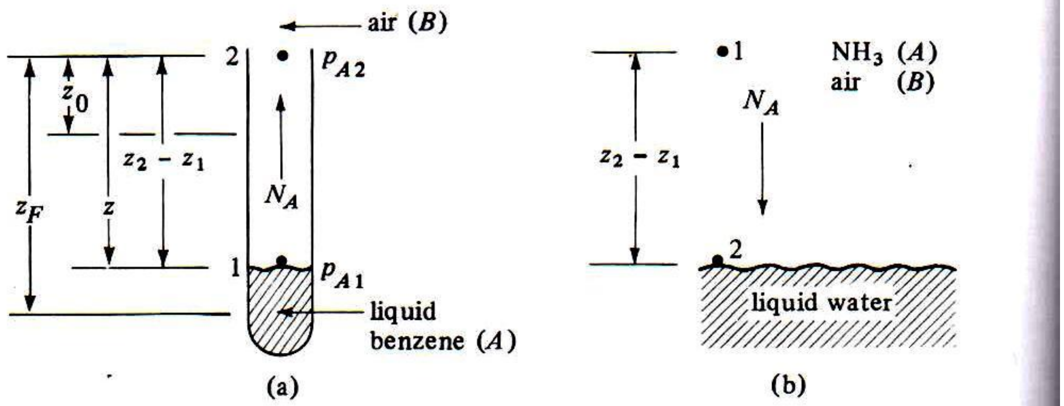


Figure 12 *Diffusion of A through stagnant, nondiffusing B: (a) benzene evaporating into air, (b) ammonia in air being absorbed into water.*

- **One example, shown in Fig. 12(a), is in the evaporation of pure liquid such as benzene (*A*) at the bottom of a narrow tube, where a large amount of inert or nondiffusing air (*B*) is passed over the top.**

- **The benzene vapor (*A*) diffuses through the air (*B*) in the tube. The boundary at the liquid surface at point 1 is impermeable to air, since air is insoluble in benzene liquid.**

- **Hence, air (*B*) cannot diffuse into or away from the surface. At point 2 the partial pressure P_{A2} = 0, since a large volume of air is passing by.**

- **Another example, shown in Fig. 12(b), occurs in the absorption of NH_3 (*A*) vapor which is in air (*B*) by water.**

- **The water surface is impermeable to the air, since air is only very slightly soluble in water. Thus, since *B* cannot diffuse, N_B = 0.**

- **To derive the case for *A* diffusing in stagnant, nondiffusing *B*, N_B = 0 is substituted into the general equation (24)**

$$N_{\mathrm{A}} = -cD_{AB}\frac{\mathrm{d}x_A}{\mathrm{d}z} + \frac{c_A}{c}\left(N_A + 0\right) \qquad \text{.....(38)}$$

- **The convective flux of *A* is (c_A/c) ($N_A + 0$). Keeping the total pressure *P* constant, substituting $c = P/RT$, $p_A = x_AP$, and $c_A/c = p_A/P$ into the above equation**

$$N_A = -\frac{D_{AB}}{RT}\frac{dp_A}{dz} + \frac{p_A}{P}N_A \qquad \text{.....(39)}$$

- **Rearranging and integrating,**

$$N_A\left(1-\frac{p_A}{P}\right)=-\frac{D_{AB}}{RT}\frac{dp_A}{dz} \qquad \text{.....(40)}$$

$$N_A\int_{z_1}^{z_2} dz=-\frac{D_{AB}}{RT}\int_{p_{A1}}^{p_{A2}}\frac{dp_A}{\left(1-p_A/P\right)} \qquad \text{.....(41)}$$

$$N_A=\frac{D_{AB}P}{RT\left(z_2-z_1\right)}ln\left(\frac{P-p_{A2}}{P-p_{A1}}\right) \qquad \text{.....(42)}$$

- **The above equation is the final equation to be used to calculate the flux of *A*.**

