

Introduction to Mass Transfer

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So far, we have dealt basically with pure component systems. When we have more than one species present, and composition gradients occur, individual species will move from one location to another, leading to species fluxes, just like the heat flux that occurs in the presence of a temperature gradient. Some examples are listed below.

Solid dissolving in a liquid: When we add water to salt in a beaker, the salt dissolves. This process begins with the dissolution of salt from the surface of each crystal into the neighboring liquid. The salt in solution is then transported across the liquid by convection and diffusion. Convection here is caused by natural means, i.e., density variations caused by composition and temperature variations in the solution, acting in conjunction with gravity. We also can stir the liquid to hasten the process of mixing, as we do when we add sugar to coffee, leading eventually to a uniform solute concentration everywhere.

Gas Absorption in a liquid: This is a common industrial process, carried out in batch vessels or in continuous columns. For example, in a packed column, the liquid is admitted at the top and flows down the column. In doing so, it covers the packing material in the form of a film of liquid flowing down. In the interstitial region among the packing particles, the gas flows upward contacting the liquid film. As an example, consider the dissolution of ammonia from an air-ammonia mixture into water flowing down the column. At any given cross-section of the column, the layer of liquid at the interface with the gas is saturated with ammonia, corresponding to the prevailing partial pressure of ammonia in the gas at that location. But the water farther away from the interface will typically have less ammonia in it, so that the ammonia will diffuse across the water film into the bulk of the liquid. This is mass transfer. As the water flows further down the column, the concentration of dissolved ammonia in it will continually increase, while as the air-ammonia mixture flows up the column, the mole fraction of ammonia in the gas phase will continually decrease as ammonia is transferred out of the gas into the liquid. This picture is somewhat simplified, because the partial pressure of ammonia in the bulk of the air-ammonia mixture will be larger than that at the interface, providing a driving force for ammonia to diffuse across the air-ammonia mixture to the interface, but this difference will be small. We'll discuss this topic in detail later in the course.

Other mass transfer operations include distillation, humidification, liquid-liquid extraction, adsorption and ion exchange, and so on. The common denominator in mass transfer processes is that species fluxes occur within a phase when there are composition variations within that phase. Also, it is common to have two phases come into contact at an interface. Typically, equilibrium conditions prevail at the interface, but the bulk phases are out of equilibrium. Species fluxes occur across the interface, and into and out of the bulk phases.

In all the above situations, mass transfer occurs by just two mechanisms: diffusion, which is molecular in origin, and convection, which is bulk movement of fluid. Even a tiny element of fluid of microscopic dimension contains enormous numbers of molecules of the species at the local concentration of that element. When the entire element translates to a new location, it carries its contents with it.

To study and analyze mass transfer, we need to develop a nomenclature. First, we need a way to identify the concentration of each species in a multicomponent mixture. We can do this on a mass basis or a molar basis. We already know how to define the mass density of a mixture ρ . It is the mass per unit volume at a given location. Imagine taking a tiny volume element of the material and determining how much mass of species A is present. The mass density or concentration of species A (mass of A per unit volume of the material at that location) would be ρ_A , and that of B would be ρ_B and so on. We can designate the mass concentration of species i as ρ_i . If the total number of species is n when we sum up all the individual mass concentrations, we must get the mass density of the mixture ρ .

$$\sum_{i=1}^n \rho_i = \rho$$

Incidentally, we commonly use the term “mixture” in mass transfer, even though the species may be completely mixed at the molecular level. Thus, a solution of salt in water is a mixture.

It is common to use mass fractions to designate mass concentration in a mixture. The mass fraction $\omega_A = \rho_A / \rho$. The individual mass fractions must always add up to unity.

$$\boxed{\sum_{i=1}^n \omega_i = 1}$$

Can you figure out why?

