that water films forming on the oxygen electrode under conditions of limited evaporation lead to poor performance at low temperature. Temperature effects are more pronounced near the maximum power point than at low or very high current densities. Life tests of cell performance at 85°C. with platinum electrodes showed no decrease in performance after 1 month. Palladium cells on the other hand fell off in performance, and the electrode material was found to have partially dissolved in the water product effluent.

The hydrogen-oxygen ion exchange membrane fuel cell has a practical operating current density of about 30 ma./sq. cm. and can be expected to deliver about 40 amp.-hr./sq. cm. at room temperature. Failure has been due to formation of pinholes in the membrane electrolyte. Platinoid elements insoluble in strong sulfuric acid are adequate electrode materials.

ACKNOWLEDGMENT

Grateful acknowledgment is made to Drs. D. E. Sargent and J. G. Murray of the Organic Chemistry Section for help in resin preparations and modifications, and to Mr. W. D. Shea for help in preparing a portion of the cells. Thanks are expressed to Messrs. M. M. Safford and R. W. Beers who developed and produced graphite-loaded plastic current collectors. We are grateful to Drs. H. A. Liebhafsky and W. T. Grubb for helpful discussions. Messrs. P. R. Schmidt of the Research Laboratory and F. H. Smyser of the Aircraft Accessory Turbine Department aided in the collection of data. Financial support for this work was obtained in part from the Missile and Space Vehicle Department of the General Electric Company.

NOTATION

C_p = specific heat at constant pressure, cal./mole °C.
E = terminal voltage of a cell, v.
$E°$ = reversible electromotive force at standard conditions. v.
F = Faraday constant, 96,517 coulombs/equiv.
$G°$ = standard Gibbs free energy, cal./mole
$H°$ = standard enthalpy, cal./mole
i = current delivered by a cell
n = number of equivalents per mole
n' = number of equivalents of fuel consumed in time θ
$S°$ = standard entropy cal./mole °C.
t = temperature, °C.
T = absolute temperature, °K.
θ = time

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Manuscript received October 25, 1960; revision received February 17, 1961; paper accepted February 20, 1961. Paper presented at A.I.Ch.E. Washington meeting.

Multicomponent Mass Transfer

I. Theory

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As the primary phase in the development of multicomponent mass transfer theory, equations are derived which predict the rate of mass transfer of each species from an interface to a ternary gas mixture in turbulent flow for equimolal-countercurrent transfer and for transfer with one of the three gases stagnant.

The mass transfer equations obtained, regardless of whether a film, Prandtl-Taylor, or modified Chilton-Colburn model is used, differ in form from the usual binary equations and predict qualitative as well as large quantitative differences between binary and ternary transfer.

A criterion is obtained which any consistent multicomponent mass transfer theory must satisfy, and although the ternary film and Prandtl-Taylor models satisfy this criterion, the modified ternary Chilton-Colburn model does not.

Although the essential features of binary mass transfer are fairly well understood, there is a rather startling dearth of knowledge of multicomponent mass transfer. The general differential equations which describe multicomponent mass transfer are easily obtained, at least for ideal gases, by combining the Maxwell-Stefan equations with a continuity equation for each species, but these equations are intractable in all but the simplest situations. Nevertheless the marked differences between the binary and multicomponent forms of the Maxwell-Stefan equations imply that there will be significant differences between binary and multicomponent mass transfer, whether the flow be laminar or turbulent.

In flow systems of the type commonly encountered there is an impressed flow which has velocity components parallel to and velocity gradients normal to the interface across which transfer is taking place. It is these hydrodynamic complications which make even a moderately rigorous prediction of the transfer rates in multicomponent systems difficult. The term "convective mass transfer" is used to describe these systems.

Methods based on the use of an effective diffusivity for each species in a multicomponent mixture have been proposed for handling multicomponent convective mass transfer *(7, 19, 11, 1)*, but these methods will be seen to be inadequate for the types of systems studied here. (The inadequacy does not arise, except for one case, in a failure of these methods to approxi-

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mate the Maxwell-Stefan equations for steady state transfer through a film, but rather arises in the method of application of the methods to convective mass transfer.)

Although multicomponent diffusion experiments have been carried out which have confirmed the Maxwell-Stefan equations for ideal gas mixtures (*5, 6, 8, 4*), no experiments have been carried out which would allow a significant test of convective mass transfer theories for multicomponent systems.

The object of this work is to develop a convective mass transfer theory which will describe the mass transfer from an interface to a three component gas mixture moving in turbulent flow for two important cases, equimolal countercurrent transfer and transfer with one component stagnant. Since, as far as diffusion is concerned, a three-component mixture is much more closely related to the general multicomponent mixture than it is to a binary mixture, success in handling these three-component problems should also aid in the solution of the general multicomponent convection mass transfer problem.

In this paper ternary film, Prandtl-Taylor, and modified Chilton-Colburn models will be developed. In addition some criteria will be obtained which any rigorous multicomponent mass transfer theory must satisfy. The theories will be compared to experiment in part II of this work.

MOLECULAR DIFFUSION

The Maxwell-Stefan equations for diffusion in an isothermal, isobaric, ideal gas mixture are (*10, 1*)

$$C\nabla y_j = \sum_{i=1}^{n} \frac{\underline{N}_i y_j - \underline{N}_j y_i}{D_{ij}}, j = 1,2 \ldots n \quad (1)$$

The equation for $j=n$ is not independent. With a constant molar density the continuity equation for each species is

$$C\frac{\partial y_j}{\partial \theta} + \nabla \cdot \underline{N}_j = R_j, j = 1,2 \ldots n \quad (2)$$

These equations with the determinancy condition, boundary conditions, and equations of motion describe multicomponent mass transfer in isothermal, isobaric, ideal gas mixtures.

