

Diffusion in general physics and the theory of the convective diffusion

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ABSTRACT

In this article, basic ideas of the diffusion in the gases and liquids are presented. In the last part of it, the problem of diffusion in the concentrated mixtures- when the concentration of components is not considered minor admixtures- is examined. In this case, Onsager's equations are utilized in molecular physics.

Key words: Probability, standard deviation, concentration, interdiffusion, chemical potential, activity coefficient.

INTRODUCTION

The thermal motion of atoms and molecules in the substance leads to their continuous mixing, which depends on density, temperature T , pressure P , and other values.

In the gases, the molecules disorderly collide. These collisions are not similar to the collisions of elastic spheres. Molecules are complex systems, their collisions are caused by repulsive forces with the approachment up to the small distances $r \sim 3 \cdot 10^{-8} \text{ cm}$, equal to a sphere radius of influence of molecular force. Mean free path λ among the collisions is

$$\lambda \sim \frac{1}{r \cdot T n},$$

where $n = \frac{1}{P}$ - the density of the number of particles. Under normal conditions, the collision frequency $z \sim 3 \cdot 10^9 \text{ sec}^{-1}$, the velocity of the free flight $v \sim 3 \cdot 10^4 \text{ cm/sec}$, in air $\lambda \sim 7 \cdot 10^{-5} \text{ cm}$.

In the liquids, which is in contrast to the gases, the thermal motion presents disorderly vibration about the positions of equilibrium. The mean lifetime τ of these positions depends on temperature and pressure. After time τ , the molecule is migrating to the new position of equilibrium locating from former to mean distance so that the mean velocity from its translational motion exists, moreover

$$\delta^3 \sim \frac{1}{\tau}, n = N_{av}, \frac{\rho}{\mu}, c \frac{\delta}{\tau},$$

where N_{av} , ρ , and μ - Avagadro's number, mass density, and the molar mass. For water $\delta \sim \sqrt[3]{\frac{18}{6 \cdot 10^{23}}} \sim 3 \text{ \AA}$ on the average, in 1 second, the molecule passes way equal to $\delta \cdot \frac{1}{\tau}$. It, of course, is not straight-line and similar to the Brownian motion. In this sense, liquid near order exists, and long-range order is absent. Values δ and c are analogous to length and velocity of free flight in gas. The mean time of molecular vibration in the position of equilibrium (oscillating cell) substantially

depends on the temperature. Approximately

$$\tau \cong \tau_0 \exp\left(\frac{\Delta W}{kT}\right),$$

$$\tau_0 \sim 10^{-13} \text{ sec},$$

where τ_0 - the oscillatory period ΔW , - the activation energy necessary for passing the molecule from one position of equilibrium into another. Molecule can change this position having only obtained the energy ΔW , sufficient in order to move apart the adjacent molecules with it and to create place for its displacement. Due to the energy ΔW the molecule leaves from its environment and falls into the new. Value ΔW is intermediate between the heat of evaporation and melting. For water, as an example, at $T \sim 300 \text{ K}$ $\Delta W = 3 \cdot 10^3 \frac{\text{cal}}{\text{mol}}$ i.e. taking into account one particle, moreover

$$\frac{\Delta W}{kT} \sim 5, \quad \tau \sim e^5 \cdot \tau_0 = 10^{-11} \text{ sec},$$

$$c = \frac{\delta}{\tau} \sim \frac{3 \cdot 10^3 \text{ A}}{10^{-11}} \sim 3 \cdot 10^3 \frac{\text{cm}}{\text{sec}},$$

the vibration frequency in the position of equilibrium is

$$\nu \sim \frac{1}{\tau_0} \sim 10^{13} \text{ Hz}$$

Diffusion in the liquid and gas mixture

Two different contiguous gases by means of the molecular motion mutually penetrate and get mixed. This process is called the diffusion. It continues to the formation of the uniform mixture of molecules, in all parts of volume of which leveled the partial gas pressures, their density, temperature and other values. They all are uniformly distributed in the volume of mixture. If initially there existed a layer of gas with different speeds, in which by the way of the exchange of momentum, fast layers slow down, slow are accelerated, and as a result, the motion of gases either ceases or their all mass moves as single entirely. This motion is called

