(ϕ in Thomas' notation)

$$e^{Y+Z}(T_1 - T_2) = I_0(2\sqrt{YZ})$$

$$e^{Y+Z}T_2 = e^Z \int_0^Z e^{-u} I_0 \; (2\sqrt{Yu}) \, du = \phi(Z, Y)$$

Some well-known relations in the field (see Thomas) can now be easily proved (by stepping left or down in the diagram) or memorized:

1. e^{Y+Z} = sum of three component parts.

2. $$\frac{\partial \phi(Y, Z)}{\partial Y} = \phi(Y, Z) + I_0(2\sqrt{YZ}).$$

By differentiating the terms of the upper part of the table with respect to Y one gets back those same terms plus those along the diagonal.

3. $$\frac{\partial \phi(Y, Z)}{\partial Z} = \phi(Y, Z) - \frac{\partial I_0(2\sqrt{YZ})}{\partial Z}.$$

4. Similar equations for derivatives of $\phi(Z, Y)$.

5. Limiting cases of $\phi(Y, Z)$ and $\phi(Z, Y)$ for both $Y = 0$ and $Z = 0$.

For numerical use the series expansions are inconvenient because of slow convergence. However since they converge for all Y and Z, they remain suited for mathematical proofs of the above kind.

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A Correlation Between Single Fiber Efficiencies of Fibrous Filters and Operating Variables

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Industrially as well as in laboratories fibrous filters are extensively used for the collection of aerosol particles. Packed beds of glass fibers in particular are being applied to the removal of air-borne microbes in the fermentation industry. For a successful design and maintenance of fibrous filters both values of pressure drop and collection efficiency have to be predicted under any operating condition in practice.

The procedure of calculating the pressure drop of air flow through fibrous beds has been well established (*5*). The effects of various factors, particle size, fiber diameter, air velocity, and so forth, on the collection efficiencies of fibrous filters have also been studied experimentally and theoretically (*1, 2, 4, 6, 7, 8, 9, 10, 11, 12, 13*). However all of the experimental data ever reported on this latter subject remain to be reviewed before reasonable calculations on the collection efficiencies can be made. This situation should have emerged from the fact that the collection efficiencies of fibrous filters are affected not only by the above-mentioned factors but also by the physicochemical interactions which are expected to exist between fibers and particles concerned and which are left open for further discussion and experimentation.

An approach attempted in this paper to correlate between single fiber efficiencies of fibrous beds and operating variables will eventually be of help in clarifying the degree of divergences of data points which have been reported so far and in pointing out a possibility of the existence of other mechanisms, if any, than the inertial impaction, interception, and diffusion of aerosol particles.

If fibrous filters are applied to the removal of air-borne contaminants, for instance bacteria, viruses and so on, they are usually operated satisfying certain conditions under which the deposition of particles due to their inertial impactions are kept minimum. The sizes of bacteria and viruses in question are in a range from about 0.5 to 3.0 μ and from 40 to 80 mμ, respectively. Therefore the following discussions which are exclusively concerned with the interception and diffusion of aerosol particles are not prohibitive in terms of generalization and practical application.

SEMITHEORETICAL CORRELATION BETWEEN SINGLE FIBER EFFICIENCIES AND OPERATING VARIABLES

In accordance with Langmuir (*2*) a critical value ψ_c of the inertial parameter ψ, below which the deposition of aerosol particles due to their inertial impactions in a single and isolated cylindrical fiber cannot be expected, is as follows:

$$\psi = \psi_c = 1/16 = \frac{C \cdot \rho_p \cdot d_p^2 \cdot v_c}{18 \, \mu d_f} \tag{1}$$

From Equation (1)

$$v_c = (1.125) \frac{\mu \cdot d_f}{C \cdot \rho_p \cdot d_p^2} \tag{2}$$

A region, in which the linear velocity of air does not exceed v_c expressed by Equation (2), will be considered tentatively in this paper. Because Equation (2) is based on a potential (nonviscous) flow around cylinders, the real critical velocity may differ from that given by Equation (2) owing to the filtration practice which is usually carried out in the laminar or near laminar region. The determination of the critical velocity is up to pertinent experiments, at any rate (Figure 1).

