$\mathbf{v}_B$ = species velocity for species B, m/s
$\mathbf{v}$ = mass average velocity, m/s
$\mathbf{v}^*_A$ = velocity for species A created by a chemical reaction, m/s
x_A = mole fraction for species A
x_B = mole fraction of species B
x_A^e = mole fraction of species A in equilibrium with the liquid phase
z = distance, m

Greek Letters

ϵ = vector associated with the mass-average momentum equation, N/m^3
ϵ_A = small vector associated with the species momentum equation for species A, N/m^3
ϵ_B = small vector associated with the species momentum equation for species B, N/m^3
ρ = total density, kg/m^3
ρ_A = density of species A, kg/m^3
ρ_B = density of species B, kg/m^3
μ = viscosity of the gas phase, N s/m^3
$\tau_A = \mathbf{T}_A - \mathbf{I}p_A$, viscous stress tensor for species A, N/m^2

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Improved Constraints for the Principle of Local Thermal Equilibrium

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When heat- and mass-transfer processes occur in multiphase systems, one would like to know under what conditions a *single temperature* or a *single concentration* is sufficient to describe the transport process. One-equation models are easily developed by adding the local volume averaged equations for the individual phases; however, one is always forced to neglect various terms that are related to the *difference* between the temperatures or concentrations in the individual phases. In addition, one is forced to make constitutive assumptions concerning the *spatial deviation* temperatures or concentrations. Thus the final form of a one-equation model is based on simplifications *both* in the local volume averaged transport equation and in the closure problem. Information contained in the closure problem is *filtered* when it appears in the local volume averaged transport equation. In this work we distinguish between *filtered* and *unfiltered* constraints in the closure problem, and we show how to derive an approximate governing differential equation for the *difference* between the temperatures of two individual phases. The heat-transfer process in a packed bed catalytic reactor is used to illustrate the development of constraints associated with local thermal equilibrium, and the same approach can be used to understand the concept of local mass equilibrium.

1. Introduction

Multiphase transport processes are ubiquitous in the discipline of chemical engineering and in many other areas of science and technology. Trickle-bed and slurry reactors (Carberry, 1976) are examples of three-phase transport processes that are well-known to chemical engineers, while heat pipes (Tien and Chung, 1978) provide a comparable example of interest to mechanical engineers. Unsaturated groundwater flows represent a three-phase transport process of concern to soil scientists, while petroleum engineers routinely deal with the same type of problem from a different perspective. Agricultural engineers encounter their own version of this process in their studies of drying (Fortes and Okos, 1980), and the mathematicians (Bensoussan et al., 1978) have developed an extensive literature in the course of their studies of multiphase transport phenomena.

The treatment of transport processes in multiphase systems always *begins* with separate transport equations for every identifiable phase. Under certain circumstances,

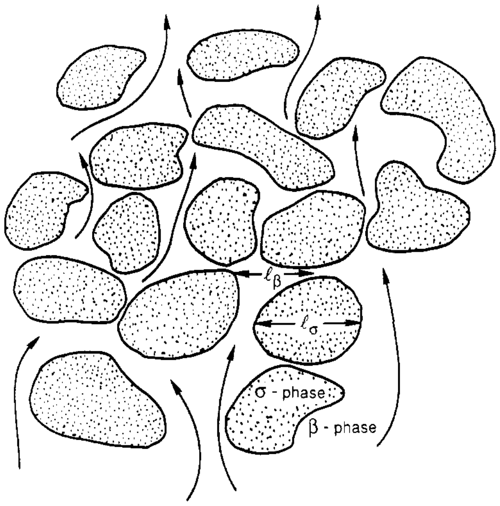

Figure 1. Fluid–catalyst pellet system.

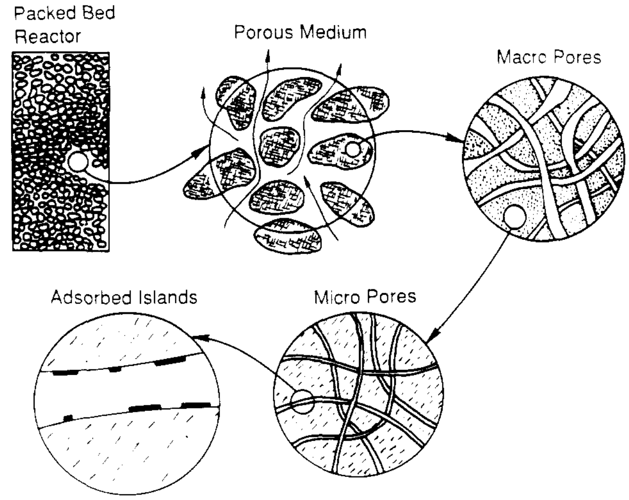

Figure 2. Averaging volumes for a packed bed catalytic reactor.

the local volume averaged transport equations for the individual phases can be combined in order to reduce the complexity of the analysis. For example, the *three* thermal energy equations used to describe the temperature fields (solid, liquid, and gas) in a drying process can usually be combined to produce a *single* transport equation for the spatial averaged temperature. This greatly simplifies the analysis of this coupled heat, mass, and momentum transport process, and the *constraints* that must be satisfied in order to accomplish this simplification have been the subject of several previous studies (Whitaker, 1977, Section III; Whitaker, 1980, Section 3.3; Nozad et al., 1985; Whitaker, 1986a; Ochoa et al., 1986). The key to the development of these constraints is the estimation of the difference between local volume average quantities associated with the separate phases. All previous studies have based this estimate on the diffusive or conductive flux between the phases. In this work we extend the previous efforts and develop the *governing differential equation* for the difference between local volume averaged temperatures in a packed bed reactor. This equation leads to constraints associated with the principle of local thermal equilibrium, and these constraints contain certain *required* features that are not found in the previous studies of local thermal equilibrium or local mass equilibrium.

