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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 $\mathbf{v}$, 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

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

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

The 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 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

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

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

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 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 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 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

$$\nabla x_A = -\frac{c_A \mathrm{v}_A}{c}\left(\frac{x_B}{D_{AB}} + \frac{x_C}{D_{AC}}\right)\frac{\partial \ln x_A}{\partial \ln a_A} \quad (10)$$

or

$$\mathrm{N}_A = c_A \mathrm{v}_A = - c\, \mathcal{D}_{Am} \nabla x_A \quad (11)$$

where

$$\frac{1}{\mathcal{D}_{Am}} = \frac{\nabla \ln x_A}{\nabla \ln a_A}\left(\frac{x_B}{\mathrm{D}_{AB}} + \frac{x_C}{\mathrm{D}_{AC}}\right) \quad (12)$$

Now if A does not dissociate or react with the solvent, $\mathcal{D}_{Am}$ should be very nearly constant over the system for any given ratio of x_B to x_C in the reservoirs.

This was indeed found to be the case by Holmes, Olander, and Wilke (*1*) for diffusion of traces of toluene in binary hydrocarbon solvents. Unfortunately the concentration of toluene in their experiments, never over about 5 μg./liter, was not sufficient to provide a very convincing test of Equation (8). These authors also found that fairly good estimates of $\mathcal{D}_{Am}$ could be obtained by using the binary diffusivities $\mathcal{D}_{AB}$ and $\mathcal{D}_{AC}$ for D_{AB} and D_{AC}. Discrepancies of up to 30% between measured and predicted values were obtained with cyclohexane-*n*-hexane mixtures as solvent, but considerably better agreement was obtained with *n*-hexane-*n*-tetradecane and cyclohexane-*n*-decane solvents.

EXAMPLE TWO: THE SYSTEM WATER-GLYCINE-POTASSIUM CHLORIDE

This system has been very carefully investigated by Woolf, Miller, and Gosting (*2*) to demonstrate the validity of the Onsager reciprocal relationships. The phenomenological coefficients they use to express the behavior of their system are defined by

$$\mathrm{J}_{10} = c\, x_1(\mathrm{v}_1 - \mathrm{v}_0) = (L_{11})_0 X_1 + (L_{12})_0 X_2 \quad (13)$$

$$\mathrm{J}_{20} = c\, x_2\, (\mathrm{v}_2 - \mathrm{v}_0) = (L_{12})_0 X_1 + (L_{22})_0 X_2 \quad (14)$$

$$X_1 = - RT \nabla \ln a_1 = - (RT/x_1)\left(\frac{\nabla \ln a_1}{\nabla \ln x_1}\right)\nabla x_1 \quad (15)$$

$$X_2 = - (RT/x_2)\left(\frac{\nabla \ln a_2}{\nabla \ln x_2}\right)\nabla x_2 \quad (16)$$

Here the subscript 0 refers to water, 1 to glycine, and 2 to potassium chloride. One may very readily develop expressions for the D_{ij} in terms of the three $(L_{ij})_0$:

$$\mathrm{D}_{01} = (x_0 DRT/c) / [x_1(L_{22})_0 - x_2(L_{12})_0] \quad (17)$$

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INFORMATION RETRIEVAL

Key Words: A. Error-3, Compromise Control-8, Probability-8, Regulate-8, Satisfactory Operation-9, Over-Determined-. B. Control-8, Inventory-9, Manufacturing-9, Operations-9, Short-Range Planning-9. C. Gaussian-8, Least Squares-8, Linear-9, Minimax-8, Optimization-8, Statistical-8. D. Control Limits-1, Exterior-6, Uncontrolled-6, Indirectly Controlled-7, Interior-7, Simultaneous-8, Manipulated-10.

Abstract: This paper considers overdetermined systems in which, by adjusting a single manipulated parameter, it is possible to regulate many controlled variables simultaneously within prescribed limits. Two novel control schemes are developed and are then compared with more conventional techniques in an illustrative example, a manufacturing and inventory system which requires short-range planning of production. The compromise methods developed here yield probabilities of satisfactory operation which are consistently higher than those arrived at by the more standard control schemes.