If we divide the mass concentration of A, ρ_A , by the molecular weight of A, M_A , we obtain c_A , the molar concentration of species A. Just as the individual mass concentrations add up to the total mass concentration, which we term mass density, the individual molar concentrations in a multicomponent mixture add up the total molar concentration, c .

$$\sum_{i=1}^n c_i = c$$

As with mass fractions, we can define mole fractions. Usually we use $x_A = c_A / c$ to designate mole fractions in liquids, and $y_A = c_A / c$ in gases. As in the case of mass fractions, when we have n species in a mixture, the individual mole fractions must always add up to unity.

Liquids: $\boxed{\sum_{i=1}^n x_i = 1}$

Gases:

$$\sum_{i=1}^n y_i = 1$$

Diffusion

Consider a binary mixture containing two molecular species in a gas phase. We are aware that the individual molecules are always in motion, with velocities distributed in magnitude and direction in a random manner about a mean that depends on the temperature of the mixture. At any given location, if we imagine a small area element that is still huge when compared with molecular dimensions, an equal number of molecules will cross that area in unit time in both directions. If the composition of the mixture is spatially uniform at that location, then the number of molecules of species A crossing the area in unit time in the two opposite directions will be the same when averaged over statistical fluctuations, and the same is true of species B. If there is a species composition gradient at that location, however, this will no longer be the case. Imagine that to the left of the area element, the proportion of the molecules of A in the mixture is larger than that on the right. Then, more molecules of A will cross from left to right than from right to left per unit time. The opposite will be true of the molecules of species B. More molecules of B will cross from right to left than from left to right in unit time. Thus, there will be a net molar flux of A and that of B in opposite directions across the area element. By dividing the number of moles of A crossing the area from left to right in unit time by the area, we can calculate a molar flux of A from left to right, and likewise the molar flux of B from right to left. The molar fluxes of A and B will be equal in magnitude, but point in opposite directions.

We have described the process of molecular diffusion in a gas. Molecular diffusion in liquids and solids occurs by a similar mechanism, with the exception that molecules are more densely packed together in these phases than in gases, and each molecule experiences interactions from neighboring molecules virtually all the time as it executes its random thermal motion. Regardless of whether we are dealing with a gas, liquid, or a solid, diffusion is driven by departure from equilibrium conditions. Therefore, a proper description of diffusion requires relating the species fluxes to chemical potential gradients of the individual species. For practical purposes, however, we can consider diffusion as being driven by composition gradients. Whenever there is a gradient in mole fraction present at a point, there will be a molar flux of the species. This idea is not restricted to binary mixtures. There can be any number of individual species present, and the concept applies to each of them, so long as a composition gradient exists at a given location.

Molecular velocities are randomly distributed in magnitude about a mean, and also randomly distributed in direction. In the presence of a composition gradient, if we can monitor the velocity of each individual molecule of A crossing our imaginary area element at a location, and average all of these velocities, we should end up with a net velocity of species A from left to right if the mole fraction on the left is larger than that on the right, because there is a net flux of species A in that direction. Likewise, species B in the binary mixture will have a net velocity in the opposite direction. Thus, the velocities of individual species in a mixture can be different in magnitude and in direction at a given location.

Because the individual species velocities at a location can be different, we must define an average velocity over all the molecules, such as that measured by a Pitot tube, or by following a tracer particle at that location. The velocity that we used in the earlier part of this course in fluid mechanics and heat transfer is called the “mass average velocity.” It is designated by a lower case \mathbf{v} in the context of mass transfer. To define this average, we first consider the mass flux \mathbf{n} at a point. If the material moves at a velocity \mathbf{v} at a point, imagine an area element dA normal to the direction of the flow. Then, the volume of fluid crossing the area per unit time in the direction of \mathbf{v} is the product of the velocity and the area, namely $\mathbf{v} dA$, where v is the magnitude of the vector velocity \mathbf{v} . If we multiply by the density of the fluid at that point, we obtain the rate at which mass flows across the area element per unit time, $\rho \mathbf{v} dA$. Dividing by the area yields the magnitude of the flux of mass, $n = \rho v$, which is the mass flow rate per unit area per unit time at that location. This mass flux has both a magnitude and a direction, which is the same as that of the vector velocity \mathbf{v} . Therefore, we define the mass flux as the vector $\mathbf{n} = \rho \mathbf{v}$. Now, we can extend the concept to individual species. In a diffusing mixture in which species A has a velocity \mathbf{v}_A at some location, if the mass of species A per unit volume at that location is ρ_A , then the mass flux \mathbf{n}_A of species A at that location can be written as

$$\mathbf{n}_A = \rho_A \mathbf{v}_A$$

Again, we note that the individual species mass flux \mathbf{n}_A also is a vector. The total mass flux is the sum of the individual mass flux vectors.

