

## MATHEMATICAL FORMULATIONS OF THE BASIC DIFFUSION EQUATION: A DISCUSSION

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### ABSTRACT

A discussion is made on the possible forms of mathematical formulations for the basic diffusion equation. The formulations have been derived from the law of motion. It is shown that the assumption of Stokes resistance leads to paradoxical conclusions in some specific cases of diffusion processes. It is argued that the expression for resistant forces in transport processes is empirical, and hence the form of the diffusion equation depends on the expression chosen in describing the resistant forces. Evidences are collected from literature in favor of both thermodynamic and Fickian formulation of the diffusion equation. It is concluded that ideal form of diffusion equation is absent, and the choice of the form of diffusion equation would depend on the specific circumstances being studied.

**Keywords:** Diffusion, Fick's law, chemical potential, concentration gradient, diffusion coefficient

### I. INTRODUCTION

As early as 1855, Fick stated that he could apply Fourier's law for heat conduction and Ohm's law for the electric conduction to diffusion processes, and proposed that the diffusion flux  $J$  ( $\text{mol.m}^{-2}.\text{s}^{-1}$ ) is proportional to the concentration gradient (Eq. 1) [1].

$$J = -D \frac{dC}{dx} \quad (1)$$

where  $D$  ( $\text{m}^2.\text{s}^{-1}$ ) is the diffusion coefficient,  $C$  ( $\text{mol.m}^{-3}$ ) is the concentration of the permeating species and  $x$  (m) is the position coordinate along the flow direction. The Eq. (1) is known as Fick's first law. The diffusion coefficient  $D$  is a constant, and is numerically equal to the flux for unit concentration gradient. It might depend on the nature of the medium and the diffusing components, temperature and some other factors; but by no means, on the concentration. Under steady state flow, the concentration gradient is constant i.e. the concentration decreases linearly. For about 150 years, Fick's law has been the fundament for all theoretical and experimental studies on diffusion transport. When viewed

superficially, one finds no dissimilarity between the formulation of Fick's law and those of Fourier and Ohm's law. However, when viewed strictly, one finds that the Fick's law suggests a driving force far different from those in the other two. Ohm's law is clear-cut in its formulation - the driving force is the electrical potential gradient. The electrical potential gradient is the field intensity i.e. it is the force acting on unit charge (N/ unit charge). Under steady state flow, this force is balanced by resistant forces, which are proportional to electric current/ electron flux. In Fourier's law, the driving force is the temperature gradient (which equivalent to thermal potential gradient), and the resistant forces could be viewed to be proportional to the thermal energy flux. Thus, the driving and the resistance forces in Fourier and Ohm's laws are similar. The concentration gradient in Eq. (1), however, does not represent the force on unit mass. Thus, the mass flux in the Fick's law is proposed to be proportional to a parameter, which is dissimilar to the driving forces in the transport of thermal and electrical energy. This dissimilarity could be avoided, if the diffusion flux were presented as proportional to the chemical potential gradient (Eq.2).

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$$J = -\kappa \frac{d\mu}{dx} \text{ with } \mu(P, T) = \mu^0(P^0, T) + RT \ln C + \vartheta(P - P^0) \quad (2)$$

where  $\kappa$  ( $\text{mol}^2 \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{J}^{-1}$ ) is the constant of proportionality (independent of concentration) and  $\mu$  ( $\text{J} \cdot \text{mol}^{-1}$ ) is the chemical potential,  $T$  (K) is the temperature,  $P^0$  (Pa) is the pressure of the reference state,  $R$  ( $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ) is the universal gas constant,  $\mu^0$  ( $\text{J} \cdot \text{mol}^{-1}$ ) is the chemical potential at the pressure  $P^0$  and temperature  $T$ , and  $\vartheta$  ( $\text{m}^3/\text{mol}$ ) is the partial molar volume of the species. According to the Eq. (2), under steady state flow, the chemical potential decreases linearly, and the concentration exponentially. The flux equation expressed by the Eq.(2) is similar to Ohm's and Fourier's law not only in the form of mathematical formulations, but also in physical significance of the terms. Recently Islam [2] made a controversial conclusion that the both the equations (Eqs. 1 & 2) could be justified from thermodynamic viewpoint. Islam and Buschatz [3] have shown that the Eq. (2) might appear more convenient in describing the diffusion processes accompanied by chemical or physico-chemical interactions.