2. Theory

In this development we consider the heat-transfer process associated with the fluid–catalyst pellet system illustrated in Figure 1. The fluid is represented by the β-phase and the rigid, catalyst phase is identified as the σ-phase. The heat-transfer process is described by the following equations and boundary conditions

$$(\rho c_p)_\beta \left(\frac{\partial T_\beta}{\partial t} + \mathbf{v}_\beta \cdot \nabla T_\beta \right) = \nabla \cdot (k_\beta \nabla T_\beta) \qquad (2.1)$$

$$\text{B.C.1} \qquad T_\beta = T_\sigma, \quad \text{at } \mathcal{A}_{\beta\sigma} \qquad (2.2)$$

$$\text{B.C.2} \qquad \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta = \mathbf{n}_{\beta\sigma} \cdot k_\sigma \nabla T_\sigma + \Omega, \quad \text{at } \mathcal{A}_{\beta\sigma} \qquad (2.3)$$

$$(\rho c_p)_\sigma \frac{\partial T_\sigma}{\partial t} = \nabla \cdot (k_\sigma \nabla T_\sigma) + \Phi_\sigma \qquad (2.4)$$

Only laminar flows are considered in this analysis; thus *time averaging of the β-phase transport equation is not required.* In the flux boundary condition given by eq 2.3, we have used $\mathbf{n}_{\beta\sigma}$ to represent the unit normal vector pointing *from* the β-phase *toward* the σ-phase, and we have used $\mathcal{A}_{\beta\sigma}$ to represent the β–σ interface in the packed bed shown in Figure 2. The nomenclature for the unit normal vectors requires that $\mathbf{n}_{\beta\sigma} = -\mathbf{n}_{\sigma\beta}$.

If we are dealing with a nonporous catalyst, the heat of reaction will give rise to a heterogeneous thermal source identified as Ω in eq 2.3. On the other hand, if the σ-phase represents a typical porous catalyst, we need to consider the homogeneous thermal source identified as Φ_σ in eq 2.4.

It is of some importance to understand that eq 2.4 is actually a local volume averaged transport equation when the σ-phase is a porous catalyst, and that the principle of local thermal equilibrium must be imposed in order to derive eq 2.4. A detailed derivation is available elsewhere (Whitaker, 1989); however, the constraints associated with local thermal equilibrium in the σ-phase are best obtained from the development presented in this paper. Since eq 2.4 is a local volume averaged transport equation, the boundary conditions given by eqs 2.2 and 2.3 represent conditions in which point quantities (temperature and heat flux) are used in conjunction with local volume averaged quantities. The validity of this approach has been analyzed in detail by Prat (1989).

In order to develop the two-equation model for a packed bed catalytic reactor, one considers the first averaging volume illustrated in Figure 2 and develops the local volume averaged forms of eqs 2.1 and 2.4. This has been done by Whitaker (1986a, 1989) and we list the result as

$$\epsilon_\beta (\rho c_p)_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} + \epsilon_\beta (\rho c_p)_\beta \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle T_\beta \rangle^\beta + (\rho c_p)_\beta \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{T}_\beta \rangle = \nabla \cdot \left[\epsilon_\beta k_\beta \left(\nabla \langle T_\beta \rangle^\beta + \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{T}_\beta \, \mathrm{d}A \right) \right] + \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta \, \mathrm{d}A \qquad (2.5)$$

$$\text{B.C.1} \qquad T_\beta = T_\sigma, \quad \text{at } \mathcal{A}_{\beta\sigma} \qquad (2.6)$$

$$\text{B.C.2} \qquad \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta = \mathbf{n}_{\beta\sigma} \cdot k_\sigma \nabla T_\sigma + \Omega, \quad \text{at } \mathcal{A}_{\beta\sigma} \qquad (2.7)$$

$$\epsilon_\sigma (\rho c_p)_\sigma \frac{\partial \langle T_\sigma \rangle^\sigma}{\partial t} = \nabla \cdot \left[\epsilon_\sigma k_\sigma \left(\nabla \langle T_\sigma \rangle^\sigma + \frac{1}{V_\sigma} \int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta} \tilde{T}_\sigma \, \mathrm{d}A \right) \right] + \epsilon_\sigma \langle \Phi_\sigma \rangle^\sigma + \frac{1}{\mathcal{V}} \int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta} \cdot k_\sigma \nabla T_\sigma \, \mathrm{d}A \qquad (2.8)$$

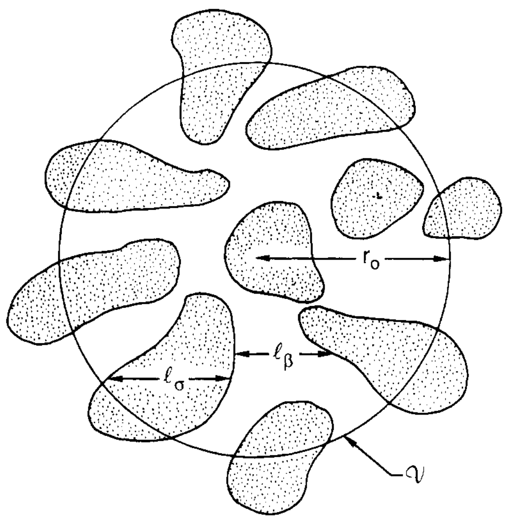

Figure 3. Averaging volume for a packed bed.

