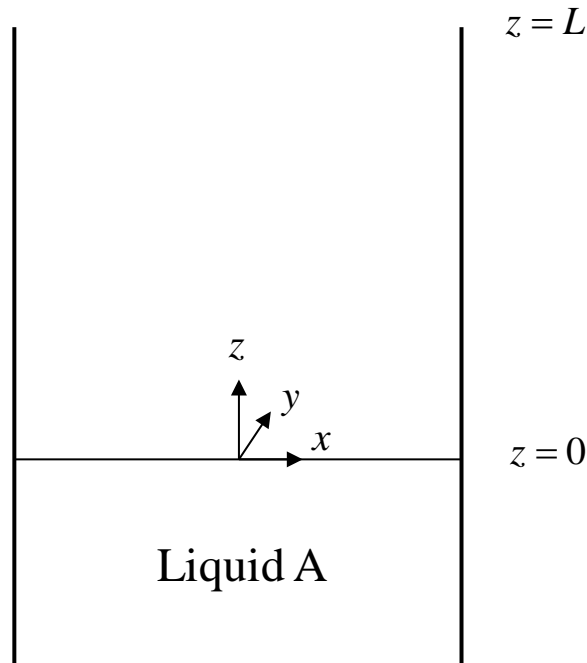


Steady One-Dimensional Diffusion of One Species A through a Second Non-Transferring Species B

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Consider a simple situation where a pure liquid A, such as water, held in an open container, evaporates into air B that is flowing over the container. A small stationary pool of liquid is present in a container. The liquid is sufficiently volatile that it exerts a significant vapor pressure at the prevailing room temperature. A gentle flow of air is maintained at the top so that the vapor is carried away by air. The liquid is assumed to be already saturated with air, so that there is no net transfer of air into the liquid from the air-vapor mixture above the liquid layer.

Gas B containing some A \longrightarrow



At the surface of the liquid, equilibrium is assumed between the gas and the liquid phases, so that the partial pressure of the vapor A in the gas phase at the interface is equal to the vapor pressure of the liquid at the prevailing temperature. We assume the gas mixture to be ideal and write

$$x_A(0) = x_{A1} = \frac{P_A}{P_t}$$

where P_A is the equilibrium vapor pressure of A and P_t is the total pressure in the gas, assumed uniform throughout the system.

It is assumed that the evaporation rate is sufficiently small that the mole fraction of A in the air stream, x_{A2} , remains virtually unchanged during its transit over the top of the container.

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

At steady state, the vapor A diffuses through the gas column because the mole fraction of A at the liquid-gas interface, x_{A1} , is larger than that at the top of the container, x_{A2} . As the liquid continues to evaporate, the height of the liquid column will gradually go down, and this change can be monitored with suitable optics. By measuring the rate of evaporation of the liquid, we can calculate the diffusivity of the vapor A in the non-transferring gas B. In order to do this, we wish to construct a model of the diffusion process in the gas column above the liquid surface.

This problem can be approximated as one-dimensional diffusion of species A through non-transferring species B. We can see from physical arguments, or from a shell balance over a differential shell in the z -direction that

$$\frac{dN_{Az}}{dz} = 0$$

This means that $N_{Az} = \text{constant}$ everywhere. Of course, we do not know the value of this constant molar flux of A. To determine its value, we must proceed to use the component of Fick's law in the z -direction.

$$N_{Az} = \underbrace{x_A(N_{Az} + N_{Bz})}_{\text{Convective flux}} - \underbrace{c D_{AB} \frac{dx_A}{dz}}_{\text{Diffusive flux}}$$

We had assumed that species B (air) is non-transferring. This means that the steady flux of species B, $N_{Bz} = 0$. Note that this does not mean that B is “non-diffusing” or “stagnant” as described incorrectly in some textbooks. We shall return to this topic at the end of the analysis.

With $N_{Bz} = 0$, Fick's law can be simplified to the following form.

$$\frac{1}{1-x_A} \frac{dx_A}{dz} = - \frac{N_{Az}}{cD_{AB}} = C_1, \text{ where } C_1 \text{ is a constant.}$$

In the analogous one-dimensional conduction problem, there would be no convective transport term, and the gradient of temperature in the z -direction is simply a constant, leading to a linear temperature profile.

If the mole fraction $x_A \ll 1$, which implies that the mixture of A and B in the column of gas-vapor is dilute in A, we can simplify the above equation to

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

which yields a linear mole fraction profile in the gas-vapor column.

$$x_A(z) = C_1 z + C_2$$

Here, C_2 is a constant of integration. To evaluate the two unknown constants, we can use the two boundary conditions

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

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

Using these conditions yields

$$C_1 = - \frac{x_{A1} - x_{A2}}{L} \quad C_2 = x_{A1}$$

Substituting for the constants and rearranging leads to the following final result for the mole fraction distribution of A.

$$\boxed{\frac{x_{A1} - x_A}{x_{A1} - x_{A2}} = \frac{z}{L}}$$

It is seen that when the mole fraction of A is plotted against distance z from the liquid surface, this result yields a straight line with constant slope. We can evaluate the steady molar flux of A through the gas-vapor column from

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

Consider the analogous heat conduction problem through the same region. If the temperature at $z=0$ is T_1 , and that at $z=L$ is T_2 , we can write the steady state conduction temperature distribution as

$$\boxed{\frac{T_1 - T}{T_1 - T_2} = \frac{z}{L}}$$

It is seen that this is entirely analogous to the mole fraction profile we obtained in the present problem. If the thermal conductivity of the material in the region $z = 0$ to L is k , we can write the steady heat flux q_z as follows.

