Mass Transfer
CHEN 331

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Fundamentals of Mass Transfer

What is mass transfer?

When a system contains two or more components whose concentrations vary from point to point, there is a natural tendency for mass to be transferred, minimizing the concentration differences within a system (to reach equilibrium).

The transport of one constituent from a region of higher concentration to that of a lower concentration is called mass transfer.

i.e. mass transfer is meant to be the tendency of a component in a mixture to travel from a region of higher concentration to that of lower concentration.

Examples:

Many of our day to day experiences also involve mass transfer, for example:

a) A lump of sugar added to a cup of coffee eventually dissolves and then eventually diffuses to make the concentration uniform. This process begins with the dissolution of sugar from the surface of each crystal into the neighboring liquid. The sugar in solution is then transported across the liquid (by diffusion and convection) from the higher concentration area to the lower concentration area..

b) Water evaporates from ponds to increase the humidity of passing-air-stream

c) Perfumes present a pleasant fragrance which is imparted throughout the surrounding atmosphere.

Note: There is a difference between mass and momentum transfer.

What is the difference between momentum and mass transfer?

Momentum transfer involves bulk transport of the continuum while mass transfer involves the transport of species within the bulk continuum. Continuum could be stationary or itself mobile.

Importance of mass transfer:

What is the importance of mass transfer?

Field of mass transfer involves some of the most typical chemical engineering problems:

➤ Design and operation of chemical process equipment involves preparation of reactants, carrying out chemical reactions (diffusion controlled reactions), and separation of the resultant products.

➤ Ability to carry out the above operations largely rests on the proficiency of principles of mass transfer, which is largely the domain of chemical engineers.

The transfer of mass within a fluid mixture or across a phase boundary is a process that plays a major role in many industrial processes (biological and chemical). Examples of such:

Name the important processes involving mass transfer.

- **Distillation:** Differential distillation, equilibrium flash vaporization, steam distillation, batch and continuous fractionation, binary and multi-component distillation, azeotropic and extractive distillation, and so on.

- **Absorption:** Used for separation of acidic impurities from mixed gas streams, for example, CO_2, H_2S, SO_2 , other organics such as carbonyl sulfide (COS) and mercaptans, NH_3, HCN, and NOx, VOC control in environmental cleanup, odor control, wastewater stripping, and so on.

- **Adsorption** (absorption and adsorption play an important role in environmental engineering)

- **Liquid–Liquid and Solid–Liquid Extraction:** Pharmaceuticals and foods, extraction and refining of fats and oils, dewaxing and aromatic extraction from lube oils, leaching of ores, and so on.

- **Crystallization.**

- **Drying.**

- **Ion exchange.**

- **Membrane Separation Processes:** Based on molecular size differences:
  - ➤ Gas–gas, gas–liquid, liquid–liquid.
  - ➤ Liquid membranes, for example, for H_2S removal.

- **Reverse osmosis**.

- **Biological processes:** include the oxygenation of blood and the transport of ions across membranes within the kidney.

Mechanism of mass transfer

The mechanism of mass transfer depends upon the dynamics of the system in which it occurs.

Mass can be transferred by two mechanisms, namely:

a. Molecular diffusion (Random molecular motion in quiescent fluids)
b. Convection (where mass is transferred from a surface into a moving fluid, aided by the dynamic characteristics of the flow)

These two distinct modes of transport, molecular mass transfer and convective mass transfer, are analogous to conduction heat transfer and convective heat transfer.

1. Molecular mass transfer

1.1. Properties of a mixture

Mass transfer always involves mixtures. Consequently, we must account for the variation of physical properties which normally exist in a given system. When a system contains three or more components, as many industrial fluid streams do, the problem becomes un-widely very quickly. The conventional engineering approach to problems of multi-component system is to attempt to reduce them to representative binary (i.e., two components) systems.

In order to understand the future discussions, let us first consider definitions and relations which are often used to explain the role of components within a mixture.

1.2. Concentration of Species

Concentration of species in multi-component mixture can be expressed in many ways.

a. Mass concentration

For species A, mass concentration denoted by ρ_A is defined as the mass of A, m_A per unit volume of the mixture.

$$\rho_A = \frac{m_A}{V} \qquad (1)$$

The total mass concentration density ρ is the sum of the total mass of the mixture in unit volume:

$$\rho = \sum_i \rho_i$$

where ρ_i is the concentration of species i in the mixture.

b. Molar concentration

Molar concentration of, A, c_A is defined as the number of moles of A present per unit volume of the mixture.

By definition,

$$Number\ of\ moles = \frac{mass\ of\ A}{molecular\ weight\ of\ A}$$

$$n_A = \frac{m_A}{M_A} \tag{2}$$

From equations 1 and 2:

$$c_A = \frac{n_A}{V} = \frac{m_A}{V\ M_A} = \frac{\rho_A}{M_A} \tag{3}$$

Note:

For gas phase: PV = n R T from which $c = \frac{n}{V} = \frac{P}{RT}$

$$\therefore c_A = \frac{P_A}{RT}$$

Q: What is the relation between mass and molar concentration?

1.3. Velocities

In a multi-component system the various species will normally move at different velocities; and evaluation of velocity of mixture requires the averaging of the velocities of each species present. If v_i is the absolute velocity of species i with respect to stationary fixed coordinates, then <u>mass-average velocity</u> for a multi-component mixture defined in terms of mass concentration is;

$$v = \frac{\sum_{i=1}^{n} \rho_i v_i}{\sum_{i=1}^{n} \rho_i} = \frac{\sum_{i=1}^{n} \rho_i v_i}{\rho} \tag{4}$$

$$v = \sum_{i=0}^{n} w_i v_i$$

By similar way, <u>molar-average velocity</u> of the mixture V is:

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$$V = \frac{\sum_{i=1}^{n} c_i v_i}{\sum_{i=1}^{n} c_i} = \frac{\sum_{i=1}^{n} c_i v_i}{c} \tag{5}$$

$$V = \sum_{i=0}^{n} x_i v_i$$

The velocity of a particular species relative to the mass-average or molar average velocity is termed as diffusion velocity

i.e.

