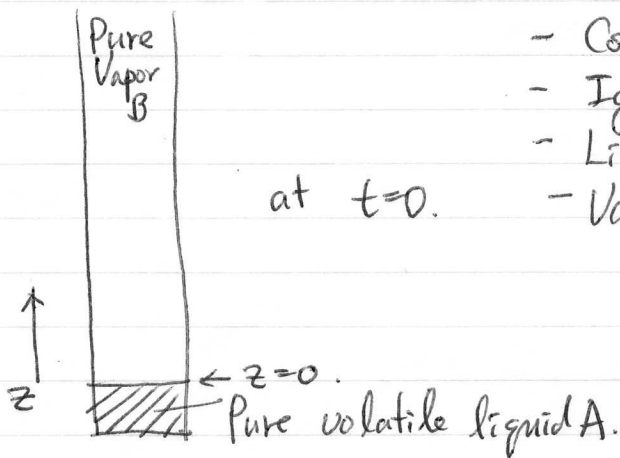


Binary Diffusion Example



- Constant and Uniform T, P .
- Ignore radial transport.
- Liquid A evaporates
- Vapor B is non-condensable

* Determine molar concentration profiles of A and B in vapor phase as functions of time, position, and evaporation rate of A.

Area = A_t

$$A_t \left[- \left(\dot{N}_A'' + \frac{\partial \dot{N}_A''}{\partial z} dz \right) + \dot{N}_A'' \right] = \frac{\partial C_A}{\partial t} \cdot dz \cdot A_t$$

- flux out + flux in = Accumulation

$$\Rightarrow - \frac{\partial \dot{N}_A''}{\partial z} = \frac{\partial C_A}{\partial t} \quad \dots \textcircled{1}$$

Similarly,
$$- \frac{\partial \dot{N}_B''}{\partial z} = \frac{\partial C_B}{\partial t} \quad \dots \textcircled{2}$$

$$\textcircled{1} + \textcircled{2} \quad - \frac{\partial (\dot{N}_A'' + \dot{N}_B'')}{\partial z} = \frac{\partial (C_A + C_B)}{\partial t} = \frac{\partial C}{\partial t} = 0$$

C = total mole number per volume
= constant and uniform ($\because T, P$ are constant)

$$\frac{\partial (\dot{N}_A'' + \dot{N}_B'')}{\partial z} = \frac{\partial \dot{N}''}{\partial z} = 0 \Rightarrow \text{sum of molar flux depends only on time, not } z. \quad \dot{N}''(t)$$

At $z=0$, $\dot{N}_B''(z=0, t) = 0$ (vapor B is non condensable.)

$$\therefore \dot{N}_A''(0, t) + \dot{N}_B''(0, t) = \dot{N}_A''(0, t) = \dot{N}''(t)$$

$$\dot{N}_A'' = \overbrace{-C D_{AB} \nabla X_A}^{\text{diffusive}} + \overbrace{X_A C v^*}_{\text{convective}}$$

$$= \frac{\partial X_A(z,t)}{\partial z}$$

$$\dot{N}_A''(0,t) = -C D_{AB} \frac{\partial X_A(0,t)}{\partial z} + X_A(0,t) C v^*$$

$$\dot{N}''(t) \equiv C v^* \quad (\text{since only A is evaporating})$$

$$\Rightarrow \dot{N}_A''(0,t)$$

$$\therefore C v^* = -C D_{AB} \frac{\partial X_A(0,t)}{\partial z} + X_A(0,t) C v^*$$

$$\Rightarrow C v^* = \frac{-C D_{AB}}{1 - X_A(0,t)} \cdot \frac{\partial X_A(0,t)}{\partial z} \dots (3)$$

$\rightarrow X_A(0,t)$ is the value corresponding to the saturated vapor, which is a function of temperature only

$$X_A(0,t) = X_A^{\text{SAT}}(T) = p^{\text{SAT}}(T)/p_0$$

$$\frac{\partial C_A}{\partial t} = - \frac{\partial \dot{N}_A''}{\partial z} \Rightarrow \left(\frac{1}{C} \frac{\partial C_A}{\partial t} \right) = - \frac{1}{C} \frac{\partial \dot{N}_A''}{\partial z} = D_{AB} \frac{\partial^2 X_A}{\partial z^2} - v^* \frac{\partial X_A}{\partial z}$$

$$\Rightarrow \boxed{\frac{\partial X_A}{\partial t} = D_{AB} \frac{\partial^2 X_A}{\partial z^2} - v^* \frac{\partial X_A}{\partial z}} \dots (4)$$

$$\text{from (3)} \quad v^* = \frac{-D_{AB}}{1 - X_A^{\text{SAT}}(T)} \cdot \frac{\partial X_A(0,t)}{\partial z} \dots (5)$$

* Boundary & initial condition

$$X_A(0,t) = X_A^{\text{SAT}}(T), \quad \lim_{z \rightarrow \infty} X_A(z,t) = 0, \quad X_A(z,0) = 0$$

* PDE soln of eqn (4) gives $X_A(z,t)$, then (5) gives v^* as a function of time.