250 years have passed since Fick proposed his famous diffusion law. Since then enormous theoretical and experimental works have been done on diffusion transport, and the Fick's law has always been the basis of analyses. Till today the investigation on the issue does not die down [4-15]. With the accumulation of experimental data, showing deviation of the diffusion flux from the Fick's law, the analysis of the diffusion processes has again been performed by the Eq. (1), but not with  $D = \text{constant}$ , rather  $D = D(C)$ . Ash et al. [14] presented a number of expressions relating the diffusion coefficient  $D$  to the concentration  $C$ . Since  $D = D(C)$  is a freely chosen empirical relation, it is quite expected that with such modification of the Eq. (1), the diffusion flux could always be described. Thus, the investigators seem do not intend to cross the boundary of thinking that the real driving force is the concentration gradient, and any deviation of the experimental data from the Eq. (1) should be attributed to the change in the diffusion coefficient with the change in concentration. It is worth mentioning that the non-equilibrium thermodynamics utilizes entropy-producing character of spontaneously occurring processes to provide a link between classical thermodynamics and the rate of processes. It shows

that the gradient of the chemical potential is the proper thermodynamic force conjugate to the diffusion flux. The linear law relating the diffusion flux and the chemical potential (Eq.2) should have been then the correct relationship irrespective of the diffusion process considered. In spite of that, in all literatures (to authors' knowledge) on non-equilibrium thermodynamics [16-19], it is assumed that the driving force in the diffusion transport is the chemical potential gradient, but the flux is proportional to concentration gradient. It appears that the diffusion flux could not be described if not somehow expressed in terms of concentration gradient. In formulating the diffusion equation in the present work, we shall apply an approach, which is different from the previous investigators. We shall consider that the chemical potential gradient is the true driving force for diffusion processes. However, we shall bear in mind that the thermodynamic parameters as chemical potential do not establish the rates of processes, and the rates depend on both the driving forces and the resistances. Although chemical potential is a thermodynamic variable, resistances are not. In the present analysis, we shall make a brief discussion on 'how a diffusion equation would look like, if the diffusion resistances follow the same laws as hydrodynamic resistances'. Thus, we are attempting to derive different forms of diffusion equation applying Newton's law of motion. Such discussion would inspire researchers not to keep their thinking confined in a boundary drawn by some apparently established law. In the present case, for example, one (who is not pre-convinced in the validity of the Eq. (1)) could easily find that the credibility of the law suffers, if the proportional constant  $D$  is almost always empirically related to concentration, the gradient of which is considered to be the driving force of the process. In the present paper, we shall also discuss evidences in favor of the Eq. (1 or 2), and make comments on the interpretation on the concentration dependence of the diffusion coefficients when the analysis of the diffusion flux is based on the Eq. (1). It is found that the consideration of the hydrodynamic law for resistances results in the diffusion equations, which are completely different from the mentioned two. It appears that the form of the diffusion equation depends on how the resistances are described. It is concluded that for experimental systems treated with Eq. (1), the observation that 'the diffusion coefficient decreases as the concentration increases', dictates that the Eq. (2) is most likely to be the true diffusion equation.

## II. FORM OF THE DIFFUSION EQUATION WITH RESISTANCES DESCRIBED AS THOSE IN HYDRODYNAMICS

In this section, we shall discuss about what the form of the diffusion equation would be, if the diffusion resistances were described in terms of velocity as practiced in describing the hydrodynamic resistances.

