Forced and Natural Convective Mass Transfer in Multicomponent Gaseous Mixtures

HERBERT E. CARLTON and JOSEPH H. OXLEY

Battelle Memorial Institute, Columbus, Ohio

The use of the Chilton-Colburn analogy to obtain an effective film thickness over which the Stefan-Maxwell equations can be integrated was confirmed for binary mixtures and found applicable for ternary, quaternary, and presumably higher order mixtures under conditions of nonequimolal counterdiffusion in a differential convective flow system. A method of averaging binary diffusivities was developed for use in computing the Schmidt number in these multicomponent systems. It was also found necessary to modify the usual Sherwood number, if there was a large molecular weight change across the diffusion barrier when the Chilton-Colburn analogy was employed.

One of the most difficult current problems in chemical engineering involves mass transfer in multicomponent gaseous mixtures under conditions of convective flow. For many years the concept of a film resistance to diffusion, originally proposed by Noyes and Whitney (*1*) and subsequently extended by Nernst (*2*), was sufficient for most applications involving systems with two components or one diffusing component in a mixture of nondiffusing components (*3*). Whitman (*4*) proposed the additive resistances of these films, and Fischbeck (*5*) and Tu et al. (*6*) extended their utility to interfaces at which a chemical reaction is occurring. However, Bischoff and Froment (*7*) have pointed out the difficulty of treating simultaneous reaction and kinetic resistances for real systems without the use of computational equipment. In recent years the penetration theory of Higbie (*8*), with suitable modifications, has been gaining in popularity (*9* to *12*), and Sherwood et al. have recently suggested turbulent film (*13*, *14*) and parallel eddy and molecular diffusion (*15*) models. However, the film concept is still widely used industrially and is quite satisfactory for many applications.

The use of analogies between momentum, heat, and mass transfer is especially helpful in defining a resistance to mass transfer, and one of the best surveys on this subject is by Sherwood (*16*). However, if these analogies are to be employed with the kinetic theory of gases to solve multicomponent diffusion problems, a model such as effective film, surface renewal, etc., must be employed. In addition, multicomponent systems present problems, because the analogies between momentum and heat transfer no longer bear a direct similarity with mass transfer. The diffusion rates of various components in a mixture are not necessarily directly related to the heat and momentum transport rates. For instance, the diffusion rates of a given component, or of the mixture as a whole, can vary in both sign and magnitude under conditions where the heat or momentum transfer is relatively invariant. Ackerman (*17*) first reported this difficulty and showed how total heat transfer was affected by the diffusion rates of each component, as well as by the transport parameters of the bulk stream. Mickley et al. (*18*) extended this concept to the case where the flow to or from an interface was essentially independent of bulk stream conditions. Such a situation can occur, for instance, in transpiration or ablative cooling. Bedingfield and Drew (*19*) derived a correction factor for direct analogy between mass and heat transfer in binary systems and using dilute systems obtained good correlation. Heinrich (*20*), working with a more concentrated system, was unable to find a general analogy.

The purpose of this study was to show that the Chilton-Colburn (*21*) analogy could be used as the basis for extracting an effective film thickness, which could then be substituted in the Stefan-Maxwell (*22*, *23*) equations to predict local transport rates in convective multicomponent gaseous systems. At the same time, the general utility of the Chilton-Colburn analogy and the Stefan-Maxwell equations could be demonstrated.

THEORETICAL ANALYSIS

The equations for diffusion of ideal gases were developed during the latter part of the nineteenth century by Maxwell (*22*) and Stefan (*23*). For an n component mixture, there is one equation of the form

$$-(P/RT)(dy_1/dZ) = (J_1y_2 - J_2y_1)(1/D_{12}) + (J_1y_3 - J_3y_1)(1/D_{13}) + \dots \quad (1)$$

for each of the n components, relating the molar flux of the given component with all the other component fluxes in terms of the mole fractions of the components, the binary diffusivities, the pressure, gas constant, and system temperature, and the gradient of the component of interest. However, only $n - 1$ of these equations are independent, since one of the equations is dependent upon the others by the relationship

$$y_n = 1 - y_{n-1} - y_{n-2} - \dots \quad (2)$$

Mathematically, the Stefan-Maxwell equations are a set of simultaneous, linear, first-order differential equations. There are a number of analytical solutions of these equations available for binary and ternary systems. Lewis and Chang (*3*) have summarized these binary solutions, and ternary solutions have been derived by Gilliland (*24*), Hoopes and Drew (*25*), Benedict and Boas (*26*), Cichelli et al. (*27*), Keyes and Pigford (*28*), Toor (*29*), Heubner (*30*), and Hsu and Bird (*31*). However as the number of components increases, the solutions become increasingly difficult to derive as well as to use, and various approximate methods have been proposed by Hougen and Watson (*32*), Wilke (*33*), Stewart (*34*), Shain (*35*), etc. The binary solutions of the Stefan-Maxwell equations have been exhaustively tested (*36*) in cross-flow convective flow systems like that used in the present study. However, no ternary or higher order system under flow conditions has been satisfactorily investigated heretofore.

The problem in experimentally verifying the Stefan-Maxwell equations in multicomponent systems is the boundary conditions. Usually, the compositions at one boundary are known, for instance, the bulk stream conditions for diffusion across a boundary layer at an interface. However, the interfacial compositions and the diffusion rates of each species in the mixture must be obtained from additional sources of data. In chemical kinetic processes, the individual rates of diffusion are related to each other by reaction stoichiometry, and the interfacial compositions must assume values which are defined by chemical kinetic and/or thermodynamic considerations. This system of constraints is the one of interest for the present study, and a computer solution for integrating the Stefan-Maxwell equations was developed for a reacting mixture of any number of components under control of diffusion and/or kinetic resistances at one boundary with numerical integration techniques used (see Appendix *A*).