$$\mathbf{n} = \sum_{i=1}^n \mathbf{n}_i$$

Substitute for the total mass flux and individual species mass fluxes in the above result.

$$\mathbf{n} = \rho \mathbf{v} = \sum_{i=1}^n \rho_i \mathbf{v}_i$$

which defines a “mass average velocity” \mathbf{v} . From the above result, we can obtain its definition.

$$\mathbf{v} = \frac{\sum_{i=1}^n \rho_i \mathbf{v}_i}{\rho} = \frac{\sum_{i=1}^n \rho_i \mathbf{v}_i}{\sum_{i=1}^n \rho_i} = \sum_{i=1}^n \omega_i \mathbf{v}_i$$

But this is not the only average velocity. We also can define a molar average velocity in an analogous fashion.

First, we start with molar fluxes, designated by capital letters.

$$N_A = c_A \mathbf{v}_A$$

This molar flux N_A measures the number of moles of species A crossing a differential area normal to the direction of motion of species A per unit time, divided by that differential area. It is obtained by dividing the mass flux of A by the molecular weight of that species, M_A . That is, $N_A = \mathbf{n}_A / M_A$. As with mass fluxes, the individual species molar fluxes must add up to the total molar flux at the location.

$$N = \sum_{i=1}^n N_i$$

Again, substitute for the total molar flux and the individual species molar fluxes in this result to get

$$N = c \mathbf{V}^* = \sum_{i=1}^n c_i \mathbf{v}_i$$

defining the “molar average velocity” \mathbf{V}^* . Using the above result, we can obtain its definition.

Liquid:
$$\mathbf{V}^* = \frac{\sum_{i=1}^n c_i \mathbf{v}_i}{c} = \frac{\sum_{i=1}^n c_i \mathbf{v}_i}{\sum_{i=1}^n c_i} = \sum_{i=1}^n x_i \mathbf{v}_i$$

Gas:
$$\mathbf{V}^* = \frac{\sum_{i=1}^n c_i \mathbf{v}_i}{c} = \frac{\sum_{i=1}^n c_i \mathbf{v}_i}{\sum_{i=1}^n c_i} = \sum_{i=1}^n y_i \mathbf{v}_i$$

Besides these two averages, other averages are defined and used as well, but that is an advanced topic, which we shall not discuss here.

Again, remember that it is the mass average velocity in a multicomponent mixture that is used in the conservation of momentum principle applications, and the one which appears in the earlier material in this course in fluid mechanics and heat transfer where we simply called it the velocity.

Now, we can move on to diffusion!

Simply having diffusion occur can lead to motion as we have seen. It is rather tiny motion, but it is important to put yourself in a reference frame translating instantaneously with this average motion at a given location in order to be able to come up with a simple “model” of the diffusion process, called Fick’s Law, which applies to a binary mixture of A and B.

We first define a molar flux of A with respect to the molar average velocity. In other words, we write

$$\mathbf{J}_A^* = c_A (\mathbf{v}_A - \mathbf{V}^*) = N_A - c_A \mathbf{V}^*$$

for this molar flux in the moving reference frame.

Fick's law, obtained based on empirical observation of diffusing mixtures, states that

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

where x_A generically designates mole fractions either in gases or liquids. In this course, we shall usually be concerned only with a one-dimensional version of this equation.