### A. Diffusion equation with the Stokes law describing the resistances

According to Stokes law, the resistant force is proportional to the velocity of the individual particles. Einstein [20] applied Stokes law in describing diffusion resistances (Such consideration coincides with the hydrodynamic resistances in laminar regime) and apparently justified Fick's law from thermodynamic viewpoint. Thus, to a particle considerably larger than solvent molecules, the frictional resistance is assumed to be  $Fu$ ,  $F$  being the frictional constant and  $u$  – the velocity of a particle. The work done in moving one mole of the solute at a distance  $dx$  is  $N_A F u dx$ ,  $N_A$  being the Avogadro number. This work is equal to  $-d\mu$ . Thus, for a system with constant pressure and temperature

$$N_A F u dx = -d\mu \Rightarrow -\frac{d\mu}{dx} - N_A F u = 0 \quad (3a)$$

Then for the diffusion flux  $J$ , we can write

$$J = uC = -\frac{RT}{N_A F} \cdot \frac{dC}{dx} \quad (3b)$$

For spherical particles of radius  $r$ , Stokes law gives  $F = 6\pi\eta r$  (3c)

where  $\eta$  is the viscosity of the medium. Combining Eqs. (3b & 3c) we have

$$J = -D \frac{dC}{dx} \quad \text{with } D = \frac{RT}{N_A F} = \frac{RT}{6N_A \pi \eta r} \quad (3d)$$

The viscosity  $\eta$  is a function of the concentration and hence the diffusion coefficient  $D$  will appear concentration-dependent. But for a small concentration difference,  $D$  might be assumed constant. Thus, defining the resistant forces in a manner different from that in Ohm's law, Fick's law was derived assuming that the chemical potential gradient was the driving force in the diffusion process. Since then it has been assumed that the Eqs.(1) & (2) are identical, and as such the transport coefficients  $\kappa$  and  $D$  are related as in Eq.(4).

$$\kappa = DC/(RT) \quad (4)$$

where  $D$  is a constant and  $\kappa$  is concentration-dependent. The relation expressed in the Eq. (4) is very attractive only if the concentration contributes to the chemical potential. In the cases, when pressure and temperature also contribute to chemical potential gradient, substitution of the Eq. (4) into the Eq. (2) would make the flux equation complicated.

Is the Eq. (3b) properly derived? Now we shall review the derivation of the Eq.(3b), which has validated the Eq. (1) from the viewpoint of thermodynamics. At the first glance, the derivation of the Eq. (3d) was clean and smooth. Let's discuss first whether the starting equation (3a) was written properly? Under steady state flow, at every point  $uC = J = \text{constant}$ .  $C$  is a continuously decreasing function of  $x$ . Consequently  $u$  is a continuously increasing function of  $x$ . Then the motion of the particles in the diffusion field is an accelerating one. Does the Eq. (3a) have magical power then? - At every point the net force acting on the particle is zero, but the velocity is increasing! Therefore, it must be accepted that the particles perform an accelerating motion, and the corresponding equation of motion should be described by the Eq.(5a) instead of the Eq. (3a).

$$-\frac{d\mu}{dx} - N_A F u = N_A m \frac{du}{dt} \quad (5a)$$

Obviously, the Eq. (5a) could not lead exactly to the Fick's law (Eq. 1) as the Eq. (3a) did. Let's see how the steady state flux  $J$  (=constant) is related to concentrations according to the Eq.(5a). For this purpose, the following substitutions are made in the Eq. (5a):

$$dt = dx / u \quad \text{and} \quad u = J / C \quad (5b)$$

Solving the Eq. (5a) for the boundary conditions: for  $x=0$ ,  $C=C_0$  and for  $x=L$ ,  $C=C_L$ ; we have

$$J(1 + J.A) = \frac{D(-\Delta C)}{L} \quad \text{with } \Delta C = C_L - C_0. \quad (5c)$$

$$D = \frac{RT}{N_A F} \quad \text{and} \quad A = \frac{m}{F} \cdot \frac{1}{C_0 C_L} \cdot \frac{(-\Delta C)}{L}$$