The problem in using the Stefan-Maxwell equations in most industrial applications is how to obtain a value for the film thickness for use in integrating Equation (1), that is, how to use a suitable analogy derived for binary systems for the more usual case of multicomponent mixtures. The validity of the Chilton-Colburn analogy between heat and binary mass transfer for flow across a cylinder is fairly well established (*21*) and recently has been given some theoretical justification for turbulent systems (*14*). This familiar analogy involves

$$j_h = j_d \tag{3}$$

where

$$j_h = (h/c_pG)(N_{Pr})^{2/3} \tag{4}$$

and

$$j_d = (k_gM_b/G)(N_{Sc})^{2/3} \tag{5}$$

Multiplication of both sides of Equation (4) by the Reynolds number yields

$$j_hN_{Re} = N_{Nu}/N_{Pr}{}^{1/3} \tag{6}$$

This grouping has been found to be related to the convective parameters of the system by equations of the form

$$N_{Nu}/N_{Pr}^{1/3} = f\ (N_{Re}, N_{Gr}) \tag{7}$$

where Chilton-Colburn specified physical properties were to be evaluated at film conditions (*21*). For cross-flow over a cylinder, the forced and natural convection heat transfer data presented by McAdams (*37*) can be correlated to yield the functional relationship

$$f(N_{Re}, N_{Gr}) = 0.50 + 0.49\ (N_{Re}^2 + N_{Gr})^{0.26} \tag{8}$$

Similarly, multiplying Equation (5) by Reynolds number and assuming perfect gas behavior, we obtain

$$j_dN_{Re} = N_{Sh}/N_{Sc}^{1/3} \tag{9}$$

where

$$N'_{Sh} = (k_gdRT/D_fP)(M_b/M_f) \tag{10}$$

The correction of the Sherwood number for the molecular weight ratio between that of the bulk stream and that of the film should be noted. This modification arises because film properties are specified in the analogy which is used as the basis for the transport correlation. As will be shown later, this ratio can be an important correction.

If the Chilton-Colburn analogy is valid for multicomponent diffusion, the function which relates $N'_{Sh}/N_{Sc}^{1/3}$ to the Reynolds and Grashof numbers of the system must be the same as the function which relates $N_{Nu}/N_{Pr}^{1/3}$ to the Reynolds and Grashof numbers. One difficulty with application of this analogy to multicomponent systems is the choice of the proper diffusivity in the Sherwood and Schmidt numbers, as has been discussed in some detail by Toor and Sebulsky (*38*). For an n component mixture, there are $(n^2 - n)/2$ binary diffusivities and obviously an infinite number of possible combinations. Fortunately, the Sherwood and Schmidt numbers appear as ratios in most analogies, and the actual value of an average multicomponent diffusivity does not need to be known with great accuracy, since its overall effect is usually only to about the one-third power. However, one must obviously be consistent in using the same average value in computing the Sherwood and Schmidt numbers of the system.

To avoid such an inconsistency, and since in using the Stefan-Maxwell equations with a film model one is interested in the effective film thickness and not the mass transfer coefficient, per se, it appears desirable to use the film definition of the mass transfer coefficient

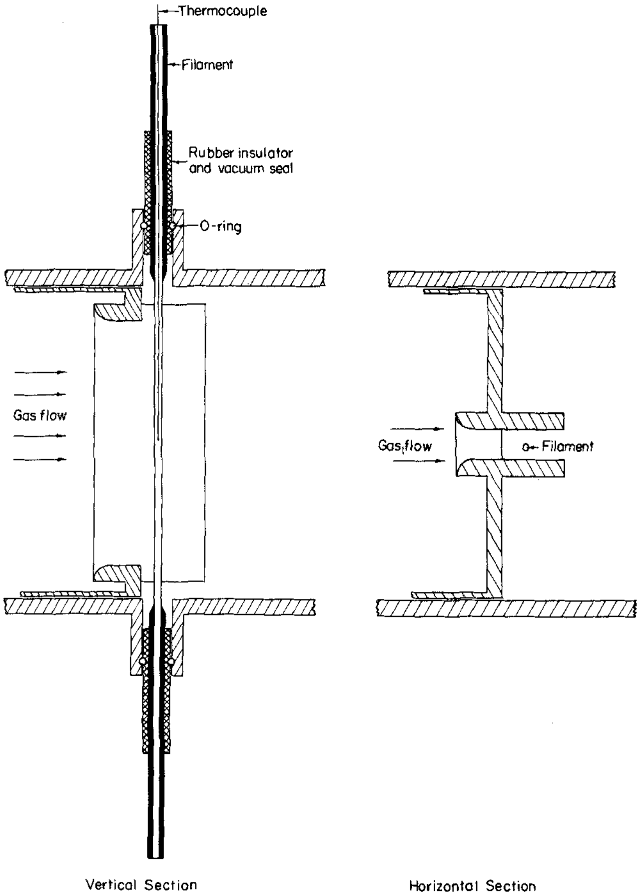
$$k_g \equiv D_f\ P/ZRT \tag{11}$$

to eliminate the diffusivity term in the Sherwood number, that is

$$N'_{Sh} = dM_b/ZM_f \tag{12}$$

If the Chilton-Colburn analogy can be verified for multicomponent systems, the film thickness is then

$$Z = dM_b/M_f\ N_{Sc}^{1/3}\ f(N_{Re}, N_{Gr}) \tag{13}$$



Vertical Section

Horizontal Section

Fig. 1. Filament and orifice detail.

