Coupled Energy and Multicomponent Mass Transfer in Dispersions and Suspensions with Residence Time and Size Distributions

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An analytical solution for the transport equation is presented for the case of coupled energy and multicomponent mass transfer in an ensemble of spherical drops, bubbles or solid particles. The solution is used to evaluate the total interfacial transfer rates in a population with particle size and residence time distributions. Using matrix notation and appropriate transformations, the partial differential equations are solved for each phase by using an integral operator whose kernel is the residence time distribution for the flow system. The method of attack is illustrated by solving the transport equations for fine dispersions or suspensions with high hold-up values and presence of adventitious surface active agents.

Studies on mass transfer to or from drops, bubbles, or solid particles in continuous media have primarily been limited to studies of isothermal, uncoupled transfer mechanism for a single particle in a binary system. To achieve a useful analysis the assumption is commonly made that the particles have uniform size and residence time distributions. This permits calculation of the total interfacial area, and the total transfer rate based on the average size and the average residence time. However, it is well known that in actual practice the particle size as well as the residence time distributions are not uniform and the assumption of uniformity may lead to error.

In many practical cases one must also consider the simultaneous transfer of heat and mass in a multicomponent, multiphase system where coupling effects among the various fluxes involved may take place. Hence it is the aim of this study to generalize previous works in uncoupled transport in binary systems (*1, 7* to *9, 15*) to cases that involve coupled heat and multicomponent mass transfer in continuous flow dispersed systems with nonuniform particle size and residence time distributions.

MECHANISM OF INTERFACIAL TRANSPORT

Transfer is considered in a multiphase system that contains a large number of spherical particles (that is, drops, bubbles, or solid particles). In the case of dispersions of two immiscible fluid phases a continuous breakup and coalescence of drops and bubbles may take place. However, under constant operating conditions, a dynamic equilibrium is ultimately established between breakage and coalescence rates and a time invariant spectrum of particle size results. This time invariant size distribution may be described by a normalized particle size distribution, $f(a)$, as described in previous works (*7, 10, 15*). The description of the extremely complicated mechanisms of breakage and coalescence themselves lies outside the scope of the present formulation. Thus we assume that the direct effect of coalescence and breakage on the transfer mechanism is negligible and indirect effects are reflected by changes in the particle size distribution under different operating conditions. This can be done by expressing the size distribution in terms of the average size of the population and following its variations as a function of the Weber number (*10*). Some other indirect effects of coalescence and breakage will be encountered in the following formulation by expressing the residence time distribution in terms of the average residence time whose functional dependence on the operating conditions is assumed to be known experimentally.

The following formulation is given for an unsteady state simultanous (coupled) heat and mass transfer in an n-component particulate system. The proposed method can be adopted also for multicomponent mass transfer in reacting systems (*16*).

The appropriate partial differential equations for multicomponent coupled mass and heat transport for each phase, α, can be written in the compact matrix form (*10*):

$$\mathbf{\Omega}^\alpha \nabla^2 \boldsymbol{\xi}^\alpha = \frac{D\boldsymbol{\xi}^\alpha}{Dt} \tag{1}$$

where D/Dt is the substantial time derivative and $\boldsymbol{\xi}^\alpha$ is an n-dimensional state vector of material quantities transported;

$$\boldsymbol{\xi}^\alpha = (C_1, C_2, \ldots, C_{n-1}, T)^T \tag{2}$$

Here $(\ldots)^T$ denotes the transposed n-dimensional vector with components C_1, C_2, ... C_{n-1}, T_n. C_i^α is the concentration of the ith component in phase α and T^α the temperature in phase α at the point in question. The superscript α refers to the phase, namely, D (dispersed phase), C (continuous phase). $\mathbf{\Omega}^\alpha$ is a nonsymmetrical n-dimensional square matrix of the transport coefficients:

$$\mathbf{\Omega}^\alpha = \begin{vmatrix} \omega^\alpha{}_{11} & \omega^\alpha{}_{12} & \cdot & \cdot & \cdot & \omega^\alpha{}_{1,n-1} & \omega^\alpha{}_{1,T} \\ \omega^\alpha{}_{21} & \omega^\alpha{}_{22} & \cdot & \cdot & \cdot & \omega^\alpha{}_{2,n-1} & \omega^\alpha{}_{2,T} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \omega^\alpha{}_{n-1,1} & \omega^\alpha{}_{n-1,2} & \cdot & \cdot & \cdot & \omega^\alpha{}_{n-1,n-1} & \omega^\alpha{}_{n-1,T} \\ \omega^\alpha{}_{T,1} & \omega^\alpha{}_{T,2} & \cdot & \cdot & \cdot & \omega^\alpha{}_{T,n-1} & \omega^\alpha{}_{T,T} \end{vmatrix} \tag{3}$$

which are assumed constant for the range of operating

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conditions prevailing in the system considered. The quantities *off the main* diagonal are the coupling coefficients among the various fluxes involved (*10*).