Also in accordance with Langmuir (*2*) the collection efficiencies η_o'' and η_o''' for an isolated cylindrical fiber due to the interception and diffusion of spherical particles are given by Equations (3) and (4), respectively:

$$\eta_o'' = \frac{1}{2[2.00 - \ln N_{Re}]} \left[2(1 + N_R) \ln (1 + N_R) - (1 + N_R) + \frac{1}{1 + N_R} \right] \tag{3}$$

where

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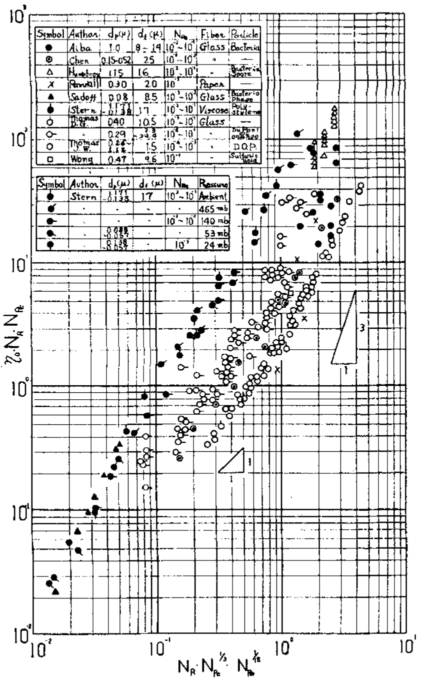

Fig. 1.

$$N_{Re} = \frac{d_f\, v\, \rho}{\mu}$$

$$N_R = \frac{d_p}{d_f}$$

$$\eta_o''' = \frac{1}{2[2.00 - \ln N_{Re}]} \left[2\left(1 + \frac{2x_o}{d_f}\right) \ln\left(1 + \frac{2x_o}{d_f}\right) - \left(1 + \frac{2x_o}{d_f}\right) + \frac{1}{1 + \frac{2x_o}{d_f}} \right] \tag{4}$$

where

$$\frac{2x_o}{d_f} = \left[1.12 \times \frac{2(2.00 - \ln N_{Re}) D_{BM}}{v \cdot d_f} \right]^{1/3}$$

$$D_{BM} = \frac{C \cdot k \cdot T}{3\pi\mu d_p}$$

In reproducing Equations (3) and (4) an assumption was made that the linear velocity v of air is equal to the upstream velocity v_o. An approximation for values of N_{Re} extending from 10^{-4} to 10^{-1} was made as follows:

$$\frac{1}{2.00 - \ln N_{Re}} \propto N_{Re}^{1/6} \tag{5}$$

Both terms of N_R and $2x_o/d_f$ in the brackets of Equations (3) and (4) were expanded on the assumption that both values were small enough compared with unity so that second and higher orders of each term could be neglected. Therefore

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INFORMATION RETRIEVAL

Key Words: Heat Transfer Coefficient-7, Condensation-8, Immiscible Liquids-8, Water-5, **n**-Heptane-5, Methanol-5, Carbon Tetrachloride-5, Benzene-6, Temperature Difference-6, Composition-6, Condenser-10.

Abstract: Heat transfer coefficients for condensing vapors of the immiscible systems benzene-water, **n**-heptane-water, carbon tetrachloride-water, and methanol-heptane have been measured on a short vertical surface. Three types of condensation were noted: film drop, film lens, and channeling. An explanation based on the concept of the spreading coefficient is proposed for these phenomena, and correlations based on modifications of Nusselt's equation are made for the different mechanisms.

Reference: Akers, W. W., and M. M. Turner, **A.I.Ch.E. Journal, 8,** No. 5, p. 587 (November, 1962).

Key Words: Sublimation-8, Evaporation-8, Evaporation Coefficient-9,7, Vapor Pressure-6,7, Vacuum-5, Naphthalene-1, Biphenyl-1, Camphor-1, Thymol-1, Hexadecanol-1, Bolometer-10, Surface Temperature-6, Temperature-6.

Abstract: Rates of sublimation of five solids were measured at very low pressures. Evaporation coefficients at 0°C. ranged from 0.14 for thymol to 1.0 for hexadecanol. The unique feature of the work was the use of a thermistor bolometer to measure the temperature of the evaporating surface, so avoiding the possibility of errors by the use of thermocouples, which have led some writers to question the validity of all reported evaporation coefficients less than unity.