Or for cross-flow over a cylinder with $N_{Re} < 1{,}000$

$$Z = dM_b/M_f \; N_{Sc}^{1/3} \, [0.50 + 0.49 \, (N_{Re}^2 + N_{Gr})^{0.26}] \quad (14)$$

The molecular weight correction can now be tested with binary data; a method of calculating the effective diffusivity in the Schmidt number for multicomponent systems can be obtained from ternary data; and the general utility of the Stefan-Maxwell equations and the Chilton-Colburn analogy can be checked with quaternary data.

EXPERIMENTAL PROCEDURE

The experimental systems selected for study were based on chemical stoichiometric control of the relative diffusion rates to and from a heated interface in a convective, differential reactor system. A similar chemical technique was used by Hoopes and Drew (*25*) in their nonconvective ternary studies based on the decomposition of ammonia. Kesler (*39*) employed the dissociation of TiI_4 in a flow system similar to that used in the present studies, but obtained results which were about 40% greater than he predicted on the basis of full diffusion control.

Two carbonyl systems, which decompose, precipitate metal, and liberate carbon monoxide at the heated interface, were employed in the present study (*40, 41*):

$$Ni(CO)_4 \rightarrow Ni + 4CO \quad (15)$$

and

$$Fe(CO)_5 \rightarrow Fe + 5CO \quad (16)$$

These reactions provide two independent ratios between diffusing reactant and products, and could be further generalized by the addition of diluents. The results were then to be tested on a more complicated system involving a hydrogen reduction reaction:

$$WF_6 + 3H_2 \rightarrow W + 6HF \quad (17)$$

The deposition experiments were conducted on resistance-heated 3½-in. lengths of ⅛-in. O.D. tubular filaments supported in a ½-in. wide rectangular orifice, as shown in Figure 1. The reactant vapors, sometimes diluted with other gases, were passed at known rates and pressures through the orifice and horizontally over the deposition surface. Approximately three-fourths of the experiments with iron carbonyl and one-half of those with nickel carbonyl were run with a horizontal filament; all other runs employed vertical filaments. There was no significant difference with orientation of filament on deposition rates for the particular length/diameter used. The deposition rate and hence diffusion rates were determined from the weight gain and initial surface area of the filament and the length of the run.

The kinetics of the two carbonyl reactions were studied to define fully both the interfacial compositions which exist in a dynamic system and also the boundaries between the so-called kinetic- and diffusion-controlled regions. The kinetics of the hydrogen-reduction reaction, although not studied in detail, are known with sufficient accuracy to define adequately the diffusion-controlled region (*42*). The tungsten was deposited at conditions where mass transport rather than reaction kinetics was limiting deposition rates.

Under the flow conditions employed, the reaction rates in carbonyl systems were controlled primarily by surface reactions involving adsorbed reactants and products at temperatures below about 200°C. for iron deposition and 175°C. for nickel, as indicated by a carbonyl concentration at the interface of more than 50% of the concentration in the inlet gas. The deposition kinetics were correlated over a three-order magnitude of rate, with a standard deviation of about 29% by rate expressions of the form (*40, 41*)

$$r_w = \frac{k_o k_a^m \, [\exp(E_o/RT)] \, [\exp(m \, E_a/RT)] \, [P_{ai}^m - (P_{ri}^x/K_{eq})^m]}{[1 + k_a P_{ai} \exp(E_a/RT) + k_r P_{ri} \exp(E_r/RT) + k_c P_{ci} \exp(E_c/RT)]^n} \quad (18)$$

where m has a value of about 1 for iron deposition and 2 for nickel deposition and n has a value of about 2 for both systems.

At temperatures above 200° for iron, 175° for nickel, and 750°C. for tungsten, the deposition rates were primarily limited by gas phase diffusion processes. It is this region which is of primary interest in this paper, and because of the volume and complexity of the experimental data the results are shown graphically and discussed in later sections. The transport characteristics in this diffusion region, and to some extent in the lower temperature, kinetic region, were determined by both forced and natural convection, and a suitable parameter to establish the transport level was obtained by vectorial combination on the Reynolds and Grashof numbers for the particular experimental system (*41*):

$$N_{Cf} = \sqrt{N_{Re}^2 + N_{Gr}} \quad (19)$$

Because of the extreme changes in density of the gas in the film, due to both reaction-induced composition changes and the temperature gradient, the Grashof number was calculated to account for both temperature and composition gradients in the system. The Reynolds number included the blockage term of Perkins and Leppert (*43*) to account for the reduction in effective area of the orifice caused by the presence of the filaments.

Handbook viscosities of hydrogen, argon, helium, carbon monoxide, and carbon dioxide (*44*) were used in the calculations, and the viscosities of the carbonyls, tungsten hexafluoride, and hydrogen fluoride were calculated by the method of Hirschfelder et al. (*45*) with the use of force constants estimated by the procedures recommended by Reid and Sherwood (*46*). At the temperatures of direct interest to this study, measurement of physical properties of the volatile metal compounds is impossible because of decomposition. Viscosities of the gas mixture were estimated from those of the pure components by the method of Bromley and Wilke (*47*). The binary diffusion coefficients were calculated from the force constants derived from the viscosity data as outlined by Hirschfelder et al. (*45*). For example, a typical mixture in the film containing 71 He, 10 $Fe(CO)_5$, and 19% CO at 155°C. and 1 atm. was calculated to have a mixture viscosity of 0.022 centipoise, and diffusion coefficients of 0.13, 1.3, and 0.55 sq. cm./sec. for the $Fe(CO)_5$–CO, CO–He, and $Fe(CO)_5$–He component pairs.

