

## Notes on Stefan-Maxwell Equation *versus* Graham's Diffusion Law\*

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**Abstract** Certain prerequisite information on the component fluxes is necessary for solution of the Stefan-Maxwell equation in multicomponent diffusion systems and the Graham's law of diffusion and effusion is often resorted for this purpose. This article addresses solution of the Stefan-Maxwell equation in binary gas systems and explores the necessary conditions for definite solution of concentration profiles and pertinent component fluxes. It is found that there are multiple solutions for component fluxes in contradiction to what specified by the Graham's law of diffusion. The theorem of minimum entropy production in the non-equilibrium thermodynamics is believed instructive in determining the stable steady state solution out of infinite multiple solutions possible under the specified conditions. It is suggested that only when the boundary condition of component concentration is symmetrical in an isothermal binary system, the counter-diffusion becomes equimolar. The Graham's law of diffusion seems not generally valid for the case of isothermal ordinary diffusion.

**Keywords** ordinary diffusion, Stefan-Maxwell equation, Graham's law of diffusion, theorem of minimum entropy production, nonequilibrium thermodynamics

### 1 PREREQUISITE FOR SOLUTION OF STEFAN-MAXWELL EQUATION

It is generally accepted that when gas components are diffusing countercurrently under isothermal and equimolar conditions, the Fick's first law describes well the molar diffusion flux of component A

$$N_A^d = -cD\nabla x_A \quad (1)$$

which is believed to be the mole flux relative to the molar average velocity. Thus, the net flux relative to the fixed physical reference frame should include the part due to bulk convection of gas mixture and for the case of one-dimensional diffusion in a binary system, it reads

$$N_A = -cD_{AB} \frac{\partial x_A}{\partial z} + x_A(N_A + N_B) \quad (2)$$

which is actually the simplified form of the Stefan-Maxwell equation

$$-c\nabla x_A = \sum_{i=1}^n \frac{1}{D_{Ai}} (x_i N_A - x_A N_i) \quad (3)$$

for binary systems<sup>[1]</sup>. Eqs. (2) and (3) play quite important roles in the theory and practice of chemical engineering.

As a set of ordinary differential equations of mole fraction  $x_i$  of component  $i$ , the Stefan-Maxwell equation consists of  $n - 1$  independent first-order differential equations and only boundary values of concentrations at  $z = 0$  are required to integrate the equation

set. However,  $n$  fluxes contained in Eq. (3),  $N_i$ , should be specified beforehand or determined during the solution process. For the one-dimensional example in Fig. 1, if the chemical reaction



proceeds in steady state at the wall surface ( $z = 0$ ), then the ratio of  $N_A$  to  $N_B$  is decided by the stoichiometric constants of the reaction

$$\frac{N_A}{N_B} = -\frac{\nu_A}{\nu_B} \quad (4)$$

If no reaction occurs, the Graham's law of diffusion and effusion is often cited to provide such information<sup>[2-5]</sup>, namely

$$\left| \frac{N_A}{N_B} \right| = \sqrt{\frac{M_B}{M_A}} \quad (5)$$

or in a more generalized form

$$\sum_{i=1}^N N_i \sqrt{M_i} = 0 \quad (6)$$

How to obtain enough knowledge on the unknown fluxes when there is no chemical reaction is to be addressed in this paper. In the analysis to follow, the necessary conditions to get a definite solution of fluxes and concentration profiles of binary gaseous systems are explored and the validity and applicability of Graham's diffusion law is discussed.

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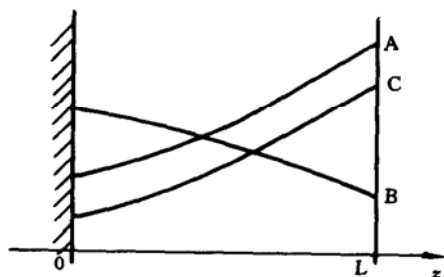


Figure 1 Sketch of concentration profiles in a ternary gas system with C being stagnant component