Recalling that any asymmetric matrix with distinct eigenvalues can be diagonalized by a similarity transformation (*12*), one can decouple Equation (1) by the transformation

$$\boldsymbol{\Omega}^{\alpha} = [\mathbf{M}^{\alpha}]^{-1} \boldsymbol{\Lambda}^{\alpha} \mathbf{M}^{\alpha} \tag{4}$$

where $\mathbf{M}^{\alpha}$ is the modal matrix and $\boldsymbol{\Lambda}$ is the diagonal matrix of the eigenvalues, diagonal $(\lambda^{\alpha}_{1}, \lambda^{\alpha}_{2}, \ldots \lambda^{\alpha}_{n-1}, \lambda^{\alpha}_{T})$.

Application of transformation (4) to (1), yields (*10*):

$$\boldsymbol{\Lambda}^{\alpha}\nabla^{2} (\mathbf{M}^{\alpha} \boldsymbol{\xi}^{\alpha}) = \frac{D}{Dt} (\mathbf{M}^{\alpha} \boldsymbol{\xi}^{\alpha}) \tag{5}$$

In the case of a nonisothermal binary system, for example, Equation (3) is reduced to

$$\boldsymbol{\Omega}^{\alpha} = \begin{bmatrix} \omega^{\alpha}{}_{cc} & \omega^{\alpha}{}_{cT} \\ \omega^{\alpha}{}_{TC} & \omega^{\alpha}{}_{TT} \end{bmatrix} \tag{5a}$$

whose eigenvalues are

$$\lambda^{\alpha}{}_{1,2} = \frac{1}{2} \{ (\omega^{\alpha}{}_{cc} + \omega^{\alpha}{}_{TT}) \pm \sqrt{(\omega^{\alpha}{}_{cc} - \omega^{\alpha}{}_{TT})^{2} + 4\, \omega^{\alpha}{}_{cT} \cdot \omega^{\alpha}{}_{TC}} \} \tag{5b}$$

It follows from the second law of thermodynamics, Onsager relations and stability conditions (*3, 10*), that $\lambda^{\alpha}{}_{1,2}$ are real and non-negative, where we have also used the fact that $\omega^{\alpha}{}_{cc} \cdot \omega^{\alpha}{}_{TT} \geqq \omega^{\alpha}{}_{cT} \cdot \omega^{\alpha}{}_{Tc}$ (*3, 11*). This assures the existence of real analytical solutions in the subsequent development of the problem.

To solve Equations (5) one can generate the expected values $<\boldsymbol{\xi}^{\alpha}(\hat{\tau}^{\alpha})>$ of the vector $<\boldsymbol{\xi}^{\alpha}(t)>$ over the kernel $K^{\alpha}(\hat{\tau}^{\alpha}, t)$ by using the integral operators

$$<\boldsymbol{\xi}^{\alpha}(\hat{\tau}^{\alpha})> = \int_{0}^{\infty} K(\hat{\tau}^{\alpha}, t)\, \boldsymbol{\xi}^{\alpha}(t)\, dt \tag{6}$$

which have been introduced recently in a general theory for transport dynamics in particulate systems (*10*). The application of the integral operators, Equation (6) to the decoupled Equations (5) yields ordinary differential equations. These can then be solved with appropriate initial and boundary conditions to give the expected concentrations and temperatures as functions of the space coordinates. The advantage of this method is that the kernel $K^{\alpha}(\hat{\tau}^{\alpha}, t)$ can be chosen to be the residence time distribution function for the particles as well as for the continuous phase. $\hat{\tau}^{\alpha}$ can be interpreted as a parameter of the residence time distribution in phase α. Since the inverse transformation becomes an unnecessary procedure, the proposed method removes a considerable mathematical difficulty in obtaining analytical solutions for coupled heat and multicomponent mass transfers in particulate systems.

For a perfectly mixed dispersion or suspension one can choose the kernel

$$K^{\alpha}(\hat{\tau}^{\alpha}, t) = \frac{\exp(-t/\hat{\tau}^{\alpha})}{\hat{\tau}^{\alpha}} \tag{7}$$

For any real system the modified kernel

$$K^{\alpha}(\hat{\tau}^{\alpha}, \eta^{\alpha}, \epsilon^{\alpha}, t) = \frac{\exp(-s^{\alpha}\, t)}{\hat{\tau}_{*}{}^{\alpha}}\; s^{\alpha} = \eta^{\alpha}/\tau^{\alpha}$$

$$s^{\alpha} = \eta^{\alpha}/\hat{\tau}^{\alpha};\; \hat{\tau}_{*} = \hat{\tau}^{\alpha} \exp\, [-\, \eta^{\alpha}\, \epsilon^{\alpha}/\hat{\tau}^{\alpha}] \tag{8}$$

has been proposed (*10*) to replace Equation (7). Here η is a measure of the efficiency of mixing and ϵ a measure of the phase shift in the system as reported by Wolf and Resnick (*6*). Normalization gives $\epsilon\eta = \hat{\tau} = \ln \eta$.