Conversion levels in experiments under mass transfer control varied from about 3 to 20%. Pressure levels were varied from 0.5 to 500 torr, mass flow rates from 3 to 250 g./(hr.) (sq.cm.) (based on total orifice area), Reynolds numbers from 2 to 220, and Grashof numbers from 1 to 1,600.* Bulk stream compositions were always based on an arithmetic average of inlet and outlet compositions. In the carbonyl systems, residual kinetic resistances and, hence interfacial compositions, were calculated from the previously established kinetic rate expressions, that is, specific solutions of Equation (18). The correction for kinetic resistances was negligible for most iron deposition experiments, but was 10 to 50% for the nickel carbonyl experiments. In the WF_6 system, the concentration of WF_6 at the deposition surface was assumed to be negligibly small. Film properties were calculated from the arithmetic average composition and temperature of the bulk stream and the interface.

Due to the deposition of metal, there was always a net radial mass flow of material toward the interface of up to about 6% of the total mass flow through the reactor. However, the volumetric radial flow was always away from the deposition surface due to the stoichiometry of the reactions studied. Under some conditions, this radial flow was as large as the total volumetric flow to the reactor. No attempt was made to measure simultaneous heat transfer during a mass transfer experiment, although the heat transfer characteristics of the system in the absence of mass transfer were reported previously (*40*).

---

* Tabular material has been deposited as document 9323 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington, D. C. 20025, and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

RESULTS

Binary Tranport Data

Binary transport data were obtained for both the nickel and iron deposition systems. These data include experiments in which the carbonyl vapor was fed into the reactor either pure or diluted with carbon monoxide. Figure 2 is a correlation of all these data in terms of the dependence of the modified Sherwood number divided by the Schmidt number to the one-third power as a function of the combined Reynolds and Grashof numbers of the system. The partial pressures of the deposition gases at the interfaces were calculated from the measured deposition rate and the kinetic equations previously established. Only those experiments in which the deposition rate was primarily diffusion controlled are included. The solid line represents the previously derived heat transfer function for cross-flow. The standard deviation of the data from the theoretical curve is about 14%.

In Figure 3 the data are correlated without the molecular weight correction of the Sherwood number. It is obvious that the nickel data do not correlate well with an equation derived from the iron data or vice versa. Likewise, neither the iron nor nickel data could be correlated by the Chilton-Colburn analogy with the modified McAdams heat transfer function used. This is strong evidence in confirmation of the fact that the ratio of molecular weight in the bulk stream to the molecular weight in the diffusion film should be included when the Sherwood number is used to correlate data based on the Chilton-Colburn analogy. The ability to correlate these binary results also indicates that nucleation resistance to metal deposition was not an important factor under the conditions studied.

Ternary Transport Data

Ternary transport data were obtained in the $Fe(CO)_5$–CO system with Ar, He, or CO_2 as nondiffusing diluents; in the $Ni(CO)_4$–CO system with Ar or He diluents; and in the H_2–WF_6–HF system. With the theory presented previously as background and the binary transport systems fully analyzed, the major problem associated with the ternary data was to estimate the diffusivity to be used in the Schmidt number. All other diffusivities in the diffusional relationships are binary diffusivities and are fixed by solution of the appropriate set of Stefan-Maxwell equations. The possible correlations were limited to those which could be used in more complex systems and to those which degenerated into a simple binary diffusivity as the amount of the third and higher numbered components approached zero. Of the many average diffusivities tested, the most appropriate method of averaging was based on the following definition:

$$D_f = \frac{\Pi_j (1 - w_j)}{\sum_{j \neq k} \frac{w_j w_k}{D_{jk}}} \qquad (20)$$

When this definition is used, the standard deviation of the data is 16%, only a trace higher than the 14% deviation of the binary data. Figure 4 presents the ternary transport data with the use of this correlation.

Quarternary Transport Data

Two four-component systems were tested to determine if the equations developed for the binary and ternary systems also apply to more complex systems. The data are presented in Figure 5. The agreement between the predicted and experimental deposition rates, as indicated by the line and the data points, is good. The two systems were $Fe(CO)_5$–CO–He–Ar and WF_6–HF–H_2–Ar. The

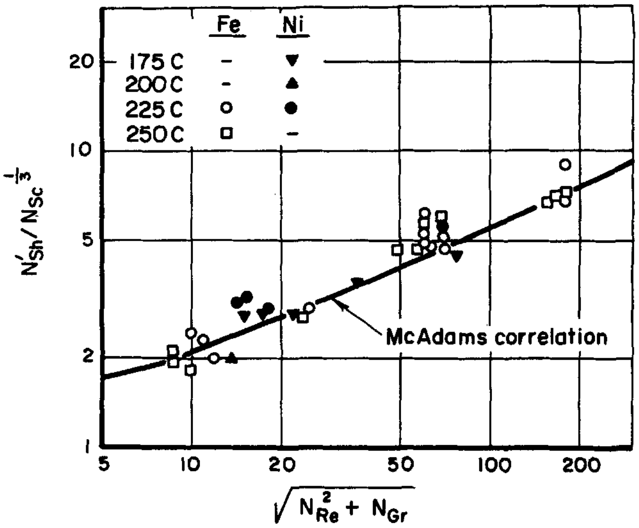


Fig. 2. Binary transport correlation with M_b/M_f correction.