## 2 APPLICABILITY OF GRAHAM'S DIFFUSION LAW

There was a continuous discussion on the applicability of Graham's laws in the literature of chemistry and chemical engineering. In 1833, Graham proposed his diffusion law based on his experimental investigation and claimed that when two gases diffused countercurrently under the isothermal and isobaric conditions, the ratio of their diffusion fluxes was in reverse proportion to the square root of the ratio of their molecular weights, namely Eq. (5)<sup>[6]</sup>. In another paper published in 1846, he proposed his effusion law that the flux of effusion of gas through micropores was inversely proportional to the square root of its molecular weight<sup>[7]</sup>. Two laws bear the same form despite of different underlying mechanisms and the range of application. In view of many errors in presenting and interpreting Graham's laws existing in introductory textbooks, Journal of Chemical Education published a series of discussion papers<sup>[8-10]</sup>. For the effusion law, the opinion is rather convergent: the Graham's effusion law is valid for the case that gas molecules under isothermal and isobaric conditions obey the Maxwell distribution of linear velocity and diffuse through very fine pores where flux due to viscous convection is negligible. In this case, the free path of gas molecule is much larger than the pore diameter and the flux is not influenced by the collision between molecules. Thus, the rate of effusion is decided by the molecular velocity and is consistent with the Knudsen diffusion mechanism. However, the misunderstanding and misuse of Graham's diffusion law, which was supposed to be applied in the range of ordinary diffusion, is not well clarified to date<sup>[11]</sup>.

Mason *et al.*<sup>[8,9]</sup> claimed that Graham's diffusion law was valid at all pressures, ranging from free molecules region at low pressures to normal diffusion region where collision between molecules dominated the rate process, and up to the hydrodynamic (viscous flow) region. They gave a theoretical explanation using an approach similar to the reasoning by Hoogschagen<sup>[12]</sup>, and repeated the diffusion-

tube experiments to confirm the validity of Graham's diffusion law. On the other hand, Kirk noted that Graham's law was not applicable in many cases and pointed out that when two gases interdiffused under uniform pressure in a binary system, their fluxes were equal but in contrary directions<sup>[10]</sup>. A well-known experiment was conducted to demonstrate the Graham's diffusion law: pure gaseous ammonia and hydrogen chloride diffuse into a glass tube filled with air separately from both ends, and a smoke ring was formed in the middle location in the tube. The ratio of relative diffusion distance for two gases was alleged to be reversely proportional to the square root of the ratio of their molecular weights. Hawkes claimed that the experimentally obtained ratio of relative rates of diffusion of HCl and NH<sub>3</sub> was  $D_{\text{NH}_3\text{-air}}/D_{\text{HCl-air}}$ , instead of  $\sqrt{M_{\text{HCl}}/M_{\text{NH}_3}}$  as suggested by the Graham's law<sup>[11]</sup>. He even advised to exclude Graham's laws from the introductory chemistry textbooks and discuss them in the course of physical chemistry later in the curriculum.

It is considered necessary to further clarify misunderstanding and misuse of Graham's diffusion law existing in the literature of chemical engineering. In this paper, the validity of Graham's diffusion law is addressed while effort is made to solve the Stefan-Maxwell equation in binary systems of ideal gas mixture under isothermal and isobaric conditions to get concentration profiles and transport flux of components. The theorem of minimum entropy production in non-equilibrium thermodynamics is resorted in the due course to single out the stable steady state of diffusion from infinite number of possible solutions.

## 3 STEFAN-MAXWELL EQUATION FOR BINARY SYSTEMS

Many research work starts from the well-known Stefan-Maxwell equation, which is generally accepted as the fundamental equation for dealing with multiple component diffusion in porous media<sup>[13,14]</sup>. For example, Krishna propose a unified approach to model the bulk, Knudsen and surface diffusion in solid adsorbent<sup>[15]</sup>; Frank *et al.* applied the Stefan-Maxwell equation to the simultaneous mass and heat transfer with chemical reaction in a liquid phase<sup>[16]</sup>; Do and Do analyzed multicomponent transient diffusion in a capillary and adsorption of hydrocarbons in activated carbon particles<sup>[17]</sup>. Analysis of binary gas systems is the focus in this paper.

In a binary system, the Stefan-Maxwell equation is simplified to Eq. (2) for the condition of  $x_A + x_B = 1$ . Eq. (2) is a differential equation with unknown fluxes

$N_A$  and  $N_B$ . For normal diffusion in such a binary system with nonzero net flux ( $N_A + N_B \neq 0$ ), integration of Eq. (2) utilizing the boundary conditions  $x_A = x_{A0}$  and  $x_B = x_{B0}$  at  $z = 0$  results in

$$\begin{cases} \frac{N_A - x_A(N_A + N_B)}{N_A - x_{A0}(N_A + N_B)} = \exp\left(\frac{N_A + N_B}{cD_{AB}}z\right) \\ \frac{N_B - x_B(N_A + N_B)}{N_B - x_{B0}(N_A + N_B)} = \exp\left(\frac{N_A + N_B}{cD_{AB}}z\right) \end{cases} \quad (7)$$

Even for interdiffusion of two pure gases in the domain ( $x_{A0} = 0$  and  $x_{BL} = 0$ ), unique solution of  $x_A$  and  $x_B$  is not available for judging if the Graham's law of diffusion is consistent with the Stefan-Maxwell equation.