Liquids:
$$\boxed{J_{A,z}^* = -c D_{AB} \frac{dx_A}{dz}}$$

Gases:
$$\boxed{J_{A,z}^* = -c D_{AB} \frac{dy_A}{dz}}$$

What if we want to use mass concentrations and mass fractions? There is an analogous version of Fick's law.

$$\boxed{j_{A,z} = -\rho D_{AB} \frac{d\omega_A}{dz}}$$

Here, $j_{A,z}$ is the z -component of a vector mass flux \mathbf{j}_A , which is the mass flux with respect to the mass average velocity at a point.

$$\mathbf{j}_A = \rho_A (\mathbf{v}_A - \mathbf{v})$$

Note the similarity of Fick's law to Fourier's law for describing heat conduction and Newton's law of viscosity. The symbol D_{AB} that appears in Fick's law is called the binary diffusivity of species A in species B. It is the same entity regardless of whether we write Fick's law for the mass flux or the molar flux of species A. It is easy to show that the binary diffusivity of B in A under the same conditions is the same! Because we shall be discussing only binary mixtures here, we shall drop the prefix "binary" in "binary diffusivity" and refer to D_{AB} simply as the diffusivity. The diffusivity is a material property of the pair, and depends on thermodynamic variables such as temperature, pressure, and composition in general.

What are the units and dimensions of diffusivity? Let us work with the one-dimensional version to figure them out.

$$D_{AB} = - \frac{J_{A,z}^*}{c \frac{dx_A}{dz}}. \text{ So putting in the units for the numerator and denominator, we get}$$

$$D_{AB} = \frac{\text{moles} / (\text{length}^2 \times \text{time})}{\text{moles} / (\text{length}^3) \times (1 / \text{length})} = \boxed{\frac{\text{length}^2}{\text{time}}}$$

Thus, we report diffusivities in m^2 / s in SI, and in ft^2 / hr in the British system. In the old CGS system, the units are cm^2 / s . You need to be comfortable with all three systems.

Values of diffusivities in a variety of systems are given in Appendix J of the book by Welty et al. (1). At room temperature, gas phase diffusivities are the largest, and are typically of the order of $10^{-5} m^2 / s$ at atmospheric pressure, while liquid phase diffusivities are four orders of magnitude smaller, typically being of the order of $10^{-9} m^2 / s$. Diffusivities in solids are another three orders of magnitude smaller than those in liquids.

In gases at ordinary densities, the diffusivity is nearly independent of composition, depending only on the choice of the specific pair of species (such as oxygen in nitrogen, or ammonia in nitrogen, and so on) and the temperature and pressure. Gas phase diffusivities increase with increasing temperature, being usually proportional to $T^{1.75}$, and depend inversely on the pressure, i.e., $D_{AB} \propto 1/P$.

Welty et al. (1) and Bird et al. (2) discuss detailed predictive models for gas phase diffusivities. A commonly used prediction is that of Hirschfelder, Bird, and Spotz, presented on page 443 in the textbook (1). But information on the Lennard-Jones parameters used in the Hirschfelder-Bird-Spotz equation is not readily available in many situations. In those cases, the textbook recommends the Fuller-Schettler-Giddings correlation on page 445. Liquid phase diffusivities are more difficult to predict, especially because they depend on the composition, in addition to temperature. Also, a lot depends on the nature of the solute and solvent, and whether the solute is ionized. For non-electrolytes, one can use the Wilke-Chang correlation. Also, Welty et al. mention the Hayduk and Laudie correlation for nonelectrolytes diffusing in water, which is simpler to use than that of Wilke and Chang. Both correlations are for dilute systems (in principle, infinite dilution). Other correlations for dilute solutions in both aqueous and non-aqueous systems that are sometimes more accurate are discussed in Taylor and Krishna (3). Some techniques for estimating diffusivities in concentrated solutions are available, and are discussed in Welty et al. (1), as well as in Taylor and Krishna (3).

For conducting solutions, in some cases, it is possible to relate the diffusivity to ionic conductance. The Nernst equation given in the text is an example.