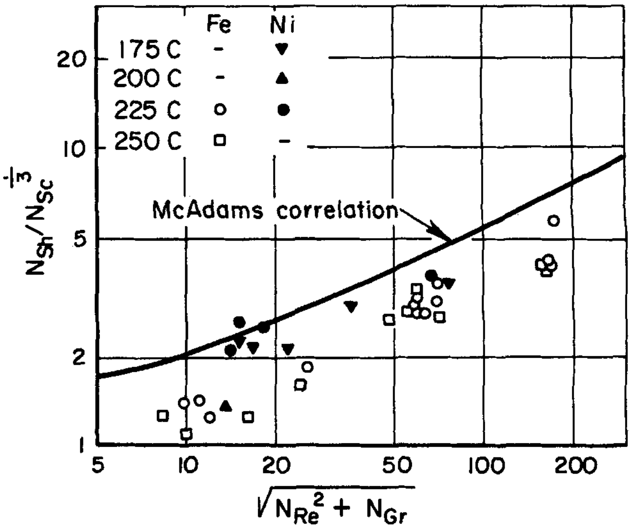


Fig. 3. Binary transport correlation without the M_b/M_f correction.

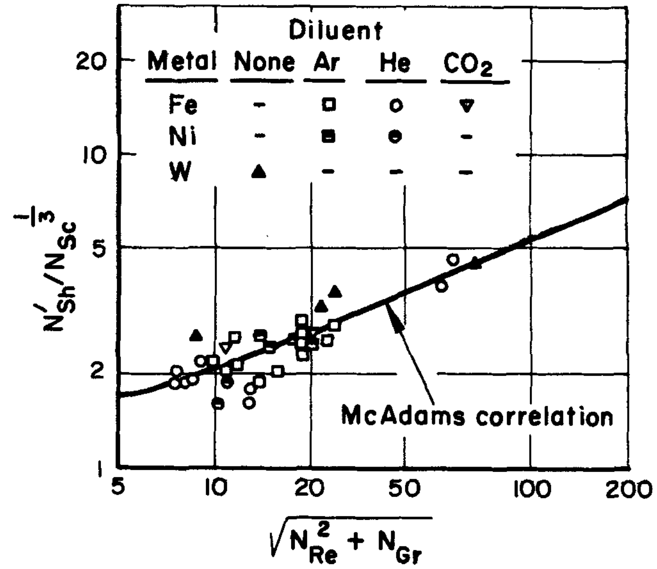


Fig. 4. Deposition rates in ternary transport systems.

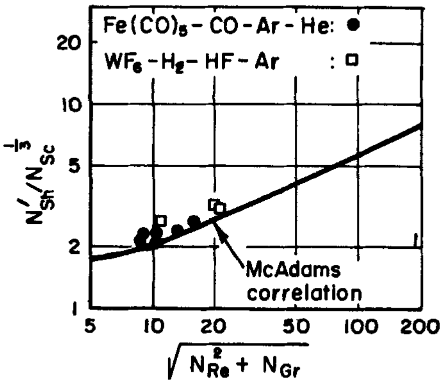


Fig. 5. Deposition rates in quarternary transport systems.

standard deviation of these data is 15%, essentially the same as the binary and ternary data.

General Correlation

As stated previously, if the Chilton-Colburn analogy is valid for multicomponent diffusing systems, the function which related $N'_{Sh}/N_{Sc}^{1/3}$ to a combined Reynolds and Grashof number for mass transfer must be the same as the function which relates $N_{Nu}/N_{Pr}^{1/3}$ to a combined Reynolds and Grashof number by heat transfer. All the experimental data in the diffusion-controlled region for the pyrolysis of $Fe(CO)_5$, including the pure feed cases and the additions of He, Ar, CO, CO_2, or He plus Ar; for the pyrolysis of $Ni(CO)_4$, both as an undiluted feed and with additions of CO, Ar, or He; and for H_2 reduction of WF_6, both with and without Ar additions are shown in Figure 6. The standard deviation of the experimental data around the heat transfer curve is about 16%, which is just a few percentage points higher than the estimated error involved in obtaining the experimental data. In addition, there does not appear to be any consistent deviation which could be corrected by using a different method for averaging diffusivity. It therefore appears that prediction of local mass transfer rates in multicomponent gas systems under forced or forced and natural convective conditions can now be made with a relatively high degree of confidence.

By use of the improved calculational procedures for diffusion rates developed in the present study, the pertinent data of Kesler (*39*) in the binary TiI_4–I system were now found to be about 60% of the predicted rates assuming complete conversion of iodide at the interface. Since in his iodide system there were undoubtedly some thermodynamic limitations and possibly some kinetic restraints on the reaction, the predicted value under conditions of full diffusion control would be expected to be significantly higher than the experimental rates. The previous inconsistency in the fact that the experimental data for the TiI_4–I system were higher than the predicted data therefore has now been resolved by the improved correlation procedures.