In the derivation of eq 2.5 we have used of the following definitions:

$$\langle\psi_\beta\rangle = \frac{1}{\mathcal{V}}\int_{V_\beta}\psi_\beta\,\mathrm{d}V \qquad \text{superficial phase average} \tag{2.9a}$$

$$\langle\psi_\beta\rangle^\beta = \frac{1}{V_\beta}\int_{V_\beta}\psi_\beta\,\mathrm{d}V \qquad \text{intrinsic phase average} \tag{2.9b}$$

$$\tilde{\psi}_\beta = \psi_\beta - \langle\psi_\beta\rangle^\beta \qquad \text{spatial deviation} \tag{2.9c}$$

$$\epsilon_\beta = V_\beta/\mathcal{V} \qquad \beta\text{-phase volume fraction} \tag{2.9d}$$

in which ψ_β is either T_β or $\mathbf{v}_\beta$. In eqs 2.9 the volume $\mathcal{V}$ represents the averaging volume shown in Figure 3 and V_β represents the volume of the β-phase contained within $\mathcal{V}$. Similar definitions were used in the derivation of eq 2.8, and in both cases we have neglected variations of the physical properties within the averaging volume. Implicit in the derivation of eqs 2.5 and 2.8 are the length-scale constraints given by

$$\ell \ll r_0 \ll L \tag{2.10}$$

Here ℓ represents either ℓ_σ or ℓ_β as illustrated in Figure 1, r_0 represents the radius of the averaging volume shown in Figure 3, and L represents the characteristic length associated with volume average quantities. In the development of eq 2.5 the flow has been treated as incompressible and laminar, and we will make use of these simplifications through the remainder of our analysis.

One-Equation Model. In order to develop a one-equation model of the heat-transfer process, we follow the original analysis (Whitaker, 1977, Section III) and decompose the intrinsic phase average temperatures according to

$$\langle T_\beta\rangle^\beta = \langle T\rangle + \hat{T}_\beta, \quad \langle T_\sigma\rangle^\sigma = \langle T\rangle + \hat{T}_\sigma \tag{2.11}$$

Here $\langle T\rangle$ represents the *spatial average temperature* which is defined by

$$\langle T\rangle = \frac{1}{\mathcal{V}}\int_{\mathcal{V}} T\,\mathrm{d}V = \epsilon_\beta\langle T_\beta\rangle^\beta + \epsilon_\sigma\langle T_\sigma\rangle^\sigma \tag{2.12}$$

One now substitutes eqs 2.11 into eqs 2.5 and 2.8 and *adds* those two equations to obtain a *total* thermal energy equation given by

$$\langle\rho\rangle C_p\frac{\partial\langle T\rangle}{\partial t} + \epsilon_\beta(\rho c_p)_\beta\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T\rangle + (\rho c_p)_\beta\nabla\cdot\langle\tilde{\mathbf{v}}_\beta\tilde{T}_\beta\rangle = \nabla\cdot\left[(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)\nabla\langle T\rangle + \frac{k_\beta}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{T}_\beta\,\mathrm{d}A + \frac{k_\sigma}{\mathcal{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\,\mathrm{d}A\right] + \epsilon_\sigma\langle\Phi_\sigma\rangle^\sigma + a_\mathrm{v}\langle\Omega\rangle_{\beta\sigma} - \left[\epsilon_\beta(\rho c_p)_\beta\frac{\partial\hat{T}_\beta}{\partial t} + \epsilon_\sigma(\rho c_p)_\sigma\frac{\partial\hat{T}_\sigma}{\partial t} + \epsilon_\beta(\rho c_p)_\beta\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\hat{T}_\beta - \nabla\cdot(\epsilon_\beta k_\beta\nabla\hat{T}_\beta + \epsilon_\sigma k_\sigma\nabla\hat{T}_\sigma)\right] \tag{2.13}$$

Here $\langle\rho\rangle$ represents the spatial average density which is defined in accordance with eq 2.12, and C_p is the mass fraction weighted heat capacity defined by

$$C_p = \frac{\epsilon_\beta(\rho c_p)_\beta + \epsilon_\sigma(\rho c_p)_\sigma}{\langle\rho\rangle} \tag{2.14}$$

In eq 2.13 we have used a_v to represent the area per unit volume, $A_{\beta\sigma}/\mathcal{V}$, and $\langle\Omega\rangle_{\beta\sigma}$ represents the area average of the heterogeneous thermal source.