When the mole fractions at the parallel $z=0$ and $z=l$ faces are held constant at y_{i0} and y_{il} respectively, there is no impressed flow or chemical reaction, and the steady state is obtained (the conditions for steady state diffusion through a film); the only gradients and fluxes are in the z direction. Equation (2) then shows that the z-direction fluxes are independent of z; Equation (1) becomes

$$C\frac{dy_j}{dz} = \sum_{i=1}^{n} \frac{N_i y_j - N_j y_i}{D_{ij}}, i = 1,2 \ldots n \quad (3)$$

and this equation may be immediately integrated since the D_{ij} are essentially constant.

The well-known binary solutions to Equation (3) under the above conditions for equimolal countercurrent diffusion (hereafter shortened to equimolal diffusion) and diffusion with one gas stagnant are

equimolal

$$N_1 = \frac{D_{12}C}{l}(y_{10} - y_{1l}) \quad (4)$$

and $N_2 = -N_1$.

1 through stagnant 3

$$N_1 = \frac{D_{13}C}{l}\ln\frac{y_{3l}}{y_{30}} = \frac{D_{13}C}{l}\frac{(y_{10} - y_{1l})}{(y_3)_m} \quad (5)$$

The analogous solutions for ternary systems are also available (*13, 15*). However these exact solutions are cumbersome for both computational and analytical purposes, and in most practical situations approximate solutions are sufficient.

The available approximate solutions for the above conditions of steady diffusion through a film fall into two classes: those based on an average effective diffusivity over the film (*7, 19, 11*) and those based on ternary solutions which are exact in certain special cases (*15*).

Of the three effective diffusivity methods the earliest, that of Hougen and Watson (*7*), must be rejected, since their effective diffusivity does not have the proper behavior. The effective diffusivity method of Wilke (*19*) and the second method on the average approximate the exact solutions with about the same accuracy, and Stewart's (*11*) method of obtaining an average effective diffusivity seems to give about the same results as Wilke's. (Some difficulties arise in both effective diffusivity methods in the vicinity of the osmotic diffusion point however. Furthermore all the approximate methods considered here give very large percentage errors near a diffusion barrier.)

The equations based on the second method for steady state diffusion through a film are (*15*)

ternary, equimolal

$$N_i = \frac{D_{i3}C}{l}\phi_e(\delta_e y_{i0} - y_{il}) \quad (6)$$

and

$$N_3 = -(N_1 + N_2) \quad (7)$$

ternary, 1 and 2 through stagnant 3

$$N_i = \frac{D_{i3}C}{l}\phi_S(\delta_S y_{i0} - y_{il}) \quad (8)$$

where

$$\phi_e = \frac{y_{30} - y_{3l}}{(1 - y_{3l}) - \delta_e(1 - y_{30})} \quad (9)$$

$$\phi_S = \frac{\ln(y_{30}/y_{3l})}{(1 - y_{3l}) - \delta_S(1 - y_{30})} \quad (10)$$

$$\delta_e = \exp[(1 - r)(y_{30} - y_{3l})] \quad (11)$$

$$\delta_S = (y_{3l}/y_{30})^r \quad (12)$$

$$r = (D_{13} + D_{23})/(2D_{12}) \quad (13)$$

In the above and subsequent equations the index i, unless otherwise stated, takes on the values 1 and 2. The flux is positive when the diffusion is from plane 0 to l. The ternary solutions are rigorous when two or three of the binary diffusion coefficients are equal; otherwise, although they are approximate, they show the important characteristics of the diffusion. In equimolal transfer component 3 is chosen so that D_{13} is as close as possible to D_{23} (*15*).

The analogous equations based on an effective diffusivity are (*7, 19*)

$$N_i = \frac{\overline{D_i}'C}{l}\frac{(y_{i0} - y_{il})}{(y_i)'} \quad (14)$$

The average effective diffusivity over the region 0 to l is given as a function of composition and flux ratios by Wilke's method and as a function of composition by Stewart's method. The film pressure factor is $(y_i)'$ times total pressure and is a function of composition and flux ratios (*7, 19*). For equimolal transfer $(y_i)'$ is one. For ternary equimolal transfer i takes on the values 1 to 3, and for ternary transfer with component 3 stagnant Wilke lets i take on the values 1 and 2. Equation (14) was obtained by Hougen and Watson and Wilke. As pointed out earlier Hougen and Watson's method of evaluating $\overline{D_i}'$ is generally inadequate. Equation (14) should apply to the general multicomponent system.

Since the justification for this study is that there are significant differences between multicomponent and binary diffusion, it is convenient, at least for the types of diffusion considered here, to compare the behavior of a multicomponent system with the related binary system, that is to the binary system with the same determinancy condition. Thus in the present instance ternary equimolal diffusion is compared with binary equimolal diffusion, and ternary diffusion with one gas stagnant is compared with binary diffusion with one gas stagnant.

The major differences between these ternary and binary systems is that in the former case the direction of diffusion depends upon the sign of the generalized driving force $(\delta y_{i0} - y_{iI})$, since the interaction terms given by Equations (9) to (12) are all positive numbers, while in the latter case the direction of diffusion depends upon the sign of the binary driving force $(y_{i0} - y_{iI})$. Consequently in a ternary system the diffusion may take place from low to high concentrations (reverse diffusion), it may take place when the concentration gradient is zero (*osmotic diffusion*), or in the presence of a concentration gradient the flux may be zero (diffusion barrier). One of the interesting questions one would like to answer is whether these qualitative differences between binary and ternary diffusion give rise to similar differences between binary and ternary convective mass transfer.

Of course phenomena superficially similar to the above can be made to occur in binary systems with the proper choice of determinancy conditions, in the condensation of mixed vapors for example (*3*). In binaries the phenomena can be visualized simply, for the diffusivity is a positive, essentially constant, system property so the rate of transfer with respect to a fixed coordinate can be separated into a diffusion flux with respect to a coordinate moving at the mean molar velocity plus the convective flux caused by the system motion. What has been called *reverse diffusion* can then be interpreted in binaries as the situation in which the convective flux of a species in the direction of increasing concentration of that species is of greater magnitude than the diffusion flux in the direction of decreasing concentration. Thus in binary systems the apparent interaction phenomena can always be removed by choosing a frame of reference moving at the mean molar velocity of the system.