As noted by Welty et al., binary diffusivities in solids increase with increasing temperature according to an Arrhenius relationship of the form

$$D_{AB} = D_0 \exp\left(-\frac{Q}{RT}\right)$$

where D_{AB} is the binary diffusivity of species A in solid B, D_0 is a constant with the units of diffusivity, Q is an activation energy for diffusion, R is the universal gas constant, and T is the absolute temperature. Some values of D_0 and Q can be found in Tables 24.7 and 24.8 in the textbook by Welty et al. (1).

Fick's Law in Laboratory Reference Frame

We can rewrite Fick's law for the vector fluxes N_A and n_A in the stationary (laboratory) reference frame or their components in a given direction. This just requires a bit of algebra.

For example,

$$N_A = c_A V^* + J_A^*$$

from the relationship between the two fluxes. We can write

$$c_A V^* = x_A c V^* = x_A N = x_A (N_A + N_B) \text{ so that}$$

$$N_A = x_A (N_A + N_B) + J_A^* = x_A (N_A + N_B) - c D_{AB} \nabla x_A$$

An analogous form can be obtained for the mass flux of A in the laboratory reference frame.

$$n_A = \rho_A v + j_A$$

$$\rho_A v = \omega_A \rho v = \omega_A n = \omega_A (n_A + n_B) \text{ so that}$$

$$n_A = \omega_A (n_A + n_B) + j_A = \omega_A (n_A + n_B) - \rho D_{AB} \nabla \omega_A$$

Usually, we tend to use the molar version in gases, because the total molar concentration is constant at constant pressure and temperature, whereas the density can vary with spatial position. In liquids, so long as the solution is dilute, it does not make any difference whether we use mass or molar concentrations. If the liquid is comprised mostly of solvent, its density, whether molar or mass, will remain sensibly constant over space.

Multicomponent mixtures

When a mixture contains more than two species, diffusion is not described by Fick's law. Instead, one must use the Maxwell-Stefan equations to describe multicomponent diffusion in general (2). This is because the flux of each species is affected by the gradients in mole fraction

of all the species, and it is even possible for a species to diffuse against its composition gradient. If a system consists primarily of solvent, however, and other species that diffuse in the solvent are present in relatively small concentrations, it is possible to assume that the fluxes of each species depend only on the gradient of the mole fraction of that species in the solvent, neglecting the presence of other solutes. Thus each solute plus the solvent can be regarded as a binary pair to which Fick's law applies. You can consult references (3,4) to learn more about multicomponent diffusion.

Mass Transfer Coefficient

When mass transfer occurs between a fluid and a surface due to a combination of convective and diffusive transport, in analogy with heat transfer, we define a mass transfer coefficient to describe the mass flux or molar flux. For example, if a liquid flows over a solid surface that is dissolving in the liquid, one might write

$$N_A = k_c (c_{A,s} - c_{A,\infty}) = k_c \Delta c_A$$

where $c_{A,s}$ is the concentration of the solute A in the liquid in contact with the solid surface and $c_{A,\infty}$ is the concentration of A in the liquid far from the solid surface. We assume equilibrium to prevail at the interface between the solid and the liquid (in analogy with heat transfer), which would mean that $c_{A,s}$ is the equilibrium solubility of the solid in the liquid at the prevailing temperature. Of course, the concentration is not this equilibrium value at other locations in the liquid, which is the reason why mass transfer occurs. Solute will diffuse from the high concentration region in the liquid in contact with the solid to the lower concentration regions away from the solid, and will be carried away by the flowing liquid. One can see how the flow conditions as well as the molecular diffusivity can influence the mass transfer rate between the solid and the liquid. Also, the geometry will play a role. As we saw in heat transfer, whether the flow is a boundary layer flow or one within a conduit will make a difference as well, and in flow through conduits, instead of using $c_{A,\infty}$ in the above result, we would use a bulk average concentration at the location where we are defining the mass transfer coefficient k_c . The above definition of k_c , which is called the mass transfer coefficient based on a concentration driving force Δc_A , serves as a template that we can use where needed. Note that we can use other driving forces, and define suitable versions of the mass transfer coefficient.