Or

$$J = \frac{-1 + \sqrt{1 + 4A.J_{\text{Fick}}}}{2A} \quad \text{with } J_{\text{Fick}} = \frac{D(-\Delta C)}{L} \quad (5d)$$

where  $L$  is the membrane thickness, and  $C_0$  and  $C_L$  are the concentrations respectively at the feed

interface ( $x=0$ ) and the permeate interface ( $x=L$ ). Now compare the Eq.(3d) with the Eq. (5d). In fact, if Stokes law describes the diffusion resistances, it is the Eq. (5d) (and not the Eq. 3d), which appears to be the basic diffusion equation. If  $4AJ_{\text{Fick}}$  is very small, the equation is approximated to the Fick's law (Eq. 5e).

$$J = \frac{-1 + \sqrt{1 + 4A \cdot J_{\text{Fick}}}}{2A} \quad (5e)$$

$$= \frac{-1 + (1 + 2A \cdot J_{\text{Fick}} + \dots)}{2A} \approx J_{\text{Fick}}$$

The value of  $C_L$  plays the decisive role in determining the value of  $A$  (For  $C_L \rightarrow 0$ ,  $A \rightarrow \infty$ ). Let's see what would happen if  $C_L \rightarrow 0$ .

$$\lim_{C_L \rightarrow 0} J = \lim_{A \rightarrow \infty} \frac{-1 + \sqrt{1 + 4A \cdot J_{\text{Fick}}}}{2A} = 0 \quad (5f)$$

The permeate side concentration  $C_L$  is usually kept very small to ensure a high flux. The Eq.(5f) shows that for  $C_L \rightarrow 0$ ,  $J \rightarrow 0$  (a paradox!). It might be assumed that in a real diffusion process, infinitely small value of  $C_L$  could not be realized, and the factor  $4AJ_{\text{Fick}}$  would always be negligible in practice. What would it mean then? If it were possible to realize infinitely small concentration on the permeate side, we could have realized 'no flux regime' whatever high concentration is maintained on the feed side! It is true that a number of known and unknown factors might affect a real process, and the experimentally observed relations could deviate from the proposed laws. But it is very confusing that the investigators aim at the realization of high fluxes for  $C_L \rightarrow 0$ , and under this condition the Eq. (5d) predicts ironically 'no flux regime'. Where might the error lie in? It is probable that the frictional force is not described properly i.e. Stokes law does not describe the diffusion resistances.

Let's have a look on the Eq. (3a or 5a) again. For colloidal systems, it is considered that the concept 'diffusion velocity' coincides with the velocity of individual particles. In the description of the diffusion of colloidal particles, Stokes law has been applied to describe the resistance forces. To apply Stokes law, the solvent molecules must be negligibly smaller than the moving particles [21]. It is disputable whether colloidal particles (not to speak of the molecular, atomic or ionic species, which are the usual species in diffusion flow) satisfy this requirement properly. If the velocity of the particles could be calculated by Stokes law, the

diffusion process of such species would be seemingly very slow and even negligible. Thus, the application of Stokes law in describing the resistances has the following drawbacks:

1. The concept 'diffusion' is related usually to molecular, atomic or ionic species. For such species, the concept 'individual velocity  $u$ ' is not well defined.
2. For very small values of  $C_L$ , the predicted flux (from Eq.5d) is paradoxical.

It seems that Stokes expression is not much appropriate to describe the resistance to diffusion flow for general cases. But the investigators are encouraged by the 'apparent derivation' of the Fick's law from the Eq.(3a), and assume that the resistant forces to the diffusion flow of atomic, molecular or ionic species could also be described by the same equation as that for the colloidal particles. For this reason, may be, irrespective of the sizes of the diffusing species, the Eqs. (1 & 2) have been always thought to be identical with the transport coefficients related by the Eq. (4).