This is not the case in multicomponent systems. In these systems the effective diffusivities [called the *effective binary diffusivities in* (*1*)] in general do not have the physical significance of a diffusivity since in systems of the present type they can take on any value from minus to plus infinity.

In ternary equimolal transfer with the conditions corresponding to those of Equation (6), for example, it can be seen by comparing Equations (6) and (14) that the average effective diffusivity over the region 0 to l is zero at the diffusion barrier, negative in the region of reverse diffusion, and has a singularity at the osmotic diffusion point. In ternary diffusion with one gas stagnant it has a singularity at the osmotic diffusion point and can take on zero and negative values in the reverse diffusion region.

Consequently the effective diffusivity in multicomponent systems must be considered to be a defined quantity which in general has no physical significance, and care must be used in drawing analogies between this quantity and the binary diffusivity. Only when the effective diffusivity is positive, bounded, and not a strong function of composition is it possible to draw this analogy, and this restriction excludes many of the really interesting multicomponent problems.

Since in general it is not possible to treat multicomponent systems as if they were analogous to binaries, the viewpoint described earlier in which the differences between the multicomponent system and the related binary system are considered is preferred. Although in steady state diffusion through a film this is mainly a matter of viewpoint, it will be seen below that when it comes to convective mass transfer the two viewpoints can lead to quite different results.

EFFECTIVE FILM MODEL

The intractability of Equations (1) and (2) when applied to convective mass transfer is avoided by the use of simplified hydrodynamic models. The simplest, which is the effective film model, assumes that all the resistance to transfer from the interface to the bulk of the gas may be considered to be caused by a laminar film of thickness l which is so thin that the flux within the film is independent of distance from the boundary. If this concept is valid, then the above equations for film diffusion can be applied directly to the gas phase; N_i is the flux at the boundary, l is the effective film thickness, y_{i0} becomes y_{iI}, and y_{iI} becomes $\overline{y_i}$. Thus the model suggests that all the phenomena predicted by the equations for diffusion through a physical film apply directly to convective mass transfer as well.

If Equation (4) is compared with the Chilton-Colburn equation for binary convective mass transfer (*2*), one obtains

$$\frac{D_{13}\,C}{l} = \frac{f}{2}\,G_m\left(\frac{\mu}{\rho\,D_{13}}\right)^{-2/3} = k_1 \qquad (15)$$

This effective film thickness is ambiguous since it depends upon the molecular diffusivity. Because of this, generalization to multicomponent systems are not straightforward. However comparison of Equations (4), (5), (6), (8), and (15) suggest the following ternary convective mass transfer equations:

equimolal

$$N_i = k_i\,\phi_e\,(\delta_e\,y_{iI} - \overline{y_i}) \qquad (16)$$

species 3 stagnant

$$N_i = k_i\,\phi_3\,(\delta_3\,y_{iI} - \overline{y_i}) \qquad (17)$$

where

$$k_i = \frac{f}{2}\,G_m\left(\frac{\mu}{\rho\,D_{i3}}\right)^{-2/3} \qquad (18)$$

Although the Chilton-Colburn equation was used here to obtain k_i, in general k_i would be obtained from the coefficient which applies in binary equimolal or dilute stagnant gas transfer under conditions such that the hydrodynamics and geometry are the same as in the ternary system under consideration. [Equations (16) to (18) satisfy the consistency condition presented later.]

The effective film model was used by earlier authors (*7, 19, 11*) in conjunction with the effective diffusivity concept, but they obtained different results because of the inherent ambiguity of the model and their attempt to treat $\overline{D_i}'$ as if it were analogous to the binary diffusivity. Thus if the earlier approach is taken, but Equation (14) is used in place of Equations (6) and (8), and $\overline{D_i}'$ is interpreted as an effective diffusivity, the resulting multicomponent convective mass transfer equations are

$$N_i = \frac{f}{2}\,G_m\left(\frac{u}{\rho\,\overline{D_i}'}\right)^{-2/3}\left(\frac{y_{iI} - \overline{y_i}}{(y_i)'}\right) \qquad (19)$$

It is seen immediately that when $\overline{D_i}'$ is negative, the mass transfer coefficient is a complex number.

What has happened of course is that the effective film thickness has become complex because the binary equations cannot be extrapolated to negative values of the Schmidt number. Obviously the complex behavior might be avoided by fitting the binary data with functions other than a power function, but then there is no way of predicting from the film model how to extrapolate to negative values of the Schmidt number. In this sense the method fails to predict multicomponent convective mass transfer from binary convective mass transfer.

Furthermore, even when the effective diffusivities are positive, the method is not completely satisfactory, for it fails to satisfy the consistency criterion developed later.

The above arguments are not meant to apply to every multicomponent system. In a system where all components but one are stagnant for example, the effective diffusivity behaves reasonably, the system acts like a binary one with one gas stagnant, and Equation (19) is indeed self-consistent.

A somewhat different method of approach based on a point effective diffusivity has also been suggested (*1*). When the Chilton-Colburn equation applies, this method leads to essentially the same result as the previous effective diffusivity methods.

The difficulties mentioned above in connection with the effective diffusivity approach will generally arise whenever the appropriate binary convective mass transfer equation contains a Schmidt number to a fractional power. Since this includes practically all convective mass transfer situations, it is concluded that the earlier effective diffusivity methods are satisfactory for the present types of systems only in the absence of convective mass transfer, that is when there is diffusion through a physical film.

The shortcomings of the effective diffusivity methods as they have been applied to convective mass transfer lead to a rejection of these methods in the present study.