convection. The levelling off of speeds of layers is accompanied by the transformation of kinetic energy of the regulated motion of fast layers into the energy of disorder motion, i.e., thermal motion. This process is of dissipating the energy. The mechanism of the levelling off of all values is caused by the appearance of the preferred direction of molecular collisions. Growing the collision rate of molecules with the speeds, directed to those parts of the volume of mixtures, in which are less density, temperature, pressure, etc. The gradients of these macroscopic characteristics of the state of the gas mixture as a result, decrease. With the description of diffusion, molecular ideas presented above are conserved, and at the same time, substance is considered as continuous medium with the macroscopic characteristics. Respectively, the possibility to describe the directivity of molecular motion at the macroscopic level appears. For this, the quantity of substance, introduced the concept of the flow of diffusion passing through the single area in 1 second.

$$\vec{j} = -D \nabla c,$$

$\frac{dc}{dx}$

where D - the diffusion coefficient, ∇c - concentration gradient. In the one-dimensional case the flow along the axis is determined by replacement,

$$\nabla c \rightarrow \left(\frac{dc}{dx}\right), \text{ i.e.}$$

$$j = -D \frac{dc}{dx}.$$

This formula is called Fick law.

Concentration gradient (or derivative) is the motive power of the diffusion, in which the molecular theory corresponds to the preferred directivity of the molecular motion. In general physics, it proves that for gases

$$D = \frac{1}{3} \nu \lambda,$$

But for the liquids

$$D = \frac{1}{6} c \cdot \delta, \quad c = \frac{\delta}{\tau}.$$

Diffusion in the hydrodynamics

The motion of liquid with uniform composition is described, as is known, by the equations of the hydrodynamics. In the case of the mixture of several different liquids, these equations change. Mixture is described by the concentrations, defined as the ratio of a quantity of particles of the component (or their mass) in the given volume of mixture to its total quantity of the particles. In the course of time, particle distribution in the volume can change with two methods. During the macroscopic motion each section of liquid (drop of liquid) mechanically is moved as single entirely with the constant composition. In spite of its conservation, concentrations in the section can change. In the absence of thermal conductivities and viscosities, this change is thermodynamically reversed and does not lead to the dissipation of the energy.

However, a change in the concentrations is possible and by the molecular transfer of components of one section to another. This levelling off of concentrations due to a direct change of the composition of drop in the hydrodynamics is also called the diffusion. It is not reversed, and together with the thermal conductivity and the viscosity serves as one of the sources of the dissipation of energy in the liquid mixture. Energies of the particles of different sections are unequal and their transition lead to its scattering. Accordingly, the form of Fick law given above is generalized. The flow of diffusion taking into account the energy interaction factors of particles into the mixture and the external field influences is determined by the formula

$$\vec{j} = -L\nabla\mu,$$

where L - Onsager's coefficient,
 μ - Chemical potential.

Theory of Onsager of mass transfer in the concentrated multicomponent mixtures

The processes of isothermal mass transfer in the liquid component mixtures are described by the densities of the flows of the electrodiffusion of components, which generalize Fick laws

$$\begin{cases} \vec{j}_k = -\sum_{(i)} (L_{ki} \nabla \mu_i), \\ L_{ki} = u_{ki} c_i, \quad i = 1, 2, \dots, m \\ \nabla \mu_i = \sum_{(j)} \left(\frac{\partial \mu_i}{\partial c_j} \right) \nabla c_j + \frac{\partial \mu_i}{\partial P} \nabla P, \\ \frac{\partial \mu_i}{\partial c_j} = \frac{\partial}{\partial c_j} \ln(c_i \gamma_i) = \frac{1}{c_j} \left(\delta_{ij} + \frac{\partial \ln \gamma_i}{\partial \ln c_j} \right). \end{cases} \quad \dots(1)$$