➢ Diffusion velocity relative to the mass average velocity $= v_i - v$ (**mass diffusion velocity**)

➢ Diffusion velocity relative to the molar average velocity $= v_i - V$ (**molar diffusion velocity**)

1.4. Mole and mass fraction

The mole fraction for liquid and solid mixture is denoted by x_A and for gaseous mixtures it is denoted by y_A are the molar concentrations of species A divided by the molar density of the mixtures.

$$x_A = \frac{c_A}{c} \tag{6}$$

and

$$y_A = \frac{c_A}{c} \tag{7}$$

by similar way, mass fraction of A in a mixture is;

$$w_A = \frac{\rho_A}{\rho} \tag{8}$$

A summary of the various concentration terms and of the interrelations for a binary system containing species A and B is given in Table 1.

Table 1 Concentrations in a binary mixture of A and B

Mass concentrations

ρ = total mass density of the mixture
ρ_A = mass density of species A
ρ_B = mass density of species B
ω_A = mass fraction of species A = ρ_A/ρ
ω_B = mass fraction of species B = ρ_B/ρ
$\rho = \rho_A + \rho_B$
$1 = \omega_A + \omega_B$

Molar concentrations

Liquid or solid mixture

c = molar density of mixture = n/V
c_A = molar density of species A = n_A/V
c_B = molar density of species B = n_B/V
x_A = mole fraction of species A = $c_A/c = n_A/n$
x_B = mole fraction of species B = $c_B/c = n_B/n$
$c = c_A + c_B$

$1 = x_A + x_B$

Gas mixture

$c = n/V = P/RT$
$c_A = n_A/V = p_A/RT$
$c_B = n_B/V = p_B/RT$
$y_A = c_A/c = n_A/n = p_A/p$
$y_B = c_B/c = n_B/n = p_B/p$

$c = c_A + c_B = \dfrac{p_A}{RT} + \dfrac{p_B}{RT} = \dfrac{P}{RT}$

$1 = y_A + y_B$

Interrelations

$$\rho_A = c_A M_A$$

$$x_A \quad \text{or} \quad y_A = \frac{\omega_A/M_A}{\omega_A/M_A + \omega_B/M_B} \tag{24-10}$$

$$\omega_A = \frac{x_A M_A}{x_A M_A + x_A M_A} \quad \text{or} \quad \frac{y_A M_A}{y_A M_A + y_B M_B} \tag{24-11}$$

1.5. Flux

Definition: The mass (or molar) flux of a given species is a vector quantity denoting the amount of the particular species, in either mass or molar units, that passes per given increment of time through a unit area normal to the vector. (Flux = concentration x velocity)
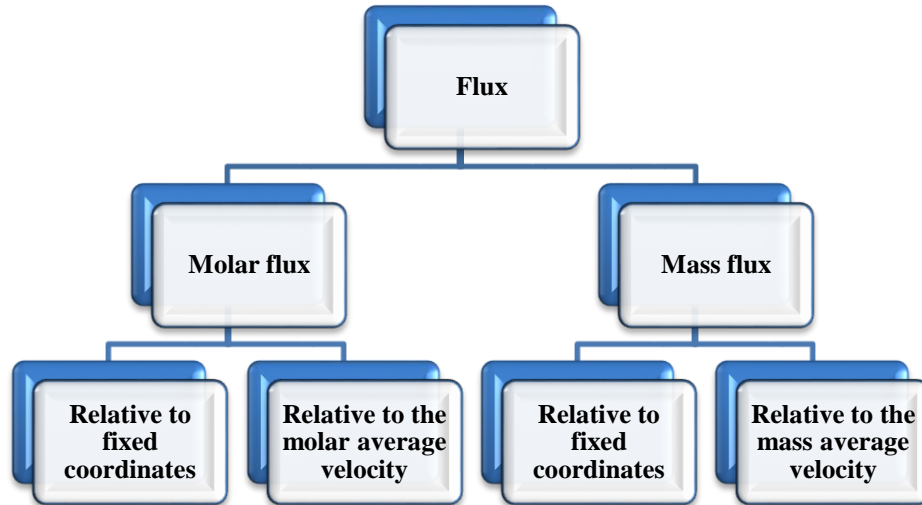
Equations describing flux

a. Molar flux

The molar flux is defined by two methods:

1. Relative to the molar average velocity
2. Relative to a fixed coordinates

- **Molar flux relative to the molar average velocity**

The basic relation for molecular diffusion <u>defines the molar flux relative to the molar average</u> velocity, J_A. An <u>empirical relation</u> for this molar flux, first postulated by Fick and, accordingly, often referred to as <u>Fick's first law</u>, defines the diffusion of component A in an <u>isothermal</u>, <u>isobaric</u> system:

$$J_A = -D_{AB}\nabla c_A \qquad (9)$$

For diffusion in only the z direction, the Fick's rate equation is:

$$J_{A,z} = -D_{AB}\frac{dc_A}{dz} \qquad (10)$$

where:

J_A: is the molar flux in the z direction relative to the molar average velocity,

$\frac{dc}{dz}$: is the concentration gradient in the z direction and

D_{AB}: the proportionality factor, is the mass diffusivity or diffusion coefficient for component A diffusing through component B.

