MASS TRANSFER BY DIFFUSION

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Contents

Summary

Diffusion is the motion of a chemical species in a fluid mixture caused by random molecular mixing process being the consequence of thermally induced agitation which finally leads to complete homogenization of the mixture. The range of application of this phenomenon is extremely broad in chemical industry, in the field of bioengineering as well as in the processes of environmental protection, forming the basis of separation and purification processes of fluid mixtures. Therefore mass transfer by diffusion is a substantial part of the fundamentals of “ Chemical Engineering”.

In the article basic concepts of the physics of diffusion have been presented which enable the design and optimalization of many unit operations such as absorption distillation, extraction and adsorption. The velocities of species as well as the mass and molar fluxes have been defined on the basis of which equivalent forms of the Fick’s first law of diffusion could be presented.

These relations define the binary diffusion coefficient. Equations have been given for the estimation of binary diffusion coefficients for gases, liquids and polymers. On the basis of the generalized mass balances derived the development of mathematical models of mass transfer processes has been discussed. As examples, problems of binary mass transfer in stagnant systems and in laminar flow have been solved. Special attention has been devoted to the coupling of diffusion with chemical reaction in a porous catalyst pellet.

General forms of the equations of multicomponent diffusion have been presented derived from the kinetic theory of gases as well as from the thermodynamics of irreversible processes leading to the generalized Fick’s law. The structure of the matrix of multicomponent diffusion coefficients has been discussed. The generalized driving force of multicomponent diffusion encompasses three driving forces which can generate the molecular movement i.e.: the concentration gradient, the pressure gradient, the externat force acting on a species and the temperature gradient. An alternative formulation of diffusion in multicomponent mixtures namely the Maxwell-Stefan relations has been discussed and compared with the formulation of the generalized Fick’s law. An example illustrates the results obtained by both formulations.

1. Introduction

By mass transfer which is one of the unit operations in chemical engineering we mean the movement of a chemical species in a fluid mixture caused by some form of “driving force”. For instance, dissolving the crystals of $KMnO_4$ in non-stirred water the colour will spread throughout the bottle moving from a region of high concentration to a region of low concentration. Thus the established concentration gradient is in this case the “driving force” of the species movement called diffusion. Generally speaking mass transfer includes not only molecular diffusion but also mass transport by convection and simple stirring, though the mechanism of these processes is much more complex.

We should be aware of the fact that mass transport can be encountered everywhere in the nature in form of various phenomena in the atmosphere, in the oceans, in living systems as well as in the industry. It is a spontaneous mixing process aiming at homogenization of the fluid mixture.

The range of application of the phenomenon of mass transfer is extremely broad not only in the processes of the chemical industry but also in petrochemical industry and in refineries. Recently, it has also been frequently used in the field of biotechnology as well as in the processes of environmental protection. Preparation of reactants for chemical syntheses, separation of products from the reaction mixture and purification of gases and liquids are all associated with mass transfer. Such unit operations like absorption, rectification, extraction and adsorption, in which mass transfer plays the dominant role form the basis of the separation and purification processes of fluid mixtures. In a number of industrial processes the exchange of matter is accompanied by heat transfer. Often, as in condensation, evaporation and sublimation these two phenomena are taking place simultaneously. The heterogeneous catalytic process has also to be mentioned, in which the diffusion in the pores of the catalyst plays a crucial role. When the mass transfer process occurring in a sequence of other phenomena (like in catalytic reactions) is the slowest step, it can constitute the controlling mechanism of the overall rate of the process.

As mentioned before there are two main mechanisms of mass transfer:

Diffusion and Convection

Diffusion is caused by a random molecular motion being the consequence of thermally induced agitation of molecules, which finally tends to complete homogenization of the mixture.

Though the translational velocities of molecules are very high (hundreds of meters per second), the molecular motion of a species is very slow. In gases the diffusion propagates (in normal conditions) at a velocity of about 5cm in a minute, in liquids its velocity is 0.05cm min^{-1} and in solids 10^{-5}cm min^{-1}. The very low rate of diffusion is caused by molecular collisions which occur at a rate of millions per second per cm^3, producing extremely strong hindering of the movement of molecules. Hence, the distance traveled by a molecule in the gaseous phase between two subsequent collisions, called the mean free path, is very low (~10^{-5}cm).

Therefore diffusion occurs more intensively at high temperatures (high mean molecular velocities) and at low pressures (lower concentration of molecules, fewer collisions). The molar mass of the molecule also influences the rate of diffusion as light molecules move more rapidly than the heavy ones.

Convection is a macroscopic process in which portions of fluid are moved over much larger distances than in the diffusion process, carrying the transferred component from regions of high concentration to regions of low concentrations. This process is generated by agitation or by currents and eddies of the turbulent flow. However, the mass transfer between the newly adjacent currents of fluid proceeds by means of diffusion which mixes the portions of fluids.