Reference: Sherwood, Thomas K., and Conrad Johannes, **A.I.Ch.E. Journal, 8,** No. 5, p. 590 (November, 1962).

Key Words: A. Dynamics-8, Process Dynamics-8, Mathematical Model-8, Transfer Functions-8, Frequency Response-8, Transient Response-8, Laplace Transform-10, Input Function-1, Forcing Function-1, Output Function-2, Response Function-2, Inlet Temperature-1, Outlet Temperature-2, Heat Exchangers-10, Boilers-10, Condensers-10, Heaters-10, Lumped System-, Distributed System-, Parallel-, Counter-, Parallel-Counter, Counter-Parallel-.

Reference: Hsu, James P., and Nathan Gilbert, **A.I.Ch.E. Journal, 8,** No. 5, p. 593 (November, 1962).

Key Words: Fluid Flow-8, Velocity-7, Mass Flow-7, Pressure Drop-7, Opening Angle-6, Viscosity-6, Duct Size-6, Triangular Duct-5.

Abstract: The characteristics of fully-developed laminar flow in ducts of isosceles triangular cross section have been determined by analysis for a wide range of duct-opening angles. Numerical results are reported for the friction factor, velocity distribution, and local wall shear stress. The friction-factor predictions agree very well with experiment. It is also found that the friction factor-Reynolds number product varies only slightly with duct-opening angle, but its numerical value is different from that of a circular tube.

Reference: Sparrow, E. M., **A.I.Ch.E. Journal, 8,** No. 5, p. 599 (November, 1962).

Key Words: Thermodynamics-8, Phase Equilibria-8, Vapor-Liquid Equilibria-8, Phases-8, Equilibrium-8, Binary-8, Correlations-8, Vapor Pressure-9, Critical Pressure-9, Critical Temperature-9, Solutions (Mixtures)-9, Mixtures-9, Ethane-1, Heptane-1, Butane-1, Hydrocarbons-1, Boiling Point-6, Temperature-6, Pressure-6, Compositions-7.

Abstract: A series of reduced state correlations for the prediction of equilibrium constants for the components of binary hydrocarbon systems have been developed with experimental data reported in the literature for the ethane—**n**-heptane, ethane—**n**-butane, and **n**-butane—**n**-heptane systems. Each correlation applies for a specific value of the ratio of the normal boiling points of the two components. The correlations involve the reduced vapor pressure of the pure substance, the pseudo vapor pressure of the substance in the mixture, the critical pressure of the mixture, and the reduced temperature. The reliability of the proposed method is tested with a number of binary systems.

Reference: Mehra, Vinod S., and George Thodos, **A.I.Ch.E. Journal, 8,** No. 5, p. 604 (November, 1962).

(Continued on page 707)

$$\eta_o'' \propto N_R^2 \cdot N_{Re}^{1/6} \qquad (6)$$

$$\eta_o''' \propto N_{Sc}^{-2/3} N_{Re}^{-11/18} \qquad (7)$$

It was postulated that

$$\eta_o = \eta_o'' + \eta_o''' \qquad (8)$$

When one multiplies both sides of Equations (6) and (7) by $N_R \cdot N_{Pe}$, they could be modified to Equations (9) and (10) respectively:

$$\eta_o'' \cdot N_R \cdot N_{Pe} \propto (N_R \cdot N_{Pe}^{1/3} N_{Re}^{1/18})^3 \qquad (9)$$

$$\eta_o''' \cdot N_R \cdot N_{Pe} \propto N_R \cdot N_{Pe}^{1/3} N_{Re}^{1/18} \qquad (10)$$

PROCEDURE AND RESULT OF THE CORRELATION

With reference to Equation (2) data concerning $\bar{\eta}$ (overall collection efficiency) which corresponds presumably to interception and diffusion mechanisms were selected out of the papers thus far presented. In the calculation with Equation (2) C was determined by using Equations (11) and (12), while μ of air was assumed to be that at room temperature (20° to 25°C.):

$$C = 1 + 2(\lambda/d_p)\,[1.23 + 0.41 \exp(-0.44\, d_p/\lambda)] \qquad (0.05 < \lambda/d_p < 67) \quad (14) \qquad (11)$$

where

$$\lambda = \text{mean free path of gas molecule} = \frac{3\mu}{\rho}\sqrt{\frac{\pi M}{8RT}} \qquad (12)$$

The values of density ρ_p (ranging from 1.0 to 1.4 g./cc.) were taken from each of relevant original papers. At the same time the Pèclet number $\dfrac{v\, d_f}{D_{BM}}$ and the Reynolds number $\dfrac{d_f v \rho}{\mu}$ were evaluated in accordance with each experimental condition described by respective authors.