However in the end the difference between these methods and the present one is essentially only in the technique of evaluating the effective film thickness. Consequently by dropping all attempts to treat D_i' as a diffusivity and using Equation (15) as it stands to obtain the effective film thickness one can develop convective mass transfer equations which will give results much the same as Equations (16) to (18). Although Equations (16) to (18) are chosen for use in the present work because they are felt to be more convenient, it should be emphasized that the effective diffusivity equations for diffusion through a physical film [Equation (14)], and for that matter the exact solutions to the Maxwell-Stefan equations for the same conditions, could be used. As long as the transition to convective mass transfer is carried out in the same manner in all cases, all the methods should give essentially the same results as Equations (16) to (18).

This study is not an attempt to investigate the validity of the approximate equations for diffusion through a film—they are valid only insofar as they approximate the Maxwell-Stefan equations to within the desired accuracy—but rather is in essence an attempt to apply known solutions of the Maxwell-Stefan equations (in approximate form) to convective mass transfer.

Although the procedure used earlier to obtain the effective film thickness does avoid the complex mass transfer coefficients and the inconsistencies of the earlier methods, it is by no means unique, for there is a definite arbitrariness in the manner in which the D_{is} arrive in Equation (18). This is a consequence of the unrealistic nature of the effective film model, and the arbitrariness can only be removed by use of more realistic models. Consequently it is necessary to consider the effect of turbulent as well as molecular transport.

TURBULENT DIFFUSION

It has been argued (*17*) that if molecular diffusion has no effect on turbulent transport, then turbulent diffusion can be described by Equation (1) if all the D_{ij} are replaced by ϵ, the turbulent diffusivity common to all species. Thus

$$\underline{N}_i = \underline{N}\, y_i - \epsilon\, C \nabla y_i,\ i = 1,2 \ldots n \tag{20}$$

and all quantities are now time averaged values. If there are interactions between molecular and turbulent diffusion, then ϵ in general has a different value for each species (*17*) and the turbulent diffusion equations tend to take on the characteristics of the molecular diffusion equations. [In a sense the turbulent equations are bounded between the limits of Equation (1) and Equation (20)].

Writing Equation (20) for the z direction, assuming that the fluxes vary with z in the same manner as the shear stress and application of the analogy between turbulent transport of matter and momentum, one obtains for the cases of interest (*17*) equimolal

$$N_i = \frac{\overline{\epsilon C}}{L}(y_{i0} - y_{iL}),\ i = 1,2 \ldots n \tag{21}$$

component n stagnant

$$N_i = \frac{\overline{\epsilon C}}{L}\frac{y_{n0}}{(y_n)_m}(\delta_T\, y_{i0} - y_{iL}),\quad i = 1,2 \ldots n-1 \tag{22}$$

where

$$\delta_T = (y_{nL}/y_{n0}) \tag{23}$$

and

$$\frac{\overline{\epsilon}}{L} = \frac{\frac{f}{2}V^2}{\int_0^L du} \tag{24}$$

In the above equations the N_i are the fluxes at the boundary of the fluid, and subscripts O and L refer to any two points in the turbulent region a distance L apart along a line normal to the boundary of the fluid.

Since the above equations apply to an n component fluid, it is seen that in equimolal transfer there is no difference between binary and multicomponent turbulent transfer (within the limitations of the present assumptions), but when one gas is stagnant, there is an interaction among the various species. This interaction is due to the bulk flow caused by the diffusion, and although it leads to interaction effects such as reverse diffusion, these interactions are similar to those obtained in binaries and are much weaker than the interactions which can be obtained in molecular gaseous diffusion (*15*).

The Reynolds analogy is obtained when the turbulence is assumed to extend to the fluid boundary so the velocity at point O is zero, when L is taken as the position where the local velocity equals the mean velocity, and when it is further assumed that at this latter point all the local concentrations have the same values as the bulk mean concentrations. Equations (24) then becomes (*17*)

$$\frac{\overline{\epsilon}}{L} = \frac{f}{2}V \tag{25}$$

which in conjunction with Equations (21) and (22) gives the multicomponent Reynolds analogy for the systems under consideration.

It would be expected that the multicomponent Reynolds analogy is of more limited utility in gaseous mass transfer than the binary Reynolds analogy, for in the multicomponent case the molecular and turbulent diffusion equations, Equations (1) and (20), differ in form, while in the binary case they are of the same form. [Equations (1) and (20) can be considered to be the limiting cases of the time average of Equation (1). At the limit of negligible turbulent transport the various species interact in a manner described by Equation (1); at the opposite limit they interact only through the total flux as described by Equation (20).] This difference is pointed out by the fact that in binary systems the Reynolds analogy and film model give essentially the same results [Equations (4) and (21)], while in ternary systems these two approaches give very different results [Equations (6) and (21)]. Consequently in analyzing multicomponent mass transfer it appears necessary to consider both molecular and turbulent diffusion simultaneously. The simplest approach of this type is that used by Prandtl (*12*) and Taylor (*14*) for heat transfer (the analogue of binary mass transfer).

PRANDTL-TAYLOR ANALOGY

The Prandtl-Taylor analogy is obtained by combining the film model with the Reynolds analogy, the transfer mechanism in the film adjacent to the wall being assumed to be entirely molecular diffusion and that away

from the wall entirely turbulent diffusion. In this case the velocity at the film turbulent core boundary is not zero but has a value given by the choice of position of the boundary. With this change Equation (24) yields

$$\frac{\overline{\epsilon}}{L} = \frac{(f/2)V}{1 - \frac{u_F}{V}} \qquad (26)$$

Since the variation of flux with position can be neglected in the film adjacent to the wall, the steady state molecular diffusion equations presented earlier apply, and the group D_{ij}/l which appears in these equations is given by

$$\frac{D_{ij}}{l} = \frac{(f/2)\,V}{(\mu/\rho\, D_{ij})\,(u_F/V)} \qquad (27)$$

Thus applying Equations (4), (5), (6), and (8) with Equation (27) across the film (I to F), Equations (21) and (22) with Equation (26) from F to the bulk, and then eliminating the mole fractions at F which appear explicitly in the driving forces, one gets the transfer rates from the interface to the bulk of the gas:

binary equimolal

$$N_1 = k_b\,(y_{1I} - \overline{y}_1) \qquad (28)$$

where

$$k_b = (f/2)\,G_m/\left[\left(\frac{\mu}{\rho\, D_{12}} - 1\right)\frac{u_F}{V} + 1\right] \qquad (29)$$

or

$$k_b = (f/2)\,G_m/\Phi\left(\frac{\mu}{\rho\, D_{12}}, u_F/V\right) \qquad (30)$$

binary 1 through stagnant 2

$$N_1 = k_b\frac{(y_{1I} - \overline{y}_1)}{(y_2)_m} \qquad (31)$$

ternary equimolal

$$N_i = k_{ie}\,(\delta_{ef}\,y_{iI} - \overline{y}_i) \qquad (32)$$

where

$$k_{ie} = (f/2)\,G_m/\Phi\left(\frac{\mu}{\rho\, D_{i3}\,\psi_e}, u_F/V\right) \qquad (33)$$

$$\delta_{ef} = \exp\left[(1-r)\,(y_{3I} - y_{3F})\right] \qquad (34)$$

$$\psi_e = \phi_{ef} = \frac{y_{3I} - y_{3F}}{(1 - y_{3F}) - \delta_{ef}(1 - y_{3I})} \qquad (35)$$

and Equation (7) holds.

Ternary 1 and 2 through stagnant 3

$$N_i = k_{iS}\frac{(\delta_S'\,y_{iI} - \overline{y}_i)}{\gamma} \qquad (36)$$

where

$$k_{iS} = (f/2)\,G_m/\Phi\left(\frac{\mu}{\rho\, D_{i3}\,\psi_S}, u_F/V\right) \qquad (37)$$

$$\delta_S' = \delta_{Sf}\,\delta_T = \delta_{Sf}\,(\overline{y}_3/y_{3F}) \qquad (38)$$

$$\delta_{Sf} = (y_{3F}/y_{3I})^r \qquad (39)$$

$$\gamma = (y_3)_{mT}/y_{3F} = \frac{1}{y_{3F}}\left[\frac{\overline{y}_3 - y_{3F}}{\ln\,(\overline{y}_3/y_{3F})}\right] \qquad (40)$$

$$\psi_S = \frac{(y_3)_{mT}}{\overline{y}_3}\left[\frac{\ln\,(y_{3I}/y_{3F})}{(1 - y_{3F}) - \delta_{Sf}(1 - y_{3I})}\right] \qquad (41)$$

(The new functions introduced above can be shown to be always positive.)

Equations (28) and (31), the binary mass transfer equations, are of the same form as the equations obtained either by use of a film model or an all turbulent model, so the model choice only affects the predictions of the coefficient. In the ternary equations however the driving forces in the three cases are the same only when all the D_{ij} are equal, so in general the choice of a model affects both the coefficients and the driving forces.

Equations (32) to (41) give the rates of mass transfer in a ternary system from the interface to the bulk of the gas. They are not symmetrical and must be altered when written from the bulk to the interface. Since the film and/or core equations are nonlinear, the mole fraction of species 3 at the film-core boundary appears in the final equations, and in general this mole fraction must be obtained by trial and error with the individual film and core equations. Before this problem is considered it is important to consider the form of the equations.

In both Equations (32) and (41) the driving forces retain the same form as the molecular diffusion equations, so the qualitative differences between binary and ternary film diffusion are also predicted by this model. In equimolal transfer [Equation (32)] the interaction term δ_{ef} is based on the film only [Equation (34)], since there are no interactions in the core, and in general the effect of the noninteracting core is to make the interactions less than they would be if the transfer were controlled entirely by a film.

When there is a stagnant species [Equation (36)], the film and core interactions combine as given by Equation (38), and when the D_{ij} are equal, $r = 1.0$, the film and core interactions are the same, and δ_S' is the same as given by an all film or all core equation. When r is greater than 1.0, as obtained when the stagnant gas is the light component, the film interactions are greater than the core interactions and the effect of the core is to reduce the over-all strength of the interactions. When the converse is true, $r < 1.0$, the core interactions are stronger than the film interactions and the effect of the core is to increase δ_S'. In this latter case however the interactions will be relatively small.

Unlike the effective film model, the Prandtl-Taylor model is unambiguous (in the sense used earlier), so essentially the same results will be obtained if the effective diffusivity equations [Equation (14)] are used for the film region in place of Equations (6) and (8).

Simplified Prandtl-Taylor Analogy

The ternary equations presented above are inconvenient insofar as they contain a mole fraction at the film-core boundary. This mole fraction appeared because of the difference in form between the molecular and turbulent equations, but there is one instance (aside from the one in which all the D_{ij} are equal) where the molecular and turbulent equations are of the same form. This occurs when two of the molecular diffusion coefficients are equal, $D_{13} = D_{23}$, for here the sum of N_1 and N_2 is, from Equation (6) for equimolal transfer

$$N_1 + N_2 = \frac{D_{13}\,C}{l}\,(y_{3F} - y_{3I}) \qquad (42)$$

where the equation is written across the film, I to F.

The turbulent equations always have this form, since all the turbulent diffusion coefficients are equal; therefore Equation (21) yields

$$N_1 + N_2 = \frac{\overline{\epsilon}C}{L}\,(\overline{y}_3 - y_{3F}) \qquad (43)$$

Eliminating $\overline{y}_{3F}$ from the last two equations and using Equations (26) and (27) one gets

$$N_1 + N_2 = k_b\,(\overline{y}_3 - y_{3I}) \qquad (44)$$

and k_b is given by Equation (29) with the diffusion coefficient in that equation equal to D_{13}. Since $(\overline{y}_3 - y_{3I})$ is the normal binary driving force for species 1 and 2, in this instance the sum of the fluxes of the two similar species follows the normal binary equation even though the individual fluxes may deviate considerably from this form.