Note: (see example 1)

$$D_{AB} = D_{BA} \text{ (Only for gases)}$$

A more general flux relation that <u>is not restricted</u> to isothermal, isobaric systems (general form) is:

$$J_{A,z} = -cD_{AB}\frac{dy_A}{dz} \tag{11}$$

where: $c_A = c\, y_A$

Important note:

For a binary system with a constant average velocity in the z direction, the molar flux in the z direction relative to the molar average velocity may also be expressed by:

$$J_{A,z} = c_A(v_{A,z} - V_z) \tag{12}$$

Initial experimental investigations of molecular diffusion were unable to verify Fick's law of diffusion. This was apparently due to the fact that mass is often transferred simultaneously by two possible means:

(1) as a result of the concentration differences as postulated by Fick and

(2) by convection currents induced by the density differences that resulted from the concentration variation. Steffan (1872) and Maxwell (1877), using the kinetic theory of gases, proved that the mass (mole) flux relative to a fixed coordinate was a result of two contributions: the <u>concentration gradient contribution</u> and the <u>bulk motion contribution</u>.

Clarification:

If a balloon, filled with a color dye, is dropped into a large lake, the dye will diffuse radially as a concentration gradient contribution. When a stick is dropped into a moving stream, it will float downstream by the bulk motion contribution. If the dye-filled balloon were dropped into the moving stream, the dye would diffuse radially while being carried downstream; thus both contributions participate simultaneously in the mass transfer.

- **Molar flux relative to a fixed coordinates**

Fluxes of components A and B relative to a fixed z coordinate; accordingly, we symbolize this new type of flux that is relative to a set of stationary axes by:

$$N_A = c_A v_A \tag{13}$$

and

$$N_B = c_B v_B \tag{14}$$

where v_A *and* v_B are velocities relative to the fixed axis.

By equating equations 11 and 12 we obtain

$$J_{A,z} = c_A(v_{A,z} - V_z) = -cD_{AB}\frac{dy_A}{dz}$$

which, upon rearrangement, yields

$$c_A v_{A,z} = -cD_{AB}\frac{dy_A}{dz} + c_A V_z$$

For this binary system, V_z can be evaluated by equation (5)

$$V_z = \frac{\sum_{i=1}^{n} c_i v_i}{c} = \frac{1}{c}(c_A v_{A,z} + c_B v_{B,z})$$

or

$$c_A V_z = y_A(c_A v_{A,z} + c_B v_{B,z})$$

Substituting this expression into our relation, we obtain

$$c_A v_{A,z} = -cD_{AB}\frac{dy_A}{dz} + y_A(c_A v_{A,z} + c_B v_{B,z})$$

Substitute from equations (13) and (14) into the above equation we obtain:

$$N_{A,z} = -cD_{AB}\frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z}) \tag{15}$$

This relation may be generalized and written in vector form as:

$$N_A = -cD_{AB}\nabla y_A + y_A(N_A + N_B) \tag{16}$$

It is important to note that the above equations (15 and 16) the molar flux relative to fixed coordinates, N_A, is a resultant of the two vector quantities:

➤ $-c\,D_{AB}\nabla y_A$: the molar flux, J_A, resulting from the concentration gradient : This term is referred to as the <u>concentration gradient contribution</u>; and

➤ $y_A(N_A + N_B) = c_A V$: the molar flux resulting as component A is carried in the bulk flow of the fluid : This flux term is designated the <u>bulk motion contribution</u>. For stagnant medium this term will be zero

Note:

If species A were diffusing in a multicomponent mixture, the expression equivalent to equation (16) would be:

$$N_A = -cD_{AM}\nabla y_A + y_A \sum_{i=1}^{n} N_i$$

b. Mass flux

The mass flux is defined by two methods similar to molar flux:

1. Relative to the mass average velocity
2. Relative to a fixed coordinates

➢ **Mass flux relative to the molar average velocity**

For isothermal and isobaric system

$$j_{A,z} = -D_{AB}\frac{d\rho_A}{dz}$$

General form

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

➢ **Mass flux relative to a fixed coordinates:**

For component A

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

and for component B

$$\mathbf{n}_B = \rho_B \mathbf{v}_B$$

The mass flux, N_A, relative to a fixed spatial coordinate system, is defined for a binary system in terms of mass density and mass fraction by

$$\mathbf{n}_A = -\rho D_{AB}\nabla\omega_A + \omega_A(\mathbf{n}_A + \mathbf{n}_B)$$

where

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

and

$$\mathbf{n}_B = \rho_B \mathbf{v}_B$$

Under isothermal, isobaric conditions, this relation simplifies to:

$$\mathbf{n}_A = -D_{AB}\nabla\rho_A + \omega_A(\mathbf{n}_A + \mathbf{n}_B)$$

Table 2, Equivalent forms of the mass flux equation for binary system A and B

Flux	Gradient	Fick rate equation	Restrictions
$\mathbf{n}_A$	$\nabla\omega_A$	$\mathbf{n}_A = -\rho D_{AB}\nabla\omega_A + \omega_A(\mathbf{n}_A + \mathbf{n}_B)$	
	$\nabla\rho_A$	$\mathbf{n}_A = -D_{AB}\nabla\rho_A + \omega_A(\mathbf{n}_A + \mathbf{n}_B)$	Constant ρ
$\mathbf{N}_A$	∇y_A	$\mathbf{N}_A = -cD_{AB}\nabla y_A + y_A(\mathbf{N}_A + \mathbf{N}_B)$	
	∇c_A	$\mathbf{N}_A = -D_{AB}\nabla c_A + y_A(\mathbf{N}_A + \mathbf{N}_B)$	Constant c
$\mathbf{j}_A$	$\nabla\omega_A$	$\mathbf{j}_A = -\rho D_{AB}\nabla\omega_A$	
	$\nabla\rho_A$	$\mathbf{j}_A = -D_{AB}\nabla\rho_A$	Constant ρ
$\mathbf{J}_A$	∇y_A	$\mathbf{J}_A = -cD_{AB}\nabla y_A$	
	∇c_A	$\mathbf{J}_A = -D_{AB}\nabla c_A$	Constant c

Example 1:

Starting with Fick's equation for the diffusion of A through a binary mixture of species A and B as given by:

$$N_{A,z} = -cD_{AB}\frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z})$$

and Fick's equation for the diffusion of B through the same binary mixture given by:

$$N_{Bz} = -cD_{BA}\frac{dy_B}{dz} + y_B(N_{Bz} + N_{Az})$$

Example: Prove the two gas diffusivities, D_{AB} and D_{BA}, are equals.