In the next section, we will develop the constraints that are necessary in order that the terms in eq 2.13 involving $\hat{T}_\beta$ and $\hat{T}_\sigma$ are negligible. When these constraints are satisfied, eq 2.13 reduces to

$$\langle\rho\rangle C_p\frac{\partial\langle T\rangle}{\partial t} + \epsilon_\beta(\rho c_p)_\beta\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T\rangle + (\rho c_p)_\beta\nabla\cdot\langle\tilde{\mathbf{v}}_\beta\tilde{T}_\beta\rangle = \nabla\cdot\left[(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)\nabla\langle T\rangle + \frac{k_\beta}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{T}_\beta\,\mathrm{d}A + \frac{k_\sigma}{\mathcal{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\,\mathrm{d}A\right] + \epsilon_\sigma\langle\Phi_\sigma\rangle^\sigma + a_\mathrm{v}\langle\Omega\rangle_{\beta\sigma} \tag{2.15}$$

Under certain circumstances the spatial deviation temperatures $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ are linear functions of $\nabla\langle T\rangle$, and the closure problem is relatively straightforward. An example of this situation is given by Nozad et al. (1985), and that study encourages *closure representations* of the form

$$(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)\nabla\langle T\rangle + \frac{k_\beta}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{T}_\beta\,\mathrm{d}A + \frac{k_\sigma}{\mathcal{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\,\mathrm{d}A = \boldsymbol{K}_\mathrm{eff}\cdot\nabla\langle T\rangle \tag{2.16a}$$

$$(\rho c_p)_\beta\langle\tilde{\mathbf{v}}_\beta\tilde{T}_\beta\rangle = -\boldsymbol{K}_\mathrm{D}\cdot\nabla\langle T\rangle \tag{2.16b}$$

Here $\boldsymbol{K}_\mathrm{eff}$ is the effective thermal conductivity tensor and $\boldsymbol{K}_\mathrm{D}$ is the thermal dispersion tensor. The distinction between *conduction* and *dispersion* for a laminar flow heat-transfer process is identical with the distinction between *diffusion* and *dispersion* for a laminar flow mass-transfer process (Whitaker, 1967, 1971). Use of eqs 2.16 in eq 2.15 leads to the following one-equation model of thermal energy transport (Carberry, 1976, eq 4-12; Froment and Bischoff, 1979, eq 11.7b-1; Smith 1981, eq 13-19).

$$\langle\rho\rangle C_p\frac{\partial\langle T\rangle}{\partial t} + \epsilon_\beta(\rho c_p)_\beta\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T\rangle = \nabla\cdot[(\boldsymbol{K}_\mathrm{eff} + \boldsymbol{K}_\mathrm{D})\cdot\nabla\langle T\rangle] + \epsilon_\sigma\langle\Phi\rangle^\sigma + a_\mathrm{v}\langle\Omega\rangle_{\beta\sigma} \tag{2.17}$$

The constraints associated with eqs 2.16 are developed in section 4 and there we encounter both *filtered* and *unfiltered* constraints associated with the closure problem.

The unfiltered constraints are imposed on the boundary value problem for $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ while the filtered constraints are imposed directly on eq 2.15. The filter to which we refer is represented by the two area integrals in eq 2.15 since all the information contained in the $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ fields does not pass through these area integrals.

For a packed bed catalytic reactor, the model represented by eq 2.17 would appear to be acceptable when the coupling between heat and mass transfer occurs only at the *local volume average level.* If $\langle c_A\rangle^\sigma$ represents the intrinsic phase average concentration of species A in the σ-phase, coupling at the local volume average level means that the transport equations for $\langle c_A\rangle^\sigma$ and $\langle T\rangle$ are coupled through the thermal source term, $\langle \Phi_\sigma\rangle^\sigma$. If coupling occurs at a smaller length scale, one finds that the transport equations for $\tilde{c}_A$ and $\tilde{T}_\sigma$ are coupled and the closure suggested by eqs 2.16 is no longer acceptable. Some aspects of the *coupled* closure problem involving $\tilde{c}_A$ and $\tilde{T}_\sigma$ have been discussed by Whitaker (1989).

3. Local Equilibrium

In order to extract eq 2.15 from eq 2.13, we require that the last term in brackets be *negligible* and this naturally leads to the question: Negligible relative to what? In a previous study (Whitaker, 1986a) it was assumed that *negligible* could be described by the following level II restrictions (Whitaker, 1988a):

$$\epsilon_\beta(\rho c_p)_\beta \frac{\partial \hat{T}_\beta}{\partial t} \ll \langle\rho\rangle C_p \frac{\partial\langle T\rangle}{\partial t},\quad \epsilon_\sigma(\rho c_p)_\sigma \frac{\partial \hat{T}_\sigma}{\partial t} \ll \langle\rho\rangle C_p \frac{\partial\langle T\rangle}{\partial t} \tag{3.1}$$

$$\epsilon_\beta(\rho c_p)_\beta\langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla\hat{T}_\beta \ll \epsilon_\beta(\rho c_p)_\beta\langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T\rangle \tag{3.2}$$

$$\nabla\cdot(\epsilon_\beta k_\beta\nabla\hat{T}_\beta) \ll \nabla\cdot(\epsilon_\beta k_\beta\nabla\langle T\rangle),\quad \nabla\cdot(\epsilon_\sigma k_\sigma\nabla\hat{T}_\sigma) \ll \nabla\cdot(\epsilon_\sigma k_\sigma\nabla\langle T\rangle) \tag{3.3}$$