In fact, the above solution of integral concentration profile presents infinite multiple solutions. Substituting the boundary conditions  $x_A = x_{AL}$  and  $x_B = x_{BL}$  at  $z = L$  into the above equations leads to

$$\frac{N_A - x_{AL}(N_A + N_B)}{N_A - x_{A0}(N_A + N_B)} = \frac{N_B - x_{BL}(N_A + N_B)}{N_B - x_{B0}(N_A + N_B)} = \exp\left(\frac{N_A + N_B}{cD_{AB}}L\right) \quad (8)$$

Since  $x_A + x_B \equiv 1$ , the first equal sign holds identically. Non-dimensionalize  $N_A$  and  $N_B$  to  $J_A$  and  $J_B$  using  $cD_{AB}/L$ , we obtain

$$\frac{J_A - x_{AL}(J_A + J_B)}{J_A - x_{A0}(J_A + J_B)} = \exp(J_A + J_B) \quad (9)$$

with  $J_i = N_iL/cD_{AB}$  and  $\xi = z/L$  being the dimensionless diffusion distance. The values of  $J_A$  and  $J_B$  corresponding different total flux  $J_A + J_B$  are listed in Table 1, each set of which satisfy the Stefan-Maxwell equation but correspond to different concentration profiles (Fig. 2). The concentration profiles are expressed by

$$\begin{cases} x_A = \frac{J_A - [J_A - x_{A0}(J_A + J_B)] \exp[(J_A + J_B)\xi]}{J_A + J_B} \\ x_B = \frac{J_B - [J_B - x_{B0}(J_A + J_B)] \exp[(J_A + J_B)\xi]}{J_A + J_B} \end{cases} \quad (10)$$

Table 1 Multiple solution of mole fluxes in a typical binary system

$J_A + J_B$	Case 1		Case 2	
	$J_A$	$J_B$	$J_A$	$J_B$
-1.0	-1.5603	0.5603	-1.4180	0.4180
0	-1.0000	1.0000	-0.8900	0.8900
0.5	-0.7503	1.2503	-0.6810	1.1810
1.0	-0.5603	1.5603	-0.5080	1.5080

Case 1:  $x_{A0} = x_{BL} = 0.01$ ,  $x_{B0} = x_{AL} = 0.99$ ;

Case 2:  $x_{A0} = 0.01$ ,  $x_{B0} = 0.99$ ,  $x_{AL} = 0.9$ ,  $x_{BL} = 0.1$

with  $x_A + x_B = 1$  being satisfied everywhere in the diffusion domain. Therefore, the Stefan-Maxwell equation is indefinitely determined and other physicochemical conditions are required to get a unique solution. Deduction of equimolar diffusion from the isobaric condition to justify the Fick's first law of diffusion is too intuitive, since the Graham diffusion experiments demonstrated that under the same isobaric conditions  $N_A \neq -N_B$ <sup>[8]</sup>.

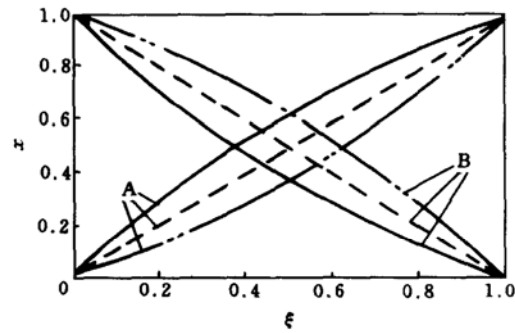


Figure 2 Multiple concentration profiles in a binary system (Case 1)  
 —  $J_A + J_B = 1.0$ ; - - -  $-J_A + J_B = 0$ ;  
 - · -  $-J_A + J_B = -1.0$