< Multi-Component Transport >

* Diffusive flux of any particular species depends on the concentration fields of all other species in the system.

ref. Ch 12, Bird, Stewart and Lightfoot, "Transport Phenomena"

$$J_i'' = \left(\frac{C^2}{\rho} \right) \sum_{j=1}^N \tilde{M}_i \tilde{M}_j \theta_{ij} \nabla X_j$$

\tilde{M} : molar weight.

C : total molar concentration

θ_{ij} : diffusion coefficient of the pair $i-j$
multi-component diffusion coefficient.

gradient of species j conc.

affects J_i (flux of species i)

* θ_{ij} are concentration dependent.

Stefan - Maxwell relation

$$\nabla X_i = \sum_{j=1}^N \frac{X_i X_j}{\theta_{ij}} (\underbrace{V_j - V_i}_{\text{total velocity}}) = \sum_{j=1}^N \frac{1}{C \theta_{ij}} (X_i \dot{N}_j'' - X_j \dot{N}_i'')$$

For a binary system, $\theta_{ij} = \theta_{ji} = \theta$.

\therefore S-M relation becomes.

$$C \theta \nabla X_1 = X_1 \dot{N}_2'' - X_2 \dot{N}_1'' = X_1 \dot{N}_2'' + X_1 \dot{N}_1'' - \underbrace{(X_1 + X_2)}_{=1} \dot{N}_1''$$

$$\therefore \dot{N}_1'' = -C \theta \nabla X_1 + X_1 \sum_{j=1}^2 \dot{N}_j''$$

If the diffusivities of all species are the same,

$$\dot{N}_i'' = \underbrace{-C \theta \nabla X_i}_{\text{Fickian term}} + \underbrace{X_i \sum_{j=1}^N \dot{N}_j''}_{\text{convective component}}$$

If the diffusivities are unequal.

in a three-component mixture that satisfies.

$$D_{23} = D_{32} = D$$

$$D_{12} = D_{21} = D_{31} = D_{13} = fD \quad (f < 1)$$

$$\dot{N}_1'' = -fD \cdot C \nabla X_1 + X_1 \sum_{j=1}^N \dot{N}_j''$$

$$\dot{N}_2'' \left\{ 1 + X_1 \left(\frac{1}{f} - 1 \right) \right\} = -C D \nabla X_2 + X_2 \left\{ \left(\frac{1}{f} - 1 \right) \dot{N}_1'' + \sum_{j=1}^N \dot{N}_j'' \right\}$$

$$\dot{N}_3'' (1 + (f-1)X_2) = -fD C \nabla X_3 + X_3 \left((f-1) \dot{N}_2'' + \sum_{j=1}^N \dot{N}_j'' \right)$$

⇒ Numerical approach is required

Simplified form

$$* \dot{N}_i'' = -C \underbrace{D_{im}}_{\text{effective binary diffusivity}} \nabla X_i + X_i \sum_{j=1}^N \dot{N}_j''$$

effective binary diffusivity depending on the fluxes of all species

↓
position in flow determines the fluxes where the gradient of conc. is non-uniform.

This works when with.

(1) nearly pure species 1. so that $D_{im} = D_{i1}$.

(2) all binary diffusivities are same, $D_{im} = D$.

$$(3) \frac{1-X_1}{D_{im}} = \sum_{j=1}^N \frac{X_j}{D_{ij}}$$

approximate

$$D_{im} = \frac{1-X_i}{\sum_{j \neq i} \frac{X_j}{D_{ij}}}$$

@ Other Brownian Mass Transport Mechanism.

$$J_i'' = J_i^{(C)''} + J_i^{(P)''} + J_i^{(g)''} + J_i^{(T)''}$$

\uparrow Ordinary diffusion flux (Stefan-Maxwell)
 \uparrow pressure diffusion ($\nabla p \neq 0$)
 \uparrow forced diffusion (body force)
 e.g. ion diffusion
 \uparrow thermal diffusion (Soret effect)
 $J_i^{(T)''} = - \left(\frac{D_i}{T} \right) \nabla \ln T$
 \uparrow thermal diffusion coef. ($|\nabla T| \gg 1$)

@ Energy transport in multi-component system.