Equation (44) is exact when D_{13} and D_{23} are equal, and if they are unequal but do not differ too greatly the equation may be used as an approximation if the mean diffusion coefficient

$$D_m = \frac{D_{13} + D_{23}}{2} \qquad (45)$$

is used as the diffusion coefficient in evaluating k_b from Equation (29).

A similar treatment when one gas is stagnant, with Equations (8), (22),

(26), and (27) used, yields for the film

$$N_1 + N_2 = \frac{D_{13} C}{l} \ln \frac{y_{3F}}{y_{3I}} \quad (46)$$

for the core

$$N_1 + N_2 = \frac{\epsilon C}{L} \ln \frac{\bar{y}_3}{y_{3F}} \quad (47)$$

and over-all

$$N_1 + N_2 = k_b \ln \frac{\bar{y}_3}{y_{3I}} = k_b \frac{(\bar{y}_3 - y_{3I})}{(y_3)_m} \quad (48)$$

Here the flux of species 1 and 2 is the total flux, and as before it has the same form as the binary convective mass transfer equation when species 1 and 2 is considered to be a single component. Again if D_{13} and D_{23} are unequal, an approximation is obtained if Equation (45) is used as the diffusion coefficient in Equation (29).

Elimination of the fluxes from Equations (42) and (43) for equimolal countercurrent transfer relates the mole fraction of species 3 at the film-core boundary to the interfacial and bulk mole fractions:

$$\frac{y_{3F}}{y_{3I}} = s \frac{\bar{y}_3}{y_{3I}} + (1 - s) \quad (49)$$

where

$$s = \frac{k_b}{k_f} \quad (50)$$

k_b is the binary coefficient and k_f the film coefficient $D_m C/l$.

If s is evaluated on the basis of the Prandtl-Taylor analogy, using equations (27) and (29) one obtains

$$s = \frac{\frac{u_F}{V} \frac{\mu}{\rho D_m}}{\left(\frac{\mu}{\rho D_m} - 1\right) \frac{u_F}{V} + 1} \quad (51)$$

Similarly from Equations (46) and (47) for one gas stagnant

$$\frac{y_{3F}}{y_{3I}} = \left(\frac{\bar{y}_3}{y_{3I}}\right) \quad (52)$$

Equations (49) and (52) describe the manner in which y_{3F} varies with the relative resistances in the film and core for their respective cases. When s is 1.0, the resistance is entirely molecular and $y_{3F} = \bar{y}_3$, while when s is zero, the resistance is all turbulent and $y_{3F} = y_{3I}$.

Equations (49) and (52) may be used to remove y_{3F} from the ternary mass transfer equations, thus allowing explicit determination of the separate fluxes as functions of the terminal compositions. Equations (32), (33), (36), and (37) are unchanged, but the remaining equations become

$$\delta_{ef} = \exp\left[s\,(1 - r)\,(y_{3I} - \bar{y}_3)\right] \quad (53)$$

$$\psi_e = \frac{s(y_{3I} - \bar{y}_3)}{(1 - \bar{y}_3) - \delta_{ef}(1 - y_{3I}) - (1 - s)(y_{3I} - \bar{y}_3)} \quad (54)$$

$$\delta_s' = (\bar{y}_3/y_{3I})^{1+s(r-1)} \quad (55)$$

$$\delta_T = (\bar{y}_3/y_{3I})^{1-s} \quad (56)$$

$$\gamma = \frac{\delta_T - 1}{\ln \delta_T} \quad (57)$$

$$\psi_S = \frac{s}{1 - s} \frac{(1 - \delta_T)}{(\delta_T - \bar{y}_3) - \delta_s'(1 - y_{3I})} \quad (58)$$

Equations (53) and (54) in conjunction with Equations (32), (33), (7), and (5) allow explicit determination of the separate fluxes as functions of terminal compositions in ternary equimolal transfer, and similarly Equations (55) to (58) with Equations (36), (37), and (51) give the fluxes when one gas is stagnant. In addition to the usual assumptions in the Prandtl-Taylor analogy it is assumed that D_{13} and D_{23} lie close enough to each other to allow Equations (49) and (52) to be used. This requirement does not appear to be too restrictive. As the parameter s varies from zero to 1, the equations shift from an all turbulent to an all film model. [When $D_{13} = D_{23}$ the flux $(N_1 + N_2)$ obtained from the above equations must, and indeed does, satisfy Equation (44) or (48)].

MODIFIED CHILTON-COLBURN ANALOGY

The Prandtl-Taylor analogy contains the ratio u_F/V, and although there was much early discussion of the value of this ratio, it became clear that unless it was made a function of Prandtl number (an assumption inconsistent with the model) the analogy would agree with experiment only when the Prandtl number was in the vicinity of 1. This limitation is caused by the neglect of the region of the fluid in which the molecular and turbulent diffusivities are of the same order of magnitude, the buffer layer. Later developments of von-Karman (9) and many others showed that inclusion of the buffer layer gave results in accord with experiment over much wider ranges of Prandtl number. Although it is clear that there is no true laminar film as assumed in these models, since the eddy diffusivity merely approaches zero as the wall is approached, recent work which takes this viewpoint shows that in binary systems the small eddy diffusivity in the film can be neglected for the relatively low Schmidt numbers encountered in gas mixtures (2, 7).

Thus the next logical step in developing the multicomponent analogy would be to include the buffer layer. Although this might be done numerically by carrying out a constant flux analogy calculation based on the time averaged multicomponent diffusion equations, the calculations are tedious, and for the time being an attempt might be made to bypass this step in a manner similar to that used by Chilton and Colburn to bypass the complete analysis of binary transfer (2). They assumed that the coefficient in binary transfer is given not by Equation (29), (the Prandtl-Taylor result), but by the empirical equation

$$k_b = \frac{f}{2} G_m \left(\frac{\mu}{\rho D_{12}}\right)^{-2/3} \quad (59)$$

Comparison of Equations (30), (33), and (37) shows that the same functional form for k_b appears in both binary and ternary transfer when the Prandtl-Taylor approach is taken—the ternary coefficients differ from the binary coefficient only in that modified ternary Schmidt numbers replace the binary Schmidt number.

