CE/ESR
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TRANSPORT OF SOLUTES
ADVECTION-DISPERSION EQUATION

by
William Fish

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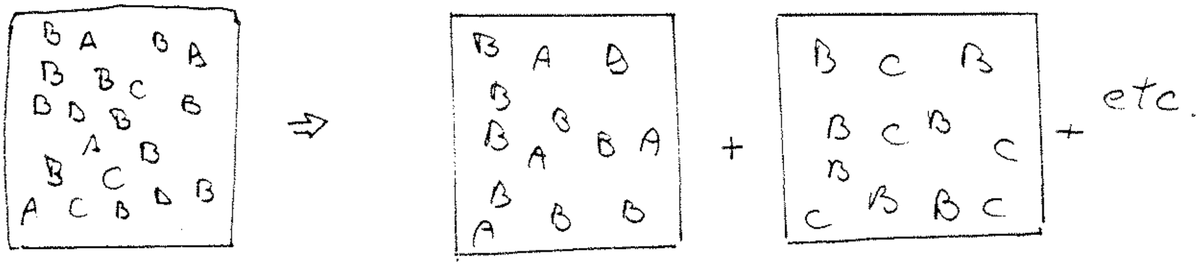
V.1 . INTRODUCTION

MASS TRANSPORT IN BINARY FLUID SYSTEMS

Early in this course we developed the conservation of mass equation for a fluid and obtained the continuity equation. A second sort of mass conservation equation can be developed for dissolved mass. In this case, we speak of mass conservation in a "binary system" meaning that two components are present: the constituent A dissolved in a solvent fluid B. B, of course, may be either a gas or liquid. In general, there are n components in natural fluids, but if we initially assume no reactions among the constituents, and assume the dissolved components do not significantly affect the momentum balance of the fluid (i.e., minimal buoyancy effects), then we can isolate the behavior of each constituent and treat it independently of the others. Thus, we can easily reduce an n-component fluid to a set of (n - 1) binary fluids: A + B + C + D = {(A + B), (B + C), (B + D)}, where B is the solvent fluid.

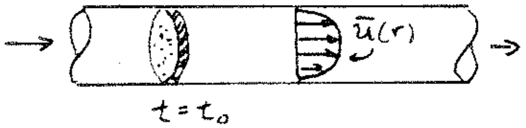


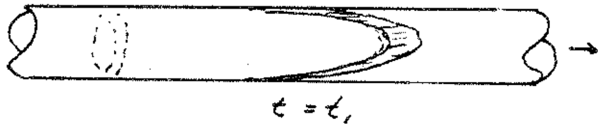
<u>Nomenclature</u>: The transport of a dissolved constituent can proceed by random molecular motions, by advection on turbulent eddies, by advection with bulk motion of the fluid. These are three almost unrelated processes. Yet, it is convenient in many cases to link the transport of dissolved mass by all of these processes. We will note the following, fairly standard nomenclature applied to the classes of transport:

> <u>Diffusion</u>: Transport effected by the random motions of molecules. Such motion depends on the molecular properties of the fluid, and thus is influenced by temperature and (to a much lesser extent) density, but is not influenced by the velocity distribution or "bulk" behavior of the fluid. Diffusion is thus sort of a "state function" in that it is independent of location in the fluid, and is perfectly isotropic. And, while we are thinking in thermodynamic terms, note that diffusion is an irreversible, entropy-driven process. Once a constituent has diffused, no ordinary fluid motion can reverse the process and put the system back to its original state. Philosophically, then, diffusion is an "arrow of time".
>
> <u>Advection</u>: Transport of a dissolved constituent as a passive component of a fluid in bulk motion. If A is passively carried by B, then as B goes, so goes A.
>
> <u>Turbulent Diffusion</u>: Transport effected by chaotic advective motions of eddies within a fluid. From a fundamental point of view, this is strictly advection, but as Reynolds noted, when you time-average these advections, the net result looks rather like speeded-up diffusion, and can be modeled

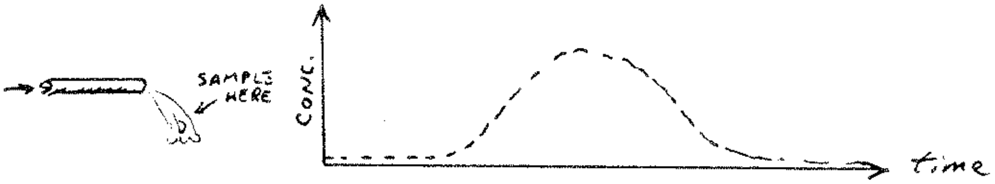
by the same equations governing diffusion. Thus, by the "duck test" we call this diffusion, but distinguish it as turbulent diffusion. (The analogy to molecular viscosity and eddy viscosity should be apparent). As with eddy viscosity, great simplification is achieved, but at a cost of having to define diffusivity coefficients that depend strongly on the intensity and anisotropy of local turbulence. Turbulent diffusion is minimally affected by molecular properties, but is strongly influenced by the velocity distribution and buoyant stability of the fluid. Turbulent diffusion is thus, in general, a function of location and direction. However, as long as a reasonable estimate of diffusivity can be attained, the use of the Fickian analogy between turbulent and molecular mixing is conceptually well founded. Like diffusion, you can think of turbulent diffusion as irreversible, but not so much for thermodynamic reasons as for reasons of chaos. In practice, no exact reversal of chaotic eddy motions is possible because of the extreme sensitivity to initial conditions.

<u>Dispersion</u>: Transport effected by spatial variation in the mean velocity field. This is most easily described with a simple illustration. Suppose you mark a narrow "disk" of water in a pipe with a dye tracer, and then follow the movement of the tracer as the water flow through the pipe. Note the effect of the velocity distribution on the dye distribution:

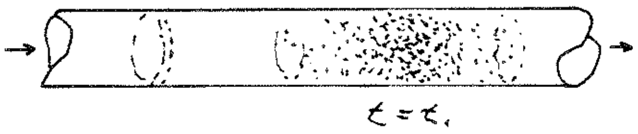




In the figure above we pretend that molecular and turbulent diffusion does not occur. Now, measure the mean concentration of dye in the water as it comes out of the pipe:



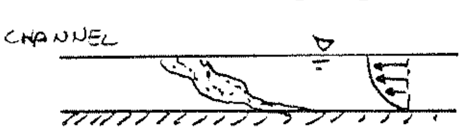
The famous British hydrodynamicist Sir Geoffrey I. Taylor reckoned that the output of the pipe, which is in effect the radially integrated average concentration, could be modelled <u>as if</u> the disk of dye were diffusing in a Fickian manner, rather than spreading out due to velocity variations:

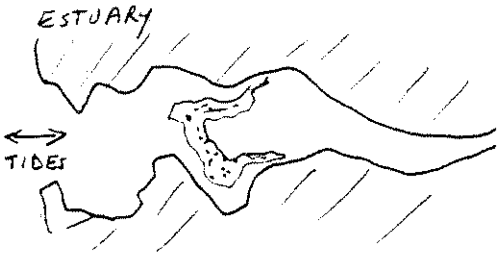


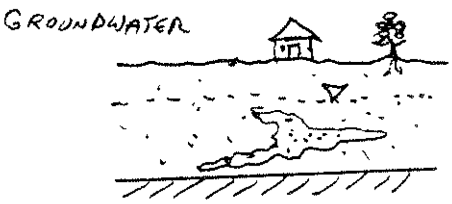
This imaginary "diffusion" is vastly greater than molecular diffusion, and is much greater than even eddy diffusion:

Note that, in a real pipe, the total spreading of the dye is the summation of the molecular diffusion, eddy diffusion, and advective spreading, all of which occur simultaneously. The relative contributions of each process depends on the velocity in the pipe: at very low velocity nearly all of the spreading is molecular, at high velocity nearly all is advective.

In the particular case above, the spreading out of the dissolved mass due to the radial distribution of velocities in a pipe is called Taylor pipe dispersion, in honor of Sir Geoffrey. Because turbulent flow in pipes has been well studied and is geometrically simple, a number of accurate formulas have been developed to specify the effective diffusivity or "Taylor dispersivity" of flow in pipes and associated fittings. The idea also has been extended to open channels, rivers, estuaries, and groundwater, with decreasing degrees of accuracy:







We will discuss the issues surrounding the use of dispersivity in such systems, but essentially, dispersivity is used to compensate for a lack of knowledge or understanding of the velocity distributions in complex flow fields. As António Baptista puts it: Dispersion is the shame of the fluid physicist. But, when one must come up with some sort of assessment in these cases, one often must put aside one's shame and rely on "dispersivity". Be aware though, that the science in this area is increasingly moving away from empirical dispersion models, although some sort of "dispersivity" normally must be retained in any model that is not fully three-dimensional.

Note that the definitions given above, particularly the latter two, are not universally agreed upon. Some authors refer to turbulent diffusion as turbulent dispersion, and use the term longitudinal dispersion to describe the last phenomenon. I will probably slip up and use dispersion and diffusion interchangeably. I suppose we should not get too hung up on nomenclature. It is more important to know that only the molecular form is really well defined, and that varying degrees of empiricism are needed in forcing other processes into a mold that Fick never envisioned for them.

So what is that mold? As we have discussed previously, for any fluid, whether stagnant, laminar, or turbulent, if a gradient of a fluid constituent exists, then there will be net transport of that constituent in a direction that opposes the direction of the gradient. Furthermore, the flux of the constituent (flow rate per unit area) is proportional to the magnitude of the gradient, where the constant of proportionality is called the diffusivity and which has dimensions of L^2/T. The most general statement of Fick's Law of Diffusion is:

$$J_z^A = -k_d^A \frac{\partial \overline{C}_A}{\partial z} \qquad (1)$$

where J_z^A is the flux of A in the z direction (units = mass of A/area/time), k_d^A is the diffusivity of A in the fluid, and $\overline{C}_A$ is the dimensionless concentration of A. (We will review concentration units in a moment). All of the diffusions and dispersions discussed above are fitted to this simple equation. For molecular diffusion, Eq.1 is perfectly accurate for all purposes. In the turbulent and dispersive extensions of this theory the key problems and computations arise in the definition of the diffusivity (what processes are lumped under that parameter) and in the definition of the averaging for the "average concentration" (time-averaged or space-averaged? depth-averaged or width-averaged? time-and-space averaged?)

You may find it useful at this point to review the class handout entitled "Generic Statement of Fickian Flux Equation" to be certain that you understanding the underpinnings of this seminal formula.

> Adolf Eugen Fick: (1829-1901) He articulated Fick's Law of Diffusion in 1855. Interestingly, Fick was an M.D. and most of his research was devoted to human anatomy and physiology. He did much work on the mechanics of the body and the dynamics of blood circulation. He got interested in diffusion as it related to the question of oxygen transfer in the blood and pulmonary systems. Evidently his law was the subject of some controversy at the time, because he initially did not work out an underlying theory. I imagine its verity and general usefulness were documented in short order.

Units of Concentration

Some authors like to distinguish between the concentration of a constituent and its density. Unfortunately, this is confusing because most common "concentration" units are actually densities. Under the strict definition, concentration is the dimensionless ratio of the mass of the i-th component divided by the sum of the masses of all components:

$$C_A = \frac{\text{Mass A}}{\text{Mass (A + B)}}$$

$$C_B = \frac{\text{Mass B}}{\text{Mass (A + B)}}$$

In this system, a solution that has 1 part of A for every 1 million parts of B is said to have a concentration of $C_A = 1 \times 10^{-6}$. In such a dilute solutions, the mass of A is negligible and can be omitted from the sum in the denominator. Strictly dimensionless concentrations are rarely used outside of computational systems. Within a numerical model, it may be convenient to carry concentrations as these dimensionless forms, but chemists and biologists and engineers and government regulators prefer to think in terms of more intuitive units. (A rare exception is the "mole fraction" which is a dimensionless concentration used by chemists). Thus, proportionality factors are normally applied to define the order of magnitude of the dimensionless concentration. For example, $C_A = 1 \times 10^{-6}$ is expressed as "1 ppm" (part per million) where the 10^6 proportionality factor is implied. Other common "proportional-dimensionless" units are:

%-A (w/w) = parts A per hundred parts solution, weight/weight basis

%-A (v/v) = parts A per hundred parts solution, volume/volume basis

°/oo-A = parts A per thousand parts solution, usually w/w

ppb = parts per billion (at that level w/w or v/v is irrelevant)

ppt = parts per trillion (in some contexts, parts per thousand)

ppq = parts per quadrillion (you laugh? The proposed standard for dioxin in the Columbia River is 0.013 ppq).

The other familiar way of expressing "concentrations" is as densities, which of course are defined as a mass divided by a unit volume:

$$\rho_A = \frac{\text{Mass A}}{\text{Volume (A + B)}}$$

$$\rho_B = \frac{\text{Mass B}}{\text{Volume (A + B)}}$$

Examples of density units for dissolved solids are mg/L, kg/m^3, mg/m^3 (common unit for air pollutants, and "mixed" weight/volume percentages such as %-A (w/v).