By multiplying Equation (5) by the kernel (7) or (8) and integrating over the entire spectrum of the residence time distributions one obtains

$$\boldsymbol{\Lambda}\nabla^{2}(\mathbf{M}^{\alpha} < \boldsymbol{\xi}^{\alpha} >) = (\mathbf{V}^{\alpha} \cdot \nabla)(\mathbf{M} < \boldsymbol{\xi}^{\alpha} >) + \int_{o}^{\infty} \frac{\exp(-\, s^{2t})}{\hat{\tau}_{*}{}^{\alpha}} \mathbf{M}^{\alpha} \frac{\partial \boldsymbol{\xi}^{\alpha}}{\partial t}\, dt \tag{9}$$

To solve Equations (9) one should know the functional form of $\mathbf{V}^{\alpha}$ — a quantity which is very difficult to evaluate by experimental or theoretical methods. Nevertheless, it is possible to estimate the relative contribution of the convective term by employing a simplified model. If the concentrations, temperatures, and shear flow stresses around any two adjacent particles in an ensemble of many particles are superimposed, the resulting profiles must exhibit an extremum value at a point between any two adjacent particles. In dispersions, emulsions, suspensions, etc., where a large number of spherical particles are present, a particle chosen at random can be expected (statistically) to be surrounded by a spherically symmetric cluster of particles. If the radius of such a spherical "cloud" is P, then one can approximate the locus of points at which the resultant profiles exhibit an extremum, by a spherical surface of radius $b = P/2$ (that is, all the profiles exhibit an extremum value at points midway between adjacent particles). Apparently, this assumption does not prevent each element of the vector $<\boldsymbol{\xi}^{\alpha}(\hat{\tau}^{\alpha})>$ to exhibit different values on the surface midway between adjacent particles. This assumption is expected to be a good approximation, especially in the case of evenly distributed particles (that is, when the local dispersed phase holdup fraction is the same everywhere in the system and is equal to the overall dispersed phase holdup fraction, Φ). Hence, each surface with extremum conditions effectively isolates each particle. The result is a cell model which has been used successfully by Happel (*17*) in his "free surface model" for the prediction of the terminal velocity of an ensemble of spherical solid particles. The cell model has also been used (*1, 7, 8*) in predicting mass and heat transfer in dispersions as well as in a recent generalization (*2*) of Levich's work (*13*) (on the velocity of a single drop) to that of an ensemble of drops moving in the presence of surfactants. The result of this study by Gal-Or and Waslo (*2*) for the free surface cell model is

$$U_{\text{ensemble}} = \frac{2(\rho^{D} - \rho^{C})ga^{2}}{9\mu^{C}} \cdot \frac{3\mu^{C}(1 - \Phi^{1/3})(1 - \Phi^{5/3}) + (K + \mu^{D})\left(3 - \frac{9}{2}\Phi^{1/3} + \frac{9}{2}\Phi^{5/3} - 3\,\Phi^{2}\right)}{2\mu^{C}(1 - \Phi^{5/3}) + (K + \mu^{D})(3 + 2\,\Phi^{5/3})} \tag{10}$$

Here $K = 1/a \cdot \Gamma_o/3\alpha \cdot \partial\sigma/\partial\Gamma$ is the retardation coefficient due to the presence of surfactants. When $\Phi \to 0$, Equation (10) reduces to Levich's solution (*13*) for a single drop (or bubble). When $\Phi \to 0$, $K \to 0$ Equation (10) is reduced to the celebrated Hadamard solution (*14*). When $(K + \mu^D) \to \infty$ one gets Happel's solution (*17*) for an ensemble of solid particles (which has been verified experimentally). Finally, when $(K + \mu^D) \to \infty$ and $\Phi \to 0$, one obtains Stokes solution for a single solid particle. Hence Equation (10) can be considered as a generalization for all the aforementioned solutions.

Now, it is a well known fact that dispersions and emulsions with fluids having clean interfaces are relatively rare in actual practice. Many unsuspected impurities in a system can be surface-active agents and even the equipment itself can supply enough impurities to make a considerable change in the experimental results. The transfer coefficients may be reduced to a small fraction (*5, 19*) in the presence of minute amounts of surfactants. Both Equations (10) and Levich's solution (*13*) show that as the drop or bubble diameter decreases, the quantity of surfactants necessary to make a drop or bubble behave like a solid particle, becomes smaller. Thus the velocity of drops or bubbles is decreased in the presence of traces of surfactant. Under these conditions we define a domain where most industrial dispersions or emulsions (small and medium size particles in liquid-liquid or gas-liquid systems) behave essentially as a dispersion of so-called "solid" particles (that is, according to Equation (10), when $K \to \infty$ all internal circulation stops). For high Φ values, Equation (10) predicts that the particle in Stokes velocity (which is already very small for relatively fine dispersions and emulsions) should be further reduced to a negligible value due to hindering effects of the neighbor particles (for $\Phi = 0.5$, for example, the resulting Stokes velocity should be multiplied by the factor 1/38). Hence, in the domain of high Φ values and relatively fine dispersions or emulsions in actual practice, where surfactants are present, we assume that the particles are completely entrained by the continuous phase eddies resulting in a negligible effect of the convective term in Equation (9). Evidently this assumption does not preclude the possibility of finite relative velocities among the eddies themselves.* In any case, the solution of Equation (9) without the convective term provides the designer with the lowest bound of the transfer rates to be expected in a given particulate system. This conclusion is also in good agreement with various experimental studies (*19* to *21*) which show that the mass transfer coefficient in agitated dispersions is unaffected by the turbulence intensity.

