THE ROLE OF DIFFUSION CREEP IN ELEMENTARY MASS TRANSFER ANALYSIS

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ABSTRACT

The analysis of equimolar counterdiffusion, diffusion with one component stationary, and equimass/isobaric counterdiffusion in a binary gas mixture is introduced using the stagnant film model. To obtain corresponding results for continuum diffusion in a tube, the phenomenon of diffusion creep is introduced and rigorous analytical results obtained where possible. Finally, usual textbook presentations of these topics are reviewed and critiqued.

Biographical Sketch:

Anthony Mills has been on faculty at UCLA since 1966. He received his engineering education at the University of Cape Town, the Imperial College of Science and Technology, and the University of California, Berkeley. In the 1980's he spent three years at the University of Auckland. His research has covered a broad range of heat and mass transfer topics, and he is the author of textbooks on heat transfer and mass transfer.

1. INTRODUCTION

When teaching transport phenomena, students are first exposed to simple and well posed problems of some engineering relevance. Poiseuille flow in fluid mechanics is an example, as are one-dimensional conduction problems in heat transfer. Textbooks usually do an excellent job presenting such analyses. In the case of mass transfer, the situation is rather different. Meaningful simple diffusion problems are not straightforward and textbooks often give incorrect analyses that can only serve to hinder the learning process. Three diffusion problems of significance are:

1. Equimolar counterdiffusion
2. Diffusion with one component stationary
3. Equimass/isobaric counterdiffusion

The first two are examined in most elementary texts. The third is only indirectly mentioned in perhaps two or three texts, but, as will become evident, should receive more attention. Nearly all texts consider the diffusion to take place in a capillary tube, and then perhaps extend consideration to a porous solid. In this paper we will first present correct analyses of appropriate model problems and then conclude with an examination of what is found in textbooks. The focus will be continuum diffusion in isothermal, ideal, binary gas mixtures. Texts usually deal with diffusive mass transfer before continuing with convective mass transfer. For convective mass transfer, chemical engineering texts introduce the equivalent stagnant film model before advancing to rigorous solutions of the governing conservation equations. Mechanical and aerospace engineers have preferred to use the Couette flow model which yields results identical to those of the film model, e.g. [1]. We will first examine diffusion problems in the context of the stagnant film model because the analyses are relatively simple and the results very useful.

2. *EQUIVALENT STAGNANT FILM MODEL*

In using the stagnant film model, the true convective transfer process is imagined to be equivalent to one-dimensional diffusion across a stagnant fluid film of thickness δ_f.

2.1 Equimolar counterdiffusion

The physical problem could be distillation involving two species whose molar latent heats are essentially equal, that is, obey Trouton's rule, or it could be a chemical reaction such as oxidation of carbon to carbon dioxide by oxygen where one mole of CO_2 is produced for each mole of O_2 consumed. The solution is:

$$N_A = J_A = \frac{c\mathcal{D}_{AB}}{\delta_f}(x_{A,s} - x_{A,e}) = -N_B \tag{1}$$

$$\frac{x_A - x_{A,s}}{x_{A,e} - x_{A,s}} = \frac{z}{\delta_f} \tag{2}$$

2.2 Diffusion with one component stationary

The physical problem could be evaporation of a liquid into a gas flow when the gas is negligibly soluble in the liquid (or the liquid is saturated with the gas). The solution on a molar basis to take advantage of the nearly constant molar density is:

$$N_A = \frac{c D_{AB}}{\delta_f} \ell n \frac{1 - x_{A,e}}{1 - x_{A,s}}; N_B = 0 \tag{3}$$

$$\frac{1 - x_A}{1 - x_{A,s}} = \left(\frac{1 - x_{A,e}}{1 - x_{A,s}}\right)^{z/\delta_f} \tag{4}$$

2.3 Equimass Counterdiffusion

The physical problem could be a catalytic reaction $A \rightarrow B$. If both A and B are in small concentrations in a carrier gas C, the mixture density may be assumed constant, and an effective binary diffusion coefficient $\mathcal{D}_{Am}$ used to give:

$$n_A = j_A = \frac{\rho \mathcal{D}_{Am}}{\delta_f}\left(\omega_{A,s} - \omega_{A,e}\right) = -n_B \tag{5}$$

$$\frac{\omega_A - \omega_{A,s}}{\omega_{A,e} - \omega_{A,s}} = \frac{z}{\delta_f} \tag{6}$$

If we consider a true binary mixture and allow for a variable mass density ρ, the result is more complicated.