The concentrations can be related to densities via the bulk density of the fluid (ρ): $C_A = \rho_A/\rho$. This equation shows that a simple relationship between concentrations and densities holds only if the bulk density of the fluid is essentially constant. If the density of the fluid is apt to differ vary by more than about 1% (as it does in estuaries and in the oceans on large scales) it is better to use some sort of concentration units. For example, chemical oceanographer define seawater constituents in units like mg/kg or μg/kg.

Remember:

- In very dilute solutions <u>numerical</u> equivalences can be assumed between concentrations and densities:

$$1 \text{ ppm} = 1 \text{ mg/L} = 1 \text{ g/m}^3$$
$$1 \text{ ppb} = 1\ \mu\text{g/L} = 1 \text{ mg/m}^3$$

- But, the units may trip you up in calculations, especially if you are using an empirical formula.

- In stronger solutions, concentrations and densities are not equivalent, even numerically: 1% w/v $\neq$ 1% w/w. Also, if "background" salts cause bulk density variation, then even trace concentrations $\neq$ densities.

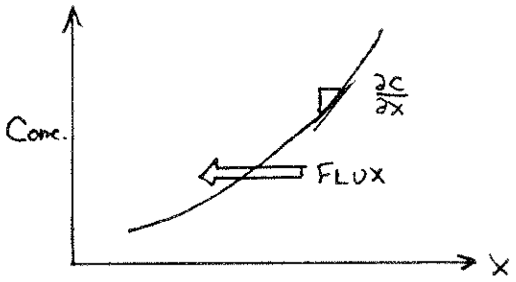
GENERIC STATEMENT OF FICKIAN FLUX EQUATION

To get the right start on diffusion fluxes and the material that follows, it is important to have a good grasp of the way fluxes are computed, and in particular to fully understand the so called Fickian model of flux equations.

Adolph Eugen Fick, a 19th century scientist, developed Fick's Law of diffusion, which states that the (molecular) flux of a dissolved constituent is linearly proportional to the opposite of the spatial gradient of the concentration of that constituent. For example, for a dissolved constituent "A":

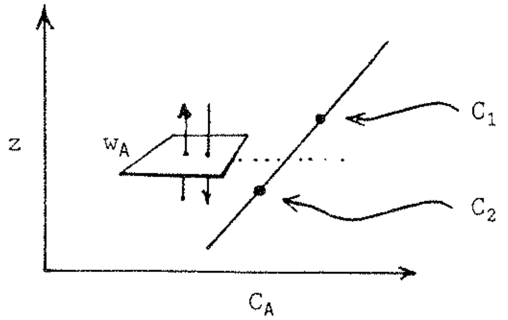
$$J_z^A \quad -k_d^A \frac{\partial C_A}{\partial z} \tag{1}$$

where J_z^A is the flux of A in the z direction (units = mass of A/area/time), k_d^A is the diffusivity of A in the fluid, and C_A is the dimensionless concentration of A (e.g., the kg of A dissolved per kg of fluid; in dimensionless units, 1 part per million would be expressed as 1×10^{-6}). This law expresses the idea that diffusion occurs "down a gradient", i.e., flows spontaneously from an area of high concentration to low concentration.



Fick based this law on experiments, but it is easy to prove its logic. Assume that in a fluid, the dissolved molecules always travel the same average distance in a unit time. E.g., the molecules might travel 1 cm in 1 sec, on the average. That is, the molecules possess an average velocity. In a gas, we would say that the molecules travel across the "mean free path" distance in the average interval between collisions, and we could compute this mean velocity. In a liquid we would probably have to experimentally measure the velocity. In any case, for molecular motions, this velocity is a well defined characteristic of the fluid because even very brief averaging intervals encompass millions of molecular collisions. Of course, for the entire fluid, this average molecular velocity has no preferred direction, and the molecules are equally likely to travel in any direction (perfect isotropy).

Now, dissolve some molecules of A in the fluid, and assume that there is no special attractive forces among the molecules. The molecules of A must move with the same mean velocity as the molecules of the bulk fluid. The molecules of A (like the bulk fluid) have no preferred direction to their velocity. If, however, there is a gradient of concentration of A, then we can show that there will be a net motion of A along the direction of the gradient. Suppose there is a gradient of A in the z direction as shown in the figure below:



where $C_1 > C_2$

The mean velocity of the A molecules in the z-direction is w_A, which as we said above is equal in either the positive or negative direction. Now, consider the number of molecules that pass through a perpendicular "window" of unit area in a given amount of time. The molecules of A above the window travel downward with the same velocity that molecules of A below the window travel upward. But because of the concentration gradient, there are more A's above the window than there are below the window. Thus,

Number of A's Moving Up through the Window/Unit Time $\propto$ $w_A C_2$
Number of A's Moving Down through the Window/Unit Time $\propto$ $w_A C_1$

and because $C_1 > C_2$, more A's are moving down through a unit area in a unit time than are moving upward. That is, the downward flux is greater than the upward flux, and the <u>net</u> flux is given by:

$$J_z^A \propto (C_2 - C_1) w_A \tag{2}$$

If we define the "mean distance travelled" by the molecules as l_m , then we can state the concentration difference across this distance as:

$$(C_2 - C_1) = -l_m \frac{\partial C_A}{\partial z} \tag{3}$$

Substitute Eq.3 into Eq. 2 to obtain:

$$J_z^A \propto -l_m w_A \frac{\partial C_A}{\partial z} \tag{4}$$

To convert the proportionality into an equivalence, we note that J is in units of mass flux (mass/area/time), and we can convert the statistical proportions given by the dimensionless concentration C into actual mass proportions by multiplying C by the (constant) bulk density of the fluid:

$$J_z^A = -\rho\, l_m w_A \frac{\partial C_A}{\partial z} \tag{5}$$

As stated above, for a gas, the mean velocity and the mean free path can be computed, but for a liquid it must be measured. For either case we can assume that $\rho l_m w_A$ = constant which is characteristic of the fluid and say that

$$\rho l_m w_A = k_d$$

which when substituted into Eq.5 gives us Fick's Law (Eq.1). This definition of k_d is used if dimensionless concentrations are used. If "density" concentrations (such as g/m^3 or mg/L) are used, as they so often are, then the multiplication by the bulk density is implicit and we redefine k_d (with different units of course) as

$$l_m w_A = D$$

So, this is Fick's Law, and it makes sense that a quantity of "A" will exhibit a flux in the direction of the (opposite) of the gradient. Later on, probably about the time that Prandtl was starting to think about mixing lengths in turbulent fluids, scientists began to realize that Fick's approach was equally applicable to the diffusion of quantities other than just dissolved mass. Newton's Law was formulated two centuries earlier for shear stress in a fluid, but if you think of shear stress as the molecular diffusion of momentum, you recognize that the transport of momentum down a velocity gradient is essentially "Fickian"; i.e., analogous to Fick's Law.