## B. Diffusion equation with resistances proportional to the square of the diffusion velocities

Moelwyn-Hughes [22] described in details Einstein and Smoluchowski's treatment of Brownian motion. It is interesting to remember what Smoluchowski proposed about the resistant forces. As per Moelwyn-Hughes [22], Smoluchowski considered that the diffusion process is related usually to the motion of very small particles and proposed that for small particles, Stokes expression would be rejected in favor of a resistance factor, which is proportional to the square of the velocity (Such consideration coincides with the hydrodynamic resistances in turbulent regime). Obviously, Smoluchowski was not talking about some general form of the diffusion equation. Let's see what might be the form of the diffusion equation, if the resistant forces were expressed as proposed by Smoluchowski. Then the equation of motion of the particles will be given by Eq.(6a) and the steady state flux- by Eq. (6b)

$$-\frac{d\mu}{dx} - N_A F v^2 = N_A m \frac{dv}{dt} \quad (6a)$$

$$J = \sqrt{\left( \frac{RT}{N_A F} \cdot \frac{C_0^2 - C_L^2}{2L} \right) \left/ \left( 1 + \frac{m}{F} \cdot \frac{\ln(C_0/C_L)}{L} \right) \right.} \quad (6b)$$

The form of the Eq. (6a) is far different from the usual form of the diffusion equation (Eq.1). Undoubtedly, the question of describing the resistant forces is open.

In diffusion flow, Einstein proposed Stokes law to describe the resistant forces- a linear relationship between the velocity of the permeating species and the resistance force. Smoluchowski recommended that the resistance force would be proportional to the square of the velocity. In fact, these relations are the limiting cases (at very low and high velocities) of the resistant forces experienced by particles moving through a fluid. In convective flow, the drag force experienced by a body immersed in a flowing fluid is proportional to the free stream velocity [23]. From the principle of transfer of momentum, the flowing fluid also experiences a resistant force equal and opposite to this drag force. The concept 'free stream velocity' is related more to the flux or area averaged velocity than to the velocity of the molecules itself. Therefore, in such cases the resistant force is considered to be proportional to the flux. According to D'Arcy's law, the driving force is the pressure gradient (Force per unit volume permeate). For the flow of incompressible fluid through a highly porous membrane, the concentration would not have contribution to the chemical potential. Then the pressure-gradient multiplied by partial molar volume of the permeating fluid in the membrane equals to the chemical gradient. Therefore, for the convective flow obeying D'Arcy's law, the resistant force is proportional to the flux itself, and the flux is virtually proportional to the chemical potential gradient. Thus, for the convective flow, the resistance is considered to be proportional to the flux. However, as discussed above, if the resistance forces are expressed as some function of the velocity of individual particles, the motion must be considered to be accelerating. Consequently, different inconvenient formulations of the diffusion law will be obtained (e.g. Eqs. 5d & 6b). To escape from such a situation, the resistant forces could be described as those in the convective flow. Usually the flux  $J$  ( $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1} = \text{m/s}$ ) is defined as the volume of the species permeating through unit area of the membrane in unit time. If the flux is expressed in terms of  $\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$  or  $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ , still the dimension is related to m/s by a coefficient. So, it is reasonable to consider that in steady state diffusion flow the resistant force is approximately proportional to the flux  $J$  itself, and then the Eq. (2)

represents the diffusion flux equation. Unlike the velocity of the individual particles, the steady state flow velocity or flux is not accelerating. The Eq. (2) could be applied to describe the diffusion flux of all kinds of diffusing species- small or large, atomic, molecular, ionic or colloidal. The Eq. (2) is now really similar to the Ohm and Fourier's laws, which state that the mass or the energy flux is proportional to the potential gradient. But it should always be remembered that the form of the resistant forces described so far are approximations, and the resulting diffusion equations (Eqs. 1, 2, 5d or 6d) are also approximations. In fact, the diffusion is a complex process, and the resistant forces could merely be expressed in a single form equally valid for all cases of diffusion transport.