Reference: Wilde, Douglass J., and Andreas Acrivos, **A.I.Ch.E. Journal, 8,** No. 5, p. 629 (November, 1962).

Key Words: Methane-1, **n**-Pentane-1, Silica-1, Phase Behavior-2, Equilibrium-2, Adsorption-4, Surface-4, Conditioning Temperature-6, Agitation-6, Pressure Excess-7.

Abstract: Measurements of the phase behavior of two mixtures of methane and **n**-pentane in contact with silica are reported. The results indicate that a much longer period is required for the attainment of equilibrium at the surface between the hydrocarbons and the silica than between the hydrocarbon phases. The bubble-point pressure of the three-component system is dependent upon the prior conditioning history.

Reference: Reamer, H. H., J. H. Lower, and B. H. Sage, **A.I.Ch.E. Journal, 8,** No. 5, p. 635 (November, 1962).

Key Words: Size Distribution-7, Crystallization-8, Transient Behavior-7, Crystal Suspension-8, Crystal Magma-8, Mixed Suspension-5, Computer-10, Draw-Down Time-6, Holding Time-6, Seed Crystal Dissolving-6, Nuclei Dissolving-6, Nucleation-6, Growth Rate-6, Periodic Upsets-6, Dynamic Behavior-7, Cascaded Tanks-10, Crystallizer-10, Population Density-7, Supersaturation-6, Amplitude Ratio-7.

Abstract: Dynamic behavior of size distribution in a mixed crystal suspension was studied by the use of a mathematical model of the suspension under the constraint of constant total mass of crystals in suspension. The basic equations were developed and solved on a digital computer for upsets in feed rate and nuclei dissolving rate with a nucleation function reported previously for ammonium sulfate. Dynamic behavior is largely determined by the sensitivity of the nucleation rate. The size distribution equation was also solved analytically for the steady state size distribution leaving the **k**'th stage of **k**-cascaded crystallizing tanks with perfect mixing in each tank.

Reference: Randolph, A. D., and M. A. Larson, **A.I.Ch.E. Journal, 8,** No. 5, p. 639 (November, 1962).

Key Words: Mass Transfer-8, Transport-8, Diffusion-8, Multicomponent-8, Liquids-8, Mixtures-9, Solvents-9, Hydrocarbons-9, Toluene-1, Hydrocarbon-1, Hexane-5, Cyclohexane-5, Decane-5, Hydrocarbons-5, Cells-10, Diaphragms-10, Theory-10, Absolute Rate-.

Abstract: A diaphragm cell technique has been utilized to investigate the diffusivity of dilute toluene in the two-component hydrocarbon solvent mixtures **n**-hexane—**n**-tetradecane, **n**-hexane—cyclohexane, and cyclohexane—**n**-decane. The mixed solvents were found to behave as single solvents with a molecular weight or molar volume equal to the mole fraction average of the two components. The $\mathbf{D}\mu/\mathbf{T}$ group was shown to be linear in solvent composition (expressed as mole fraction), except for the cyclohexane—**n**-decane mixture, which exhibited a definite minimum. The data could be satisfactorily interpreted by a modified form of the absolute rate theory model of binary diffusion.

Reference: Holmes, John T., D. R. Olander, and C. R. Wilke, **A.I.Ch.E. Journal, 8,** No. 5, p. 646 (November, 1962).