A little thought will indicate that these restrictions can be replaced by

$$\frac{\partial \hat{T}_\beta}{\partial t} \ll \frac{\partial\langle T\rangle}{\partial t},\quad \frac{\partial \hat{T}_\sigma}{\partial t} \ll \frac{\partial\langle T\rangle}{\partial t} \tag{3.4}$$

$$\nabla\hat{T}_\beta \ll \nabla\langle T\rangle,\quad \nabla\hat{T}_\sigma \ll \nabla\langle T\rangle \tag{3.5}$$

Use of eqs 3.4 and 3.5 leads to a plausible set of constraints; however, these constraints are not *automatically* satisfied by the following conditions:

$$(\rho c_p)_\beta = (\rho c_p)_\sigma,\quad k_\beta = k_\sigma,\quad \mathbf{v}_\beta = 0 \tag{3.6}$$

Since these conditions reduce the problem described by eqs 2.1–2.4 to one of transient heat conduction in a single phase, it seems reasonable that the principle of local thermal equilibrium should be satisfied by eqs 3.6. Because the previous constraints are not automatically satisfied by eqs 3.6, they are overly severe and we are motivated to reconsider the restrictions given by eqs 3.1–3.3.

If one thinks about eq 2.13 and the processes that it describes, one could conclude that the leading portion of the conductive transport term represents one of the smallest *but nonzero* terms in the thermal energy balance. This suggests the following restrictions represent an acceptable basis for simplifying eqs 2.13–2.15:

$$\epsilon_\beta(\rho c_p)_\beta \frac{\partial \hat{T}_\beta}{\partial t} + \epsilon_\sigma(\rho c_p)_\sigma \frac{\partial \hat{T}_\sigma}{\partial t} \ll \nabla\cdot[(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)\nabla\langle T\rangle] \tag{3.7}$$

$$\epsilon_\beta(\rho c_p)_\beta\langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla\hat{T}_\beta \ll \nabla\cdot[(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)\nabla\langle T\rangle] \tag{3.8}$$

$$\nabla\cdot(\epsilon_\beta k_\beta\nabla\hat{T}_\beta + \epsilon_\sigma k_\sigma\nabla\hat{T}_\sigma) \ll \nabla\cdot[(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)\nabla\langle T\rangle] \tag{3.9}$$

In order to determine under what circumstances these restrictions are satisfied, we need estimates of $\hat{T}_\beta$ and $\hat{T}_\sigma$. To do this, we first return to eqs 2.11 and 2.12 and use those definitions to obtain

$$\hat{T}_\beta = \langle T_\beta\rangle^\beta - \langle T\rangle = \epsilon_\sigma(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) \tag{3.10a}$$

$$\hat{T}_\sigma = \langle T_\sigma\rangle^\sigma - \langle T\rangle = \epsilon_\beta(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta) \tag{3.10b}$$

Here it becomes clear that we need an estimate of the *temperature difference*, $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$, if we are to produce useful constraints on the basis of eqs 3.7–3.9. The first estimates of this temperature difference were based on an order of magnitude analysis of the interfacial flux terms in eq 2.5 and 2.8 (Whitaker, 1980, Section 3.3). While those first estimates were reasonable, and they led to reasonable results, an idea of obvious fundamental importance was overlooked. We state this idea as follows:

If one seeks information about a field, such as $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$, one should derive the governing differential equation for the field.

In the previous section, we *added* eqs 2.5 and 2.8 in order to obtain the governing differential equation for the *sum*, $\epsilon_\beta\langle T_\beta\rangle^\beta + \epsilon_\sigma\langle T_\sigma\rangle^\sigma$. Now it seems logical that we should *subtract* eq 2.8 from 2.5 in order to obtain the governing differential equation for the *difference*, $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$. Before doing this, it is some interest to use eqs 3.10 in eqs 3.7–3.9 to obtain

$$\epsilon_\beta\epsilon_\sigma[(\rho c_p)_\beta - (\rho c_p)_\sigma] \frac{\partial}{\partial t}(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) \ll \nabla\cdot[(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)\nabla\langle T\rangle] \tag{3.11}$$

$$\epsilon_\sigma\epsilon_\beta(\rho c_p)_\beta\langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) \ll \nabla\cdot[(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)\nabla\langle T\rangle] \tag{3.12}$$

$$\nabla\cdot[\epsilon_\beta\epsilon_\sigma(k_\beta - k_\sigma)\nabla(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma)] \ll \nabla\cdot[(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)\nabla\langle T\rangle] \tag{3.13}$$

Here we see that the restrictions associated with local thermal equilibrium are automatically satisfied when the conditions indicated by eqs 3.6 are imposed. We also see that the thermal sources, Φ_σ and Ω, play no *direct* role in the above constraints.