### III. EVIDENCES IN FAVOR OF THE EQ. (1) OR THE EQ. (2)

The question of the type "Which equation is more appropriate to describe a diffusion process- Eq.(1) or Eq. (2)?" is difficult to be answered. It depends on how the resistant forces are realized in a diffusion process. If the concentration distribution of the diffusing species in the membrane were known/measured reliably, some information could have been acquired about the true diffusion equation. If the steady state concentration profile is linear, the governing equation is the Eq.(1); and if the steady state concentration profile is exponentially decreasing, the governing equation is the Eq. (2). However it is a very tough task to measure the concentration profile across an operating membrane. Few efforts have been made in this regard [24-27] with stacked films rather than a single film. The stacked films were peeled and the component-films were separated for the measurement of averaged concentration in each film, after the permeation experiment had already been over. Naturally, the method throws some shadow on the reliability of the results. Most reliable method is, to fit the steady state flux data directly to Eqs. (1) & (2), and to verify whether  $D$  or  $\kappa$  is constant. This method is also complicated, as the true concentrations at the interfaces are usually not known. As a usual practice, in estimating the interface concentrations, it is assumed that surface reaction is very fast and is in equilibrium. Thus, fitting the flux data to the Eq.(1), the diffusion coefficient is determined. There are also some other methods for the determination of diffusion coefficient (e.g. time lag, sorption and desorption kinetics), but the

coefficient determined from steady state flow seems most reliable to verify the validity of the diffusion equation. Regarding the diffusion coefficient, Mears [28] stated, "When  $D$  is determined by using Eq.(1), it is found that  $D$  varies with concentration. This may be due to variation of mobility with concentration or to the force departing from chemical potential". Some interpretation had always been looked for to explain the concentration dependence of the diffusion coefficient. No effort is made yet however, to fit the data to Eq.(2), and to verify whether  $\kappa$  is a constant. This is also difficult, as  $C_L$  is always very small and difficult to be measured. Thus the probability of finding suitable literature data to fit to the Eq. (2) is fade.

#### IV. CONCENTRATION DEPENDENCE OF THE DIFFUSION COEFFICIENT

Barrie [29] has thoroughly discussed the concentration dependence of the diffusion coefficient through polymers. The diffusion coefficient could increase, decrease or remain constant depending on the processes. To explain the increase in the diffusion coefficient, it is assumed that with an increase in the concentration of the permeating species, the energy of the activation of the diffusion process decreases and hence  $D$  is an exponentially increasing function of concentration (Eq.7a) [30, 31].

$$D = D_0 \exp(\alpha C) \quad (7a)$$

where  $D_0$  and  $\alpha$  are empirical constants.

Combining Eqs. (1 & 7a), we have,

$$J = D_0 \exp(\alpha C) \frac{dC}{dx} \quad (7b)$$

The Eq. (7b) is considered to be the modified form of the Fick's law. Thus, two adjustable parameters ( $D_0$  and  $\alpha$ ) appeared in Eq. (7b) instead of a constant diffusion coefficient. We could go further with the modification of the Fick's law transforming the Eq. (7b) into Eq. (8).

$$J = D_R \frac{d\zeta}{dx} \text{ with } D_R = (D_0/\alpha) \text{ and } \zeta = \exp(\alpha C) \quad (8)$$

The Eq. (8) has the properties to represent a new formulation of the diffusion law: (a) The quantity  $d\zeta/dx$  (and not  $dC/dx$  as in Fick's law) is the driving force for the diffusion flux. Both the quantities  $d\zeta/dx$  and  $dC/dx$ , however, are not related to the concept 'force per unit mass'. (b) The proportionality constant  $D_R$  is independent of  $\zeta$  (or  $C$ ). (c) Under the steady state flow, the parameter  $\zeta$  (and not the concentration  $C$ ) decreases linearly.

From the mathematical viewpoint, the Eqs. (7b & 8) are equivalents, but the 'driving forces' are expressed differently.