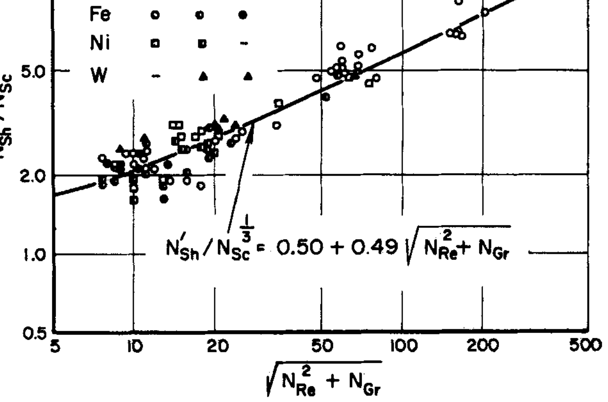


Fig. 6. Correlation of all mass transfer-limited data with modified McAdams' heat transfer function.

The difference between the present method of correlation and all others proposed to date for multicomponent systems is in the use of the complete set of Stefan-Maxwell equations to describe the fluxes and concentration gradients of all components. Although in many cases this necessitates the use of computing machinery, it obviates many severe objections which arise with the approximate methods. No singularities are present in the solution; imaginary values for a negative Schmidt number raised to a fractional exponent are avoided; the effective film thickness or boundary-layer resistance to diffusion is the same for each component in the mixture; the effective film thickness is relatively independent of the magnitude and presumably the direction of the individual fluxes; and there is no uncertainty in including a correction factor, such as film pressure, to a transfer coefficient.

CONCLUSIONS

1. A method of using the Chilton-Colburn analogy to obtain an effective film thickness over which the Stefan-Maxwell equations can be integrated in flow processes was established for a number of multicomponent gaseous systems in a differential system.
2. The use of a relatively unrecognized correction for molecular weight differences between the film and bulk stream was found important when the Chilton-Colburn analogy was used in establishing diffusion rates in many practical systems.
3. A method of establishing an average multicomponent diffusivity to be used in computing the Schmidt number was found to correlate satisfactorily the ternary and quaternary data.

ACKNOWLEDGMENT

The authors express their appreciation to the many companies that cooperatively sponsored the fundamental program on chemical vapor deposition at Battelle during 1962-64 for their financial support. We also wish to thank Dr. John M. Blocher, Jr., who encouraged and contributed to this work, and Mrs. Joan V. Bossenbroek for assistance in computer programming.

NOTATION

c_p = specific heat at constant pressure, cal./(g.) (°K.)
D_{jk} = diffusivity of mixture of j^{th} and k^{th} components, sq.cm./hr.
D_f = film diffusivity, sq.cm./hr.
d = filament diameter, cm.
E_j = adsorption energy, cal./g.-mole
E_o = activation energy, cal./g.-mole
G = mass flow rate, g./(sq.cm.) (hr.)
g = acceleration due to gravity, cm./hr.^{2}
h = heat transfer coefficient, cal./(sq.cm.) (°K.)
J_j = molar flux of j^{th} component, g.-mole/(sq.cm.)(hr.)
j_d = mass transfer factor
j_h = heat transfer factor
k = thermal conductivity, cal./(cm.) (hr.) (°K.)
K_{eq} = reaction equilibrium constant, torr^{x-1}
k_g = mass transfer coefficient, g.-mole/(sq.cm.) (hr.)

k_j = adsorption coefficient for j^{th} component, torr^{-1}
k_o = rate coefficient, g./(sq.cm.) (hr.)
M_j = molecular weight for j^{th} component, g./g.-mole
m = order of surface reaction
N_{Cf} = combined flow parameter $\sqrt{N^2{}_{Re} + N_{Gr}}$
N_{Gr} = Grashof number, $d^3g(\rho_f/\mu_f)^2(\rho_b - \rho_i)/\rho_b$
N_{Nu} = Nusselt number, dh/k_f
N_{Pr} = Prandtl number, $c_p\mu_f/k_f$
N_{Re} = Reynolds number, dG/μ_f
N_{Sc} = Schmidt number, $\mu_f/\rho_f D_f$
N_{Sh} = Sherwood number, $k_g dRT/D_f P$ or d/Z
N'_{Sh} = modified Sherwood number, $k_g dRTM_b/D_f PM_f$ or dM_b/ZM_f
m = reaction order
n = number of sites in surface reaction
P = total pressure, torr
P_{ji} = partial pressure at interface
R = gas constant, cal./(g.-mole) (°K.)
r_w = deposition rate, g./(sq.cm.) (hr.)
T = temperature, °K.
w_j = weight fraction of j^{th} component
x = moles of gaseous product per mole of reactant
y_j = mole fraction of j^{th} component
Z = film thickness, cm.
μ = gas viscosity, g./(cm.) (hr.)
ρ = gas density, g./cc.
Π = multiplication operator
Σ = summation operator

Subscripts

a = value for carbonyl
b = value in bulk stream
c = value for inert component
f = value in film
i = value at interface
j = value for j^{th} component
k = value for k^{th} component
r = value for carbon monoxide