Translational energy is considered here. $E_{trans} = \frac{3}{2} k_B T$ per molecule

* Recall the previous discussion on a flux of property \tilde{a} .

$$\Lambda_{\tilde{a}}'' = -\frac{1}{3} n \langle c \rangle \int_{msfp} \frac{d\tilde{a}(x_0)}{dx_2} : \text{flux at } x_2 = x_0$$

x_2 is an arbitrary spatial coordinate

$m C_v T$ is thermal energy (translational energy)

$C_v = \frac{3}{2} R$: mass-based specific heat.

$$\therefore \dot{q}'' = -\frac{1}{3} n m \langle c \rangle \int_{msfp} C_v \frac{\partial T}{\partial x_2}$$

$\lambda \equiv \frac{1}{3} \rho \langle c \rangle \int_{msfp} C_v$: thermal conductivity.

" molecule velocity $\propto \sqrt{T}$.

however the dependence also depends on molecular weight.

It including rotational / vibrational energy.

$$\lambda = \lambda_{trans} + \lambda_{rot/vib}$$

$$C_{v,rot/vib} = C_v - \frac{3}{2} R.$$

An empirical mixture rule for λ

$$\lambda_{\text{mixture}} = \frac{1}{2} \left(\sum_{i=1}^N X_i \lambda_i + \frac{l}{\sum_{i=1}^N \frac{X_i}{\lambda_i}} \right)$$

Remember dimensions of diffusion coefficient (cm^2/sec)
and thermal conductivity ($\text{W}/\text{m}\cdot\text{K}$)

for stable

< Premixed Laminar Flame >

* One of the simplest combustion phenomena.

The burned gas state is located on deflagration branch of P-H.

* Weak deflagration \Rightarrow Not a single solution

Consider one-dimensional combustion wave propagation

Slope of Rayleigh line $(\frac{dP}{dv}) = m''^2 = (\rho u u)''^2$
 specific volume = v/ρ

$u_u = S_u = \text{laminar flame speed} = -\frac{1}{\rho u} \sqrt{\frac{dP}{dv}}$

Recall that the slope of deflagration is much smaller than that of detonation. $S_{u \text{ laminar}} = \text{subsonic} \ll S_{u \text{ detonation}}$

* A steady, one-dimensional combustion wave.

Mass conservation $\frac{d}{dx}(\rho u) = 0$, $m'' = \rho u = \text{constant}$.

Momentum eqn. $\frac{dP}{dx} + \rho u \left(\frac{du}{dx}\right) = 0$

* recall general conservation equation from a previous hour for a steady, inviscid flow without body force

\Rightarrow Euler's eqn. $\nabla P + \rho \vec{v} \cdot \nabla \vec{v} = 0$

$= \frac{\partial P}{\partial x} \vec{i} + \frac{\partial P}{\partial y} \vec{j} + \frac{\partial P}{\partial z} \vec{k} + \rho(u \vec{i} + v \vec{j} + w \vec{k}) \cdot \left(\frac{\partial u}{\partial x} \vec{i} + \frac{\partial v}{\partial y} \vec{j} + \frac{\partial w}{\partial z} \vec{k} \right)$

in one-dimensional system with x

$= \frac{dP}{dx} + \rho u \frac{du}{dx} = 0$

$$\therefore \Delta p = -\rho_u \left(\frac{\Delta u}{\Delta x} \right) \cdot \Delta x = -\rho_u u_u (u_b - u_u) \text{ across the flame}$$

$$\frac{d\rho}{dx} \cdot \Delta x \quad \frac{du}{dx} \cdot \Delta x \approx \frac{\Delta u}{\Delta x} \cdot \Delta x$$

$$\therefore \Delta p = -\rho_u u_u^2 \left(\frac{u_b}{u_u} - 1 \right) = -\rho_u u_u^2 \left(\frac{\rho_u}{\rho_b} - 1 \right)$$

for an ideal gas.

$\frac{\rho_u}{\rho_b} \propto \frac{T_b}{T_u}$ and assume constant/homogeneous pressure p ($\Delta p \ll 1$)
with same gas constants, ($\because N_2$ is dominant species in most cases)

$$\Delta p = -\rho_u u_u^2 \left(\frac{T_b}{T_u} - 1 \right)$$

$$u_u \sim 15 \sim 40 \text{ cm/s}, \quad T_b/T_u \sim 5 \sim 7.$$

$$\rho_u \sim 1 \text{ kg/m}^3$$

$$-\Delta p \approx 10^{-6} \sim 10^{-5} \text{ bar.} \ll 1.$$