Governing Equation for $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$. The governing equation for $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ can only be developed in an approximate sense, and in order to simplify this development without imposing a severe limitation on the physics of the process, we neglect the variations in ϵ_β and ϵ_σ. This allows us to express eqs 2.5 and 2.8 as

$$(\rho c_p)_\beta \frac{\partial\langle T_\beta\rangle^\beta}{\partial t} + (\rho c_p)_\beta\langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T_\beta\rangle^\beta + (\rho c_p)_\beta\nabla\cdot\langle\tilde{\mathbf{v}}_\beta\tilde{T}_\beta\rangle^\beta = \nabla\cdot\left[k_\beta\left(\nabla\langle T_\beta\rangle^\beta + \frac{1}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{T}_\sigma\, dA\right)\right] + \frac{\epsilon_\beta^{-1}}{\mathcal{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla T_\beta dA \tag{3.14a}$$

$$(\rho c_p)_\sigma \frac{\partial\langle T_\sigma\rangle^\sigma}{\partial t} = \nabla\cdot\left[k_\sigma\left(\nabla\langle T_\sigma\rangle^\sigma + \frac{1}{V_\sigma}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\, dA\right)\right] + \langle\Phi_\sigma\rangle^\sigma + \frac{\epsilon_\sigma^{-1}}{\mathcal{V}}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla T_\sigma\, dA \tag{3.14b}$$

We now subtract eq 3.14b from eq 3.14a to obtain

$$(\rho c_p)_\beta \frac{\partial \langle T_\beta\rangle^\beta}{\partial t} - (\rho c_p)_\sigma \frac{\partial \langle T_\sigma\rangle^\sigma}{\partial t} + (\rho c_p)_\beta \langle \mathbf{v}_\beta\rangle^\beta \cdot \nabla \langle T_\beta\rangle^\beta + (\rho c_p)_\beta \nabla\cdot\langle \tilde{\mathbf{v}}_\beta \tilde{T}_\beta\rangle^\beta = \nabla\cdot[k_\beta \nabla\langle T_\beta\rangle^\beta - k_\sigma \nabla \langle T_\sigma\rangle^\sigma] + \frac{k_\beta}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{T}_\beta \, dA - \frac{k_\sigma}{V_\sigma}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\tilde{T}_\sigma \, dA + (\epsilon_\beta\epsilon_\sigma)^{-1}\frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla T_\beta \, dA - \epsilon_\sigma^{-1} a_v \langle \Omega\rangle_{\beta\sigma} - \langle \Phi_\sigma\rangle^\sigma \quad (3.15)$$

Use of eqs 2.11 allows us to express this result in the form

$$(\rho c_p)_\beta \frac{\partial \hat{T}_\beta}{\partial t} - (\rho c_p)_\sigma \frac{\partial \hat{T}_\sigma}{\partial t} + [(\rho c_p)_\beta - (\rho c_p)_\sigma] \frac{\partial \langle T\rangle}{\partial t} + (\rho c_p)_\beta \langle \mathbf{v}_\beta\rangle^\beta \cdot \nabla\langle T\rangle + (\rho c_p)_\beta \langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla \hat{T}_\beta + (\rho c_p)_\beta \nabla\cdot\langle \tilde{\mathbf{v}}_\beta\tilde{T}_\beta\rangle^\beta = \nabla\cdot\left[k_\beta\nabla\hat{T}_\beta - k_\sigma\nabla\hat{T}_\sigma + (k_\beta - k_\sigma)\nabla\langle T\rangle + \frac{k_\beta}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{T}_\beta\, dA - \frac{k_\sigma}{V_\sigma}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\tilde{T}_\sigma \, dA\right] + (\epsilon_\beta\epsilon_\sigma)^{-1}\frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla T_\beta\, dA - \epsilon_\sigma^{-1} a_v\langle\Omega\rangle_{\beta\sigma} - \langle\Phi_\sigma\rangle^\sigma \quad (3.16)$$

and if the representations for $\hat{T}_\beta$ and $\hat{T}_\sigma$ given by eqs 3.10 are employed, we begin to see a governing differential equation for $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$. This is given by

$$[\epsilon_\sigma(\rho c_p)_\beta + \epsilon_\beta(\rho c_p)_\sigma]\frac{\partial}{\partial t}(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) + [(\rho c_p)_\beta - (\rho c_p)_\sigma]\frac{\partial\langle T\rangle}{\partial t} + (\rho c_p)_\beta\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T\rangle + \epsilon_\sigma(\rho c_p)_\beta\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) + (\rho c_p)_\beta\nabla\cdot\langle\tilde{\mathbf{v}}_\beta\tilde{T}_\beta\rangle^\beta = \nabla\cdot\left[(\epsilon_\sigma k_\beta + \epsilon_\beta k_\sigma)\nabla(\langle T_\beta\rangle - \langle T_\sigma\rangle^\sigma) + (k_\beta - k_\sigma)\nabla\langle T\rangle + \frac{k_\beta}{V_\beta}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{T}_\beta\, dA - \frac{k_\sigma}{V_\sigma}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\, dA\right] + (\epsilon_\beta\epsilon_\sigma)^{-1}\frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla T_\beta\, dA - \epsilon_\sigma^{-1}a_v\langle\Omega\rangle_{\beta-\sigma} - \langle\Phi_\sigma\rangle^\sigma \quad (3.17)$$