- **However, it is often written in another form.**

- **A log mean value of the inert *B* is defined as follows.**

- **Since $P = p_{A1} + p_{B1} = p_{A2} + p_{B2}$, $p_{B1} = P - p_{A1}$ *and* $p_{B2} = P - p_{A2}$**

$$P_{BM} = \frac{p_{B2} - p_{B1}}{ln\left(p_{B2} / p_{B1}\right)} = \frac{p_{A1} - p_{A2}}{ln\left[\left(P - p_{A2}\right) / \left(P - p_{A1}\right)\right]} \quad \text{.....(43)}$$

Thus,

$$N_A = \frac{D_{AB} P}{RT\left(Z_2 - Z_1\right) p_{BM}} \left(p_{A1} - p_{A2}\right) \quad \text{.....(44)}$$

Compare with the earlier equation for equimolar counterdiffusion:

$$J_A = \frac{D_{AB}\left(p_{A1} - p_{A2}\right)}{RT(z_2 - z_1)}$$

Therefore, in the present case, *P/p_{BM}* can be regarded as <u>correction factor</u>.

In addition, for gases, Eq. (20) $N_A = J_A + c_A \upsilon_M$ can also be expressed using mole fraction in vapor phase (y_A), since:

$$c_A = \rho_M y_A \qquad \text{.....(45)}$$

$$\upsilon_M = \frac{N}{\rho_M} \qquad \text{.....(46)}$$

where:

- ρ_M **= molar density (kgmole/m^3)**
  = 1/22.41 kgmole/m^3 (at standard conditions, 0°C & 1 atm)
- y_A **= mole fraction of component *A* in vapor phase**
- N **= total convective flux of the whole stream relative to the stationary point (kgmole/m^2·s)**
- υ_M **= molar average velocity (ms^{-1})**
- c_A **= molar concentration of component *A* (kgmole/m^3)**

Thus the Eq. (20) becomes:

$$N_A = y_A N - D_{AB}\rho_M \frac{dy_A}{dz} \qquad \text{.....(47)}$$

Since $N = N_A + N_B$, and when only component A is being transferred (i.e.: $N_B = 0$), the total flux to or away from the interface N is the same as N_A, then the Eq. becomes:

$$N_A = y_A N_A - D_{AB}\rho_M \frac{dy_A}{dz} \qquad \text{.....(48)}$$

Rearranging and integrating:

$$N_A(1-y_A) = -D_{AB}\rho_M \frac{dy_A}{dz} \qquad \text{.....(49)}$$

$$N_A\int_{z_1}^{z_2} dz = -D_{AB}\rho_M \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{(1-y_A)} \qquad \text{.....(50)}$$

$$\mathrm{N_A} = \frac{\mathrm{D_{AB}}\rho_\mathrm{M}}{\mathrm{z_2 - z_1}} \ln\left(\frac{1-\mathrm{y_{A2}}}{1-\mathrm{y_{A1}}}\right) \qquad \text{.....(51)}$$

Similarly,

$$y_{B1} = 1 - y_{A1}$$

$$y_{B2} = 1 - y_{A2}$$

$$y_{B2} - y_{B1} = y_{A1} - y_{A2} \quad \text{and} \quad (y_{A1} - y_{A2}) / (y_{B2} - y_{B1}) = 1$$

Then,

$$N_A = \frac{D_{AB}\rho_M}{z_2 - z_1} \cdot \frac{y_{A1} - y_{A2}}{y_{B2} - y_{B1}} ln\left(\frac{y_{B2}}{y_{B1}}\right) \qquad \text{.....(52)}$$