LITERATURE CITED

1. Noyes, A. A., and W. R. Whitney, *Z. Phys. Chem.*, **23**, 689 (1897).
2. Nernst, W., *ibid.*, **47**, 52 (1904).
3. Lewis, W. K., and K. G. Chang, *Trans. Am. Inst. Chem. Engrs.*, **21**, 127 (1928).
4. Whitman, W. G., *Chem. Met. Engr.*, **29**, No. 4, 146 (1923).
5. Fischbeck, K., *Z. Elektrochem. Soc.*, **39**, 316 (1933); **40**, 517 (1934).
6. Tu, C. M., H. Davis, and H. C. Hottel, *Ind. Eng. Chem.*, **26**, 749 (1934).
7. Bischoff, K. B., and G. F. Froment, *Ind. Eng. Chem. Fundamentals*, **1**, 195 (1962).
8. Higbie, Ralph, *Trans. A.I.Ch.E. J.*, 31, 365 (1935).
9. Danckwerts, P. V., *Ind. Eng. Chem.*, **43**, 1460 (1951); *A.I.Ch.E. J.*, **1**, 456 (1955).
10. Hanratty, T. J., *A.I.Ch.E. J.*, **2**, 359 (1956).
11. Harriott, Peter, *Chem. Eng. Sci.*, **17**, 149 (1962).
12. Toor, H. L., and J. M. Marchello, *A.I.Ch.E. J.*, **4**, 97 (1958); *Ind. Eng. Chem. Fundamentals*, **2**, No. 1, 8 (1963).
13. Sherwood, T. K., and J. M. Ryan, *Chem. Eng. Sci.*, **11**, 81 (1959).
14. Vieth, W. R., J. H. Porter, and T. K. Sherwood, *Ind. Eng. Chem. Fundamentals*, **2**, 1 (1963).
15. Sherwood, T. K., comments added in review.
16. ———, *Chem. Eng. Progr. Symp. Ser. No. 25*, **55**, 71 (1959).
17. Ackerman, G., *Forschungsheft*, **382**, 1 (1937).
18. Mickley, H. S., R. C. Ross, A. L. Squyers, and W. E. Stewart, *Natl. Advisory Comm. Aeronaut. Tech. Note 3208* (1954).
19. Bedingfield, C. H., Jr., and T. B. Drew, *Ind. Eng. Chem.*, **42**, 1164 (1950).
20. Heinrich, W., *Chem. Ing. Tech.*, **36**, 269 (1964).
21. Chilton, T. H., and A. P. Colburn, *Ind. Eng. Chem.*, **26**, 1183 (1934).
22. Maxwell, J. C., "Scientific Papers," Cambridge Univ. Press, Cambridge (1890).
23. Stefan, S., *Sitz. Akad. Wiss. Wien*, **63**, (II), 63 (1871); **65**, (II), 323 (1872); **68** (II), 385 (1874).
24. Sherwood, T. K., "Adsorption and Extraction," 1 ed., McGraw-Hill, New York (1937).
25. Hoopes, J. W., Ph.D. thesis, Columbia Univ., New York (1951).
26. Benedict, M., and A. Boas, *Chem. Eng. Progr.*, **47**, 51 (1951).
27. Cichelli, M. T., W. D. Weatherford, Jr., and J. R. Bowman, *ibid.*, **47**, 63, (1951).
28. Keyes, J. J., Jr., and R. L. Pigford, *Chem. Eng. Sci.*, **6**, 215 (1957).
29. Toor, H. L., *A.I.Ch.E. J.*, **3**, 198 (1957).
30. Heubner, G. W., M.S. thesis, Univ. Wisconsin, Madison (1957).
31. Hsu, Hsien-Wen, and R. B. Bird, *A.I.Ch.E. J.*, **6**, 516 (1960).
32. Hougen, O. A., and K. M. Watson, "Chemical Process Principals," 1 ed., Pt. III, pp. 975-979, Wiley, New York (1947).
33. Wilke, C. R., *Chem. Eng. Progr.*, **46**, No. 2, 95 (1950).
34. Stewart, W. E., *A.I.Ch.E. J.*, **9**, 528 (1963).
35. Shain, S. A., *ibid.*, **7**, 17 (1961).
36. Sherwood, T. K., and R. L. Pigford, "Adsorption and Extraction," McGraw-Hill, New York (1952).
37. McAdams, W. H., "Heat Transmission,' 3 ed., McGraw-Hill, New York (1954).
38. Toor, H. L., and R. T. Sebulsky, *A.I.Ch.E. J.*, **7**, No. 4, 558 (1961).
39. Kesler, G. H., *Trans. Met. Soc. A.I.M.E.*, **218**, 197 (1960).
40. Carlton, H. E., and J. H. Oxley, *A.I.Ch.E. J.*, **11**, No. 1, 79 (1965).
41. *Ibid.*, **13**, No. 1, 86 (1967).
42. Oxley, J. H., E. A. Beidler, J. M. Blocher, Jr., C. J. Lyons, R. S. Park, and J. H. Pearson, in "Proceedings 5th Plansee Seminar," F. Benesovsky, ed., Reutte/Tyrol, Austria (1964).
43. Perkins, H. C., Jr., and G. Leppert, *Trans. Am. Soc. Mech. Engrs.*, **84C**, 257 (1962).
44. Hodgman, C. D., "Handbook of Chemistry and Physics," 41 ed., pp. 2188-2191, Chemical Rubber Publishing Co., Cleveland (1959-60).
45. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York (1954).
46. Reid, R. C., and T. K. Sherwood, "The Properties of Gases and Liquids," McGraw-Hill, New York (1958).
47. Bromley, L. A., and C. R. Wilke, *Ind. Eng. Chem.*, **43**, 1641 (1951).
48. Ralston, A., and H. S. Wilfe, "Mathematical Methods for Digital Computers," Wiley, New York (1960).