The hypothesis could now be made that the binary and ternary coefficients will also have the same functional forms in any more rigorous analogy, and since Equation (59) is such an analogy (experimentally determined), it follows from the hypothesis that for ternary equimolal transfer

$$k_{te} = (f/2)\, G_m \left(\frac{\mu}{\rho D_{13} \psi_e}\right)^{-2/3} \quad (60)$$

and for ternary transfer with one gas stagnant

$$k_{ts} = (f/2)\, G_m \left(\frac{\mu}{\rho D_{13} \psi_S}\right)^{-2/3} \quad (61)$$

The parameter s is now given by

$$s = y_F^+ \sqrt{f/2} \left(\frac{\mu}{\rho D_m}\right)^{1/3} \quad (62)$$

Although it might be hoped that use of this approach would reduce the errors caused by some of the assumptions inherent in the Prandtl-Taylor model, it will be found below that the equations developed in this section are not self-consistent, so the modified Chilton-Colburn approach cannot be used to obtain a completely satisfactory multicomponent mass transfer theory.

Since the above approach is merely a more refined guessing game than the effective film method, other answers are possible. The results obtained, just as with the effective film thickness method, really depend upon the form

of the equations used for the film. If the effective diffusivity form of the equations had been used for the film for example, ψD_{is} in Equations (60) and (61) would have been replaced by the effective diffusivity evaluated over the film. This later quantity would then replace ψD_{is} in Equation (61) giving a result similar to, and presenting the same difficulties as, Equation (19).

A THEOREM FOR n-1 SIMILAR SPECIES IN AN n COMPONENT MIXTURE

Although in general the rigorous form of the mass transfer equations for ternary transfer (or general multicomponent transfer) cannot be attained at present, some rigorous results can be obtained for certain special conditions, and it will be seen that these results set conditions which any exact mass transfer theory must satisfy.

It was shown earlier that in a ternary system in which $D_{13} = D_{23}$, the Prandtl-Taylor approach yielded equations for the flux sum $N_1 + N_2$ identical in form to the binary equation when the driving force for this flux was based on the sum of the mole fractions of species 1 and 2. Since the condition $D_{13} = D_{23}$ is equivalent to stating that species 1 and 2 are identical as far as diffusion is concerned (except for one qualification which is discussed below), species 1 and 2 together may be considered to be one component, and the three component mixture is reduced to a binary mixture made up of the 1 + 2 species and species 3. Similarly for an n component mixture with $n - 1$ similar species and one dissimilar one (say the nth), the sum of the $n - 1$ similar species can be treated as one component in a binary mixture in which the other component is the nth species. This result is confirmed by applying these conditions to the Maxwell-Stefan equations [Equation (1)] and summing the first $n - 1$ equations:

$$\underline{N}_\sigma = \underline{N}\, y_\sigma - C\, D\, \nabla y_\sigma \qquad (63)$$

where

$$\underline{N}_\sigma = \sum_{i=1}^{n-1} \underline{N}_i \qquad (64)$$

$$y_\sigma = \sum_{i=1}^{n-1} y_i \qquad (65)$$

Equation (63) is identical to the binary Maxwell-Stefan diffusion equation, and the only diffusion coefficient which appears is the diffusion coefficient for a binary mixture of any one of the similar species with species n. If Equation (63) is combined with a differential material balance on the $n - 1$ similar species, there results

$$C \frac{\partial y_\sigma}{\partial \theta} + \nabla \cdot (\underline{N}\, y_\sigma) = D\, C\, \nabla^2 y_\sigma \qquad (66)$$

This molecular equation is identical in all respects to the basic molecular diffusion equation for a binary mixture, and the equations of motion are also the same in the two systems. As in binary transfer another equation, such as the equimolal condition, is needed to make the system determinate. Since Equations (63), (66), the equations of motion, and the determinancy condition with given geometry and boundary conditions completely define the mass transfer process, whether it be laminar or turbulent, the integrated rate equation for this type of multicomponent mass transfer must be identical to the integrated binary rate equation when the conditions on the equations are the same in both cases. Specifically if the binary rate equation under any given conditions is

$$N_1 = k_b' (y_{1I}, \overline{y_1}) (y_{1I} - \overline{y_1}) \qquad (67)$$

then the multicomponent equation under the same conditions must be

$$N_\sigma = k_b' (y_{\sigma I}, \overline{y_\sigma}) (y_{\sigma I} - \overline{y_\sigma}) \qquad (68)$$

Thus Equations (44) and (48) are seen to be special cases of this general result. Equation (68) fails when one attempts to distinguish among the similar species in some manner, either by means of the boundary conditions or the determinancy condition. For example Equation (68) takes on the form of the binary stagnant gas equation when species n is stagnant or all the similar species are stagnant, but if only a fraction of the similar species are stagnant, there is no binary system analogous to this multicomponent system.

There are multicomponent systems of practical interest where Equation (68) is a good approximation, moderately high molecular weight organics being transferred through a stagnant light gas for example. Even here the equation is not of direct use, since it does not give the separate fluxes (but as will be seen in Part II it is of use in the analysis of experimental data in a system of this type). Its greatest utility however is that it sets a limiting condition which the individual rate equations must satisfy.

Thus the ternary equations developed on the basis of the Prandtl-Taylor model were seen earlier to be consistent, since the flux sum $N_1 + N_2$ satisfied the binary Prandtl-Taylor equation when $D_{13} = D_{23}$, but the binary Prandtl-Taylor equation is only consistent with experiment near a Schmidt Number of 1. It is not only necessary that any correct theory sum to equations of the form of (44) or (48) when $D_{13} = D_{23}$, but k_b in these equations must be consistent with experiment.