$$n_A = j_A = \frac{P \mathcal{D}_{AB}}{\mathcal{R}T \delta_f} \frac{M_A M_B}{M_B - M_A} \ell n \frac{M_A}{M_B} = -n_B \tag{7}$$

$$\omega_A = \frac{M_B \left(M_A / M_B\right)^{z/\delta_f} - M_A}{M_B - M_A} \tag{8}$$

Use of these results requires specification of the equivalent stagnant film thickness δ_f, which is obtained by considering the limit of zero transfer rate to relate δ_f to the mass transfer coefficient as:

$$\delta_f = \frac{\mathcal{D}_{AB}}{k}$$

where k is obtained from an appropriate Sherwood number correlation. Note that all three cases involve essentially isobaric diffusion in accord with boundary layer theory.

Using a stagnant film (or equivalently Couette flow) model to introduce the student to these fundamental diffusion situations has advantages and disadvantages. One disadvantage is that the student has already had a fluid mechanics course in which boundary layers and velocity profiles have been seen: then the concept of an equivalent stagnant film is difficult to accept since it violates physical realty rather seriously. On the other hand, an advantage is that the analyses are truly one-dimensional because wall effects, present when diffusion takes place in a tube or porous solid, are absent.

But nearly all texts introduce the elementary diffusion problems in the context of diffusion in a tube or porous solid. Thus, we will present correct analyses of appropriate model problems for diffusion in a capillary tube, and with these results as a basis, subsequently examine what is found in textbooks. Correct analysis requires the introduction of the phenomenon of diffusion creep on the walls of the capillary tube. This phenomenon is not discussed in relevant engineering texts. One might speculate that this omission was not by choice because diffusion creep was considered an advanced topic inappropriate to the beginning student: rather, the omission was because the authors were unaware of the phenomenon, or did not appreciate the role it plays.

3. DIFFUSION CREEP

The non-slip boundary condition of viscous fluid flow does not apply to a gas mixture when there is a concentration gradient along the boundary surface: there is a "diffusion creep" velocity. This phenomenon is analogous to the more well known "thermal creep" on a non-isothermal surface that was first studied by Maxwell [2] in 1877. Both phenomena are perhaps peculiar in that the kinetic theory of gases is used to describe molecule surface interactions, and yet they can play an important role when the appropriately defined Knudsen number tends to zero, and continuum analysis is indicated. Diffusion creep is also called "diffusion slip" or "concentration creep" in the literature.

A formula for the diffusion creep velocity was first derived by Kramers and Kistemaker [3] in 1944. They used a simple flow model of diffusion to examine the momentum balance at the wall, and found that the gas adjacent to

wall had to be in motion. For a binary mixture, the mass average creep velocity is

found to be [4]

$$v_w = \frac{\dfrac{1}{M_A^{1/2}} - \dfrac{1}{M_B^{1/2}}}{\dfrac{\omega_A}{M_A^{1/2}} + \dfrac{\omega_B}{M_B^{1/2}}} \mathcal{D}_{AB} \frac{d\omega_A}{dz} \qquad (10)$$

Notice that v_w is in the direction of diffusion of the heavier species. The

molar equivalent of Eq. (10) is:

$$v_w^* = \frac{M_A^{1/2} - M_B^{1/2}}{x_A M_A^{1/2} + x_B M_B^{1/2}} \mathcal{D}_{AB} \frac{dx_A}{dz} \qquad (11)$$

and v_w^* is in the opposite direction to the mass average value: it is in the direction

of diffusion of the lighter species.

More recently, there have been many more rigorous kinetic theory

analyses of diffusion creep: a review is given by Mills [4]. The simple Kramers

and Kistemaker result proves to be surprisingly accurate, particularly when the

two molecular weights are substantially different.

4. ANALYSES INCLUDING DIFFUSION CREEP

4a.   Equimolar Counterdiffusion

Most texts introduce equimolar counterdiffusion in gases by considering a

virtual experiment where two large, well stirred chambers are connected by a

capillary tube. Initially one chamber contains pure species A, and the other pure

species B. At time $t = 0$, a stopcock is opened and it is postulated that, following

an initial transient, a quasi-steady state is attained with equimolar

counterdiffusion, $N_A = -N_B$. The molar average velocity v_b^* is then zero, but the

mass average velocity v_b is not:

$$\rho v_b = n_A + n_B = \frac{N_A}{M_A} + \frac{N_B}{M_B} \neq 0 \qquad (12)$$

where N_A, N_B and v_b are averages over the tube cross-section. Thus we expect a pressure gradient along the capillary tube as was demonstrated in the experiments of Kramers and Kistemaker [3].