INITIAL AND BOUNDARY CONDITIONS

For a continuous input-output system under constant operating conditions the initial conditions $\boldsymbol{\xi}_o{}^\alpha$ are

$$\boldsymbol{\xi}^\alpha{}_o = (C^\alpha{}_{10}, C^\alpha{}_{20}, \ldots, C^\alpha{}_{n-1,0}\, T^\alpha{}_o)^T \qquad (11)$$

which are the concentrations and temperatures of the feed stream of phase α.

After integration by parts and use of Equation (11) and under the aforementioned domain of high Φ values, presence of surfactants and fine dispersions or suspensions, Equation (9) becomes

$$\hat{\tau}_*{}^\alpha \boldsymbol{\Lambda}^\alpha \nabla^2 \boldsymbol{\zeta}^\alpha = \boldsymbol{\zeta}^\alpha - \boldsymbol{\zeta}^\alpha{}_o \qquad (12)$$

where the transformations

$$\boldsymbol{\zeta}^\alpha = \mathbf{M}^\alpha < \boldsymbol{\xi}^\alpha > \qquad (13)$$

$$\boldsymbol{\zeta}^\alpha{}_o = \mathbf{M}^\alpha\, \boldsymbol{\xi}^\alpha{}_o \qquad (14)$$

have been also introduced. Due to the spherically symmetric $\boldsymbol{\zeta}^\alpha$ field, Equation (12) can be rewritten in spherical coordinates as

$$\frac{d^2}{dr^2}(r\,\boldsymbol{\zeta}^\alpha) - [\boldsymbol{\mu}^\alpha]^2\,(r\,\boldsymbol{\zeta}^\alpha) = -[\boldsymbol{\mu}^\alpha]^2\, \mathrm{r}\, \boldsymbol{\zeta}_o{}^\alpha \qquad (15)$$

where

$$\boldsymbol{\mu}^\alpha = \text{diag.}\,(\mu_1{}^\alpha, \mu_2{}^\alpha, \ldots, \mu_n{}^\alpha) \qquad (16)$$

$$\mu_\mathrm{i}{}^\alpha = (\hat{\tau}_*{}^\alpha \lambda_i{}^\alpha)^{-1/2} \qquad (17)$$

By using the spherically symmetric cell model, whose outer radius b is given by

$$b = a\,\Phi^{-1/3} \qquad (18)$$

one can formulate the following boundary conditions for $t \geqq 0$:

$$r = 0,\ \boldsymbol{\zeta}^D \text{ is finite} \qquad (19)$$

$$r = b,\ \frac{d\boldsymbol{\zeta}^C}{dr} = 0 \qquad (20)$$

$$r = a,\ \boldsymbol{\zeta}^C = \mathbf{U}\,\boldsymbol{\zeta}^D \qquad (21)$$

$$r = a,\ \boldsymbol{\Omega}^C \frac{d<\boldsymbol{\xi}^C>}{dr} = \boldsymbol{\Omega}^D \frac{d<\boldsymbol{\xi}^D>}{dr} \qquad (22)$$

Equation (19) is the requirement that at the center of the particle, the concentrations and the temperature must be finite. Equation (20) follows from the discussion of the extremum condition in the aforementioned domain and the transformation (13). Apparently condition (20) does not prevent each element of the vector $<\boldsymbol{\xi}^\alpha>$ to exhibit different values at b. The interactions among the profiles at b take place as a function of, a, and Φ since b is a yardstick for the average distance between adajcent particles. Consequently, for the same fractional holdup there are more particles per unit volume as the particle size decreases, causing b to decrease and result in more and more interaction between adjacent particles (*7*). This is one type of interaction that is taken into account in this formulation.

Equation (21) refers to the interfacial concentrations and the temperature in both phases which are related through the equilibrium partition coefficients, m_i. Hence

$$\boldsymbol{\xi}^C = \mathbf{m}\,\boldsymbol{\xi}^D \qquad (23)$$

where

$$\mathbf{m} = \text{diag.}\,(m_1, m_2, \ldots m_{n-1}, 1) \qquad (24)$$

Here m_i are assumed to be constant (that is, averaged over the interfacial temperatures prevailing in the system considered). Combining Equation (23) with (13) yields

$$\mathbf{U} = [\mathbf{M}^C]\mathbf{m}[\mathbf{M}^D]^{-1} \qquad (25)$$

which completes the definition of boundary condition (21).

Finally, the boundary condition (22) refers to the continuity of the flux $\mathbf{J} = -\,\boldsymbol{\Omega}^\alpha\, \partial\boldsymbol{\xi}^\alpha/\partial r$ at the interface.