Solution:

$$N_{A,z} = -cD_{AB}\frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z})$$

$$N_{Bz} = -cD_{BA}\frac{dy_B}{dz} + y_B(N_{Bz} + N_{Az})$$

By adding the two equations

$$N_{A,z} + N_{B,z} = -cD_{AB}\frac{dy_A}{dz} - cD_{BA}\frac{dy_B}{dz} + (y_A + y_B)(N_{A,z} + N_{B,z})$$

But:

$$(y_A + y_B) = 1$$

$$\therefore cD_{AB}\frac{dy_A}{dz} + cD_{BA}\frac{dy_B}{dz} = 0$$

$$cD_{AB}\frac{dy_A}{dz} = -cD_{BA}\frac{dy_B}{dz}$$

$$y_A + y_B = 1$$

$$\frac{dy_A}{dz} + \frac{dy_B}{dz} = 0$$

$$\frac{dy_A}{dz} = -\frac{dy_B}{dz}$$

$$\therefore D_{AB} = D_{BA}$$

Related types of mass transfer:

➤ In chemical reactions, there is a thermodynamic term called the chemical potential μ_c. The driving force in chemical thermo dynamic is $\Delta\mu_c$.

➤ The chemical potential is a function of concentration and is related by the equation:

$$\mu_c = \mu^o + RT \ln c_A$$

i.e. where a concentration difference exists there will be a chemical potential difference and there will be at tendency to move toward equilibrium (mass transfer will occur)

➤ There are a number of other physical conditions in addition to difference in concentration which will produce a chemical potential gradient (and we can obtain mass transfer by applying it) such as:

• Temperature gradient

• Pressure difference (separation of a liquid mixture in a centrifuge by pressure diffusion)

• Difference in forces applied by external field, such as:

    a. gravity (separation by sedimentation under the influence of gravity),

    b. magnetic (magnetic separation of mineral mixtures through the action of magnetic force field)and

    c. electrical field (electrolytic precipitation due to an electrostatic force field)

The diffusion coefficient (Fick's law proportionalityD_{AB})

In this part we search for:

    1. definition of diffusion coefficient

    2. factors affecting diffusion coefficient

    3. equations used to calculate the diffusion coefficient (for gas, liquid and solid)

• **Definition of D_{AB}**: the mass or molar flux per unit concentration gradient

• **Factors affecting diffusion coefficient:**

The diffusion coefficient depends on:

a) temperature   b) pressure   c) composition of the system

Experimental values of the diffusivities of gases, liquids and solids are tabulated in appendices at different conditions. See tables 3, 4 and 5.

Note: Diffusion in gases > liquids > solids

In the absence of experimental data, semitheoretical expressions have been developed which give approximations, sometimes as valid as experimental values due to the difficulties encountered in their measurement.

Table 3, Binary mass diffusivities in gases

System	T (K)	$D_{AB}P(\text{cm}^2 \text{ atm/s})$	$D_{AB}P(\text{m}^2 \text{ Pa/s})$
Air			
Ammonia	273	0.198	2.006
Aniline	298	0.0726	0.735
Benzene	298	0.0962	0.974
Bromine	293	0.091	0.923
Carbon dioxide	273	0.136	1.378
Carbon disulfide	273	0.0883	0.894
Chlorine	273	0.124	1.256
Diphenyl	491	0.160	1.621
Ethyl acetate	273	0.0709	0.718
Ethanol	298	0.132	1.337
Ethyl ether	293	0.0896	0.908
Iodine	298	0.0834	0.845
Methanol	298	0.162	1.641
Mercury	614	0.473	4.791
Naphthalene	298	0.0611	0.619
Nitrobenzene	298	0.0868	0.879
n-Octane	298	0.0602	0.610
Oxygen	273	0.175	1.773
Propyl acetate	315	0.092	0.932
Sulfur dioxide	273	0.122	1.236
Toluene	298	0.0844	0.855
Water	298	0.260	2.634
Ammonia			
Ethylene	293	0.177	1.793
Argon			
Neon	293	0.329	3.333
Carbon dioxide			
Benzene	318	0.0715	0.724
Carbon disulfide	318	0.0715	0.724
Ethyl acetate	319	0.0666	0.675

Table 3, continued

System	T (K)	$D_{AB}P(\text{cm}^2\,\text{atm/s})$	$D_{AB}P(\text{m}^2\,\text{Pa/s})$
Ethanol	273	0.0693	0.702
Ethyl ether	273	0.0541	0.548
Hydrogen	273	0.550	5.572
Methane	273	0.153	1.550
Methanol	298.6	0.105	1.064
Nitrogen	298	0.165	1.672
Nitrous oxide	298	0.117	1.185
Propane	298	0.0863	0.874
Water	298	0.164	1.661
Carbon monoxside			
Ethylene	273	0.151	1.530
Hydrogen	273	0.651	6.595
Nitrogen	288	0.192	1.945
Oxygen	273	0.185	1.874
Helium			
Argon	273	0.641	6.493
Benzene	298	0.384	3.890
Ethanol	298	0.494	5.004
Hydrogen	293	1.64	16.613
Neon	293	1.23	12.460
Water	298	0.908	9.198
Hydrogen			
Ammonia	293	0.849	8.600
Argon	293	0.770	7.800
Benzene	273	0.317	3.211
Ethane	273	0.439	4.447
Methane	273	0.625	6.331
Oxygen	273	0.697	7.061
Water	293	0.850	8.611
Nitrogen			
Ammonia	293	0.241	2.441
Ethylene	298	0.163	1.651
Hydrogen	288	0.743	7.527
Iodine	273	0.070	0.709
Oxygen	273	0.181	1.834
Oxygen			
Ammonia	293	0.253	2.563
Benzene	296	0.0939	0.951
Ethylene	293	0.182	1.844