This selection of $\bar{\eta}$ was followed by the determination of η_o (collection efficiency of an isolated cylindrical fiber) with Equations (13) and (14):

$$\eta_a = \frac{\pi d_f (1-\alpha)}{4\, L\, \alpha} \ln\left(\frac{1}{1-\bar{\eta}}\right) \qquad (13)$$

$$\eta_o = \frac{\eta_a}{1. + 4.5\alpha} \qquad (14)$$

$$(0 < \alpha < 0.1) \quad (2)$$

Equation (13) is considered to be reasonable because all of the data for the following consideration were obtained with fibrous filters relatively thin in bed thickness ($L \leq 4$ cm).

TABLE 1. MINIMUM COLLECTION EFFICIENCY (20°C. AND ATMOSPHERIC PRESSURE)

d_f	v_s	d_{pc}	$N_R \cdot N_{Pe}^{1/3} N_{Re}^{1/18}$
1.5×10^{-4} cm.	0.94 cm./sec.	0.50×10^{-4} cm.	1.34
1.5×10^{-4} cm.	0.42 cm./sec.	0.54×10^{-4} cm.	1.14
1.5×10^{-4} cm.	0.21 cm./sec.	0.58×10^{-4} cm.	0.96
1.5×10^{-4} cm.	0.094 cm./sec.	0.68×10^{-4} cm.	0.87

Sadoff et al. (*8*) reported that η_o increased contrary to the decrease of α, being incompatible with Equation (14). For convenience the data of η_a pertaining to the lower limit of α employed in the experiment of Sadoff et al. ($\alpha = 0.0174$) were assumed to represent those of η_o. It was rather difficult to select $\bar{\eta}$ out of the paper presented by Wong et al. (*13*) satisfying the condition formulated in Equation (2). Accordingly the determination of η_o in this case was made by carrying out some trial-and-error calculations with the result that one data point ($N_R < 0.125, \psi < 1/16$) was selected.

The plot thus obtained for $\eta_o \cdot N_R N_{Pe}$ against $N_R \cdot N_{Pe}^{1/3} N_{Re}^{1/18}$ is shown in Figure 1. All of the data points in the figure, unless otherwise noted, have been secured at room temperature and atmospheric pressure.

DISCUSSION

If a curve may be drawn through the data points given in Figure 1, it is inclined towards the abscissa to the extent of unity and three at lower and higher values of $N_R \cdot N_{Pe}^{1/3} N_{Re}^{1/18}$ respectively. Such a change of inclination is represented by Equations (9) and (10), which imply that at higher values of $N_R \cdot N_{Pe}^{1/3} N_{Re}^{1/18}$ the collection of aerosol particles is predominantly due to interception, while at lower values of $N_R \cdot N_{Pe}^{1/3} N_{Re}^{1/18}$ the collection due to diffusion is controlling.

Although the data points of each worker are scattered within ± 10 to ± 20%, the fact that the data points deviate considerably from case to case in the figure might be attributed to the differences in physicochemical properties of aerosol particles as well as fibrous beds employed in each experiment. Moreover a possibility that the collection mechanisms other than the diffusion, for instance electrostatic force exerted between aerosol particles and specific fibers, could not be neglected in the case of extremely fine particles.

The correlation shown in Figure 1 is similar to that reported by Friedlander who plotted the term $N_R \cdot N_{Pe}^{1/3} N_{Re}^{1/6}$ on the abscissa of the figure (*3*). The scattering and deviation of the data points were recognized to be of the same order of magnitude as those in Figure 1, even if the procedure proposed by Friedlander was employed.

It is seen from Equations (6) and (7) that the effects of d_p on η_o'' and η_o''' are reversed. Consequently a certain value of d_p ($= d_{pc}$) which reduces η_o to a minimum is expected to be found as exemplified below. Thomas et al. (*11*) and other workers (*9, 12*) pointed out experimentally to the same effect, for example, as shown in Table 1 (*11*). The last column in the table was calculated by the procedure mentioned earlier.