The ordinary differential Equation (15) can now be solved by employing the boundary conditions (19) to (22), to generate the expected value of $\boldsymbol{\xi}^\alpha(r)$ (see Appendix):

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* Numerical solutions of the nonlinear differential Equation (9) with the convective term will be reported in due time.

$$<\boldsymbol{\xi}^D(r)> = \boldsymbol{\xi}_o{}^D + \left(\frac{a}{r}\right)[\mathbf{M}^D]^{-1}\,\mathbf{T}^D(r)$$

$$\{[\mathbf{Q}^C]^{-1}\,\mathbf{Q}^D - [\mathbf{T}^C]^{-1}\mathbf{U}\mathbf{T}^D(r)\}^{-1}[\mathbf{T}]^{-1}\mathbf{M}^C(\mathbf{m}\boldsymbol{\xi}_o{}^D - \boldsymbol{\xi}_o{}^C) \qquad (26)$$

$$<\boldsymbol{\xi}^C(r)> = \boldsymbol{\xi}_o{}^C + \left(\frac{a}{r}\right)[\mathbf{M}^C]^{-1}\mathbf{T}^C(r)$$

$$\{\mathbf{I}_n - [\mathbf{T}^C]^{-1}\mathbf{U}\mathbf{T}^D[\mathbf{Q}^D]^{-1}\mathbf{Q}^C\}^{-1}[\mathbf{T}^C]^{-1}\mathbf{M}(\mathbf{m}\boldsymbol{\xi}_o{}^D - \boldsymbol{\xi}_o{}^C) \qquad (27)$$

where:

$$\mathbf{T}^\alpha(r) = \text{diag.}\ (T_1{}^\alpha(r), T_2{}^\alpha(r), \ldots, T_n{}^\alpha(r)) \qquad (28)$$

$$T_i{}^C(r) = \mu_i{}^C b \cosh\{\mu_i{}^C(r-b)\} + \sinh\{\mu_i{}^C(r-b)\} \qquad (29)$$

$$T_i{}^D(r) = \sinh(\mu_i{}^D r) \qquad (30)$$

$$\mathbf{R}^\alpha = \text{diag.}\ (R_1{}^\alpha, R_2{}^\alpha, \ldots, R_n{}^\alpha) \qquad (31)$$

$$R_i{}^C = [(\mu_i{}^C)^2 a\, b - 1]\sinh\{\mu_i{}^C(a-b)\} + \mu_i{}^C(a-b)\cosh\{\mu_i{}^C(a-b)\} \qquad (32)$$

$$R_i{}^D = \mu_i{}^D a \cosh(\mu_i{}^D a) - \sinh(\mu_i{}^D a) \qquad (33)$$

$$\mathbf{Q}^\alpha = [\mathbf{M}^\alpha]^{-1}\,\boldsymbol{\Lambda}^\alpha\mathbf{R}^\alpha \qquad (34)$$

$\mathbf{I}_n$ = n-dimensional identity matrix.

The expected value of the interfacial flux is

$$<\mathbf{J}(a)> = -\,\boldsymbol{\Omega}^\alpha\left(\frac{\partial<\boldsymbol{\xi}^\alpha>}{\partial r}\right)_{r=\alpha} \qquad (35)$$

where $\dfrac{\partial<\boldsymbol{\xi}^\alpha>}{\partial r}$ is found from Equation (26) or (27).

Hence, by using Equation (35) one obtains

$$<\mathbf{J}(a)> = -\frac{1}{a}\{\mathbf{Y}^C(a) - \mathbf{m}\mathbf{Y}^D(a)\}^{-1}(\mathbf{m}\boldsymbol{\xi}_o{}^D - \boldsymbol{\xi}_o{}^C) \qquad (36)$$

where

$$\mathbf{Y}^\alpha(a) = [\mathbf{M}^\alpha]^{-1}\{\mathbf{T}^\alpha(a)[\mathbf{R}^\alpha(a)]^{-1}\boldsymbol{\Lambda}^\alpha\}[\mathbf{M}^\alpha] \qquad (37)$$

The total interfacial transfer rate in the whole dispersed system, $\mathbf{W}$ is found by summing the interfacial transfer rate over the entire population of the particles, taking into account the variation in their sizes. Thus one obtains (*7*, *10*)

$$\mathbf{W} = \frac{\Phi V}{\frac{4}{3}\pi \hat{a}_v{}^3}\int_o^\infty 4\pi a^2 f(a)<\mathbf{J}(a)>da \qquad (38)$$

where V is the total volume of the dispersed system and a_v is the mean volume radius of the particles, defined by

$$a_v = \int_o^\infty a^3 f(a)\,da \quad ^{1/3} \qquad (39)$$

By substituting the expression for the expected interfacial flux (36), in (38) one finally obtains the required general solution for total average transfer rates in nonisothermal multicomponent particulate systems with residence time and size distributions:

$$\mathbf{W} = \frac{3\Phi V}{\hat{a}_v{}^3}\int_o^\infty \{\mathbf{Y}^C(a) - \mathbf{m}\mathbf{Y}^D(a)\}^{-1}(\boldsymbol{\xi}_o{}^C - \mathbf{m}\boldsymbol{\xi}_o{}^D)f(a)\,ada \qquad (40)$$

Equation (40) is useful for the design of particulate systems when the diffusivities, partition coefficients, feed stream conditions, dispersed-system volume, dispersed-phase holdup, average residence times, residence time distributions, average particle size, and size distributions are known. When the size distribution is not known, but the Sauter mean radius of the population is known, (40) can be approximated by

$$\mathbf{W} \approx \frac{\Phi 3V}{\hat{a}_{32}}\{\mathbf{Y}^C(a_{32}) - \mathbf{m}\mathbf{Y}^D(a_{32})\}^{-1}(\boldsymbol{\xi}_o{}^C - \mathbf{m}\boldsymbol{\xi}_o{}^D) \qquad (41)$$

where $\mathbf{W}$ represents the n-dimensional column vector of the total interfacial transfer rate of each component ($i = 1, 2, \ldots, n - 1$) and the heat flow.