Mobilities u_{ki} in (1) and coefficients of the interdiffusion of ions in the binary mixtures are connected, as is known, with the relationship of Nernst Einstein. The electrochemical potential μ_i of component with the concentration, the ionic charge z_i and the activity coefficient γ_i is equal

$$\mu_i = \mu_{i0} + kT \ln(c_i \gamma_i) + z_i \varphi, \quad \dots(2)$$

And the equation of the convective electro diffusion (convection speed)

$$\begin{aligned} \vec{V} - \frac{\partial c_i}{\partial t} + \text{div}(\vec{j}_i + c_i \vec{V}) &= 0, \\ \text{div}(\varepsilon \nabla \varphi) + 4\pi \sum_{(i)} (q_i c_i) &= 0. \end{aligned} \quad \dots(3)$$

Relationship system (1) – (3) considers interaction of components, dependence of their flows on pressure and others. It is at the same time assumed that the mass transfer occurs on medium, state of which the diffusion of components does not affect. Medium, i.e., by aqueous or another solvent, is considered as the certain thermostat, in which move small, not disturbing its state of the admixture.

But the approximation of the minor constituents (adm) becomes incorrect in the practically important case of the concentrated solutions, in which the concentrations of components are compared in the value with the concentration of the solvent. Then admixtures and solvent are equivalent in their components quantity. Accordingly, in the system of flows (1) it is necessary to include the flow of this solvent (water).

Its equations are proposed by Onsager¹

$$\sum_{k=1}^m \left[c_k c_i \nabla \mu_i + \frac{RT}{q_{ik}} (c_k \vec{j}_i - c_i \vec{j}_k) \right] = 0, \quad i=1,2,\dots,m, \quad \dots(4)$$

Where $\sum_{k=1}^m$ - the total number of components, c_i - the constants, which in (1) are equated to the coefficients of the interdiffusion. Their solutions are necessary, as an example, for examining the processes of mass transfer in the concentrated electrolytes. They include the problems of precision electrochemical metal working with the complex geometry of their surface. This is also of the problem of the extremely intensive localized (under appropriate conditions) anodic dissolution of metals in aggressive media. In these cases local anode current density reaches hundreds (A/cm^2). Accordingly, into the solution of electrolyte

enters a colossal quantity of metal ions M^{+} . On their required hydration a colossal quantity of molecules of water is spent, and in the region near the anode electrolyte dehydrates. The equations are necessary for calculating these and similar processes. They are used in²⁻⁵ with the development of the regime of forming the components of power plants and anodic dissolution in the binary electrolytes. Let us examine the structure of the equations, using for this the mean statistical or (*standard deviation*) speed of component, introduced by Onsager. It considers simultaneously all components of its motion, including the diffusion. We write

$$\vec{V}_i(\vec{r}) = \frac{1}{n} \int \vec{v}_i f(\vec{r}, \vec{v}_i) d\vec{v}_i, \\ n = \int f(\vec{r}, \vec{v}_i) d\vec{v}_i, \quad \dots(5)$$

where $\vec{v}_i$ - true. I.e. the instantaneous velocity of particle, n - phase density.

Let us designate the densities of the total fluxes of mass and number of particles of the i component and $\vec{j}_i$ the density of the diffusion flow, the molar masses of the components M_i .

We write

$$\vec{I}_i = M_i c_i \vec{V}_i, \quad \vec{J}_i = c_i \vec{V}_i, \quad \vec{j}_i = c_i (\vec{V}_i - \vec{V}), \\ \rho \vec{V} = \sum_{i=1}^m \vec{I}_i = \sum_{i=1}^m (M_i c_i \vec{V}_i), \\ \rho = \sum_{i=1}^m (M_i c_i). \quad \dots(6)$$

Using (6), let us examine the left side of expression (4)

$$c_i \vec{j}_i - c_i \vec{j}_k = c_i c_k [(\vec{V}_i - \vec{V}) - (\vec{V}_k - \vec{V})] = c_i c_k (\vec{V}_i - \vec{V}_k).$$