APPENDIX A

Any system of linear, simultaneous, first-order differential equations, such as the Stefan-Maxwell equations, can be solved numerically by computing machinery if all the parameters at one boundary are known and the parameters at the other boundary are required. A FORTRAN solution of this problem by the Runge-Kutta-Gill method (48) was therefore developed for the general multicomponent case. The values of the geometric parameters, the physical properties of the gases, the stoichiometry of the reaction, constants used in computing diffusivities, and the values of the independent variables in the deposition reaction are read into the computer at the beginning of the problem and immediately printed out for future reference and for proofreading. The various parameters and intermediate terms which are not dependent upon composition are calculated before the iterative steps. An initial estimate of the interfacial composition for the first iteration is then assumed to be the composition of the outlet gas based on 100% conversion. Each time a set of positive interfacial compositions is determined by solution of the Stefan-Maxwell equations, the estimate of interfacial composition is reset to the newest value.

The deposition conversion is estimated as the average of the lowest and highest possible conversions which, on the first time through the program, are 0 and 100%. For each iteration, the program determines if the previous conversion estimate is too high or too low by solving both the kinetic and diffusion equations, resets either the highest or lowest possible conversion to the new estimated value, and then reaverages. The conversion is soon found with a high degree of accuracy. For each conversion estimate, the bulk stream, interfacial and film compositions, and the physical properties of the bulk stream and film are recomputed.

From these values and the flow rate, the thickness of the diffusion barrier is calculated. The interfacial compositions are then determined from the Stefan-Maxwell equations. Since initially the film composition was estimated, an iterative procedure was used where the results of the previous iteration were used as the estimated interfacial composition for the next iteration. When two successive iterations agree, this set of interfacial compositions is used to calculate the deposition rate from the kinetic equations for the particular system. If this kinetic rate agrees with the rate calculated from the estimated deposition conversion, the program is completed and the interfacial compositions, conversions, etc., are printed out. If there is poor agreement, the deposition conversion is estimated again to give better agreement, and the iterative procedures repeated.

If the kinetic expression is unknown and the deposition rate is known to be diffusion controlled, such as with the tungsten–hexafluoride-hydrogen system, the test for high or low deposition rate can be a sign test on interfacial compositions. For all positive values of film composition, the deposition conversion is obviously too low, while a negative value for the concentration of any component indicates the conversion is too high. In estimating rates in systems where no experimental kinetic data are available, thermodynamic equilibria have also been employed to test if efficiency was either too high or too low.

Manuscript received June 20, 1966; revision received October 3, 1966; paper accepted October 4, 1966. Paper presented at A.I.Ch.E. Detroit meeting.

An Experimental Study of Nonequimolal Diffusion in Ternary Gas Mixtures

R. W. GETZINGER and C. R. WILKE

University of California, Berkeley, California

This work is an experimental test of the Stefan-Maxwell equations as applied to cocurrent, steady state gaseous diffusion of two species through a stagnant third component. The Stefan capillary tube method was used to measure the diffusion rates. The use of constant evaporating binary liquid mixtures made possible boundary conditions that were invariant with time. Total molar losses were compared with the predictions of the theory to demonstrate the validity of the equations under conditions of a significant convective flux.

This paper describes experimental measurements of diffusion rates in three ternary gas systems in which two gases are simultaneously diffusing through a third species. The results are used to check the validity of the Stefan-Maxwell equations under these conditions.

The Stefan-Maxwell equations describe in differential form diffusion in isothermal, isobaric ideal gas mixtures (*1* to *4*). Whereas the number of cases for which these equations have been solved is limited to a few restrictive situations in ternary systems (*5* to *10*), even fewer actual experimental tests of the validity of the solutions are available (*6*, *9* to *11*). Thus although the recent extensive work of Duncan and Toor with ternary equimolal countercurrent diffusion (*11*) does offer very convincing proof of the applicability of the Stefan-Maxwell equations in real gas systems, we wish to present further evidence of this fact from a study of cocurrent diffusion of two gases through a stagnant third species.

Cocurrent diffusion of one or more gaseous species through an additional stagnant gas can be easily studied by application of the Stefan capillary tube method of measuring diffusion coefficients (*12*). In the present work this technique was utilized to study diffusion in both binary and ternary systems at 35.0°C. involving the organic compounds methyl alcohol, ethyl alcohol, chloroform, carbon tetrachloride, and benzene, and an invariant stagnant gas, air. Since both the theoretical and experimental aspects of the capillary tube method have been discussed in detail for binary systems by Lee and Wilke (*12*), only the unique features of the present work will be described here.

EXPERIMENTAL CONSIDERATIONS

A schematic diagram of the apparatus used here appears in Figure 1 and a drawing of the diffusion unit itself is

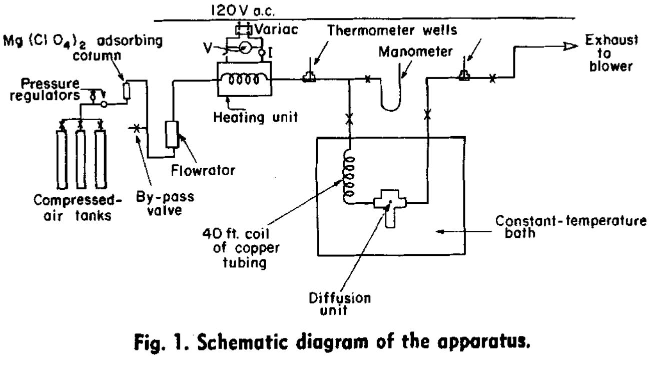


Fig. 1. Schematic diagram of the apparatus.

R. W. Getzinger is with Los Alamos Scientific Laboratory, Los Alamos, New Mexico.