THE DISPERSED PHASE CONTACTOR

The above equations can be used to predict the output $\boldsymbol{\xi}_E{}^\alpha$ in the effluent from a continuous flow two-phase contactor. Let the flow rate of phase α be F^α. Then, a macroscopic balance at a steady state, leads to the equation:

$$F^\alpha\mathbf{S}^\alpha(\boldsymbol{\xi}_E{}^\alpha - \boldsymbol{\xi}_o{}^\alpha) = \mathbf{W} \qquad (42)$$

where

$$\mathbf{S}^\alpha = \text{diag.}\ (1, 1, \ldots, 1, \rho^\alpha C p^\alpha) \qquad (43)$$

is a partitioned matrix containing identity matrix $\mathbf{I}_{n-1}$ of dimension ($n - 1$) and the volumetric heat capacity $\rho^\alpha C_P{}^\alpha$ on the diagonal. (40) and (42) can be combined to give

$$\boldsymbol{\xi}_E{}^\alpha = \boldsymbol{\xi}_o{}^\alpha + \frac{3\Phi V}{F^\alpha\hat{a}_v{}^3}[\mathbf{S}^\alpha]^{-1}\int_o^\infty \{\mathbf{Y}^C(a) - \mathbf{m}\mathbf{Y}^D(a)\}^{-1}(\boldsymbol{\xi}_o{}^C - \mathbf{m}\boldsymbol{\xi}_o{}^D)f(a)\,ada \qquad (44)$$

In the case of a perfectly mixed dispersed system

$$\hat{\tau}^D = \hat{\tau}^C = \hat{\tau} = \frac{\Phi V}{F^D} = \frac{(1-\Phi)V}{F^C} \qquad (45)$$

and the output in each phase can be obtained from (44):

$$\boldsymbol{\xi}_E{}^C = \left\{\mathbf{I}_n + \frac{\Phi}{1-\Phi}[\mathbf{S}^C]^{-1}\mathbf{P}\right\}\boldsymbol{\xi}_o{}^C$$

$$\left\{\frac{\Phi}{1-\Phi}[\mathbf{S}^C]^{-1}\mathbf{P}\mathbf{m}\right\}\boldsymbol{\xi}^D{}_o \qquad (46)$$

$$\boldsymbol{\xi}_E{}^D = \{\mathbf{I}_n - [\mathbf{S}^D]^{-1}\mathbf{P}\mathbf{m}\}\,\boldsymbol{\xi}_o{}^D + \{[\mathbf{S}^D]^{-1}\mathbf{P}\}\boldsymbol{\xi}_o{}^C \qquad (47)$$

where

$$\mathbf{P} = \frac{3\hat{\tau}}{\hat{a}_v{}^3}\int_o^\infty \{\mathbf{Y}^C(a) - \mathbf{m}\mathbf{Y}^D(a)\}^{-1}f(a)\,ada \qquad (48)$$

The integral $\mathbf{P}$ can rarely be evaluated analytically, and is to be done by the use of a digital computer.

Equations (46) and (47) depict the input-output relationships for the concentrations and the temperature in each phase for a given continuous steady-flow dispersed system. Therefore, (46) and (47) can be used in predicting the input-output relationships for a multistage system with several continuous stirred vessels in series.

Although the derivation of (46) and (47) is based on the assumption of perfect mixing, one can estimate the deviations from this ideal situation by taking into account the distribution defined by Kernel (*8*).

CONCLUDING REMARKS

The understanding of the mechanisms of transport processes is essential for the rational design and operation of industrial and biological particulate systems. This may be gained in part by constructing models amenable to a mathematical treatment. In the present mathematical characterization of particulate systems we have generalized previous works in this field by including such environmental parameters as temperatures and compositions of a multicomponent mixture in addition to dispersed-phase holdup volume, particle size and residence time distributions which (when known experimentally) describe the dependence of the total transfer rates on the operating conditions. Subject to the Curie principle (3), the derived set of partial differential equations includes the possibilities of coupling effects among the various fluxes involved. A simultaneous solution of this set of equations is presented in the domain of high dispersed-phase holdup fractions, fine dispersions (or suspensions) and presence of adventitious surfactants. It is demonstrated that under this domain one can assume that the particles are spherical in shape and completely entrained by the continuous phase eddies. The result is a characteristic set of linear partial differential equations that can be solved analytically for each phase by employing integral operators whose kernels are the residence time distributions for each phase. The computed total transfer rates for simultaneous heat and multicomponent mass transfer provide the designer with the lowest bound of the transfer rates to be expected in continuous flow dispersed systems. A knowledge of the average particle size, average residence time of each phase, size distribution, residence time distribution, mass diffusivities, heat diffusivities, (including cross coefficients), interfacial partition coefficients, feed stream conditions. dispersed-system volume, and dispersed-phase holdup is necessary to arrive at a working approximate description of the system under study. The proposed method is expected to be useful for describing the behavior of such systems and processes as colloids, biological cells, blood, aerosols, mist, cloud droplets, emulsions, spray drying, capillary-porous bodies (*4*), and a host of fluid-fluid and solid-fluid contacting systems (*10*).