Likewise, Fourier's Law of heat conduction (formulated a century before) states that heat diffuses down a gradient of temperature, which is just an indicator of the concentration of heat. The recognition of the Fickian Analogy marked the begin of the unified description of heat, mass, and momentum transport, which was perfected by Bird in the 1950s. For our immediate purposes, the Fickian Analogy allows us to define a uniform form for a set of "transport coefficients." These coefficients are expressed in the same units (m^2/s), regardless of whether they are used to describe heat, mass, momentum, or importantly, buoyancy. This uniformity of coefficient form will prove especially useful in defining fluxes in turbulent systems, which can be approximated by the Fickian equations.

General Statement of Gradient/Flux Equations

Let S be some quantity that is characteristic of a fluid, such as momentum, concentration of dissolved component, heat, or buoyancy. Define the following related variables:

J_S = Flux of S = S/unit area/unit time
Units: $J_s \longrightarrow S\ L^{-2}T^{-1}$ (e.g., $S/m^2/sec$)

s = specific S = S/unit mass
Units: $s \longrightarrow S\ M^{-1}$ (e.g., S/kg)

The general expression of flux in term of gradients is:

$$J_z^S = -\rho K_S \frac{\partial s}{\partial z} \tag{6}$$

where J_z^S is the flux of S in the z-direction; two other flux corresponding equations describe the flux in the x- and y-directions. Note that the gradient is that of *s* (specific-S). Note the dimensions of all the components:

Eqn:	J_z^S	=	$-\rho$	K_S	$\partial s/\partial z$
Dimensions:	$S\ L^{-2}T^{-1}$		$M\ L^{-3}$	$L^2\ T^{-1}$	$S\ M^{-1}\ L^{-1}$

A quick comparison reveals that this equation is consistent with the form of Fick' Law given in Eq.5, using the second definition of diffusivity, $k_d = l_m w_A$. In fact, we do not have to express diffusivity in terms of mean-path lengths and velocities; it can be simply a fitted parameter, as long as we assign in the correct units with dimensions $L^2\ T^{-1}$. Now, if other fluid properties such as heat or momentum are substituted into Eq.6, do we obtain the familiar flux laws?

MOMENTUM

Let $S = P_x$ = momentum in the x-direction. Then $s = P_x$/mass = x-velocity = u. We have defined shear stress τ_{xz} as the negative of the z-direction flux of x-momentum. Hence, $J_z^S = J_z^\tau = -\tau_{xz}$. Making these substitution into Eq.6:

$$-J_z^S = \tau_{xz} = \rho K_\tau \frac{\partial u}{\partial z} \tag{7}$$

And if we note that kinematic viscosity ν has dimensions $L^2\ T^{-1}$ and substitute it for K_τ, we obtain (after dividing out ρ)

$$\tau_{xz} = \mu \frac{\partial u}{\partial z} \tag{8}$$

which certainly looks like Newton's Law of viscosity. How about heat flux?

Momentum & Heat transfer eqn
interesting but not
reqd for this course

HEAT

Let S = Q' = heat content of the fluid. Then s = Q'/mass = Q, the specific heat. Hence, $J_z^S = J_z^Q = q/A = q'$, where q is the rate of heat transferred per unit time, and q' = q/A is the heat flux (heat transferred/unit time/unit area). (Refer back to the 3rd lecture in ESE 505 where we developed the differential energy balance equation). Make the necessary substitutions into Eq.6:

$$J_z^Q = q_z' = -\rho K_Q \frac{\partial Q}{\partial z} \tag{9}$$

Note that from elementary thermodynamics we can relate change in specific heat content to change in temperature by the relationship

$$dQ = C_v dT \tag{10}$$

where C_v is the specific heat capacity at constant volume. Substitute Eq.10 into Eq.9. Because C_v is a state property and does not vary with position, it is constant with respect to z and can be legitimately placed as a constant in from of the z-derivative:

$$q_z' = -\rho C_v K_Q \frac{\partial T}{\partial z} \tag{11}$$

Note that ρ and C_v are general characteristics of the fluid that are independent of the intrinsic heat-transfer properties of the fluid. The specific information about the ability of the fluid to transmit heat is embodied in K_Q. We use the "K" notation here to emphasize the similarity of this constant to analogous constants, but in the literature and in handbooks, K_Q is denoted by α, and is called the *thermal diffusivity*.

While α quantifies the intrinsic thermal properties of the fluid, Eq.11 indicates that for a given value of α, the density and the specific heat capacity do affect the flux of heat. The denser the fluid, the better it transmits heat. Likewise, the higher the heat capacity of the fluid, the greater the transfer of heat for a given T-gradient. So, for practical purposes, it is convenient to lump together all of these properties of a given fluid into a single parameter, $k_h \equiv \rho C_v K_Q$. Rewrite Eq.11 with this substitution:

$$q_z' = -k_h \frac{\partial T}{\partial z} \tag{12}$$

which, of course is Fourier's Law of Heat Conduction, and k_h is called the thermal conductivity.

Note that there is a pattern in the characteristics of the propotionality factors placed in front of the gradient term. If we use the most general form of the gradient/flux law (Eq.6), the proportionality K_S always has dimensions L^2T^{-1}. But some common forms of the equations may have extra parameters tacked onto K_S (see table next page).

Quantity	Proportionality Factor	Common Symbol	Common Name
DISS. MASS	ρK_A	k_d	Diffusion Coeff.
MOMENTUM	ρK_P	μ	Viscosity
HEAT	$\rho K_H C_v$	k_h	Thermal Conductivity

From this table we see that these common forms of the proportionalities are simply K_S times density. (For heat, C_v is included simply to get the gradient in terms of the more easily measured temperature, rather than specific heat content). In fact for viscosity, we often switch back and forth in our use of proportionalities that either include density (μ) or not (ν). The "common" forms simply incorporate the density of the fluid, since that factor always affects the flux. However, the "K_S" forms embody the "intrinsic" information about the transfer properties of the fluid, which gives us insights that may be masked by the density factor. For example, the "ordinary" (or dynamic) viscosity of water (μ) is much greater than the dynamic viscosity of air, and this is borne out by everyday experience. But the "intrinsic" (or kinematic) viscosity of water (ν) is <u>less</u> than the kinematic viscosity of air. This means that air is inherently more viscous than water and that our everyday perception of the viscosity of water is due to the vastly greater density of liquids compared to gases.

The intrinsic, or "K_S-type" constants can be summarized as follows:

Quantity	Proportionality Factor (as used here)	Common Symbol	Common Name
DISS. MASS	K_A	D	Diffusivity
MOMENTUM	K_P	ν	Kinematic Viscosity
HEAT	K_H	α	Thermal Diffusivity

==> TAKE-HOME MESSAGE:

If we wish to quantify or compare the inherent or intrinsic ability of a fluid to transport a constitutive property, we should use the transport coefficient in the form of K_S, with dimensions L^2T^{-1}.