We seek a one-dimensional model, so plug flow at the mass average velocity v_b can be assumed; for laminar flow in a tube of radius R :

$$v_b = v_w + \frac{R^2}{8\mu}\left(-\frac{dP}{dz}\right) \tag{13}$$

where v_w is the diffusion creep mass average velocity. The corresponding molar based result is [4]:

$$v_b^* = v_w^* + \frac{R^2}{8\mu}\left(-\frac{dP}{dz}\right) = 0 \tag{14}$$

$$\frac{dP}{dz} = \frac{8\mu}{R^2}v_w^* \tag{15}$$

Since J_A^* and $c\mathcal{D}_{AB}$ are constant, Fick's Law with $x_{A,0} = 1$, $x_{A,L} = 0$ gives:

$$\frac{dx_A}{dz} = -\frac{1}{L} \tag{16}$$

Substituting Eqs. (11) and (16) in Eq. (15) and integrating with μ assumed constant gives:

$$\Delta P = \frac{4\mu\mathcal{D}_{AB}}{R^2}\ell n\left(\frac{M_A}{M_B}\right) \tag{17}$$

which is one-half the value for Poiseuille flow ($v_w = 0$). Numerical integration of Eq. (15) allowing for variable viscosity is reported by Kramers and Kistemaker [3]; Mills [4] further refined the analysis using the creep velocity of Ivchenko et al [5]. There remains a 20% discrepancy with the experiments of [3], but an examination of the data suggests a true quasi-steady state was not attained. Other difficulties in the experiment were also noted [3]. Further experimental data would be desirable.

4b.   Isobaric Counterdiffusion

In 1833, Graham [6] reported experiments on continuum isobaric counterdiffusion of various gas mixtures through a porous plug, and concluded that the molar fluxes were inversely proportional to the square root of molecular weight.

$$\frac{N_A}{N_B} = -\left(\frac{M_B}{M_A}\right)^{1/2} \qquad (18)$$

Graham's result was confirmed in more recent work, notably by Hoogschagen in 1955 [7] and others subsequently [8,9,10], provided the molecular weights were sufficiently different. Experiments have in fact shown that Eq. (18) is valid over the whole Knudsen number range from free molecule flow to continuum diffusion. Equation (18) follows directly from Knudsen's analysis for free molecule flow, but our concern here is the continuum limit. Notice that Eq. (18) does not indicate equimass counterdiffusion for which $N_A/N_B = -M_B/M_A$, as obtained in the stagnant film analysis of 2.3, where the diffusion was both equimass and isobaric.

Consider isobaric diffusion along a tube in the continuum limit. There is a diffusion creep velocity v_w on the tube wall, and we assume plug flow at velocity v_w. The flow is strictly not one dimensional because v_w is not constant along the tube; however, the Reynolds number is very small (<<1) so that the velocity profile is very nearly uniform. The absolute flux of species A is:

$$n_A = \omega_A \rho v_w - \rho \mathcal{D}_{AB} \frac{d\omega_A}{dz} \qquad (19)$$

Writing Eq. (19) for species B with $d\omega_B/dz = -d\omega_A/dz$, dividing into Eq. (19), and using Eq. (10) for v_w gives:

$$\frac{n_A}{n_B} = \frac{\omega_A f(\omega_A) - 1}{\omega_B f(\omega_A) + 1} \tag{20}$$

where

$$f(\omega_A) = \left(\frac{1}{M_A^{1/2}} - \frac{1}{M_B^{1/2}} \right) \Big/ \left(\frac{\omega_A}{M_A^{1/2}} + \frac{\omega_B}{M_B^{1/2}} \right)$$

Substituting $\omega_B = 1 - \omega_A$ gives:

$$\frac{n_A}{n_B} = -\left(\frac{M_A}{M_B} \right)^{1/2} \tag{21}$$

$$\frac{N_A}{N_B} = -\left(\frac{M_B}{M_A} \right)^{1/2} \tag{22}$$

which is Graham's Law. Notice that it is the diffusion creep velocity given by

Eq. (10) that essentially yields Graham's Law. With Eq. (22) established we

continue on a molar basis to take advantage of the constant total molar

concentration. The absolute molar flux of species A is:

$$N_A = x_A (N_A + N_B) - c\mathcal{D}_{AB} \frac{dx_A}{dz} \tag{23}$$

Hence

$$N_A (1 - \alpha x_A) = -c\mathcal{D}_{AB} \frac{dx_A}{dz} \tag{24}$$

where $\alpha = 1 + (N_B/N_A)$. Separating variables and integrating with $x_A = x_{A,0}$ at