$$N_A = k_x (x_{A,s} - x_{A,\infty}) = k_x \Delta x_A$$

Here, we are using the driving force for mass transfer expressed in mole fraction units. Clearly,

$$k_x = c k_c$$

so that even the units for these two types of mass transfer coefficients differ. The units of k_c are those of molar flux divided by concentration.

$$\text{Units of } k_c : \frac{\text{moles of A}}{\text{m}^2 \bullet \text{s} \times (\text{moles of A} / \text{m}^3)} = \frac{\text{m}}{\text{s}}$$

As you can see, strangely enough, the units of k_c match those of a velocity, even though the meanings of these terms are completely different. It is shown in reference (3) that k_c is actually the maximum possible velocity, relative to the molar average velocity, at which species A can be transferred in a binary system. The units of k_x can be inferred from the result for the molar flux written in terms of the mole fraction driving force.

$$\text{Units of } k_x : \frac{\text{moles of A}}{\text{m}^2 \bullet \text{s} \bullet (\text{mole fraction of A})}$$

Let us explore the units of k_x more carefully. The mole fraction of A is the ratio of moles of A per mole of mixture. Substituting this result,

$$\text{Units of } k_x : \frac{\text{moles of A}}{\text{m}^2 \bullet \text{s} \bullet (\text{moles of A} / \text{mole of mixture})}$$

Because mole fraction has no dimensions, it is sometimes omitted when writing the units of k_x . But it is advisable to keep it intact.

If a solid surface sublimates into a gas flowing past it, we might use a partial pressure driving force to define a mass transfer coefficient k_G .

$$N_A = k_G (p_{A,s} - p_{A,\infty})$$

Here, $p_{A,s}$ is the partial pressure of the vapor in the gas phase at the solid surface, and is equal to the equilibrium vapor pressure of the solid surface at the prevailing temperature. The units of k_G can be inferred from the definition given above.

$$\text{Units of } k_G : \frac{\text{moles of A}}{\text{m}^2 \bullet \text{s} \bullet \text{Pa}} \quad \text{or} \quad \frac{\text{moles of A}}{\text{m}^2 \bullet \text{s} \bullet \text{atm}}$$

depending on the units chosen for representing the partial pressure driving force. The standard SI unit for mole is the gram-mole abbreviated simply to “mol.” It is common in chemical

engineering practice to use the “kg-mol” which stands for kilogram-mole as a substitute; this is sometimes abbreviated as “kmol.”

Another possibility is to use the mass concentration difference $\Delta \rho_A$ as the driving force to define a mass transfer coefficient k_ρ .

$$n_A = k_\rho (\rho_{A,s} - \rho_{A,\infty}) = k_\rho \Delta \rho_A$$

The units of k_ρ can be obtained from its definition as the ratio $n_A / \Delta \rho_A$, and also work out to be the same as those of a velocity.

$$\text{Units of } k_\rho : \frac{\text{mass of A}}{\text{m}^2 \cdot \text{s} \times (\text{mass of A} / \text{m}^3)} = \frac{\text{m}}{\text{s}}$$

Thus, unlike in heat transfer, where temperature differences are always used as the driving force, in mass transfer, because concentration can be expressed in a variety of units, mass transfer coefficients are not uniquely defined. You need to get used to this idea. Usually, convention dictates the type of mass transfer coefficient that is used in a given application. In gas absorption, we tend to use molar concentration differences in the liquid and partial pressure differences in the gas phase, and in distillation, mole fraction driving forces are used in both phases.

You can convert mass transfer coefficients from one type to another by carefully converting the units involved for the driving force.

Mass transfer coefficients are converted to a dimensionless form called the Sherwood Number, and reported in correlations in which the Sherwood Number is some function of the Reynolds Number for the flow, and a group called the Schmidt Number, which plays a role analogous to that of the Prandtl Number in heat transfer. We’ll discuss these ideas a little later.

References

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