At this point it is worth citing Maxwell’s statement: “Mass transfer is due partly to the motion of translation and partly to that of agitation”. In other words we would say that any mass flux may include both convection and diffusion because in many cases convection may be generated by diffusion.

2. Velocities and Fluxes of Mass Transfer

The thermodynamic state of a fluid system can be unequivocally defined based on the composition of the mixture and its temperature and pressure. The composition of the fluid mixture is generally expressed in problems of mass transfer by means of the following concentrations:

$\rho_i\left[kgm^{-3}\right]$	mass density of component i	$\rho_i = C_i M_i$
$\rho\left[kgm^{-3}\right]$	mixture mass density	$\rho = \sum_{i=1}^{n} \rho_i$
$u_i[-]$	mass fraction of component i	$u_i = \rho_i \Big/ \rho, \sum_{i=1}^{n} u_i = 1$
$C_i\left[kmolm^{-3}\right]$	molar density of component i	$C_i = \rho_i / M_i$
$C\left[kmolm^{-3}\right]$	mixture molar density	$C = \sum_{i=1}^{n} C_i$
$y_i[-]$	mole fraction of component i	$y_i = \frac{C_i}{C}, \sum_{i=1}^{n} y_i = 1$

In gaseous mixtures the partial pressure of a component is also often used.

The relations between these concentrations are listed in Table 1.

	Partial pressure p_i	Mass density ρ_i	Mass fraction u_i	Molar density C_i	Mole fraction y_i
p_i	p_i	$\frac{\rho_i}{M_i} RT$	$P\mathcal{U}_i \frac{M}{M_i}$	$\mathcal{C}_i RT$	$y_i P$
ρ_i	$\frac{\mathcal{P}_i M_i}{RT}$	ρ_i	$\mathcal{U}_i \rho$	$\mathcal{C}_i M_i$	$\frac{y_i M_i \rho}{M}$
u_i	$\frac{\mathcal{P}_i}{P} \frac{M_i}{M}$	$\frac{\rho_i}{\rho}$	μ_i	$\mathcal{C}_i \frac{M_i}{\rho}$	$y_i \frac{M_i}{M}$
C_i	$\frac{\mathcal{P}_i}{RT}$	$\frac{\rho_i}{M_i}$	$\mathcal{U}_i \frac{\rho}{M_i}$	C_i	$\frac{y_i \rho}{M}$
y_i	$\frac{\mathcal{P}_i}{P}$	$\frac{\mathcal{P}_i}{\rho} \frac{M}{M_i}$	$\mathcal{U}_i \frac{M}{M_i}$	$\frac{\mathcal{C}_i M}{\rho}$	y_i

Table 1. Concentration conversion table.

Let us consider a homogenous multicomponent mixture in which the concentrations of components are functions of position. Under the influence of the established concentration gradients the mass fluxes of components are generated. Thus the various components are moving at different velocities $\mathbf{w_i}$ with respect to a stationary coordinate system. By $\mathbf{w_i}$**,** the velocity of component i, we do not mean the velocity of an individual molecule of component i. It should be rather understood as the average of all velocities of molecules of component i within a small volume. Based on the defined component velocity the mass flux of component i can be determined as

$$\mathbf{n_i} = \rho_i \mathbf{w_i} \quad kgm^{-2}s^{-1} \tag{1}$$

which is the local rate at which mass of component i passes through a unit cross section perpendicular to the velocity $\mathbf{w_i}$.

Similarly, a local molar flux of component i can be defined as

$$\mathbf{N_i} = C_i \mathbf{w_i} \quad kmolm^{-2}s^{-1} \tag{2}$$

Summing equations (1) and (2) over all n components of the mixture leads to a resultant local flux of the mixture of a strictly determined direction

$$\sum_{i=1}^{n} \mathbf{n_i} = \sum_{i=1}^{n} \rho_i \mathbf{w}_i = \mathbf{n} \tag{3}$$

$$\sum_{i=1}^{n} \mathbf{N_i} = \sum_{i=1}^{n} C_i \mathbf{w_i} = \mathbf{N} \tag{4}$$

Relationship (1) forms the basis for the definition of the local mass average velocity of the mixture

$$\mathbf{w} = \frac{\sum_{i=1}^{n} \rho_i \mathbf{w_i}}{\rho} = \sum_{i=1}^{n} u_i \mathbf{w_i} \tag{5}$$

which is frequently called the velocity of the centre of mass or the barycentric velocity. This velocity is used in the momentum and energy balances.
Similarly, one can define a local molar average velocity

$$\mathbf{w^m} = \frac{\sum_{i=1}^{n} C_i \mathbf{w_i}}{C} = \sum_{i=1}^{n} y_i \mathbf{w_i} \tag{6}$$