$z = 0$ and $x = x_{A,L}$ at $z = L$ gives:

$$N_A = \frac{c\mathcal{D}_{AB}}{\alpha L} \ell n \frac{1 - \alpha x_{A,L}}{1 - \alpha x_{A,0}} \tag{25}$$

where $\alpha = 1 - (M_A/M_B)^{1/2}$ from Eq. (22). As for equimolar counterdiffusion, a

more accurate result can be obtained by using an improved diffusion creep

velocity from kinetic theory.

4c.   <u>Diffusion with One Component Stationary</u>

The usual analysis of diffusion with one component stationary is done in the context of the Stefan tube to measure diffusion coefficients eg. [11], but also in the context of a heatpipe eg. [12]. These analyses are one-dimensional and thus assume plug flow. Some years ago there was a concern about the impact of violating the nonslip boundary coalition for viscous flow. McDonald et al. [13] in 1971 obtained an exact numerical solution for a cylindrical tube heatpipe and showed the error incurred by using a plug flow model was less than 5%, even at very high mass transfer rates. In 1991 Whitaker [14] pointed out that the numerical studies ignored the presence of diffusion creep, but did not take the matter further.

To examine the possible effect of diffusion creep, consider the usual one-dimensional analysis with species B stationary. The bulk velocity is:

$$v_b = -\frac{1}{1-\omega_A}\mathcal{D}_{AB}\frac{d\omega_A}{dz} \tag{26}$$

The diffusion creep velocity v_w is given by Eq. (10) and thus:

$$\frac{v_w}{v_b} = \frac{(1-\omega_A)(1-\beta)}{\beta+\omega_A(1-\beta)} \tag{27}$$

where $\beta = (M_A/M_B)^{1/2}$. For the water vapor-air system, Eq. (27) shows that v_w is at most 25% of v_b, and is opposite to v_b. Based on the exact solutions with $v_w = 0$, a significant effect on N_A is not expected. In contrast to the previous two cases, diffusion creep cannot be included in a one-dimensional analysis. The flow has an essential two-dimensional character. For $M_A < M_B$ there is flow towards

$z = 0$ on the walls, and away from z= 0 in the core, with $|v_w| < v_b$. Also radial

concentration variations are required to satisfy species conservation.

5. *TEXTBOOK PRESENTATIONS*

5a. Equimolar Counterdiffusion

Nearly all texts eg. [15, 16, 17, 18] specify a uniform pressure when

analyzing equimolar counterdiffusion in a tube connecting two chambers. In 4a

we saw that the pressures in each chamber are constant but unequal since a

pressure differential is required to overcome viscous forces in the tube: the

diffusion is not isobaric as claimed. Not only does such a claim confuse the

student, but also the result has been to ignore the proper analysis of

equimass/isobaric diffusion as given in 2c and 4b. Perhaps it would be simpler to

replace the closed system of two chambers with an open system as was

considered for isobaric diffusion in 4b. Then the pressure differential can be

viewed as a controllable parameter: isobaric diffusion is a special case as is

equimolar diffusion, the latter corresponding to a unique value of pressure

differential that depends on the dimensions of the tube and the particular gaseous

species.

5b. Isobaric Diffusion

Geankoplis [15] first considers free molecule flow (Knudsen diffusion,

$Kn = \ell / R \gg 1$) to write

$$N_A = \frac{\mathcal{D}_{KA} P}{\mathcal{R} T L} \left(x_{A,0} - x_{A,L} \right) \tag{28}$$

where D_{KA} is the Knudsen diffusion coefficient. For temperature in kelvins and

tube radius R in meters, $D_{KA} = 97.0 R \left(T / M_A \right)^{1/2}$. Thus N_A is proportional to

$M_A^{-1/2}$ in the Knudsen regime, in accord with Graham's Law. Geankoplis goes on to consider continuum diffusion for $Kn \rightarrow 0$, and obtains Eq. (25) of 4b:

$$N_A = \frac{\mathcal{D}_{AB}P}{\alpha \mathcal{R}TL} \ell n \frac{1-\alpha x_{A,L}}{1-\alpha x_{A,0}}; \alpha = 1+\frac{N_B}{N_A} \tag{25}$$