Long [32] applied McCall's model (Eq. 7b) to describe the steady state flux of some liquid hydrocarbons through polypropylene films and found that the value of  $\alpha$  varied in the range of 20-87. The author also calculated the concentration profile in the membrane, and found that at the feed side, the concentration gradient  $dC/dx$  is very low (in absolute value), and it increases as  $x$  increases. The concentration profile calculated by Long [32] could have been disputed arguing that most probably it was the Eq. (8) (and not the Eq.7b), which was describing the steady state flow. The room for such dispute disappeared, when Kim & Kammermeyer [27] measured the actual concentration profile in diffusion processes through a stacked film packet and provided experimental data in favor of the concentration distribution predicted by McCall's model [30]. Kim & Kammermeyer [27] also reported very high values of  $\alpha$  (=17-100) for the systems under investigation. A bit earlier than Kim & Kammermeyer [27], Rosenbaum and Cotton [26] measured the concentration gradient of water through a stack of cellulose acetate films. However they found that the concentration decreased almost linearly. In fact, the measurement of actual concentration profile under steady state flow is a very difficult task, and could merely be precisely performed. On the other hand, the steady state flux can be measured in a reliable range of confidence. Thus, pretending (!) the unawareness of the concentration profile measured by Kim & Kammermeyer [27] or suspecting in the preciseness of the measured data, the steady state flux data could empirically be described by the Eq. (8) for  $\alpha$  =17-100, and the apparent driving force ( $-\Delta\zeta/\Delta x$ ) would appear much higher than ( $-\Delta C/\Delta x$ ) predicted by the Fick's law. It could easily be shown that for very small values of  $C_L$ , the value of  $\ln(C_0/C_L)$  is also always much higher than that of  $(C_0-C_L)$ . Thus, the Eq. (2) with  $\kappa$  =constant, predicts a driving force for the diffusion flux higher than  $(C_0-C_L)/L$ . Therefore, even as an empirical approach, attempts could have been made to fit the diffusion flux data to the Eq. (2) (if  $C_L$  were known). But as we are aware of the concentration profile reported by Kim & Kammermeyer [27], we have no alternative than accept that Fick's law is valid with the diffusion coefficient exponentially increasing with concentration. In fact, the positive change in  $D$  is

related to the structural change in diffusion media. The exponential model of diffusion coefficient has been discussed in literatures [1,31] and enjoys much support from the investigators.

Many investigators [33-37] studied the diffusion transport for a number of water-polymer systems. Unlike Kim & Kammermeyer [27], they found that the diffusion coefficient, obtained from an analysis of the steady state of permeation, decreased as the total concentration of water in the polymer was increased. In case of some silicon rubber [38, 39], beyond some critical concentration, the diffusion coefficient decreased as the water content increased. Wellons & Stannett [40] measured the diffusion coefficient in four ways, viz., sorption, desorption, time lag, and by dividing the permeability constants by the equilibrium solubility coefficients. The time lag gave diffusion constants that were independent of concentration, whereas the other three led to diffusion constants that steadily decreased with the increase in the concentration. Park [41] also reviewed a number of observations on the concentration dependence of diffusion coefficients. The author found that for a number of cases the diffusion coefficient decreased as the concentration increased. The concentration-distance relationship was also exponentially decreasing. The decreasing tendency of  $D$  with concentration is usually interpreted in terms of the association of the water molecules through the formation of hydrogen bonds such that the effective mobility of the water molecules was reduced as the concentration was increased. There is no doubt that the clustering of the permeating species would affect the diffusion process, and under steady state permeation, it might seem that the diffusion coefficient is decreasing as the concentration increases. The very question is whether the observations could be interpreted without assuming the cluster formation (or at least neglecting the effect of cluster formation)? From the viewpoint of the theory of molecular kinetics, the self-diffusion coefficient of a gas is given as follows [22]:

$$D = \frac{1}{\pi\sigma^2 n} \left( \frac{kT}{\pi m} \right)^{0.5} \quad (9)$$

Where  $k$  is the Boltzmann constant,  $m$  is the mass of a molecule,  $\sigma$  is the molecular radius and  $n$  is the molecules per  $\text{cm}^3$ . The Eq. (9) shows that the self-diffusion coefficient is inversely proportional to  $n$  (concentration expressed in terms of molecules. $\text{m}^{-3}$ ). This coefficient is derived assuming the validity of Fick's law. Let's now also discuss a hypothetical

situation: The Eq. (2) describes the diffusion transport properly. But an investigator is pre-convinced in the validity of Eq. (1) and applies it to treat the experimental data. What would he/she conclude about the concentration dependence of the diffusion coefficient? This can be seen rewriting Eq. (2) in terms of concentration gradient (Eq.10).

$$J = -\frac{\kappa RT}{C} \cdot \frac{dC}{dx} \quad (10)$$

Wouldn't the investigator find that the diffusion coefficient  $D$  is some decreasing function of the concentration  $C$ ? 'The diffusion coefficient  $D$  varies inversely as the concentration  $C$ ' is an indirect evidence in favor of the Eq. (2). The statement 'Under the steady state flow, the concentration profile is exponentially decreasing' made by Taylor et al. [24] and especially reproduced by Park [41] could be the strongest evidence in favor of the Eq. (2). The concentration profile reported by Gillespie & Williams [25] for water vapor diffusion through stacked cellophane films was also to some extent exponentially decreasing. But as said earlier the method of measuring concentration profile is not so reliable to validate a law convincingly. 'The diffusion coefficient  $D$  is an exponentially increasing function of the concentration with  $\alpha$  as high as 20 (see Eq. 7b or 8)' also dictates that the data could more likely be fitted to the Eq.(2).

## V. CHOICE OF THE FORMULATION OF BASIC DIFFUSION EQUATION

Virtually, the mathematical formulation of the diffusion law solely depends on how the resistant forces are defined. Only the experimental data (acquired without being pre-convinced in any model) could confirm the validity of the Eq. (1) or (2) in a given case. It is a usual practice that if experimental data do not fit to an established law, some explanation becomes eminent to justify the deviation. In diffusion processes, a number of factors (e.g. plasticization of the membrane material, clustering of the diffusing species, interaction between the permeating species and the membrane material) could actually cause deviation of the experimental data from the basic law. But the question 'whether the basic diffusion equation is chosen properly' does not get deserved attention. Before accepting any real deviation from a diffusion equation it should always be remembered how the resistance forces are defined in deriving the mathematical formulation of the equation. Both

the transport coefficients  $D$  and  $\kappa$  are phenomenological. There are no convincing evidences so as to accept for a general case that  $D$  is a constant and  $\kappa$  is directly proportional to concentration, or to accept that  $\kappa$  is a constant and  $D$  is inversely proportional to concentration. For that reason, the choice of the form of the diffusion equation (Eq.1 or Eq.2) would depend on the specific circumstances being studied. Moreover, as we have seen, the Eq. (1) & (2) might not necessarily be the only forms of diffusion equation.

## VI. CONCLUSIONS

- (1) The mathematical formulations of the diffusion law solely depend on how the resistant forces are defined. The description of resistances by Stokes law results in paradoxical prediction of diffusion fluxes in some specific cases.
- (2) Evidences are available validating both the thermodynamic and Fickian formulation of the diffusion equation.
- (3) Ideal form of diffusion equation is absent, and the choice of the form of diffusion equation would depend on the specific circumstances being studied.

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**Acknowledgement:** The authors express their deep gratitude to the Alexander von Humboldt Foundation for awarding Dr. Islam a Georg – Forster Fellowship for doing this work. M. A. Islam is highly indebted to Prof. D. Paul for ensuring pleasant research and scientific atmosphere at the GKSS Research Center Geesthacht GmbH (Germany).