Table 4, Binary mass diffusivities in liquids

Solute A	Solvent B	Temperature (K)	Solute concentration (g mol/L or kg mol/m^3)	Diffusivity (cm^2/s $\times$ 10^5 or m^2/s $\times$ 10^9)
Chlorine	Water	289	0.12	1.26
Hydrogen chloride	Water	273	9	2.7
			2	1.8
		283	9	3.3
			2.5	2.5
		289	0.5	2.44
Ammonia	Water	278	3.5	1.24
		288	1.0	1.77
Carbon dioxide	Water	283	0	1.46
		293	0	1.77
Sodium chloride	Water	291	0.05	1.26
			0.2	1.21
			1.0	1.24
			3.0	1.36
			5.4	1.54
Methanol	Water	288	0	1.28
Acetic acid	Water	285.5	1.0	0.82
			0.01	0.91
		291	1.0	0.96
Ethanol	Water	283	3.75	0.50
			0.05	0.83
		289	2.0	0.90
n-Butanol	Water	288	0	0.77
Carbon dioxide	Ethanol	290	0	3.2
Chloroform	Ethanol	293	2.0	1.25

Table 5, Binary mass diffusivities in solids

Solute	Solid	Temperature (K)	Diffusivity (cm^2/s or m^2/s $\times$10^4)	Diffusivity (ft^2/h)
Helium	Pyrex	293	4.49×10^{-11}	1.74×10^{-10}
		773	2.00×10^{-8}	7.76×10^{-8}
Hydrogen	Nickel	358	1.16×10^{-8}	4.5×10^{-8}
		438	1.05×10^{-7}	4.07×10^{-7}
Bismuth	Lead	293	1.10×10^{-16}	4.27×10^{-16}
Mercury	Lead	293	2.50×10^{-15}	9.7×10^{-15}
Antimony	Silver	293	3.51×10^{-21}	1.36×10^{-20}
Aluminum	Copper	293	1.30×10^{-30}	5.04×10^{-30}
Cadmium	Copper	293	2.71×10^{-15}	1.05×10^{-14}

- **Equations used to calculate the diffusion coefficient**

Gas Mass Diffusivity

We need to calculate the gas mass diffusivity for polar and nonpolar gases in a binary system and a multicomponent system.

Note:

The arrangement or geometry of the atoms in some molecules is such that one end of the molecule has a positive electrical charge and the other side has a negative charge. If this is the case, the molecule is called a polar molecule, meaning that it has electrical poles. Otherwise, it is called a non-polar molecule. Whether molecules are polar or non-polar determines if they will mix to form a solution or that they don't mix well together.

Examples of polar molecules of materials that are gases under standard conditions are: Ammonia (**NH$_3$**), Sulfur Dioxide (**SO$_2$**) and Hydrogen Sulfide (**H$_2$S**).

A non-polar molecule is one that the electrons are distributed more symmetrically and thus does not have an abundance of charges at the opposite sides. The charges all cancel out each other.

Common examples of non-polar gases are the noble or inert gases, including Helium (He), Neon (Ne), Krypton (Kr) and Xenon (Xe). Other non-polar gases include the Hydrogen (H$_2$), Nitrogen (N$_2$), Oxygen (O$_2$), Carbon Dioxide (CO$_2$), Methane (CH$_4$) and Ethylene (C$_2$H$_4$) molecules.

Summary:

The geometry of atoms in polar molecules is such that one end of the molecule has a positive electrical charge and the other side has a negative charge. Non-polar molecules do not have charges at their ends. Mixing molecules of the same polarity usually results in the molecules forming a solution.

For binary gas mixture

Nonpolar gases

For gas pairs of nonpolar, nonreacting molecules Hirschfelder presented an equation for the diffusion coefficient

$$D_{AB} = \frac{0.001858\, T^{3/2} \left[\frac{1}{M_A} + \frac{1}{M_B}\right]^{1/2}}{P\, \sigma_{AB}^2\, \Omega_D}$$

The above equation was developed for dilute gases consisting of nonpolar, spherical monatomic molecules. However, this equation gives good results for most nonpolar, binary gas systems over a wide range of temperatures.

where:

D_{AB}: is the mass diffusivity of A through B, in cm^2/s

T: is the absolute temperature in k

M_A , M_B are the molecular weights of A and B, respectively

P: is the absolute pressure in atmosphere

σ_{AB}: is the ''collision diameter in $\dot{A}$,(average diameter of atom A and B) (a Lennard–Jones parameter)

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

σ_A **and** σ_B are obtained from table 6

Ω_D: collision integral in ergs (The collision integral is defined as the rate of change of the distribution function) (from table 7)

From table 7 the collision integral is a function of a dimensionless temperature $\frac{kT}{\varepsilon_{AB}}$

k: is the Boltzmann constant (1.38×10^{-16} ergs/K)

ε_{AB}: the energy of molecular interaction for the binary system A and B in ergs

Note:

$$\frac{\varepsilon_{AB}}{k} = \sqrt{\frac{\varepsilon_A}{k}\frac{\varepsilon_B}{k}}$$

$\frac{\varepsilon_A}{k}$ **and** $\frac{\varepsilon_B}{k}$ are obtained from table 6

Important note:

We can predict the diffusion coefficient at any temperature and at any pressure below 25 atm from a known experimental value (from table 3) by using the equation:

$$D_{AB,T_2,P_2} = D_{AB,T_1,P_1}\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)^{3/2}\frac{\Omega_{D,T_1}}{\Omega_{D,T_2}}$$

If the temperature range is close, you can consider the ratio $\frac{\Omega_{D,T_1}}{\Omega_{D,T_2}} = 1$

Table 6, Values of the diameter of spherical molecules, σ (Lennard–Jones force constants)

Compound	Formula	ϵ_A/κ, in (K)	σ, in Å
Acetylene	C_2H_2	185	4.221
Air		97	3.617
Argon	A	124	3.418
Arsine	AsH_3	281	4.06
Benzene	C_6H_6	440	5.270
Bromine	Br_2	520	4.268
i-Butane	C_4H_{10}	313	5.341
n-Butane	C_4H_{10}	410	4.997
Carbon dioxide	CO_2	190	3.996
Carbon disulfide	CS_2	488	4.438
Carbon monoxide	CO	110	3.590
Carbon tetrachloride	CCl_4	327	5.881
Carbonyl sulfide	COS	335	4.13
Chlorine	Cl_2	357	4.115
Chloroform	$CHCl_3$	327	5.430
Cyanogen	C_2N_2	339	4.38
Cyclohexane	C_6H_{12}	324	6.093
Ethane	C_2H_6	230	4.418
Ethanol	C_2H_5OH	391	4.455
Ethylene	C_2H_6	205	4.232
Fluroine	F_2	112	3.653
Helium	He	10.22	2.576
n-Heptane	C_7H_{16}	282[‡]	8.88[3]
n-Hexane	C_6H_{14}	413	5.909
Hydrogen	H_2	33.3	2.968
Hydrogen chloride	HCl	360	3.305

Table 6, continued

Compound	Formula	ϵ_A/k, in (K)	σ, in Å
Hydrogen iodide	HI	324	4.123
Iodine	I_2	550	4.982
Krypton	Kr	190	3.60
Methane	CH_4	136.5	3.822
Methanol	CH_3OH	507	3.585
Methylene chloride	CH_2Cl_2	406	4.759
Methyl chloride	CH_3Cl	855	3.375
Mercuric iodide	HgI_2	691	5.625
Mercury	Hg	851	2.898
Neon	Ne	35.7	2.789
Nitric oxide	NO	119	3.470
Nitrogen	N_2	91.5	3.681
Nitrous oxide	N_2O	220	3.879
n-Nonane	C_9H_{20}	240	8.448
n-Octane	C_8H_{18}	320	7.451
Oxygen	O_2	113	3.433
n-Pentane	C_5H_{12}	345	5.769
Propane	C_3H_8	254	5.061
Silane	SiH_4	207.6	4.08
Silicon tetrachloride	$SiCl_4$	358	5.08
Sulfur dioxide	SO_2	252	4.290
Water	H_2O	356	2.649
Xenon	Xe	229	4.055

Table 7, Values of the collision integral Ω_D(Lennard–Jones Constants)

$\kappa T/\epsilon$	$\Omega_\mu = \Omega_k$ (for viscosity and thermal conductivity)	Ω_D (for mass diffusivity)	kT/ϵ	$\Omega_\mu = \Omega_k$ (for viscosity and thermal conductivity)	Ω_D (for mass diffusivity)
			1.75	1.234	1.128
0.30	2.785	2.662	1.80	1.221	1.116
0.35	2.628	2.476	1.85	1.209	1.105
0.40	2.492	2.318	1.90	1.197	1.094
0.45	2.368	2.184	1.95	1.186	1.084
0.50	2.257	2.066	2.00	1.175	1.075
0.55	2.156	1.966	2.10	1.156	1.057
0.60	2.065	1.877	2.20	1.138	1.041
0.65	1.982	1.798	2.30	1.122	1.026
0.70	1.908	1.729	2.40	1.107	1.012
0.75	1.841	1.667	2.50	1.093	0.9996
0.80	1.780	1.612	2.60	1.081	0.9878
0.85	1.725	1.562	2.70	1.069	0.9770
0.90	1.675	1.517	2.80	1.058	0.9672
0.95	1.629	1.476	2.90	1.048	0.9576
1.00	1.587	1.439	3.00	1.039	0.9490
1.05	1.549	1.406	3.10	1.030	0.9406
1.10	1.514	1.375	3.20	1.022	0.9328
1.15	1.482	1.346	3.30	1.014	0.9256
1.20	1.452	1.320	3.40	1.007	0.9186
1.25	1.424	1.296	3.50	0.9999	0.9120
1.30	1.399	1.273	3.60	0.9932	0.9058
1.35	1.375	1.253	3.70	0.9870	0.8998
1.40	1.353	1.233	3.80	0.9811	0.8942
1.45	1.333	1.215	3.90	0.9755	0.8888
1.50	1.314	1.198	4.00	0.9700	0.8836
1.55	1.296	1.182	4.10	0.9649	0.8788
1.60	1.279	1.167	4.20	0.9600	0.8740
1.65	1.264	1.153	4.30	0.9553	0.8694

Table 7, continued

$\kappa T/\epsilon$	$\Omega_\mu = \Omega_k$ (for viscosity and thermal conductivity)	Ω_D (for mass diffusivity)	kT/ϵ	$\Omega_\mu = \Omega_k$ (for viscosity and thermal conductivity)	Ω_D (for mass diffusivity)
1.70	1.248	1.140	4.40	0.9507	0.8652
4.50	0.9464	0.8610	10.0	0.8242	0.7424
4.60	0.9422	0.8568	20.0	0.7432	0.6640
4.70	0.9382	0.8530	30.0	0.7005	0.6232
4.80	0.9343	0.8492	40.0	0.6718	0.5960
4.90	0.9305	0.8456	50.0	0.6504	0.5756
5.0	0.9269	0.8422	60.0	0.6335	0.5596
6.0	0.8963	0.8124	70.0	0.6194	0.5464
7.0	0.8727	0.7896	80.0	0.6076	0.5352
8.0	0.8538	0.7712	90.0	0.5973	0.5256