#### 4 ENTROPY PRODUCTION IN A BINARY SYSTEM

Many reports accepted the notion of equimolar interdiffusion in a binary system of gas, but the reasoning is not theoretically strict (for example Ref. [10]). Table 1 and Fig. 2 indicate that multiple solutions exist for such a case. In the following, the theorem of minimum entropy production introduced by Prigogine<sup>[18]</sup> is used to analyze the isothermal interdiffusion in a binary system. This approach was tentatively used in examining the Danckwerts exit boundary condition for the axial dispersion model for a closed reactor<sup>[19]</sup> and the thermodynamic necessity of some velocity profiles in hydrodynamics<sup>[20]</sup>. Here, the interdiffusion is considered as a linear irreversible process not far from the equilibrium and the rate of entropy production in the binary system is expressed by<sup>[18]</sup>

$$\sigma = \sum J'_i \left[ -\nabla \frac{\mu_i}{T} \right], \quad i = A, B \quad (11)$$

where  $J'_i$  is the diffusion flux relative to the average linear velocity of the system<sup>[13]</sup>,  $J'_i = J_i - x_i(J_A + J_B)$ . If the gas system is ideal,

$$\mu_i = \mu^0 + RT \ln x_i$$

Integration of Eq. (11) over the system volume leads to the total entropy production

$$P = \int \sigma dV = -R \int_0^1 \left[ J'_A \frac{1}{x_A} \frac{dx_A}{d\xi} + J'_B \frac{1}{x_B} \frac{dx_B}{d\xi} \right] d\xi \quad (12)$$

According to the theorem of minimum entropy production<sup>[18]</sup>, the steady state constrained by the specified boundary conditions and with the minimum rate of entropy production is the most stable state. Fig. 3 presents the variation of relative value of  $P$  under the condition of  $x_{AL} = x_{B0}$  with the net total flux  $J_A + J_B$ , and it is evident that the minimum of  $P$  corresponds to the condition of  $J_A + J_B = 0$ , namely equimolar countercurrent diffusion independent of molecular weights. This result is obviously in contradiction to the Graham's diffusion law. In this occasion, Eq. (2) is simplified to

$$N_A = -cD_{AB} \frac{dx_A}{dz} = -D_{AB} \frac{dc_A}{dz} \quad (13)$$

in agreement with the Fick's first law, presenting linear concentration profiles with mirror symmetry as shown in Fig. 2.

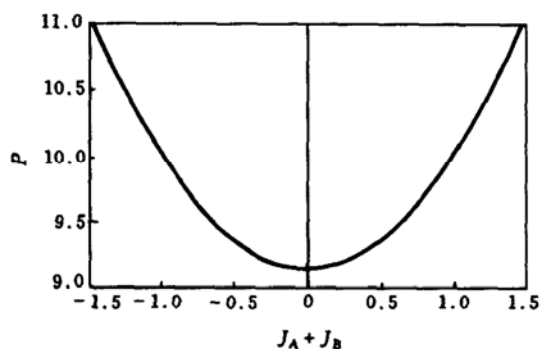


Figure 3 Variation of entropy production with the net flux  $J_A + J_B$  in a binary system with mirror symmetry in the boundary conditions

If  $x_{AL} \neq x_{B0}$ , the concentration profile chart loses its symmetry since there is no more symmetry of the boundary conditions on  $x_A$  and  $x_B$  (Fig. 4). In this case the minimum of  $P$  is not located at the point with  $J_A + J_B = 0$  as shown in Fig. 5.

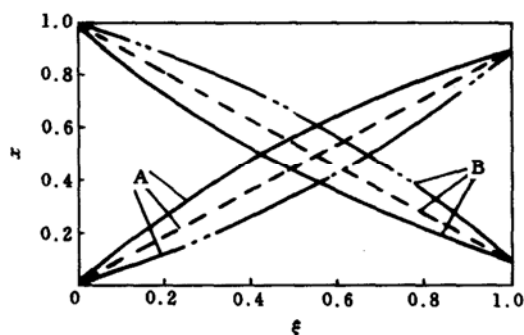


Figure 4 Concentration profiles in the binary system with  $x_{AL} \neq x_{B0}$  (Case 2)  
—  $J_A + J_B = 1.0$ ; - - -  $J_A + J_B = 0$ ; - · -  $J_A + J_B = -1.0$

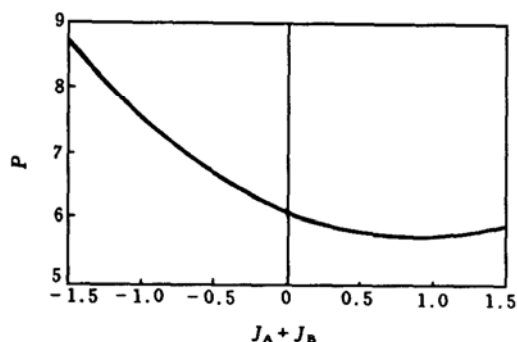


Figure 5 Variation of  $P$  with  $J_A + J_B$  in a binary system with  $x_{AL} \neq x_{B0}$