$$q_z = k \frac{T_1 - T_2}{L} = \boxed{k \frac{\Delta T}{L}}$$

Compare the results for the molar flux of A and the heat flux. You can see that the heat conduction and diffusion problem are completely analogous, so long as the assumption we made that the gas mixture is dilute in A, or $x_A \ll 1$, holds. Let us return to the original differential equation that we obtained for the distribution of $x_A(z)$.

$$\frac{1}{1-x_A} \frac{dx_A}{dz} = - \frac{N_{Az}}{cD_{AB}} = C_1$$

When we made the assumption that $x_A \ll 1$, we approximated $(1-x_A)$ in the denominator in the left side as $\boxed{(1-x_A) \approx 1}$. Now, examine the Fick's law result that we wrote for the molar flux of A, N_{Az} , after setting $N_{Bz} = 0$.

$$N_{Az} = \underbrace{x_A (N_{Az} + \cancel{N_{Bz}})}_{\text{Convective flux}} - \underbrace{c D_{AB} \frac{dx_A}{dz}}_{\text{Diffusive flux}}$$

The origin of the extra x_A in $(1-x_A)$ is seen to be the convective flux contribution in Fick's Law written for the molar flux in the laboratory reference frame. In other words, the diffusion process leads to overall motion that carries all the molecules at a molar average velocity V^* through the column. Thus, the role of this convection arising from diffusion is minimized when the system is dilute in the species A, as one might logically expect. When we retain this convection term, molecular diffusion is no longer analogous to conduction.

If we retain the effect of convection, it is possible to integrate the differential equation for the mole fraction distribution and apply the boundary conditions to obtain the following final mole fraction distribution.

$$\boxed{\frac{1-x_A}{1-x_{A1}} = \left(\frac{1-x_{A2}}{1-x_{A1}} \right)^{z/L} = \exp \left[\frac{N_{Az}}{cD_{AB}} z \right]}$$

As you can see, this is an exponential function of z . Thus, steady one-dimensional diffusion of species A through non-transferring B yields an exponential concentration profile in contrast to steady conduction in one dimension.

In this exact solution, the constant C_1 is obtained as

$$C_1 = \frac{1}{L} \ln \left(\frac{1-x_{A1}}{1-x_{A2}} \right)$$

You can compare this result with $C_1 = -(x_{A1} - x_{A2})/L$, a result that we obtained when we neglected the role of the convection that accompanies diffusion.

Substituting the exact result for C_1 in the result for the molar flux of A,

$$N_{Az} = -cD_{AB}C_1 = -\frac{cD_{AB}}{L} \ln \left(\frac{1-x_{A1}}{1-x_{A2}} \right) = -\frac{cD_{AB}}{L} \ln \left(\frac{x_{B1}}{x_{B2}} \right)$$

This can be recast as follows.

$$N_{Az} = -\frac{cD_{AB}}{L} \ln \left(\frac{x_{B1}}{x_{B2}} \right) \frac{x_{A1} - x_{A2}}{x_{A1} - x_{A2}} = \frac{cD_{AB}}{L} \ln \left(\frac{x_{B1}}{x_{B2}} \right) \frac{x_{A1} - x_{A2}}{x_{B1} - x_{B2}}$$

In the above result, we first multiplied the right side by unity in the form $\frac{x_{A1} - x_{A2}}{x_{A1} - x_{A2}}$, and then substituted for the mole fraction of A in terms of the mole fraction of B ($x_A = 1 - x_B$) in the denominator. This permits us to write the molar flux of A in the following final form.

$$N_{Az} = \frac{cD_{AB}}{x_{Bm}} \frac{x_{A1} - x_{A2}}{L} = \frac{D_{AB}}{x_{Bm}} \frac{c_{A1} - c_{A2}}{L} = \boxed{\frac{D_{AB}}{x_{Bm}} \frac{\Delta c}{L}}$$

where x_{Bm} is the log mean of the concentration of B over the diffusion path, expressed in mole fraction units.

$$\boxed{x_{Bm} = \frac{x_{B2} - x_{B1}}{\ln \left(\frac{x_{B2}}{x_{B1}} \right)}}$$

Compare the result we just obtained for the molar flux with that in the dilute case, where we neglected the convection that accompanies diffusion. We see that the only difference is the appearance of the logarithmic average of the mole fraction of B over the diffusion path. Because

x_{B_m} must be less than unity, the flux of A is enhanced by the convection arising from diffusion over that which would result if this convection is ignored.

Now, let us return briefly to the term “stagnant B” used in textbooks. Because species A experiences a gradient in mole fraction in the gas column, species B must also experience a gradient in mole fraction of exactly the same magnitude and opposite sign. Thus, species B is diffusing downward in the column at the same rate as species A diffuses upward. But then, how is it that the flux $N_{B_z} = 0$? There is no mystery here, because species B is being carried upward by the motion of the entire gas mixture caused by the diffusion process. In fact, the convective flux of B upward must exactly balance its diffusive flux downward to give us a net flux of zero, and the appearance of a “stagnant” B . Thus, species B is neither non-diffusing nor stagnant. It is diffusing in one direction, and is being carried by the overall motion in the opposite direction at the same rate. A good analogy is to imagine yourself trying to walk downward in an escalator that is moving upward. If you choose the right pace, you’ll find yourself staying in place, just like species B in this experiment.

Thus, an appropriate term to use in describing this problem is “diffusion of A through non-transferring B ” and not “diffusion of A through stagnant B .”