Here we see an accumulation term, a convective transport term, and a conductive term, all of which involve the temperature difference, $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$. In addition, a portion of the interfacial flux is proportional to $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ and on the basis of previous studies (Whitaker, 1980, Section 3.3; Whitaker, 1986a) one can represent the interfacial flux as

$$\frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla T_\beta\, dA = -\mathbf{O}\left[\frac{a_v(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma)}{\dfrac{\delta_\beta}{k_\beta} + \dfrac{\delta_\sigma}{k_\sigma}}\right] + \frac{a_v\langle\Omega\rangle_{\beta\sigma}}{1 + \mathbf{O}\left(\dfrac{\delta_\beta}{\delta_\sigma}\dfrac{k_\sigma}{k_\beta}\right)} \quad (3.18)$$

Here δ_β and δ_σ represent the characteristic lengths associated with the estimates

$$\frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla T_\beta\, dA = \mathbf{O}\left[\frac{k_\beta}{\delta_\beta}(\langle T_\mathrm{i}\rangle_{\beta\sigma} - \langle T_\beta\rangle^\beta)\right] \quad (3.19a)$$

$$\frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\sigma\nabla T_\sigma\, dA = \mathbf{O}\left[\frac{k_\sigma}{\delta_\sigma}(\langle T_\sigma\rangle^\sigma - \langle T_\mathrm{i}\rangle_{\beta\sigma})\right] \quad (3.19b)$$

in which $\langle T_\mathrm{i}\rangle_{\beta\sigma}$ represents the area average interfacial temperature. For the case under consideration, it seems reasonable to replace δ_σ with ℓ_σ, which is illustrated in Figure 3. On the other hand δ_β could be thought of as a thermal boundary layer thickness over certain portions of the β–σ interface; thus we will need to consider this characteristic length in more detail later.

Substitution of eq 3.18 into 3.17 leads to an approximate form of the governing differential equation for $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ which can be expressed as

$$[\epsilon_\sigma(\rho c_p)_\beta + \epsilon_\beta(\rho c_p)_\sigma]\frac{\partial}{\partial t}(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) + \epsilon_\sigma(\rho c_p)_\beta\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) - \nabla\cdot[(\epsilon_\sigma k_\beta + \epsilon_\beta k_\sigma)\nabla(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma)] + \mathbf{O}\left[\frac{a_v(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma)}{\epsilon_\beta\epsilon_\sigma\left(\dfrac{\delta_\beta}{k_\beta} + \dfrac{\delta_\sigma}{k_\sigma}\right)}\right] = -[(\rho c_p)_\beta - (\rho c_p)_\sigma]\frac{\partial\langle T\rangle}{\partial t} - (\rho c_p)_\beta\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T\rangle - (\rho c_p)_\beta\cdot\nabla\langle\tilde{\mathbf{v}}_\beta\tilde{T}_\beta\rangle^\beta + \nabla\cdot\left[(k_\beta - k_\sigma)\nabla\langle T\rangle + \frac{k_\beta}{V_\beta}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{T}_\beta\, dA - \frac{k_\sigma}{V_\sigma}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\, dA\right] + \left\{\frac{1 - \epsilon_\beta\left[1 + \mathbf{O}\left(\dfrac{\delta_\beta}{\delta_\sigma}\dfrac{k_\sigma}{k_\beta}\right)\right]}{\epsilon_\beta\epsilon_\sigma\left[1 + \mathbf{O}\left(\dfrac{\delta_\beta}{\delta_\sigma}\dfrac{k_\sigma}{k_\beta}\right)\right]}\right\} a_v\langle\Omega\rangle_{\beta\sigma} - \langle\Phi_\sigma\rangle^\sigma \quad (3.20)$$

One can now return to eq 3.6 and note that when those three conditions are imposed, all the terms on the right-hand side of eq 3.20 will be zero except for the two integrals involving $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ and the two terms involving $\langle\Omega\rangle_{\beta\sigma}$ and $\langle\Phi_\sigma\rangle^\sigma$. Details concerning the $\tilde{T}_{\beta\sigma}$ and $\tilde{T}_\sigma$ fields are available from the closure problem which is presented in section 4, and from that development one can conclude that $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ will be negligibly small when eqs 3.6 are in force. This means that eq 3.20 leads to

$$\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma = 0 \quad (3.21)$$

when the conditions indicated by eqs 3.6 are imposed and the thermal sources are zero. Equation 3.20 also indicates that $\langle\Omega\rangle_{\beta\sigma}$ and $\langle\Phi_\sigma\rangle^\sigma$ can cause nonzero values of $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$, and this is entirely consistent with our intuition.

Our objective at this point is to obtain an estimate of the magnitude of $\langle T_\beta\rangle_\beta - \langle T_\sigma\rangle^\sigma$ for use with the restrictions given by eqs 3.11–3.13. To do this we being with estimates of the form (Whitaker, 1983, Section 2.9)

$$\frac{\partial}{\partial t}(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) = \mathbf{O}\left[\frac{\Delta(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma)}{t^*}\right] \quad (3.22a)$$

$$\nabla^2(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) = \mathbf{O}\left[\frac{\Delta(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma)}{L_c^2}\right] \quad (3.22b)$$

$$\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) = \mathbf{O}\left[\frac{\langle\mathbf{v}_\beta\rangle^\beta\Delta(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma)}{L_{\rho c_p}}\right] \quad (3.22c)$$