If we want to have a practical form of the gradient/flux law for some particular purpose, then it often makes sense to multiply K_S by another factor such as the fluid density.

TRANSPORT OF SOLUTES
ADVECTION-DISPERSION EQUATION

V.3

Excerpts from Lecture Notes
by Donald R.F. Harleman
Professor (emeritus), MIT

Chapter I

Molecular Diffusion of Mass in Binary Systems

CHAPTER 1

MOLECULAR DIFFUSION OF MASS IN BINARY SYSTEMS

1.1 Introduction

In this section the physical concepts and mathematical representation of molecular diffusion are presented. In the majority of environmental problems, in which we are interested in the distribution of pollutants introduced into the atmosphere or water bodies, the transport of mass by molecular diffusion is of little importance in comparison with transport due to the bulk motion of the air or water. In general, these bulk or ~~co~~adnvective flows possess both spatial and temporal variability. The latter, known as turbulent diffusion, dominates the molecular process by orders of magnitude. Nevertheless, it is important to understand the molecular mass transport processes since the mathematical formulations are the basis for the more complex mass transport problems to be considered.

In fluid mechanics, various mixing processes in homogeneous fluids are treated by means of momentum-transfer concepts. Examples include a jet of air or water introduced into a large body of identical fluid. The analysis of the mixing or entrainment process is based upon the equations of motion and continuity. Homogeneity implies that both the jet fluid and the ambient fluid which is entrained are identical. In situations in which the two fluids are different but approximately of the same density, volumetric flux relations may be used to determine the average dilution of one fluid discharging into another. However, in the larger group of technological problems which are concerned with fluid mixtures, it is in general necessary to determine the relative amount of a given substance at a specified point in time and space. Thus a new variable, that of concentration, is introduced into the analysis. This requires that the conservation-of-mass equation (known as the continuity equation in a homogeneous fluid) be reformulated for a nonhomogeneous fluid.

The conservation-of-mass principle must be satisfied for each component or species in a heterogeneous fluid. For simplicity, the following discussions are concerned with a binary or two-component system. Thus, if we are interested in the mixing between two different gases, one gas may be designated as species A and the other as species B. More complex cases such as mixing between

sea water and fresh water may also be treated with reasonable approximation as a binary system even though sea water is a multicomponent liquid. For example, if it is assumed that the concentration of sodium chloride is representative of the relative concentration of sea water, the mixing process may be considered a binary one with sodium chloride as component A and fresh water as component B.

1.2 Molecular Diffusion in a Binary System

Molecular diffusion is the process by which matter is transported by molecular mobility. The gradual blurring of an originally sharp interface between dis-similar fluids is a common example of ordinary or molecular diffusion. It is recognized that temperature gradients, pressure gradients, and external force fields also contribute to mass flux on a molecular scale. These effects are usually small, although it is easy to find examples in which this is not the case. Examples include the separation of compounds by high-speed centrifuges and the settling of solid-particle suspensions in liquids, where the gravitational field produces a fall velocity of the solids relative to the liquid phase. Ordinary molecular diffusion is often called gradient diffusion, because it may be described by an observational law in which the time rate of mass transfer of a substance per unit area is proportional to the spatial gradient of concentration of the substance. This is known as Fick's law and is analogous to Newton's law of viscosity or Fourier's law of heat conduction. Before continuing with a quantitative discussion of molecular diffusion processes, it is necessary to define certain fluid properties and kinematic quantities for a binary system.

Following the basic hypothesis of continuum mechanics, we define density, ρ, as the amount of mass contained in a specified volume of fluid. The sample volume of the fluid must be large compared to the cube of the average distance between diffusing molecules or particles. In a binary system we distinguish between the density of the component species A and B and the total density of the mixture. Thus,

$$\rho_A = \frac{\text{mass of component A}}{\text{volume of mixture of A and B}}, \quad \rho_B = \frac{\text{mass of component B}}{\text{volume of mixture of A and B}} \tag{1-1}$$

and,
$$\rho = \frac{\text{mass of A + mass of B}}{\text{volume of mixture of A and B}} = \rho_A+\rho_B \tag{1-2}$$

In environmental applications, species A represents the pollutant (or tracer) substance contained in a relatively small amount in the carrier fluid B (air or water). Therefore, the magnitudes of ρ_B and ρ differ by only a small amount. In order to emphasize the "small amount" of substance A in comparison with B it is convenient to define dimensionless relative densities ρ_A/ρ and ρ_B/ρ. In the literature of molecular transport processes, the density ρ_A is called the concentration of species A and quantity ρ_A/ρ is called the relative concentration, relative density or more commonly, the mass fraction of species A. In order to avoid ambiguity between dimensional and non-dimensional quantities we will consistently use the term density for ρ_A or ρ_B and concentration, c_A or c_B, to mean the dimensionless relative concentration or mass fraction. Thus,

$$c_A = \frac{\text{mass of component A}}{\text{mass of mixture of A and B}} = \frac{\rho_A}{\rho} \tag{1-3}$$

$$c_B = \frac{\text{mass of component B}}{\text{mass of mixture of A and B}} = \frac{\rho_B}{\rho}$$

The [illegible] dimensionless relative concentration

It then follows from Eqs. (1-1) and (1-2) that

$$c_A+c_B = 1 \tag{1-4}$$

Magnitudes of the densities and concentrations are given in the following example: If the density of the pollutant $\rho_A = 1$ mg/l (milligram per litre) and that of the carrier fluid (water) is $\rho_B = 1$ g/c^3 (gram per cubic centimeter) or 10^6 mg/l, the total density (to at least five decimal places) $\rho = \rho_A+\rho_B = 10^6$ mg/l and $c_A = \rho_A/\rho = 10^{-6}$. This dimensionless concentration, c_A, could be referred to as "one part per million" (1 ppm) or "a thousand parts per billion" (1000 ppb). Confusion between the density and the dimensionless concentration of the pollutant sometimes arises, when the carrier fluid is water, because the value of the density ρ_A in mg/l is numerically equal to the concentration expressed in parts per million.

We consider the flux of mass due to molecular mobility by referring to the simple fluid system shown in Figure 1.1. A linear density gradient for species A (A decreases in the positive z direction) exists in a stagnant fluid (no bulk motion*).