Hence, it is apparent, that (4) is possible to write it down in the identical form of

$$\vec{c} \nabla \mu_i = \sum_{k=1}^m Q_{ik} c_k (\vec{V}_k - \vec{V}_i), \\ \vec{c} = \sum_{i=1}^m c_i, \quad Q_{ik} = \left(\frac{RT}{q_{ik}} \right), \quad \dots(7)$$

Moreover, according to (6), we get

$$\sum_{i=1}^m (M_i \vec{j}_i) = \left[\sum_{i=1}^m M_i (\vec{J}_i - c_i \vec{V}) \right] = \left[\sum_{i=1}^m (\vec{I}_i) - \rho \vec{V} \right]. \quad \dots(8)$$

Equations (7) is the simpler form of Onsager's equations (4). From (7) we obtain the limiting case of admixtures diffusion with the small concentrations⁵. Actually, assume that in (7), concentration of one of the components (solvent) predominates, i.e. the concentrations of remaining components are considerably less. Then with it will be

$$c_i \ll c_j, \quad \vec{V}_i \approx \vec{V}, \quad c_i \sim \vec{c}, \quad \vec{c} = \sum_{i=1}^m c_i. \quad \dots(9)$$

Therefore, to the right of (7) is substantial, only one term with c_i , and we have for any other component

$$\vec{c} \nabla \mu_i = Q_{ii} c_i (\vec{V} - \vec{V}_i), \quad i \neq 1. \quad \dots(10)$$

Whence it follows, taking into account (6),

the usual expression of the flow of the convective diffusion of component in the dilute solution is

$$\vec{J}_i = \vec{V}_i c_i = - \frac{1}{Q_{ii}} c_i \nabla \mu_i + c_i \vec{V},$$

$$Q_{ii} = \frac{RT}{q_{ii}}. \quad \dots(11)$$

With $q_{ik} = D_{ik}$ it coincides with (1).

The structure of equations (7) can be explained⁵, using an idea about the force of stoke during the motion in the viscous fluid with the coefficient of the viscosity. For this, let us examine the particular expression

$$-\nabla \mu_i = \eta (\vec{V}_i - \vec{V}) \quad \dots(12)$$

and let us consider that, the force acts on the ball of stoke

$$f_i = \eta \lambda_i (\vec{V}_i - \vec{V}),$$

where λ_i - the characteristic scale of interaction, analogous $6\pi\eta r$, and $(\vec{V}_i - \vec{V})$ - the

speed of ball relative to the environment.

Left side of (12) represents the density of the thermodynamic force, which acts on the particles of component. Taking into account its one mole $-\nabla \mu_i \sim N_A f_i$.

Right side of (12) treats as the resisting force with the coefficient of braking, analogous to the force of stoke f_i with $\eta = \eta \lambda_i$.

In the general case of several components it is necessary to consider their pairwise interactions. for this, let us change in (12) the indexing of values

$$k_i \rightarrow Q_{ik}, \vec{V} \rightarrow \vec{V}_i, \eta \lambda_i \rightarrow \eta \lambda_{ik} = Q_{ik},$$

Then, let us introduce the statistical weight $\frac{c_i}{c}$ of i component and will sum up interactions of all pairs of components. As a result, we will obtain (7). According to (7), Onsager's model diffusion in the concentrated liquid mixtures presents the motion of the components, which are mutually rubbed with the force $Q_{ik}(\vec{V}_i - \vec{V}_k)$. it is possible to name it the hydrodynamic idea of diffusion.

REFERENCES

1. L. Onsager. *Ann. N.Y. Acad. Sci.* **46**: 241 (1945).
2. V.S. Krelov. *Electrochemistry*. **12**(6): 843 (1976).
3. V.S. Krelov, A.D. Davidov, E. Kozak. *Electrochemistry*. **11**(8): 1155 (1975).
4. L.I. Kheifets, A.B. Goldberg. *Electrochemistry*. **25**(1): 3 (1989).
5. Yu. A. Popov., Theory of interaction of metals with a corrosive Environment // England. Cambridge International Science Publishing. 378 (2000).