The logarithmic mean of y_{B1} and y_{B2} is given by:

$$y_{BM} = \frac{y_{B2} - y_{B1}}{ln(y_{B2}/y_{B1})} \qquad \text{.....(53)}$$

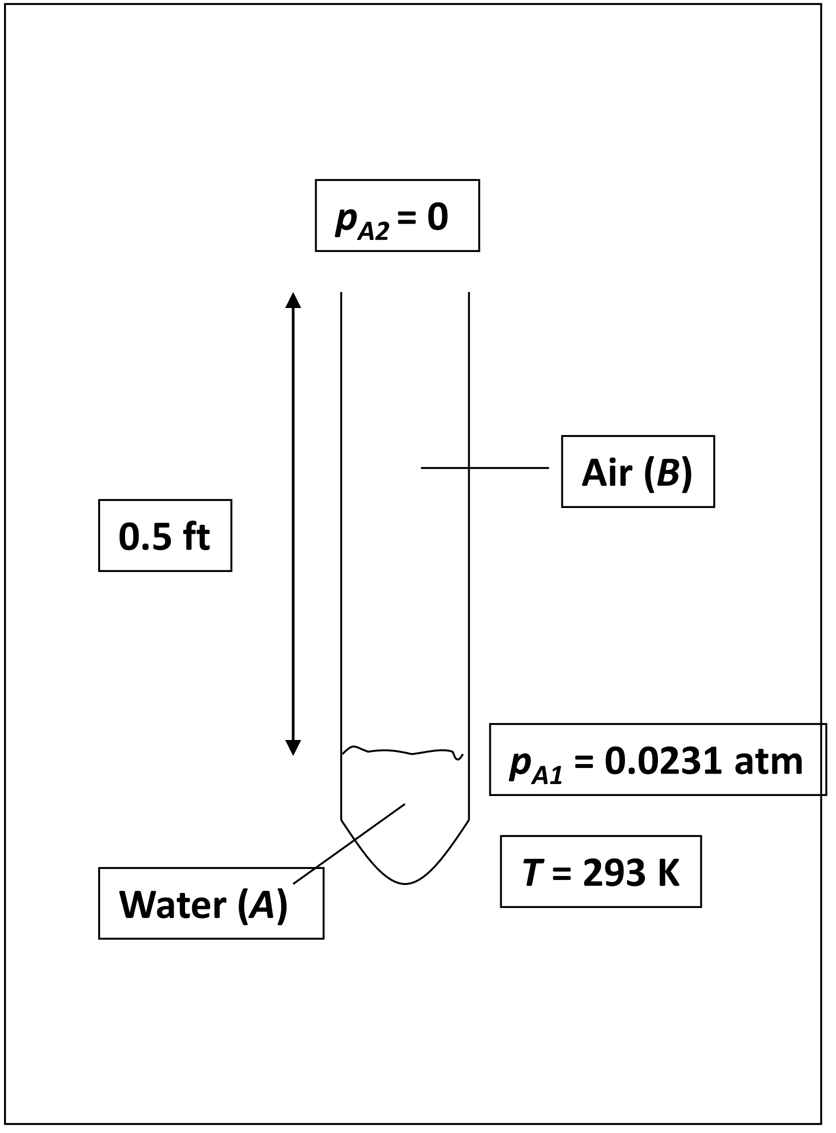
Finally, by substituting Eq. (53) into Eq. (52) gives:

$$N_A = \frac{D_{AB}\rho_M}{(z_2 - z_1)y_{BM}}(y_{A1} - y_{A2}) \qquad \text{.....(54)}$$

Example:

Water in the bottom of a narrow metal tube is held at a constant temperature of 293 K. The total pressure of air (assume dry) is 1.01325 x 10^5 Pa (1.0 atm) and the temperature is 293 K (20°C). Water evaporates and diffuses through the air in the tube and the diffusion path $z_2 - z_1$ is 0.1524 m (0.5 ft) long. The diagram is similar to the shown figure. Calculate the rate of evaporation at steady state in lb mol/ft^2·h and kgmole/m^2·s. The diffusivity of water vapor at 293 K and 1 atm pressure is 0.250 x 10^{-4} m^2/s. Assume that the system is isothermal. Use SI and English units.