There is another empirical correlation for estimating the diffusion coefficient for nonpolar, binary gas systems at low pressures such as the empirical correlation recommended by Fuller, Schettler, and Giddings which permits the evaluation of the diffusivity when reliable Lennard–Jones parameters, σ and ε are unavailable. The Fuller correlation is:

$$D_{AB} = \frac{10^{-3} T^{1.75} \left[\frac{1}{M_A} + \frac{1}{M_B}\right]^{1/2}}{P\left[(\Sigma v)_A^{1/3} + (\Sigma v)_B^{1/3}\right]^2}$$

The diffusion volume v is obtained from table 8

Table 8, Atomic diffusion volumes for use in estimating D_{AB} by method of Fuller, Schettler, and Giddings (the equation shown above)

Atomic and structure diffusion-volume increments, v			
C	16.5	Cl	19.5
H	1.98	S	17.0
O	5.48	Aromatic ring	−20.2
N	5.69	Heterocyclic ring	−20.2

Diffusion volumes for simple molecules, v					
H_2	7.07	Ar	16.1	H_2O	12.7
D_2	6.70	Kr	22.8	$CCIF_2$	114.8
He	2.88	CO	18.9	SF_6	69.7
N_2	17.9	CO_2	26.9	Cl_2	37.7
O_2	16.6	N_2O	35.9	Br_2	67.2
Air	20.1	NH_3	14.9	SO_2	41.1

Mass diffusivity in a binary polar gases mixture

For estimating diffusion coefficient for binary gas mixtures containing polar compounds,

Hirschfelder equation $\left(D_{AB} = \dfrac{0.001858\, T^{3/2} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}}{P\, \sigma_{AB}^2\, \Omega_D} \right)$ is used; however the collision integral

(Ω_D) is evaluated from equations not from table 7 (see the equations in the reference book page 413)

Mass diffusivity in gas mixture of several components

Mass transfer in gas mixtures of several components can be described by theoretical equations involving the diffusion coefficients for the various binary pairs involved in the mixture. The following relation can be used (Wilke's equation):

$$D_{1-mixture} = \frac{1}{y_2'/D_{1-2} + y_3'/D_{1-3} + \ldots + y_n'/D_{1-n}}$$

where $D_{1-mixture}$ is the mass diffusivity for component 1 in the gas mixture; D_{1-n} is the mass diffusivity for the binary pair, component 1 diffusing through component n; and y_n' is the mole fraction of component n in the gas mixture evaluated on a component-1-free basis, that is

$$y_2' = \frac{y_2}{y_2 + y_3 + \ldots + y_n} = \frac{y_2}{1 - y_1}$$

For calculating D_{1-2}, D_{1-3} and D_{1-n} use the Hirschfelder equation (for polar or nonpolar gases according to the conditions) or Fuller equation for nonpolar gases.

Important note:

For a dilute multicomponent gas mixture, the diffusion coefficient of the diffusing species in the gas mixture is approximated by the binary diffusion coefficient of the diffusing species in the carrier gas (the carrier gas is the gas of high percentage)

Liquid mass diffusivity

Compare between gas diffusion coefficient and liquid diffusion coefficient.

liquid diffusion coefficients (table 4) reveals that they are several orders of magnitude smaller than gas diffusion coefficients and that they depend on concentration due to the changes in viscosity with concentration and changes in the degree of ideality of the solution. While from the Hirschfelder equation there is no dependency on concentration for gas diffusion coefficient.

How is liquid mass diffusivity calculated?

For diffusion of nonelectrolyte solutes in low concentration solutions (dilute solutions), there are two theories for explanations:

1. The Eyring theory: according this theory the liquid is treated as a quasi-crystalline lattice model interspersed with lattice holes. The solute jumps into the holes within the lattice model.

2. The hydrodynamical theory: this theory states that the diffusion coefficient is related to the mobility of solute molecules and it defines the diffusion coefficient as the net velocity of the molecule while under the influence of a unit driving force.

Equations used to calculate the liquid mass diffusivity

A. Stokes-Einstein equation (developed from the hydrodynamical theory)

$$D_{AB} = \frac{k\,T}{6\pi r \mu_B}$$

D_{AB}: is the diffusivity of A in dilute solution, cm^2/s k: Boltzman constant (1.38×10^{-6} erg/K)

T: absolute temperature, K r: solute particle radius

μ_B: Solvent viscosity, centipoise

The above equation shows that the liquid diffusion coefficient depends on the solute radius and solvent viscosity which both affect the mobility of the molecule.

The above equation can be written in the form:

$$\frac{D_{AB}\mu_B}{T} = Constant$$

Note:

We can predict the diffusion coefficient at any temperature T_2 from an experimental value at T_1 from the equation:

$$\frac{D_1\mu_1}{T_1} = \frac{D_2\mu_2}{T_2}$$

B. Wilke and Chang equation (developed from the two theories for nonelectrolytes in dilute solution)

$$\frac{D_{AB}\,\mu_B}{T} = \frac{7.4 \times 10^{-8}(\phi_B M_B)^{1/2}}{V_A^{0.6}}$$

D_{AB}: is the diffusivity of A through liquid solvent B, cm^2/s $\qquad$ M_B:molecular weight of the solvent

T: absolute temperature, K $\qquad\qquad\qquad\qquad$ μ_B: solution viscosity, centipoises

V_A: molecular volume of solute at normal boiling point, cm^3/g.mol (from table 9 and 10)