Pasceri and Friedlander have already published their paper, in which the minimum collection efficiencies were calculated and compared with experimental data (*6*). The calculation shown in Table 1 differs from the paper presented by Pasceri et al. in that the minimum efficiencies were estimated solely from the dimensionless groups.

Since the minimum collection efficiency which is defined above is expected to be observed within an intermediate region between diffusion controlling and interception predominating referring to the collection mechanisms of aerosol particles, the value, around 1 of the abscissa in Figure 1, corresponds roughly to the transient region in this specific example presented by Thomas et al. (*11*) (Figure 1). With regard to other cases shown in the figure the regions in question were not located successfully because of the lack of pertinent data.

NOTATION

C = Cunningham's correction factor
d_f = fiber diameter, (μ)
d_p = particle diameter, (μ)
d_{pc} = particle diameter corresponding to minimum collection efficiency, (μ)
D_{BM} = diffusivity of particles, (sq. cm./sec.)
k = Boltzmann constant, (1.38×10^{-16} sq. cm. deg.$^{-1}$ g./sec.^{2})
L = bed thickness, (cm.)
M = molecular weight of gas, (air)
N_{Pe} = Pèclet number, ($vd_f/D_{BM} = N_{Sc} \cdot N_{Re}$)
N_R = interception parameter, (d_p/d_f)

N_{Re} = Reynolds number, $(d_f v \rho/\mu)$
N_{Sc} = Schmidt number, $(\mu/\rho D_{BM})$
R = gas constant, (0.08205 liter atm./deg. mole)
T = absolute temperature, (°K.)
v = linear velocity of air, $(= v_s/\epsilon$, cm./sec.)
v_s = nominal velocity of air through fibrous bed, (cm./sec.)
v_c = critical velocity of air defined by Equation (2), (cm./sec.)
v_o = upstream air velocity for isolated cylindrical fiber, (cm./sec.)
x_o = distance from isolated cylindrical fiber, aerosol particles within x_o can be collected owing to diffusion

Greek letters

α = volume fraction of fiber
ϵ = porosity of filter bed, $(= 1 - \alpha)$
η_o = collection efficiency of isolated cylindrical fiber $(= \eta_o'' + \eta_o''')$
η_o'' = collection efficiency of isolated cylindrical fiber due to interception
η_o''' = collection efficiency of isolated cylindrical fiber due to diffusion
η_α = collection efficiency of fiber in filter bed, volume fraction of which is α
$\bar{\eta}$ = overall collection efficiency of filter
λ = mean free path of gas molecule, (cm.)
μ = viscosity of air, (g./cm. sec.)
ρ = density of air, (g./cc.)
ρ_p = density of particle, (g./cc.)
ψ = inertial parameter
ψ_c = critical value of ψ

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INFORMATION RETRIEVAL

Key Words: Estimating-8, Predicting-8, Mass Transfer-8, Heat Transfer-8, Fluid Flow-8, Rates-8, Spheres-9, Beds-9, Fluidized-, Packed-, Reynolds Number-6, j-Factor-7, Correlations-10, Analogies-10.

Abstract: Mass and heat transfer data available in the literature for the flow of gases and liquids through all types of beds of spheres have been critically reviewed and found to produce unique relationships between the Reynolds number and a modified j-factor. The resulting heat and mass transfer relationships have been established for packed, extended, distended, and fluidized beds of spheres and are applicable for Reynolds number > 1. The relationships extend to include the limiting case of flow past a single sphere.

Reference: Gupta, A. S., and George Thodos, **A.I.Ch.E. Journal, 8,** No. 5, p. 608 (November, 1962).

Key Words: Thermal Conductivity-8, Properties (Characteristics)-8, Physical Properties-8, Estimating-8, Predicting-8, Mixtures-9, Polymers-9, Elastomers-9, Liquids-9, Temperature-6, Molecular Weight-6, Van der Waals Constants-6, Thermal Conductivity-7.

Abstract: A method is proposed to estimate the thermal conductivity of nonassociating liquids, their mixtures, and polymer melts including elastomers over a wide temperature range. The only information required is molecular weight, van der Waals dimensions, standard energy of vaporization group increments, and for flexible molecules the number of external degrees of freedom. Tables for the last two items are included.