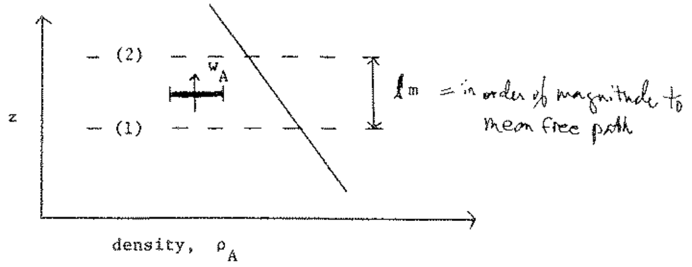


FIGURE 1.1 Concentration gradient in a stagnant fluid.

In a mixture, the various components or species are moving with different velocities. However, we do not refer to the velocity of any one molecule of a species but rather to an average velocity of all the molecules of a given component within a small volume. In reference to Figure 1.1, let w_A be this average velocity in the z direction for species A. The flux of species A passing through an element of area "window" (in the x-y plane) in the positive z direction is given by $\rho_A w_A$, i.e., the mass of A per unit time per unit area [$gs^{-1}cm^{-2}$]. Molecules pass through the window in both the positive and negative z direction. If it is assumed that the representative velocity w_A is spatially constant (no temperature gradients) and that the effective transport distance is ℓm (equal in order of magnitude to the "mean free path"), the net flux in the z direction is given by

---

*Strictly speaking, a slight bulk motion will be generated if the molecular weights of the diffusing species A and B are not equal. However, the magnitude of the error introduced by neglecting this effect is of the order of the concentration c_A. Hence, for dilute solutions in which $c_A << 1$, bulk motion due to molecular transport may be ignored. See Bird, Stewart and Lightfoot (1960) for a discussion of non-equimolar counter-diffusion.

$$(J_A)_z = (\rho_A)_1 w_A - (\rho_A)_2 w_A = w_A[(\rho_A)_1 - (\rho_A)_2] \tag{1-5}$$

The concentration gradient is linear, therefore

$$(\rho_A)_2 - (\rho_A)_1 = \ell m \frac{\partial \rho_A}{\partial z} \tag{1-6}$$

The gradient $\frac{\partial \rho_A}{\partial z}$ is negative, therefore $(\rho_A)_2 < (\rho_A)_1$ and from Eqs. (1-5) and (1-6) it follows that

$$= -w_A(\rho_{A_2} - \rho_{A_1})$$

$$(J_A)_z = -w_A \ell m \frac{\partial \rho_A}{\partial z} \quad \leftarrow \quad = -w_A \ell_m \frac{\partial \rho_A}{\partial z} \tag{1-7}$$

The net flux is in the positive z direction, i.e., in the direction of the decreasing concentration gradient.

The product $w_A \ell m$ is a property of the binary mixture and is called the molecular diffusion coefficient; thus

$$D_{AB} = w_A \ell m \tag{1-8}$$

and the net flux in the z direction can be written as

$$(J_A)_z = -D_{AB} \frac{\partial \rho_A}{\partial z} \tag{1-9}$$

In general, the net flux is a vector quantity and since molecular diffusion is isotropic (independent of the direction of the flux), Eq. (1-9) may be expressed in vector notation as

$$\vec{J}_A = -D_{AB} \nabla \rho_A \tag{1-10}$$

This is known as Fick's law.

The above relations have been obtained by considering mass transport due to molecular mobility in a stagnant fluid. If the fluid has a bulk velocity $\vec{q}$ (as would be measured by tracking the successive positions of a macroscopic "particle" or by an instrument such as a pitot tube) and if the bulk motion is in a state of stable (i.e., laminar) motion, the total flux, $\vec{N}_A$, relative to a fixed coordinate system is given by the vector sum of the mass transport by the bulk motion, $\rho_A\vec{q}$, and the diffusive flux, $\vec{J}_A$. Thus,

$$\vec{N}_A = \rho_A\vec{q}+\vec{J}_A = \rho_A\vec{q}-D_{AB}\nabla\rho_A \qquad (1\text{-}11)$$

The combination of diffusive and convective transport is illustrated in Figure 1.2 in which an aqueous solution of NaCl is convected and diffused. Both

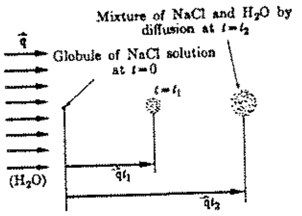


FIGURE 1.2 Molecular diffusion relative to the convective motion of the fluid.

components of the total mass flux $\vec{N}_A$ are associated with velocities; macroscopic velocities in the case of convective transport and microscopic velocities in the case of molecular diffusion. The representation of molecular diffusive flux as the product $D_{AB}\nabla\rho_A$ is simply a convenient way of avoiding the difficulties associated with introducing a representative molecular velocity and a mean free path length. In gases, the latter quantities are physically intuitive while in liquids they are much less so owing to the dense lattice structure of the liquid molecules.

Note that we could have defined the flux vector $\vec{N}_A = \rho_A\vec{q}_A$, where $\vec{q}_A$ is a representative velocity for species A. The species velocity $\vec{q}_A$ is not a quantity that can be directly measured; nevertheless, the product $\rho_A\vec{q}_A$ can be interpreted as the momentum of species A per unit volume of the mixture. In a similar manner, $\vec{N}_B = \rho_B\vec{q}_B$ and the total momentum per unit volume is the sum $\vec{N}_A+\vec{N}_B$. We are now in a position to define the bulk or hydrodynamic velocity $\vec{q}$ as the total momentum per unit mass of the mixture. Therefore, the following relationships must hold,

$$\vec{q} = \frac{\vec{N}_A+\vec{N}_B}{\rho} \qquad (1\text{-}12)$$

This relation will be used in forming the mass balances of the two species in the binary system.

The molecular diffusivity D_{AB} is a property depending on the components A and B, their relative concentration, and the temperature and pressure of the system. Table 1-1 gives some values of the diffusivity of certain binary mixtures (component A diffusing into component B).

The molecular diffusivities of gases and liquids differ by a factor of approximately 10^6, which indicates the relative molecular mobilities of these two phases of matter. Experimental data on molecular diffusivity are frequently given in terms of the Schmidt number, $S_c = \nu_B/D_{AB}$. This dimensionless number is the ratio of the kinematic viscosity to the molecular diffusivity. An empirical correlation of the Schmidt number for gas-air mixtures and dilute aquerous solutions as a function of the molecular weight of the diffusing substance is given in Figure 1.3. Values obtained in this manner are accurate within ±20% and are useful for estimating purposes. The Schmidt number for liquids is characteristically of the order of 1000; for gases it is near unity. A review of semi-empirical formulae for the prediction of molecular diffusion in liquids is given by Simons and Porter (1975).