However, at this point of the analysis, it is not mentioned how α is to be evaluated in the continuum regime. Eq. (25) is not a solution of the diffusion problem without a specification of the flux ratio α. Only subsequently in Section 7.6E does Geankoplis address the flux ratio issue. He states that Graham's Law is valid for the Knudsen, transition and continuum regimes and thus, $\alpha = 1-\left(M_A/M_B\right)^{1/2}$. He gives his own paper with Remick [10] as a reference for this result. This paper presents as excellent set of experimental data covering a wide Knudsen number range, but has an unsatisfactory treatment of the continuum limit theory.

Bird, Stewart and Lightfoot [11] restrict their discussion to two limiting situations, namely free molecule flow, and continuum flow of gases for which the "generalized Maxwell-Stefan equations for multi-component diffusion can be used." Like Geankoplis, they first introduce free molecule flow to show N_A proportional to $M_A^{-1/2}$, and state that this is Graham's Law. They subsequently state that the ratio $N_A/N_B = -\left(M_A/M_B\right)^{1/2}$ was first observed by Graham in 1833 and rediscovered by Hoogschagen in 1953, without mentioning that these two experiments were in the continuum regime. Finally, they state that, "Though derived here for Knudsen flow, this relation is valid for isobaric diffusion well outside the Knudsen region." The reader may well conclude that Graham's Law is

not expected to be valid in the continuum limit. If their advice is followed and the

Maxwell-Stefan equations used for the continuum limit, the incorrect result

$N_A/N_B = -(M_B/N_A)$ would be obtained, unless the diffusion creep wall

boundary condition were introduced. But the phenomenon of diffusion creep is

not mentioned in the text. Indeed, both thermal creep and diffusion creep are

ignored in their Example 24.2-1, to yield an erroneous result.

Cussler [19] describes Graham's 1833 experiment and notes that the

diffusion was isobaric. But he does not discuss Graham's Law and the role played

by diffusion creep.

The text by Mills [1] also does not mention diffusion creep. One of the

analyses presented involves equimass counterdiffusion in a tube where at $z = 0$

there is a catalytic reaction, and the reactants are held at a specified composition

by a gas flow over the open end at $z = L$. The solution assumes a mass average

velocity of zero and constant density to give linear mass fraction profiles. The

diffusion creep velocity is not negligible in such situations and an exact solution

must consider a two-dimensional flow. When the diffusion creep velocity is

directed towards the catalyst, there must be a core flow away from the catalyst

and vice-versa. The results of the analysis are subsequently applied in the context

of a stagnant film analysis with tube length L replaced by δ_f, for which the wall

effect is irrelevant. But the author admits that this feature was fortuitous, since he

was ignorant of diffusion creep at the time!

6. CONCLUDING COMMENTS

It should be clear from Section 4 that correct solutions of continuum mass

transfer problems can be obtained by solving classical conservation equations

with the diffusion creep wall boundary condition applied to the momentum equation. Recently, the validity of the "classical approach" has been questioned by Kerkhof and coworkers, eg. [20], but these workers failed to recognize the role played by diffusion creep. The classical approach is alive and well!

7. NOMENCLATURE

c	total molar concentration	(kmol/m^3)
$\mathcal{D}$	binary diffusion coefficient	(m^2/s)
$\mathcal{D}_K$	Knudsen diffusion coeffiecient	(m^2/s)
J	diffusive molar flux	(kmol/m^2)
j	diffusive mass flux	(kg/ m^{2}s)
k	mass transfer coefficient	(m/s)
L	tube length	(m)
ℓ	mean free path	(m)
M	molecular weight	(kg/kmol)
N	absolute molar flux,	(kmol/ m^{2}s)
n	absolute mass flux	(kg/ m^{2}s)
P	pressure	(Pa)
$\mathcal{R}$	gas constant	(J/mol K)
R	tube radius	(m)
T	temperature	(K)
V	mass average velocity	(m/s)
V^*	molar average velocity	(m/s)
x	mole fraction	
z	Coordinate	(m)

GREEK

δ_f	equivalent stagnant film thickness	(m)
μ	dynamic viscosity	(kg/ms)
ω	mass fraction	
ρ	mass density	(kg/m^3)

SUBSCRIPTS

A, B	species in a binary mixture
b	bulk
0	at z = 0
L	at z = L
e	free stream
m	effective binary
s	surface
w	creep

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