Interestingly enough the present effective film model, which is the crudest model considered, satisfies both the above conditions.

The ternary equations developed with the modified Chilton-Colburn approach are not self-consistent, for when $D_{13} = D_{23}$ the equations do not sum to the correct binary equation, although in many cases the inconsistency may not be very large. The same can be said for the earlier effective diffusivity methods.

Thus even though all the present models, except for the Reynolds analogy, lead to ternary mass transfer equations of the same basic form, none can be considered to be completely satisfactory on theoretical grounds, so a choice among the equations and a determination of their accuracy can only be made by experiment (see Part II).

NOTATION

C = molar density, lb. moles/cu. ft.
D = binary diffusion coefficient, sq. ft./hr.
$\overline{D_i'}$ = average effective diffusivity of species i, sq. ft./hr.
D_m = mean diffusion coefficient, sq. ft./hr.
f = Fanning friction factor
G_m = molar mass velocity, lb. moles/hr. sq. ft.
k = mass transfer coefficient, ft./hr.
l, L = length, ft.
n = number of species
N = total flux at interface, lb. moles/hr. sq. ft.
$\underline{N}$ = total flux vector, lb. moles/hr. sq. ft.
N_i = flux of species i at interface, lb. moles/hr. sq. ft.
$\underline{N}_i$ = vector flux of species i, lb. moles/hr. sq. ft.
r = ratio of diffusion coefficients
R = molar rate of production, lb. moles/hr. cu. ft.
s = ratio of mass transfer coefficients
u = local velocity, ft./hr.
V = mean velocity, ft./hr.
y = mole fraction
$(y_i)'$ = film pressure factor divided by total pressure
y^+ = reduced y plus distance coordinate
z = distance coordinate, ft.

Greek Letters

γ = interaction term
δ = interaction term

ϵ = turbulent diffusion coefficient, sq. ft./hr.
θ = time, hr.
μ = viscosity, lb.-mass/ft. hr.
ρ = density, lb.-mass/cu. ft.
ϕ = interaction term
Φ = functional symbol
ψ = interaction term

Subscripts

b = binary
e = equimolal transfer
f = across film
F = outer edge of film
i, j = species 1, 2, or 3
l, L, O = positions
m = log mean unless otherwise defined
n = species n
S = transfer with one gas stagnant
T = across turbulent core
σ = sum of $n-1$ similar species
1,2,3 = respective species
I = interface
— = vector if below quantity, mean or bulk value if above
∇ = del operator

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II. Experiment

Measurements have been made of the simultaneous rates of transfer of acetone and benzene between a liquid film and a turbulent three component gas mixture. The measurements were made in a wetted-wall column with both mixtures of acetone, benzene and nitrogen, and acetone, benzene and helium.

As predicted by the equations of Part I the mass transfer differs qualitatively as well as quantitatively from mass transfer in the corresponding binary system in which one component is stagnant. In several experiments acetone was transferred from low to high concentrations in accord with the predictions.

Both the ternary film and Prandtl-Taylor models satisfactorily predict the rates of transfer of acetone and benzene, and, except possibly for very high Reynolds numbers, the simpler film model is recommended.

The ternary convective mass transfer theory developed in Part I is concisely summarized by

$$N_i = k_i \phi \, (\delta \, y_{iI} - \overline{y}_i) \qquad (1)$$

where i takes on the values 1 and 2 and k_i, ϕ, and δ are functions which are positive and depend upon the type of transfer (equimolal or one component stagnant) and upon the type of model used. It is the object of this work to determine experimentally whether or not ternary convective mass transfer is described by an equation of the above form and which, if any, of the models developed in Part I is most suitable.

CHOICE OF SYSTEM

The conditions required for a satisfactory test of the rate equations are most readily obtained by contacting a volatile binary liquid below its bubble point with a ternary gas in which two of the species are common to the liquid and one is insoluble in the liquid.

This choice of a binary liquid phase greatly enlarges the choice of systems for which vapor-liquid equilibrium data are available and reduces the uncertainties concerning the mass transfer in the liquid phase. Furthermore the insoluble gas, which will be stagnant, can be readily changed to change the predicted interactions.

The system benzene-acetone, for which good equilibrium data are available (*1*), was chosen for the liquid phase, and both nitrogen and helium were used separately as the stagnant gases. The former tends to give relatively weak interactions, $r = 2.5$, and the latter relatively strong interactions, $r = 10$. [Note that r enters Equation (12), Part I, as an exponent.] In addition the choice of heavy species for those being transferred and light species for the inerts makes D_{13} close to D_{23}, so Equation (68), Part I, should hold, affording a useful check on the consistency of the theory and experiment.

EQUIPMENT AND PROCEDURE

The apparatus is shown schematically in Figure 1. A wetted-wall column similar to that used by Emmert and Pigford (3) was used to contact the gas and liquid. Operation was concurrent downwards. The 0.985-in. I.D. Pyrex glass pipe was 24 in. long measured from the knife edge at the top to the beginning of the take off flare at the bottom. The column was preceded by an 18 in. calming section made of 1-in. diameter brass pipe.

Both the gas and liquid streams were passed through preheaters and then through copper tubes in a constant temperature water bath. The gas was supplied simultaneously from a battery of four cylinders connected by a manifold. The liquid was pumped from a 50-gal. storage tank. Both the gas line from the constant-temperature bath and the calming section were insulated, the column was uninsulated, and the gas line leaving the column was electrically heated.

Provision was made for splitting the gas stream and passing a metered portion of it through a saturater which could be filled with either of the volatile species. Mixing of the saturated side stream with the main gas stream took place in a vertical packed section of pipe located in the constant-temperature bath.

The liquid and gas flow rates were measured by rotameters, and column pressure was determined by pressure taps