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TABLE 1. DIFFUSION BEHAVIOR* OF THE SYSTEM

WATER (0)-GLYCINE (1)-POTASSIUM CHLORIDE (2)

c_0	moles/liter	54.44	54.35	53.95	53.94	53.74	53.33
c_1		0.25	0.25	0.25	0.50	0.50	0.50
c_2		0.125	0.25	0.50	0.125	0.25	0.50
$(L_{11})_0$	$\times 10^8\, RT$ moles^2/cm., sec.	0.265	0.265	0.264	0.525	0.524	0.522
$(L_{22})_0$		0.123	0.249	0.501	0.119	0.241	0.482
$(L_{12})_0$		0.003_4	0.004_7	0.009_4	0.005_8	0.008_2	0.017
D_{10}	$\times 10^5$ sq. cm.^{2}/sec.	1.074	1.080	1.096	1.061	1.064	1.081
D_{20}		0.988	1.004	1.019	0.961	0.973	0.993
D_{12}		0.17	0.27	0.27	0.20	0.27	0.27

* The D_{ij} are calculated from the c_i and $(L_{ij})_0$ of reference *6*. The significance of even the first figure of the $(L_{12})_0$ is doubtful (see reference *6*).

$$D_{02} = (x_0 DRT/c)/[x_2(L_{11})_0 - x_1(L_{12})_0] \quad (18)$$

$$D_{12} = (DRT/c)/(L_{12})_0 \quad (19)$$

where $D = (L_{11})_0 (L_{22})_0 - (L_{12})_0^2$.

The results of Woolf, Miller, and Gosting are summarized in Table 1, and at the bottom of the table are shown the D_{ij} as calculated from Equations (17) through (19). It can be seen that these multicomponent diffusion coefficients are reasonably concentration independent, especially if the large experimental uncertainty of the cross term D_{12} is taken into account. It is also apparent that D_{12} is very much lower than D_{10} or D_{20}. Part of this difference may result from the relatively low molecular weight of water, but this explanation does not seem sufficient. It appears that this unexpectedly high frictional resistance may result from the electrostatic charges on potassium chloride and the glycine, which latter is almost entirely in the zwitterion form. This would be an interesting possibility to investigate further. One finds then that the D_{ij} are doubly useful in this system, first from a practical point of view, because they are much less concentration dependent than the $(L_{ij})_0$ most commonly used at present, and second because they provide a method for further and more fundamental investigation of the cross terms in the diffusion equation. Binary diffusion coefficients, based on concentration driving forces, are about 1.0 and 1.8 times 10^{-5} sq. cm./sec. respectively for glycine-water and potassium chloride-water under these conditions. The corresponding binary diffusivities based on free energy driving forces are nearly the same as the D_{10} and D_{20} of Table 1.

A few more examples of the usefulness of the D_{ij} could also be presented here, for example in explaining the behavior of the very interesting restrained quaternary system water-potassium-sodium-chlorine recently investigated by Dunlop and Gosting (*6*). Again the D_{ij} prove to be very weak functions of concentration.

Investigation of multicomponent diffusion in condensed systems is still in its infancy however, and the real test of the usefulness of the D_{ij} is still to come. The authors are now initiating an extensive series of such tests, both in true solutions and gels. Clearly one cannot expect to obtain very much information merely by such formal definitions as given above. It is hoped however that the definitions chosen here will facilitate estimation of the effects of solution properties on diffusional behavior.

NOTATION

a_i = thermodynamic activity of species i
c_i = molar concentration of species i
c = total molar density of solution $= \Sigma_i c_i$
F = Faraday's constant
g_i = body force per unit mass on species i
M_i = molecular weight of species i
N_i = molar flux of species i with respect to stationary coordinates
p = pressure
R = international gas constant
T = absolute temperature
$\tilde{V}_i$ = partial molal volume of species i
v_i = (observable) velocity of species i with respect to stationary co-ordinates
x_i = c_i/c = mole fraction of species i in the mixture
α_{ij} = Onsager phenomenological coefficient, considered to be a system property
∇ = del, or nabla, operator
μ_i = chemical potential of species i
ν_i = change of species i, for example —1 for chlorine
ϕ = electrostatic potential

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Gas Absorption with Simultaneous Irreversible First-Order Reaction

II. Comparison of Results for the Film and Penetration Models

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Considered here is the absorption of a sparingly soluble reactive gas in an agitated tank, under such conditions that the gas may be assumed to undergo irreversible first-order reaction in the absorbing liquid. It is shown that the predicted effect of chemical reaction on gas absorption rate is very nearly equivalent for stagnant-film and