Reference: Bondi, A. A., **A.I.Ch.E. Journal, 8,** No. 5, p. 610 (November, 1962).

Key Words: Natrosol-9, Hydroxyethyl Cellulose-9, Pseudoplastic Fluid-9, Non-Newtonian Fluid-9, Turbine Impellers-10, Baffles-10, Agitation-8, Mixing-8, Blending-8, Apparent Viscosity-6, Power Input-7, Vortex-6, Blend Time-7.

Abstract: Pseudoplastic aqueous solutions of Natrosol (hydroxyethyl cellulose) were agitated with turbine impellers. Despite nonconstant flow behavior indexes the power input was predictable from correlations for pseudoplastics with constant indexes. Blend times, observed visually by indicator color change during neutralization reaction, varied with acid-to-base ratio and were ten to fifty times greater than with Newtonian fluids of the same apparent viscosity. Insertion of radial baffles lengthened blend times. Blend times were shortest when a vortex formed and varied inversely with the square root of the vortex depth.

Reference: Godleski, E. S., and J. C. Smith, **A.I.Ch.E. Journal, 8,** No. 5, p. 617 (November, 1962).

Key Words: A. Reaction-8, Kinetics-8, Heterogeneous-5, Ethanol-1, Ethyl Ether-2, Dehydration-8, Catalyst-4, Ion Exchange Resin-4, Dowex 50-4, Vapor Phase-5. B. Adsorption-8, Langmuir-, Isotherms-9, Ethanol-1, Water-2, Ethyl Ether-2, Constants-, Ion Exchange Resin-5, Dowex 50-5. C. Kinetic-2, Adsorption-8, Constants-9, Comparison-. D. Dehydration-8, Dual Site-, Ethanol-10, Adsorption-10.

Abstract: Equilibrium adsorption constants for the vapor-phase dehydration of ethanol to ethyl ether have been determined directly from static adsorption measurements and from correlation of reaction kinetic data with the Langmuir-Hinshelwood model of heterogeneous catalysis. A packed bed reactor was used with ion exchange resin as catalyst. Order of magnitude agreement of the constants determined by these two independent approaches is considered to be evidence favoring validity of this model for this system. Additional interpretation of the adsorption and kinetic data via this model suggests that the deyhdration may proceed through the reaction of adjacently adsorbed ethanol molecules.

Reference: Kabel, Robert L., and Lennart N. Johansen, **A.I.Ch.E. Journal, 8,** No. 5, p. 621 (November, 1962).

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Applicability of the Stefan-Maxwell Equations to Multicomponent Diffusion in Liquids

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Up to the present time there are few reliable data (*1* to *7*) for multicomponent diffusion in liquids and almost no methods for predicting the diffusional behavior of such systems. This would then appear to be a good time to determine what useful information can be obtained from available flux equations and through use of analogies with the comparatively well-understood behavior of binary liquids and multicomponent gases. It is shown below that a generalized form of the Stefan-Maxwell equations may be useful, both as a guide in planning experimental studies and as a first approximation for predicting the diffusional behavior of multicomponent condensed systems.

The authors begin their discussion with a set of flux equations (*8*) compatible with the principles of irreversible thermodynamics. Restricting oneself to isothermal systems one may write

$$\mathbf{j}_i = -\sum_{j=1}^{n}\left(\frac{\alpha_{ij}}{c_j M_j}\right)\mathbf{d}_j \qquad \begin{pmatrix} n \text{ components} \\ \text{constant } T \end{pmatrix} \quad (1)$$

$$\mathbf{d}_j = c_j\sum_{i=1}^{n}\left(\frac{\partial \mu_j}{\partial c_i}\right)_{T,P,c_k}\nabla c_i + c_j\left(\tilde{V}_j - \frac{M_j}{\rho}\right) - c_j M_j\left(\mathbf{g}_j - \frac{1}{\rho}\sum_{j=1}^{n}\rho_i\,\mathbf{g}_i\right) \quad (2)$$