These are the most commonly used values of mixture average velocities. However, in solving special problems of mass transfer other forms of this value can be defined, for example, the volume average velocity

$$\mathbf{w^v} = \sum_{i=1}^{n} C_i \overline{V}_i \mathbf{w_i} = \sum_{i=1}^{n} \Phi_i \mathbf{w_i} \tag{7}$$

The equations of the average mixture velocities can be presented in a general way by defining an arbitrary average mixture velocity

$$\mathbf{w^a} = \sum_{i=1}^{n} a_1 \mathbf{w_i} \tag{8}$$

where $a_1, a_2 \ldots a_n$ are weighting factors which fulfil the relationship

$$\sum_{i=1}^{n} a_i = 1 \tag{9}$$

Having defined the average velocity of the mixture we are now in a position to determine the flux of component i relative to the flux of the mixture, i.e. relative to a coordinate system moving with the average velocity of the mixture. This is the so called diffusion flux or molecular flux. Thus for the mass average velocity one obtains

$$\mathbf{j_i} = \rho_i (\mathbf{w_i} - \mathbf{w}) \tag{10}$$

and relative to the molar average velocity

$$\mathbf{j_i^m} = \rho_i (\mathbf{w_i} - \mathbf{w^m}) \tag{11}$$

Both equations (10) and (11) can be expressed in moles by dividing them by M_i as $\rho_i / M_i = C_i$.

Generalizing, the flux of component i relative to the coordinate system moving with an arbitrary average velocity $\mathbf{w^a}$ can be written as

$$\mathbf{j_i^a} = \rho_i (\mathbf{w_i} - \mathbf{w^a}) \tag{12}$$

or in molar units

$$\mathbf{J_i^a} = C_i (\mathbf{w_i} - \mathbf{w^a}) \tag{13}$$

Summing Equations (10) over n components the following equality is obtained

$$\sum_{i=1}^{n} \mathbf{j_i} = 0 \tag{14}$$

so not all of the diffusion fluxes are independent.

A similar relationship applies for the molar fluxes relative to the molar average velocity

$$\sum_{i=1}^{n} \mathbf{J_i^m} = 0 \tag{15}$$

It can be proved that in the general case these relationships are as follows

$$\sum_{i=1}^{n} \frac{\mathbf{j}_\mathbf{i}^\mathbf{a} a_i}{\rho_i} = \sum_{i=1}^{n} \frac{\mathbf{j}_\mathbf{i}^\mathbf{a} a_i}{u_i} = 0 \qquad (16)$$

or

$$\sum_{i=1}^{n} \frac{\mathbf{J}_\mathbf{i}^\mathbf{a} a_i}{C_i} = \sum_{i=1}^{n} \frac{\mathbf{J}_\mathbf{i}^\mathbf{a} a_i}{y_i} = 0 \qquad (17)$$

Introducing the definition of the flux of component i (Equation (1)) into Equation (10) and transforming it one finally arrives at the expression

$$\mathbf{n}_\mathbf{i} = \mathbf{j}_\mathbf{i} + \rho_i \mathbf{w} \qquad (18)$$

or generally

$$\mathbf{n}_\mathbf{i} = \mathbf{j}_\mathbf{i}^\mathbf{a} + \rho_i \mathbf{w}^\mathbf{a} \qquad (19)$$

and in molar units

$$\mathbf{N}_\mathbf{i} = \mathbf{J}_\mathbf{i}^\mathbf{m} + C_i \mathbf{w}^\mathbf{m} \qquad (20)$$

$$\mathbf{N}_\mathbf{i} = \mathbf{J}_\mathbf{i}^\mathbf{a} + \mathbf{C}_\mathbf{i} \mathbf{w}^\mathbf{a} \qquad (21)$$

From these equations it can be seen that the total mass flux of component i (relative to the stationary coordinate system) is the sum of the molecular mass flux and the convective mass flux (bulk flow); the same conclusion is valid for the molar fluxes. Moreover it has to be stressed that the diffusion fluxes $\mathbf{j}_\mathbf{i}^\mathbf{a}$ or $\mathbf{J}_\mathbf{i}^\mathbf{a}$ cannot be defined in an absolute way, as they are strictly dependent on the local average velocity of the mixture chosen.

Equations (18) and (20) are frequently presented in an alternative form

$$\mathbf{n}_\mathbf{i} = \mathbf{j}_\mathbf{i} + u_i \sum_{k=1}^{n} \mathbf{n}_k \qquad (22)$$

$$\mathbf{N}_\mathbf{i} = \mathbf{J}_\mathbf{i}^\mathbf{m} + y_i \sum_{k=1}^{n} \mathbf{N}_k \qquad (23)$$

It is worth mentioning that for the equimolar counterdiffusion

$$\sum_{i=1}^{n} \mathbf{N}_\mathbf{i} = 0 \qquad (24)$$

hence the molar diffusion flux $\mathbf{J}_\mathbf{i}^\mathbf{m}$ is equal to the total molar flux N_i and the molar average velocity is zero. Similarly for the mass fluxes

$$\sum_{i=1}^{n} \mathbf{n}_\mathbf{i} = 0 \tag{25}$$

means that the mass average velocity equals zero and so $j_i = n_i$.