Solutions



- **The diffusivity is converted to ft²/h by using the conversion factor (refer Appendix 1, McCabe, Smith and Harriott).**

$$D_{AB} = (0.250 \text{ x } 10^{-4})(3.875 \text{ x } 10^{-4}) = 0.969 \text{ ft}^2/\text{h}$$

- **Using Appendix A.2 (Christie John Geankoplis), the vapor pressure of water at 20°C is 17.54 mmHg**

$$p_{A1} = \frac{17.54}{760} = 0.0231\, atm = 0.0231(1.01325x10^5) = 2.341x10^3\, Pa$$

$$p_{A2} = 0\, (pure\, air)$$

***T* = 460 +68 = 528°R = 293 K**

***R* = 82.057 cm³· atm/gmole· K = 0.730 ft³ · atm/lbmole· °R**

- **In order to calculate the value of p_{BM} :**

$p_{B1} = P - p_{A1} = 1.00 - 0.0231 = 0.9769$ atm

$p_{B2} = P - p_{A2} = 1.00 - 0 = 1.00$ atm

- **Therefore:**

$$p_{BM} = \frac{p_{B2} - p_{B1}}{\ln(p_{B2} / p_{B1})} = \frac{1.00 - 0.9769}{\ln(1.00 / 0.9769)} = 0.988\,\text{atm} = 1.001\,\text{x}\,10^5\ \text{Pa}$$

Since p_{B1} is close to p_{B2} , the linear mean $(p_{B1} + p_{B2})/2$ could be used and would be very close to p_{BM} .

Substituting in Eq. (44) with $z_2 - z_1$ = 0.5 ft (0.1524 m), thus:

$$N_A = \frac{D_{AB}P}{RT(z_2 - z_1)p_{BM}}(p_{A1} - p_{A2})$$

$$= \frac{0.969\left(\frac{ft^2}{h}\right)(1.0)(atm)(0.0231 - 0)(atm)}{0.730\left(\frac{ft^3 \cdot atm}{Ibmol \cdot {}^0R}\right)(528)({}^0R)(0.5)(ft)(0.988)(atm)}$$

$$= 1.175 \, x \, 10^{-4} \; lbmole/ft^2 \cdot h$$

$$N_A = \frac{D_{AB}P_T}{RT(z_2 - z_1)p_{BM}}(p_{A1} - p_{A2})$$

$$= \frac{(0.250 \, x \, 10^{-4})\left(\frac{m^2}{s}\right)(1.01325 \, x \, 10^5)(Pa)(2.341 \, x \, 10^3 - 0)(Pa)}{8314\left(\frac{m^3 \cdot Pa}{kgmol \cdot K}\right)(293)(K)(0.1524)(m)(1.001 \, x \, 10^5)(Pa)}$$

$$= 1.595 \, x \, 10^{-7} \; kgmole/m^2 \cdot s$$

Molecular Diffusion in Liquids

- **Diffusion of solutes in liquid is very important in many industrial processes especially in separation operations such as:**
  1) **Gas absorption**
  2) **Distillation**
  3) **Liquid-liquid extraction or solvent extraction**

- **Rate of molecular diffusion in liquids is considerably slower than in gases.**

- **The molecules in a liquid are very close together compared to a gas. Therefore, the molecules of the diffusing solute *A* will collide with molecules of liquid *B* more often and diffuse more slowly than in gases.**

- **For diffusion in liquids, an important difference from diffusion in gases is that the diffusivities are often dependent on the concentration of the diffusing components.**

- **Similar to those for gases, equations for diffusion in liquids can be classified in two cases:**

<u>1) Steady-state equimolar counterdiffusion,</u>

Starting from general Eq. (24): $N_A = -cD_{AB}\frac{dx_A}{dz} + \frac{c_A}{c}(N_A + N_B)$

and knowing $N_A = -N_B$, then:

$$J_A = \frac{D_{AB}c_{av}}{z_T}(x_{Ai} - x_A) = \frac{D_{AB}}{z_T}(c_{Ai} - c_A) \qquad \text{.....(55)}$$