Here $\mathbf{j}_i$ is the mass diffusion flux of component *i*, that is the mass flux of *i* with respect to the mass-average velocity **v**, and the $\mathbf{d}_j$ represent driving tendencies resulting from concentration, pressure, and potential, gradients. It may be noted that the $\mathbf{j}_i$ and $\mathbf{d}_j$ are so defined that they sum to zero and that the phenomenological coefficients α_{ij} are symmetrical. That is

$$\alpha_{ij} = \alpha_{ji} \quad (3)$$

Equations (1) through (3) give a complete description of the diffusional behavior of isothermal multicomponent systems provided the α_{ij} are known as functions of composition and that departures from equilibrium are small. Practically this last restriction requires that the fractional changes in intensive properties within a molecular mean free path be much less than unity. Almost all mass transfer processes meet this requirement, and one may therefore consider Equations (1) through (3) to be quite general. For present purposes they are however not in the most useful form.

Now solve the *n* Equations 1 for the $\mathbf{d}_j$, obtaining

$$\mathbf{d}_j = -cRT\sum_{i=1}^{n}\left(\frac{x_i x_j}{\mathcal{D}_{ij}}\right)(\mathbf{v}_j - \mathbf{v}_i) \quad (4)$$

$$\mathcal{D}_{ij} = \mathcal{D}_{ji} \quad (5)$$

The $\mathcal{D}_{ij}$ are a new set of phenomenological coefficients related in a complicated way to the α_{ij}. The important points to note here are that the symmetry of the phenomenological coefficients is maintained, and that the $\mathcal{D}_{ij}$ have the dimensions and physical significance of diffusion coefficients. One may now do several things to put Equation (2) in more familiar form. First neglect the effect of pressure gradients, normally only important during ultracentrifugation. Then write

$$\sum_{i=1}^{n}\left(\frac{\partial \mu_j}{\partial c_i}\right)_{T,p,c_k}\nabla c_i = \nabla \mu_j \qquad (\text{constant } T, p) \quad (6)$$

Next introduce the chemical activity, defined by

$$\nabla \mu_j = RT\,\nabla \ln a_j \quad (\text{constant } T, p) \quad (7)$$

Finally assume the only body forces to be those due to electrostatic and gravitational potential. Equation (2) then becomes*

$$\mathbf{d}_j = cRT\left(\frac{\nabla \ln a_j}{\nabla \ln x_j}\right)\nabla x_j + \frac{x_j \nu_j F}{RT}\nabla\phi \quad (8)$$

One may then express the diffusional behavior of this system as

$$\frac{\nabla \ln a_j}{\nabla \ln x_j}\nabla x_j + \frac{x_j \nu_j F}{RT}\nabla\phi = -\sum_{i=1}^{n}\left(\frac{x_i x_j}{\mathcal{D}_{ij}}\right)(\mathbf{v}_j - \mathbf{v}_i) \quad (9)$$

$$\mathcal{D}_{ij} = \mathcal{D}_{ji} \quad (5)$$

Equations (9) and (5) may be considered as generalizations of the Stefan-Maxwell equations. They differ from these celebrated relations only in that variable activity coefficients are permitted, and the possibility of electrodiffusion is considered. Like the diffusion coefficients in the Stefan-Maxwell equations the $\mathcal{D}_{ij}$ are symmetrical and system properties. They may however be expected to vary considerably with composition, except for such limiting cases as mixtures of unionized low-density gases.

Of most importance here, these equations reduce the question of applicability of the Stefan-Maxwell equations for condensed systems to the simpler one of how the $\mathcal{D}_{ij}$ vary with composition. Equations (9) and (5) will of course be most useful if this variation is small, or at least predictable. Now consider two systems for which the usefulness of the $\mathcal{D}_{ij}$ can be tested.

EXAMPLE ONE: DIFFUSION OF TRACE COMPONENT A THROUGH A MIXTURE OF B AND C

To begin with a very specific example, consider the pseudo steady state diffusion of trace component A through a small stagnant duct connecting two large well-stirred reservoirs. For simplicity consider that the liquid in the two reservoirs contains the same proportions of major components B and C on an A-free basis, and that diffusion results from concentration gradients alone.

For this system $\mathbf{v}_A$ will be much greater than $\mathbf{v}_B$ or $\mathbf{v}_C$, and one may write

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* In Equation (8) the normally small relaxation and electrophoretic effects accompanying electrodiffusion have been neglected. The latter should be considered for large charged species such as proteins