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NOTATIONS

a = radius of a bubble, drop, or solid particle in a population with size distribution
$\hat{a}_v$ = mean volume radius defined by Equation (39)
$\hat{a}_{32}$ = surface mean radius (Sauter-mean)
b = outer radius of cell model defined by Equation (18)
C_i = concentration of the ith component
C_p = heat capacity
D/Dt = substantial time derivative
$f(a)$ = a normalized particle size distribution function
F = flow rate
g = local acceleration
$\mathbf{I}_n$ = n-dimensional identity matrix
$\mathbf{J}(a)$ = state vector of the heat and mass transfer fluxes at the interface of a typical particle whose radius is a
$K^\alpha(\hat{\tau}^\alpha, t)$ = kernel of the integral operators defined by Equation (6)
$\mathbf{m}$ = a diagonal matrix of the partition coefficients defined by Equations (23) and (24)
$\mathbf{M}$ = modal matrix defined by Equation (4)
n = number of components present in the particulate system
$\mathbf{Q}$ = matrix defined by Equation (34)
Q^* = flux of adsorbed surfactants
P^* = flux of desorbed surfactants
$\mathbf{P}$ = matrix defined by Equation (48)
r = radius in spherical coordinates
$\mathbf{R}$ = matrix defined by Equations (31), (32), and (33)
s = defined by Equation (8). It is a parameter whose magnitude is large enough to make the integral (6) convergent
$\mathbf{S}$ = diagonal matrix defined by Equation (43)
t = time variable
T = temperature
$\mathbf{T}$ = matrix defined by Equations (28), (29), and (30)
$\mathbf{U}$ = matrix defined by Equation (25)
$\mathbf{V}$ = local velocity vector
V = total volume of the particulate system considered
$\mathbf{W}$ = total average interfacial transfer rate over the entire population of the particulate system. Defined by Equation (38) and denotes an n-dimensional vector whose components yield the total average heat and multicomponent mass transfer rates
$\mathbf{X}$ = matrix defined by Equation (A11)
$\mathbf{y}$ = state vector defined by Equation (A12)
$\mathbf{Y}(a)$ = matrix defined by Equation (37)

Greek Symbols

$\alpha = \left[\dfrac{\partial P^*}{\partial \Gamma} - \dfrac{\partial Q^*}{\partial \Gamma} \right]$
β_i = coefficients in Equation (A1), defined by Equation (A6)
γ_i = coefficients in Equation (A1), defined by Equation (A9)
$\boldsymbol{\Upsilon}$ = n-dimensional state vector defined by Equation (A9)
Γ_o = equilibrium surface concentration of surfactants
ϵ = a measure of the phase shift in Equation (8)
$\hat{\tau}$ = average residence time
$\hat{\tau}_*$ = characteristic time parameter defined by Equation (8)
$\boldsymbol{\xi}$ = an n-dimensional state vector with concentrations and temperature components defined by Equation (2)
Φ = volumetric dispersed-phase holdup fraction
η = a measure of the efficiency of mixing defined by Equation (8)
μ = viscosity
μ_i = element of $\boldsymbol{\mu}$, defined by Equation (17)
$\boldsymbol{\mu}$ = a matrix defined by Equation (16)
λ_i = the elements of $\boldsymbol{\Lambda}$
$\boldsymbol{\Lambda}$ = a diagonal matrix defined by Equation (4)
$\boldsymbol{\Omega}$ = matrix of the transfer coefficients defined by Equation (3)
$\boldsymbol{\zeta}$ = a state vector defined by Equation (14)
ρ = density
ω_{ij} = transport coefficients defined by equation (3). These include the heat and mass diffusivities ω_{ij} $(i = j)$ and the coupling coefficients ω_{ij} $(i \neq j)$

Superscripts

α = denotes the homogeneous phase considered $(\alpha = C, D)$

$(\ldots)^T$ = transposed state vector
C = refers to the continuous phase
D = refers to the dispersed phase

Subscripts

i, j = refer to component i or j of an n-dimensional state vector
C = refers to concentration field in a binary system
T = refers to temperature field in a binary system
E = at effluent stream
o = initial (feed) condition

Special Symbols

$< >$ expected values over $K^\alpha(\hat{r}^\alpha, t)$

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APPENDIX

The ordinary differential Equation (15) is solved here by employing the boundary conditions (19) to (22). For the dispersed phase, the general solution of (15) is

$$\zeta_i^D = \zeta_{io}^D + \left(\frac{1}{r}\right)\{\beta_i^D \cosh(\mu_i^D r) + \gamma_i^D \sinh(\mu_i^D r)\} \quad (i = 1, 2, \ldots, n) \qquad (A1)$$

from (19) we get that $\beta_i^D = 0$, so that (A1) takes the form

$$\zeta_i^D = \zeta_{io}^D + \frac{\gamma_i^D}{r}\sinh(\mu_i^D r) = \zeta_{io}^D + \frac{\gamma_i^D T_i^D(r)}{r} \qquad (A2)$$