## 5 DEGREE OF FREEDOM OF A BINARY DIFFUSION SYSTEM

If analyzing in view of the degree of freedom of a binary system, to determine  $J_A$  and  $J_B$  requires two more conditions, and the specified  $x_{AL}$  at  $\xi = 1$  is one of them. Due to lack of the second condition, the multiplicity of solution occurs. Non-equilibrium thermodynamics may provide the necessary condition for singling out the unique solution which is most probable in the natural situation as indicated by Fig. 3. If there is external constraint on  $J_i$ , the system has no degree of freedom and diffusion fluxes may be determined from solving Eq. (2) or (9). For example, when the Stefan tube is used for measuring the diffusion coefficient of a vaporizing component through the inert air, the flux of air  $J_B$  is fixed at zero, and the partial pressure of the diffusing component at the open end is also set by other experimental conditions. Thus, the flux of the diffusing component can be determined from Eq. (9), leaving no room for the theorem of minimum entropy production. Another case of determinacy is the chemical reaction, which decided the ratio of  $J_A/J_B$  by stoichiometry. Only when a system has some degree of freedom, the system may evolve according to the direction dictated by the minimum entropy production into the most stable steady state of interdiffusion.

In a rigorous sense, there is actually the convection resulted from  $J_A + J_B \neq 0$ , which creates pressure difference in the system due to viscosity of gas. However, the viscosity of gas is generally small and the cross sectional area for diffusion may be large as compared with the distance for diffusion, making the pressure difference often negligibly small (for example, external boundary layer around a solid particle). Therefore, the diffusion with  $J_A + J_B \neq 0$  is acceptable approximation and it is legal to estimate entropy production by Eq. (12) without considering the contribution of viscous convection. One point is worthy of mentioning: the concentration boundary conditions

are assumed ideally maintained no matter how large the component fluxes are. When the boundary conditions are incorporated with finite mass transfer coefficients, solution of Stefan-Maxwell equation and evaluation of entropy production must have this factor accounted for.

Although the theorem of minimum entropy production is applicable to binary systems with possible multiple solutions, the location for the minimum does not generally correspond to  $J_A + J_B = 0$  or other special case, and the physical meaning of this minimum is to be clarified. Nevertheless, the component flux is certainly not an explicit functions of the square roots of molecular weight of diffusing species, calling for general discretion in using Graham's diffusion law.

## 6 CONCLUDING REMARKS

In a binary diffusing system, there are multiple solutions for countercurrent diffusion for constituting components, which in general correspond not to equimolar counterdiffusion. The theorem of minimum entropy production in non-equilibrium thermodynamics may be resorted to decide the most stable steady state solution. When there is symmetry for the boundary concentration conditions, the stable solution is equimolar countercurrent diffusion; loss of symmetry leads to diffusion with nonzero net total flux. The Graham's diffusion law seems not generally effective in determining the component fluxes in the region of normal diffusion.

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## NOMENCLATURE

$c$	concentration, mol·m <sup>-3</sup>
$D_{ij}$	binary diffusion coefficient, m <sup>2</sup> ·s <sup>-1</sup>
$J$	non-dimensional diffusion flux
$J'$	non-dimensional diffusion flux relative to average velocity
$L$	length of diffusion domain, m
$M$	molecular weight, g·mol <sup>-1</sup>
$N$	flux, mol·m <sup>-2</sup> ·s <sup>-1</sup>
$n$	number of components
$P$	total rate of entropy production, J·K <sup>-1</sup> ·s <sup>-1</sup>
$R$	gas constant, 8.314 J·mol <sup>-1</sup> ·K <sup>-1</sup>
$T$	temperature, K
$V$	volume of system, m <sup>3</sup>
$x$	mole fraction
$z$	coordinate, m
$\mu$	chemical potential, J·mol <sup>-1</sup> ·K <sup>-1</sup>
$\mu^0$	standard chemical potential, J·mol <sup>-1</sup> ·K <sup>-1</sup>
$\nu$	stoichiometric coefficient
$\xi$	non-dimensional coordinate ( $z/L$ )

$\sigma$  local rate of entropy production, J·K<sup>-1</sup>·m<sup>-3</sup>·s<sup>-1</sup>

## Superscript

d diffusive

## Subscripts

A,B,i component

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