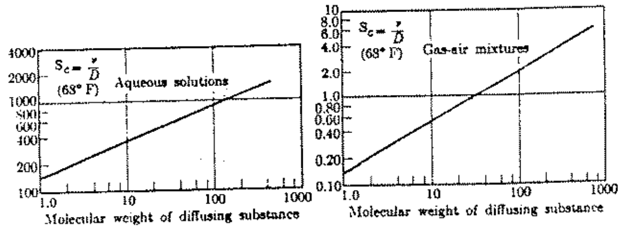


FIGURE 1.3 Schmidt number as a function of molecular weight for gas-air mixtures and dilute aqueous solutions.

Table 1-1

Molecular Diffusivity of Binary Systems

Components A-B	Temperature °C	D_{AB} cm^2/sec
Gases at 1-atm press		
ammonia - air	0°	0.20
CO_2 - air	0°	0.14
SO_2 - air	0°	0.12
water vapor - air	25°	0.26
gas - liquid		
CO_2 - water	25°	2.0×10^{-5}
O_2 - water	25°	2.4×10^{-5}
NaCl - water	0°	0.78×10^{-5}
NaCl - water	25°	1.61×10^{-5}
NaCl - water	50°	2.63×10^{-5}

Note: Diffusivities in liquids depend on the concentration of the diffusing substance. The above values are for very dilute solutions.

1.3 Convective-Diffusion Equation

The expression for the conservation of mass of one component in a binary system is obtained by summing the mass fluxes for a differential control volume. The mass flux of species A relative to a fixed-coordinate system is given by Eq. (1-11)

$$\vec{N}_A = \rho_A \vec{q} - D_{AB} \nabla \rho_A$$

The flux vector $\vec{N}_A$ has the dimensions of mass of A per unit time per unit area (normal to the direction of the flux). In Cartesian coordinates

$$\vec{N}_A = (N_A)_x \vec{i} + (N_A)_y \vec{j} + (N_A)_z \vec{k} \tag{1-13}$$

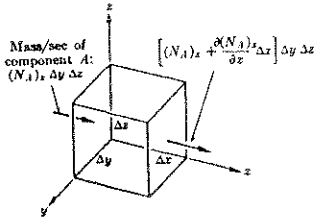


FIGURE 1.4 Mass flux of component A in x-direction.

We may now form the conservation-of-mass expression for component A in Cartesian coordinates by referring to Figure 1.4. This may be stated as follows:

$$\begin{bmatrix}\text{net flux of mass A}\\ \text{through fluid ele-}\\ \text{ment (inflow minus}\\ \text{outflow)}\end{bmatrix} + \begin{bmatrix}\text{time rate of produc-}\\ \text{tion of mass A by}\\ \text{chemical and/or bi-}\\ \text{ological reaction in-}\\ \text{side fluid element}\end{bmatrix} = \begin{bmatrix}\text{time rate of accumu-}\\ \text{lation of mass A in-}\\ \text{side fluid element}\end{bmatrix}$$

In equation form, we have

$$-\frac{\partial (N_A)_x}{\partial x}\Delta x\Delta y\Delta z - \frac{\partial (N_A)_y}{\partial y}\Delta x\Delta y\Delta z - \frac{\partial (N_A)_z}{\partial z}\Delta x\Delta y\Delta z + r_A\Delta x\Delta y\Delta z = \frac{\partial \rho_A}{\partial t}\Delta x\Delta y\Delta z \qquad (1\text{-}14)$$

Upon dividing by the element of volume, ΔxΔyΔz, and rearranging, we obtain

$$\frac{\partial \rho_A}{\partial t} + \frac{\partial (N_A)_x}{\partial x} + \frac{\partial (N_A)_y}{\partial y} + \frac{\partial (N_A)_z}{\partial z} = r_A, \qquad (1\text{-}15)$$

or in vector form,

$$\frac{\partial \rho_A}{\partial t} + \nabla\cdot\vec{N}_A = r_A \qquad (1\text{-}16)$$

In the above equations, r_A represents the time rate at which mass of A is produced per unit volume. Conversely, if the component decreases in a reaction process, r_A would be negative.

In a similar manner, the conservation of mass of substance B may be written as

$$\frac{\partial \rho_B}{\partial t} + \nabla\cdot\vec{N}_B = r_B \qquad (1\text{-}17)$$

In a binary system, the production of A can only come about at the expense of B since the total mass of the system must also be conserved. Hence

$$r_A = -r_B \qquad (1\text{-}18)$$

Therefore, adding Eqs. (1-16) and (1-17), we obtain

$$\frac{\partial \rho_A}{\partial t} + \frac{\partial \rho_B}{\partial t} + \nabla\cdot(\vec{N}_A+\vec{N}_B) = 0$$

or, using Eqs. (1-2) and (1-12), we have

$$\frac{\partial \rho}{\partial t} + \nabla\cdot(\rho\vec{q}) = 0, \qquad (1\text{-}19)$$

---

which, not surprisingly, is the general continuity equation for a fluid mixture.

Returning to the single-component conservation equation (1-16), we replace the flux vector $\vec{N}_A$ by its equivalent from Eq. (1-11), and since $\rho_A = \rho c_A$, we get

$$\left[\partial(\rho c_A)/\partial t + \nabla\cdot(\rho c_A\vec{q} - \rho D_{AB}\nabla c_A)\right] = r_A \qquad (1\text{-}20)$$

Expanding and rearranging, we obtain

$$\partial(\rho c_A)/\partial t + \rho c_A\nabla\cdot\vec{q} + \vec{q}\cdot\nabla\rho c_A = \rho D_{AB}\nabla^2 c_A + (\nabla c_A)\cdot(\nabla\rho D_{AB}) + r_A \qquad (1\text{-}21)$$

If the fluid mixture is considered to be incompressible, $\nabla\cdot\vec{q} = 0$. If, in addition, the solution is dilute, both the total density of the mixture ρ and the diffusion coefficient D_{AB} are essentially constant. Hence after division by ρ, Eq. (1-21) becomes

$$\left[\partial c_A/\partial t\right] + \vec{q}\cdot\nabla c_A = D_{AB}\nabla^2 c_A + \left[r_A/\rho\right] \qquad (1\text{-}22)$$

$\frac{\partial c_A}{\partial t} + (\vec{q}\cdot\nabla c_A$

In Cartesian form, we have

$$\frac{\partial c_A}{\partial t} + u\frac{\partial c_A}{\partial x} + v\frac{\partial c_A}{\partial y} + w\frac{\partial c_A}{\partial z} = D_{AB}\left[\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} + \frac{\partial^2 c_A}{\partial z^2}\right] + \frac{r_A}{\rho} \qquad (1\text{-}23)$$

and in cylindrical coordinates,

$$\frac{\partial c_A}{\partial t} + v_r\frac{\partial c_A}{\partial r} + \frac{v_\theta}{r}\frac{\partial c_A}{\partial \theta} + v_z\frac{\partial c_A}{\partial z} = D_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_A}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 c_A}{\partial \theta^2} + \frac{\partial^2 c_A}{\partial z^2}\right] + \frac{r_A}{\rho} \qquad (1\text{-}24)$$

This is known as the convective-diffusion equation; it is the expression for the conservation of mass of substance A undergoing ordinary diffusion in an incompressible laminar flow.