Similarly for the continuous phase, the general solution for (15) can be given as:

$$\zeta_i^C = \zeta_{io}^C + \frac{1}{r}[\beta_i^C \cosh\{\mu_i^C(r-b)\} + \gamma_i^C \sinh\{\mu_i^C(r-b)\}] \qquad (A3)$$

From (A2) and (A3)

$$\frac{d\zeta_i^D}{dr} = \frac{\gamma_i^D}{r^2}\{\mu_i^D r \cosh(\mu_i^D r) - \sinh(\mu_i^D r)\} = \frac{\gamma_i^D R_i^D(r)}{r^2} \qquad (A4)$$

$$\frac{d\zeta_i^C}{dr} = \frac{\beta_i^C}{r^2}[\mu_i^C r \sinh\{\mu_i^C(r-b)\} - \cosh\{\mu_i^C(r-b)\}] + \frac{\gamma_i^C}{r^2}[\mu_i^C r \cosh\{\mu_i^C(r-b)\} - \sinh\{\mu_i^C(r-b)\}] \qquad (A5)$$

From (20) and (A5)

$$\beta_i^C = \mu_i^C b \gamma_i^C \qquad (A6)$$

Combining (A3) and (A6)

$$\zeta_i^C = \zeta_{io}^C + (\gamma_i^C/r)[\mu_i^C b \cosh\{\mu_i^C(r-b)\} + \sinh\{\mu_i^C(r-b)\}]$$

Or,

$$\boldsymbol{\zeta}^C = \boldsymbol{\zeta}_o^C + \frac{1}{r}\mathbf{T}^C(r)\,\boldsymbol{\gamma}^C \qquad (A7)$$

Similarly (A2) can be written as:

$$\boldsymbol{\zeta}^D = \boldsymbol{\zeta}_o^D + \frac{1}{r}\mathbf{T}^D(r)\,\boldsymbol{\gamma}^D \qquad (A8)$$

where

$$\boldsymbol{\gamma}^\alpha = (\gamma_1^\alpha, \gamma_2^\alpha, \ldots \gamma_n^\alpha)^T \qquad (A9)$$

By substituting for $\boldsymbol{\zeta}^\alpha$ from (A7) and (A8) into the boundary condition (21), we can solve for $\boldsymbol{\gamma}^\alpha$:

$$\boldsymbol{\gamma}^C = a\mathbf{y} + \mathbf{X}\boldsymbol{\gamma}^D \qquad (A10)$$

where

$$\mathbf{X} = [\mathbf{T}^C(a)]^{-1}\,\mathbf{U}\,[\mathbf{T}^D(a)] \qquad (A11)$$

$$\mathbf{y} = [\mathbf{T}^C(a)]^{-1}\,\mathbf{M}^C\,(\mathbf{m}\boldsymbol{\xi}_o^D - \boldsymbol{\xi}_o^C) \qquad (A12)$$

From (A5) and (A6) we get

$$\frac{d\boldsymbol{\zeta}^C}{dr} = \frac{1}{r^2}\mathbf{R}^C(r)\boldsymbol{\gamma}^C \qquad (A13)$$

where

$$R_i^C(r) = \mu_i^C b[\mu_i^C r \sinh\{\mu_i^C(r-b)\} - \cosh\{\mu_i^C(r-b)\}] + [\mu_i^C r \cosh\{\mu_i^C(r-b)\} - \sinh\{\mu_i^C(r-b)\}] \qquad (A14)$$

Boundary condition (22) can be rewritten as:

$$[\mathbf{M}^C]^{-1}\,\boldsymbol{\Lambda}^C \left.\frac{d\boldsymbol{\zeta}^C}{dr}\right|_{r=a} = [\mathbf{M}^D]^{-1}\,\boldsymbol{\Lambda}^D \left.\frac{d\boldsymbol{\zeta}^D}{dr}\right|_{r=a} \qquad (A15)$$

By substituting (A4) and (A12) into (A15), and making use of (A9), we finally get:

$$\boldsymbol{\gamma}^D = a\{[\mathbf{Q}^C]^{-1}\mathbf{Q}^D - \mathbf{X}\}^{-1}\mathbf{y} \qquad (A16)$$

$$\boldsymbol{\gamma}^C = a\{\mathbf{I}_n - \mathbf{X}[\mathbf{Q}^D]^{-1}\mathbf{Q}^C\}^{-1}\mathbf{y} \qquad (A17)$$

so that $\boldsymbol{\zeta}^\alpha$ can be found explicitly as:

$$\boldsymbol{\zeta}^D = \boldsymbol{\zeta}_o^D + \left(\frac{a}{r}\right)\mathbf{T}^D(r)\,\{[\mathbf{Q}^C]^{-1}\mathbf{Q}^D - \mathbf{X}\}^{-1}\mathbf{y} \qquad (A18)$$

$$\boldsymbol{\zeta}^C = \boldsymbol{\zeta}_o^C + \left(\frac{a}{r}\right)\mathbf{T}^C(r)\,\{\mathbf{I}_n - \mathbf{X}[\mathbf{Q}^D]^{-1}\mathbf{Q}^C\}^{-1}\mathbf{y} \qquad (A19)$$

(A18) and (A19), when combined with (13), yield the expected concentrations and the temperature profiles in both phases.