In solving mass transfer problems it is sometimes necessary to transform fluxes from one reference velocity, say w^b, to another – w^a. The general transformation equation for the molar fluxes is as follows

$$\mathbf{J}_\mathbf{i}^\mathbf{a} = \sum_{k=1}^{n-1} \beta_{ik}^{ab} \mathbf{J}_\mathbf{k}^\mathbf{b} \tag{26}$$

where the elements of the transformation matrix are

$$\beta_{ik}^{ab} = \delta_{ik} + \frac{y_i}{y_k}\left(\frac{a_n}{b_n} b_k - a_k\right) \tag{27}$$

and for the mass fluxes

$$\mathbf{j}_\mathbf{i}^\mathbf{a} = \sum_{k=1}^{n-1} \beta_{ik}^{*ab} \mathbf{j}_\mathbf{k}^\mathbf{b} \tag{28}$$

where

$$\beta_{ik}^{*ab} = \delta_{ik} + \frac{u_i}{u_k}\left(\frac{a_n}{b_n} b_k - a_k\right) \tag{29}$$

For instance, to relate the molar diffusion fluxes relative to the volume average velocity with the molar diffusion fluxes relative to the molar average velocity the elements of the transformation matrix are:

$$\beta^{y_i \Phi_i} = \delta_{ik} + y_i\left(\frac{\overline{V}_k}{\overline{V}_n} - 1\right) \tag{30}$$

In solving the diffusion problems a question always arises what kind of average velocity of the mixture should be chosen. The best criterion for choosing the reference velocity is to considerably simplify the equations determining the mass transfer fluxes. Therefore we should choose w^a equal to zero in order to eliminate the convective terms in the flux equation.

The molar and volume average velocities are equal and in some cases also equal zero for ideal gases at constant molar density C. But the mass average velocity is not zero in such systems.

When the volume of the liquid phase is nearly constant during the diffusion process it can be assumed that the volume average velocity is close to zero. The evaluation of the two other relative velocities is not so easy. We can only presume that the mass average velocity will be nearly zero when the densities of the constituents of the solution are identical as in this case the center of mass does not move. If, similarly, the molar density of the liquid is constant the molar average velocity is also close to zero.

As the volume average velocity can be assumed close to zero in some mass transfer problems it is frequently preferred in calculations of molecular motion.

Obviously these approximate rules cannot be applied in those cases where a convective flow is superimposed on the system considered. In such cases, as well as in cases where the mass transfer problem has to be solved simultaneously with momentum and energy balances, only the mass average velocity can be used.

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Biographical Sketch

Andrzej Burghardt was born in 1928 in Warsaw, Poland. He received his B.Sc. in 1952 and finally graduated in Chemical Engineering from the Silesian Technical University, Gliwice, Poland obtaining M.Sc. degree. In 1962 he received his Ph.D. while in 1965 the degree Doctor in Technical Sciences from the same university. In 1971 he was awarded a title of Professor in Technical Sciences by the President of the Republic of Poland while some years later, in 1983, he was elected as a member of the Polish Academy of Sciences. In the years 1987-2003 he was a chairman of the Committee of Chemical Engineering at the Polish Academy of Sciences.

Currently he is a member of the Presidium of the Polish Academy of Sciences and of the Scientific Council at the Ministry of Science and Informatics. He is also an active member of the Working Party on Chemical Reaction Engineering of the European Federation of Chemical Engineering.

In the years 1954-1966 he was engaged at the Silesian Technical University, Gliwice, Poland as an Assistant Professor lecturing in Distillation, Mass Transfer and Chemical Reaction Engineering. Then, in 1966, he moved to the Institute of Chemical Engineering of the Polish Academy of Sciences where he was designated to the post of director holding this post until 2002. His field of research focuses mainly on the theory of mass transfer in multicomponent and multiphase systems as well as on chemical reaction engineering with special interest in dynamics of chemical reactors. He is author and co-author of nearly 200 scientific publications in refereed journals and of following books and chapters in collective editions: *Chemical Reactors' Engineering Vol. I and II, Examples of Reactor Design, Dynamics of Processes in a Porous Catalyst Pellet, Mass Transfer in Multicomponent Systems, Condensation of Multicomponent Mixtures in VDI-Wärmeatlas (Three Ed. in German one in English)*. He is also a member of Editorial Boards in several journals.