If the convective velocity $\vec{q}$ and production rate r_A are zero, Eq. (1-22) reduces to

$$\partial c_A/\partial t = D_{AB}\nabla^2 c_A \qquad (1\text{-}25)$$

This form of the equation is often called Fick's second law and is a well-known second-order differential equation. If the concentration is replaced by the temperature T, and D_{AB} is replaced by the thermal diffusivity α, we have the "heat equation"

$$\partial T/\partial t = \alpha\nabla^2 T \qquad (1\text{-}26)$$

which is one of the basic equations of heat-transfer theory. A large number of solutions of these equations for various initial and boundary conditions have been obtained. The Prandtl number is analogous to the Schmidt number in that it expresses the ratio between the molecular viscosity and the thermal diffusivity,

$$P_r = \nu/\alpha \qquad (1\text{-}27)$$

The Prandtl number for common gases is approximately 0.7 at atmospheric pressure. For liquids the variation is large; the Prandtl number for water at standard temperature is approximately 8.0.

In a binary system there is no need to write the conservation equation for the second species. Once c_A is determined from a solution of Eq. (1-22), c_B is given by the condition (Eq. 1-4) that $c_A+c_B = 1$. In dealing with binary systems, the subscript A on the concentration variable will be dropped with the understanding that the concentration refers to the "tracer" species. In a multi-component system of n species, a total of n-1 conservation equations must be used.

Some additional remarks should be made on the nature of the production/decay term, r_A, in Eq. (1-22). There are two types of chemical or biological reactions: homogeneous, in which the change in species occurs uniformly throughout the entire volume of the system, and heterogeneous, in which the change takes place at a specific location. Examples of heterogeneous reactions are those that take place at the surface of a catalyst, at the free surface or fixed boundaries of a river. For a homogeneous reaction, the time rate of production (or decay) of a species per unit volume appears as a source (or sink) term in the differential equation for the conservation of mass in a fluid element.

The term r_A in Eq. (1-22) represents a homogeneous reaction term. For the heterogeneous type, the time rate of production per unit surface area appears as a boundary condition at whatever surface the reaction occurs.

Boundary conditions, in addition to those discussed for heterogeneous reactions, necessary for the mathematical solution of the convective-diffusion equation must be specified. Typical boundary conditions are of the following types:

1. The concentration at a surface may be specified, e.g., $c = c_o$ at $x = o$.
2. The mass flux at a surface can be given, e.g., $J_s = -D_{AB}\left.\frac{\partial c}{\partial x}\right|_{x=o}$
    a) at an impermeable surface, $J_s = 0$ and therefore, $\left.\frac{\partial c}{\partial x}\right|_{x=o} = 0$

1.4 Diffusion and Convection in Turbulent Flow

The turbulent-flow counterpart of the molecular convective-diffusion equation is obtained by making use of an analogy between molecular and turbulent diffusion. The development is similar to that used to obtain the Reynolds equations for turbulent motion from the Navier-Stokes equation. We represent the instantaneous hydrodynamic velocity components in terms of the sum of a time-averaged and a fluctuating velocity. Thus

$$u = \bar{u}+u', \quad v = \bar{v}+v', \quad w = \bar{w}+w'$$

In addition, the concentration of the diffusing substance may be represented in a similar manner as

$$c_A = \bar{c}_A+c'_A$$

Assuming D_{AB} is a constant, one substitutes the mean and fluctuating velocities and concentrations into the convective-diffusion equation (1-23). Then each term is time-averaged according to the rules of Section 11-2 of Daily and Harleman (1966). Assuming that the total-mass density ρ is constant and making use of the continuity condition,

$$\nabla\cdot\vec{q} = \frac{\partial\bar{u}}{\partial x}+\frac{\partial\bar{v}}{\partial y}+\frac{\partial\bar{w}}{\partial z} = 0$$

Daily, J.W. and Harleman, D.R.F., Fluid Dynamics , Addison Wesley Publ. Co., Reading, Mass., 1966

From: "Encyclopedia of Fluid
Mechanics, Vol. 6"

ν = MOMENTUM DIFFUSIVITY (Eddy viscosity
K^V = Vertical diffusivity of heat or
Diss. Mass

Table 1B
Vertical Diffusivities ν, D^V (or K^V) in $[m^2/s]$

Author	Year	ν(Epilimnion)	ν(Hypolimnion)	K^V(Epilimnion)	K^V(Hypolimnion)
Jacobsen	(1913)		0.00019–0.00038 $H < 6$ m/s		0.00002–0.00006
Thorade	(1914)	$1.02 \cdot 10^{-4} W^3$ W in [m/s]			
Brennecke	(1921)	0.0160			
Durst	(1924)	0.025–0.1500			
Sverdrup	(1926)	0–0.1			
Thorade	(1928)	0.0075–0.1720			
Fjeldstad	(1929)	0.001–0.040			
Defant	(1932)			0.0320	
Fjeldstad	(1933)			0.0002–0.0016	
Suda	(1936)	0.0680–0.7500		0.0030–0.0080	
Suda	(1936)	0.0150–0.1460		0.0007–0.0090	
Munk & Anderson	(1948)	$\nu_0/(1 + \frac{10}{3}\mathrm{Ri})^{1/2}$		$K_0(1 + 10\,\mathrm{Ri})^{3/2}$	
Wüst	(1955)	0.0007–0.0050			
Mamayev	(1959)	$\nu_0 \exp(-m\,\mathrm{Ri})$		$K_0 \exp(-n\,\mathrm{Ri})$	
Nan'niti	(1964)	0.0100			
Neumann & Pierson	(1964)	$0.1825 \cdot 10^{-4} W^{5/2}$			
Hunkins	(1966)	0.0024			
Assaf	(1971)	0.0150–0.0225			
Horn	(1971)			0.024–0.031	
Csanady	(1972)	0.0065–0.0160			
Hoeber	(1972)			0.0340–0.500	
Jones	(1973)	0.0020–0.0700			
Prümm	(1974)			0.0265–0.0480	
Ostapoff & Worthem	(1974)			0.0067–0.0085	
Williams & Gibson	(1974)		0.0012–0.0025		0.000052–0.0027
Arsen'yev et al.	(1975)	0.0060–0.0750			
Imboden & Emerson	(1978)				0.000005–0.00001
Baker	(1980)	0–0.0025			

Some of the expressions show a dependence on the Richardson number Ri (see text) or wind speed W)