Equimolar Counterdiffusion

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We learned earlier that normally when diffusion occurs, convection caused purely by the diffusion process accompanies it. Under certain conditions, however, the molar average velocity can be precisely zero, so that there is no distinction between the molar flux of a species in the laboratory reference frame, $\boldsymbol{N}_A$, and the molar flux of the same species in a reference frame moving with the local molar average velocity, $\boldsymbol{J}_A^*$. Recall that in a binary system, $\boldsymbol{J}_A^*$ is related to the mole fraction gradient of A through Fick's law.

$$\boxed{\boldsymbol{J}_A^* = -c\, D_{AB} \nabla x_A}$$

The molar average velocity is related to the total molar flux in the laboratory reference frame through $\boldsymbol{N} = c\boldsymbol{V}^*$. Therefore, for $\boldsymbol{V}^*$ to be zero, the total molar flux $\boldsymbol{N}$ must be zero. Because $\boldsymbol{N} = \boldsymbol{N}_A + \boldsymbol{N}_B$ in a binary system consisting of species A and B, it follows that

$$\boxed{\boldsymbol{N}_A + \boldsymbol{N}_B = \boldsymbol{0}} \quad \text{or} \quad \boxed{\boldsymbol{N}_A = -\boldsymbol{N}_B}$$

In other words, the flux of A is precisely opposite in direction to the flux of B, and has the same magnitude. This situation is called equimolar counterdiffusion. Commonly, the concept is used in one-dimensional models, where diffusion occurs in the same direction throughout the system. If this is the $z-$direction, then we can write

$$\boxed{N_{Az} + N_{Bz} = 0}$$

You might wonder about practical situations where equimolar counterdiffusion can happen. In binary distillation applications in which the molar heats of vaporization for species A and B are approximately equal, both species are diffusing, but at equal rates in opposite directions. Therefore, when modeling the diffusion process in these applications, it is common to invoke this simplification.

Here is another example. Consider diffusion that occurs in a tube connecting two tanks containing a binary gas mixture of species A and B. If both tanks as well as the connecting tube are at a uniform pressure and temperature, the total molar concentration would be uniform throughout the tanks and the connecting tube. If x_{A1}, the mole fraction of A in tank 1, is larger than x_{A2}, the mole fraction of A in tank 2, A would diffuse from tank 1 to tank 2 through the connecting tube, while B would diffuse from tank 2 to tank 1 through the same connecting tube.

Because the temperature and pressure are uniform, the molar flux of A from tank 1 to tank 2 through the connecting tube must be the same as the molar flux of B from tank 2 to tank 1.
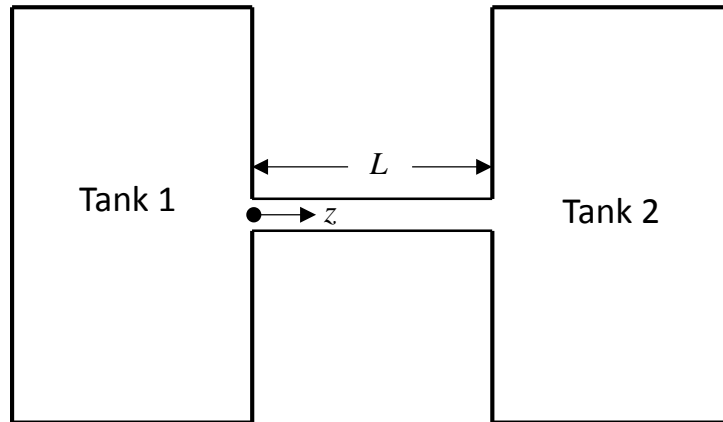
If we assume that the tanks are relatively large in volume when compared with the volume of the connecting tube, and if the connecting tube is relatively short, we can envision a scenario where when the connection between the two tanks is established, say by opening a valve, the process of diffusion through the connecting tube can reach steady state relatively quickly while the compositions in the two tanks remain practically constant. This steady diffusion process through the connecting tube can be modeled using the one-dimensional version of Fick's law.

$$N_{Az} = \underbrace{x_A \left(N_{Az} + N_{Bz} \right)}_{\text{convective transport term}} - \underbrace{cD_{AB} \frac{dx_A}{dz}}_{\text{diffusive transport term}}$$

Because we have equimolar counterdiffusion of A and B, the convective term is zero, and the above result simplifies to

$$\boxed{N_{Az} = - cD_{AB} \frac{dx_A}{dz}}$$

At steady state, it is evident that neither A nor B will be able to accumulate at any location in the tube, because that will lead to an unsteady composition at that location. Therefore, the flux of A, N_{Az}, must be independent of location in the tube, and therefore, just a constant. Hence we can write

$$\boxed{\frac{dx_A}{dz} = - \frac{N_{Az}}{cD_{AB}} = C_1}$$

where C_1 is an unknown constant that needs to be determined. Integrating this differential equation leads to

$$\boxed{x_A(z) = C_1 z + C_2}$$

Now, we proceed to write the boundary conditions.

We can assume that at the left end, $z = 0$, the mole fraction of A is at the value in tank 1, so that

$$x_A(0) = x_{A1}$$

and likewise, the mole fraction of A at the right end, which we shall designate $z = L$, is the value in tank 2.

$$x_A(L) = x_{A2}$$

Let us apply these boundary conditions to the solution we obtained.

$$x_A(0) = C_2 = x_{A1}$$

Substituting this result in the solution yields

$$x_A(z) = x_{A1} + C_1 z$$

Now, apply the boundary condition at the end $z = L$.

$x_A(L) = x_{A1} + C_1 L = x_{A2}$ so that $\boxed{C_1 = -\dfrac{x_{A1} - x_{A2}}{L}}$.   Substitute this in the result for the mole fraction distribution of A in the tube to obtain

$$\boxed{x_A(z) = x_{A1} - (x_{A1} - x_{A2})\frac{z}{L}}$$ or in a compact form, $\boxed{\dfrac{x_{A1} - x_A}{x_{A1} - x_{A2}} = \dfrac{z}{L}}$

Thus, we see that the mole fraction distribution in the duct is a straight line. This is completely analogous to a one-dimensional heat conduction problem with constant thermal conductivity, wherein the temperature distribution is linear. The molar flux of A can be written as

$$N_{Az} = -cD_{AB}C_1 = \boxed{cD_{AB}\frac{x_{A1} - x_{A2}}{L}}$$ or $\boxed{N_{Az} = D_{AB}\frac{c_{A1} - c_{A2}}{L}}$

in perfect analogy with the result for the heat flux, where we simply replace the thermal conductivity with the binary diffusion coefficient, and the end temperatures with the concentrations at the two ends.