ϕ_B: association parameter for solvent B (from table 11)

Table 9, Molecular volumes at normal boiling point for some commonly encountered compounds

Compound	Molecular volume, in cm³/g mol	Compound	Molecular volume, in cm³/g mol
Hydrogen, H$_2$	14.3	Nitric oxide, NO	23.6
Oxygen, O$_2$	25.6	Nitrous oxide, N$_2$O	36.4
Nitrogen, N$_2$	31.2	Ammonia, NH$_3$	25.8
Air	29.9	Water, H$_2$O	18.9
Carbon monoxide, CO	30.7	Hydrogen sulfide, H$_2$S	32.9
Carbon dioxide, CO$_2$	34.0	Bromine, Br$_2$	53.2
Carbonyl sulfide, COS	51.5	Chlorine, Cl$_2$	48.4
Sulfur dioxide, SO$_2$	44.8	Iodine, I$_2$	71.5

Table 10, Atomic volumes for complex molecular volumes for simple substances

Element	Atomic volume, in cm³/g mol	Element	Atomic volume, in cm³/g mol
Bromine	27.0	Oxygen, except as noted below	7.4
Carbon	14.8	Oxygen, in methyl esters	9.1
Chlorine	21.6	Oxygen, in methyl ethers	9.9
Hydrogen	3.7	Oxygen, in higher ethers	
Iodine	37.0	and other esters	11.0
Nitrogen, double bond	15.6	Oxygen, in acids	12.0
Nitrogen, in primary amines	10.5	Sulfur	25.6
Nitrogen, in secondary amines	12.0		

Table 11, Recommended values of the association parameter, ϕ_B, for a few common solvents.

Solvent	Φ_B
Water	2.26
Methanol	1.9
Ethanol	1.5
Benzene, ether, heptane, and other unassociated solvents	1.0

Note: the molecular volume = the sum of atomic volume of each elemnet present

Example: the molecular volume of $C_2H_5OH = 2V_C + 6V_H + V_O$

If data for computing the molar volume of solute at its normal boiling point, V_A, are not available, the following equation is used:

$$V_A = 0.285 \, V_C^{1.048}$$

where V_C is the critical volume of species A in cm^3/g.mol (from tabulated data)

C. Hayduk and Laudie equation (for diffusion in water)

It is a special form of Wilke equation for evaluating diffusion coefficient of nonelectrolytes in water

$$D_{AB} = 13.26 \times 10^{-5} \mu_B^{-1.14} \, V_A^{-0.589}$$

Examples:

1. The Stokes–Einstein equation is often used to estimate the molecular diameter of large spherical molecules from the molecular diffusion coefficient. The measured molecular diffusion coefficient of the serum albumin (an important blood protein) in water at infinite dilution is 5.94×10^{-7} cm^2/s at 293 K. Estimate the mean diameter of a serum albumin molecule.

Solution:

$$D_{AB} = \frac{k \, T}{6\pi r \mu_B}$$

$$r = \frac{k \, T}{6\pi \mu_B D_{AB}}$$

Water viscosity at 293 $\mu_B = 998 \times 10^{-3} \, cP$

$$r = 3.637 \, nm$$

2. Estimate the liquid diffusivity of methanol in water at 283 K.

Solution:

$$\mu_B = 1.14\ cp \qquad\qquad M_B = 18$$

$$\phi_B = 2.26 \qquad\qquad V_{CH_3OH} = 14.8 + 4(3.7) + 7.4 = 37$$

Substitute in the equation:

$$\frac{D_{AB}\ \mu_B}{T} = \frac{7.4 \times 10^{-8}(\phi_B M_B)^{1/2}}{V_A^{0.6}}$$

$$D_{AB} = 1.336 \times 10^{-5} cm^2/s$$

Note:

➢ For the above example we can apply for Stokes-Einstein equation to estimate the atomic radius

➢ the selection of the equation to be used to evaluate the liquid mass diffusivity depends on the available data.

➢ It is important to note that liquid diffusivities D_{AB_L} and D_{BA_L} are not equal as were the gas diffusivities at the same temperature and pressure.

Solid Mass Diffusivity

Applications of solid diffusion:

1. In semiconductors manufacture process: where impurity atoms, commonly called dopants, are introduced into solid silicon to control the conductivity in a semiconductor device.

2. The hardening of steel: results from the diffusion of carbon and other elements through iron
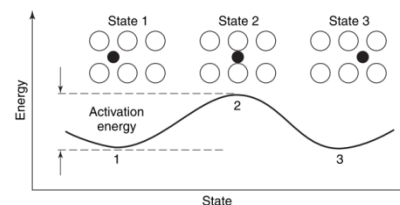
Mechanism of solid diffusion:

Vacancy diffusion and interstitial diffusion are the two most frequently encountered solid diffusion mechanisms
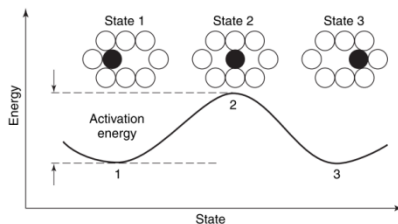
    a) Vacancy diffusion   b) Interstitial diffusion

Factors affecting solid diffusion coefficient:

1. Type of solute
2. Type of solvent (host metal)
3. Temperature

The solid-phase diffusion coefficient depends on temperature and has been observed to increase with increasing temperature according to an Arrhenius equation of the form:

$$D_{AB} = D_o e^{-Q/RT}$$

➤ D_{AB} is solid diffusion coefficient for the diffusing species A within solid B

➤ Q is the activation energy (J/mol)

➤ T is the absolute temperature (K)

➤ D_o is a proportionality constant of units consistent with D_{AB} (from tables)

➤ R is the thermodynamic constant (8.314 J/mol·K)