Note that c_T is consider as c_{av}

c_{av} **is defined as follows:**

$$c_{av} = \left(\frac{\rho}{M}\right)_{av} = \frac{\left(\frac{\rho_1}{M_1} + \frac{\rho_2}{M_2}\right)}{2} \qquad \text{.....(56)}$$

where:

c_{av} **= average total concentration of *A* + *B* (kgmole/m^3)**

M_1 **= average molecular weight of the solution at point 1 (kg mass/kgmole)**

ρ_1 **= average density of the solution at point 1 (kg/m^3)**

2) Steady-state diffusion of *A* through nondiffusing *B*

Since N_B **= 0, If Eq. (44) is rewritten in terms of concentrations by substituting,** $c_{av} = P/RT$, $c_{A1} = p_{A1}/RT$, **and** $x_{BM} = p_{BM}/P$, **we obtain the equation for liquids at steady state:**

$$N_A = \frac{D_{AB} c_{av}}{(z_2 - z_1) x_{BM}} (x_{A1} - x_{A2}) \qquad \text{.....(57)}$$

where

$$x_{BM} = \frac{x_{B2} - x_{B1}}{ln(x_{B2}/x_{B1})} \qquad \text{.....(58)}$$

Note that $x_{A1} + x_{B1} = x_{A2} + x_{B2} = 1.0$. For dilute solution, x_{BM} is close to 1.0 and c is essentially constant. Then, the Eq.(57) simplifies to:

$$N_A = \frac{D_{AB}}{(z_2 - z_1)}(c_{A1} - c_{A2}) \qquad \text{.....(59)}$$

Example:

Calculate the rate of diffusion of acetic acid (*A*) across a film of nondiffusing water (*B*) solution 1 mm thick at 17°C when the concentrations on opposite sides of the film are 9 and 3 wt %, respectively. The diffusivity of acetic acid in the solution is 0.95×10^{-9} m²/s.

Solution:

Given:

$(z_2 - z_1) = 0.001$ m

$M_A = 60.03$ kg/kmole

$M_B = 18.02$ kg/kmole

At 17 °C: Density of the 9% solution = 1012 kg/m³

Density of the 3% solution = 1003.2 kg/m³

Consider basis of solution = 1 kg,

At point 1:

$$x_{A1} = \frac{0.09/60.03}{0.09/60.03 + 0.91/18.02} = \frac{0.0015}{0.0520} = 0.0288 \text{ mole fraction acetic acid}$$

$$x_{B1} = 1 - 0.0288 = 0.9712 \text{ mole fraction water}$$

$$\text{Molecular weight of the solution}, M_1 = \frac{1}{0.0520} = 19.21 \text{ kg/kmole}$$

$$\frac{\rho_1}{M_1} = \frac{1012}{19.21} = 52.7 \text{ kmole/m}^3$$

Similarly, at point 2:

$$x_{A2} = \frac{0.03/60.03}{0.03/60.03 + 0.97/18.02} = \frac{0.0005}{0.0543} = 0.0092\,\text{mole fraction acetic acid}$$

$$x_{B2} = 1 - 0.0092 = 0.9908\,\text{mole fraction water}$$

$$\text{Molecular weight of the solution, } M_2 = \frac{1}{0.0543} = 18.42\,\text{kg/kmole}$$

$$\frac{\rho_2}{M_2} = \frac{1003.2}{18.42} = 54.5\,\text{kmole/m}^3$$

Then,

$$\left(\frac{\rho}{M}\right)_{av} = \frac{52.7 + 54.5}{2} = 53.6\,\text{kmole/m}^3$$

$$x_{BM} = \frac{x_{B2} - x_{B1}}{ln(x_{B2}/x_{B1})} = \frac{0.9908 - 0.9712}{ln(0.9908/0.9712)} = 0.980$$

Finally, substitute all known values in the Eq.:

$$N_A = \frac{0.95\ x\ 10^{-9}\left(\frac{m^2}{s}\right)}{(0.001)(m)(0.980)}(53.6)\left(\frac{kmol}{m^3}\right)(0.0288 - 0.0092)$$

$$= 1.018\ x\ 10^{-6}\ kmole/m^2 \cdot s$$