Here L_c and $L_{\rho c_p}$ represent the *conductive length* and the *convective length* which are discussed elsewhere (Whitaker, 1982, Section 1.1.3.3). The convective length represents the distance over which significant variations of $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ occur *along a volume average streamline*. For the packed bed reactor shown in Figure 2, the *convective length* could be the length of the reactor. On the other hand, if there are sharp temperature fronts moving through a reactor (Butt and Billimoria, 1978; Liu and Amundson, 1962; Liu et al., 1963; Eigenberger, 1972a,b) the characteristic length $L_{\rho c_p}$ could be much smaller than the length of the reactor. The *conductive length* represents the shortest distance over which significant variations in $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ occur. In an adiabatic reactor L_c and $L_{\rho c_p}$ will be equivalent; however, if significant radial gradients are present in a reactor, the *conductive length* will be on the order of the reactor diameter. We will use L_c and $L_{\rho c_p}$ to construct the order of magnitude estimates whenever the characteristic length is obvious. When there is some uncertainty, the macroscopic length scale will simply be identified as L.

In eq 3.22a we have used $\Delta(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma)$ to represent the change in $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ that occurs over the characteristic time t^*, while in eqs 3.22b and 3.22c we have used the same symbol to represent changes that occur over the distances L_c and $L_{\rho c_p}$. For most systems the changes in a volume average quantity that occur over t^*, L_c, and $L_{\rho c_p}$ are generally the same order of magnitude; thus the lack of a definitive nomenclature in eqs 3.22 is not a problem. In addition, we must remember that $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ represents a *macroscopic spatial deviation* as indicated by eqs 3.10. This means that the change of $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ will be on the order of $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ itself and eqs 3.22 can be expressed as

$$\frac{\partial}{\partial t}(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) = \mathbf{O}\left[\frac{\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma}{t^*}\right] \quad (3.23a)$$

$$\nabla^2(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) = \mathbf{O}\left[\frac{\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma}{L_c^{\,2}}\right] \quad (3.23b)$$

$$\langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) = \mathbf{O}\left[\frac{(\langle \mathbf{v}_\beta\rangle^\beta)(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma)}{L_{\rho c_p}}\right] \quad (3.23c)$$

If we use these estimates in eq 3.20, we can estimate the left-hand side of that result as

$$[\epsilon_\sigma(\rho c_p)_\beta + \epsilon_\beta(\rho c_p)_\sigma]\frac{\partial}{\partial t}(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) + \epsilon_\sigma(\rho c_p)_\beta\langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) - \nabla\cdot[(\epsilon_\sigma k_\beta + \epsilon_\beta k_\sigma)\nabla(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma)] + \mathbf{O}\left[\frac{a_v(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma)}{\epsilon_\beta\epsilon_\sigma\left(\frac{\delta_\beta}{k_\beta} + \frac{\delta_\sigma}{k_\sigma}\right)}\right] =$$

$$\frac{(\rho c_p)_{\beta\sigma}}{t^*}\left\{1 + \mathbf{O}\left[\epsilon_\sigma\left(\frac{k_\beta}{k_{\beta\sigma}}\right)Pe\left(\frac{d_p}{L_{\rho c_p}}\right)\left(\frac{\alpha_{\beta\sigma}t^*}{d_p^{\,2}}\right)\right] + \mathbf{O}\left(\frac{\alpha_{\beta\sigma}t^*}{L_c^{\,2}}\right) + \mathbf{O}\left[\frac{\alpha_{\beta\sigma}t^*/a_v^{-1}d_p}{\epsilon_\beta\epsilon_\sigma\left(\frac{k_{\beta\sigma}}{d_p}\right)\left(\frac{\delta_\beta}{k_\beta} + \frac{\delta_\sigma}{k_\sigma}\right)}\right]\right\} \times (\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) \quad (3.24)$$

Here we have introduced the following nomenclature:

$$(\rho c_p)_{\beta\sigma} = \epsilon_\sigma(\rho c_p)_\beta + \epsilon_\beta(\rho c_p)_\sigma \quad (3.25a)$$

$$k_{\beta\sigma} = \epsilon_\sigma k_\beta + \epsilon_\beta k_\sigma \quad (3.25b)$$

$$\alpha_{\beta\sigma} = k_{\beta\sigma}/(\rho c_p)_{\beta\sigma} \quad (3.25c)$$

$$Pe = \langle \mathbf{v}_\beta\rangle^\beta d_p/\alpha_\beta \quad (3.25d)$$

$$\alpha_\beta = k_\beta/(\rho c_p)_\beta \quad (3.25e)$$

with the intent of simplifying a complex representation.

In order to develop a useful estimate of the right-hand side of eq 3.20, we first note that the closure problem presented in the next section can be used to conclude that

$$\left\{\frac{k_\beta}{V_\beta}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{T}_\beta\, dA - \frac{k_\sigma}{V_\sigma}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\, dA\right\} = \mathbf{O}(k_\beta - k_\sigma)\nabla\langle T\rangle \quad (3.26)$$

This means that for estimating purposes we need to retain only the term $(k_\beta - k_\sigma)\nabla\langle T\rangle$ in order to represent the conductive contribution to the right-hand side of eq 3.20. In addition to this simplification, we can also simplify the heterogeneous thermal source by considering the two limiting cases:

$$\left(\frac{\delta_\beta}{\delta_\sigma}\frac{k_\sigma}{k_\beta}\right) \gg 1, \quad \left(\frac{\delta_\beta}{\delta_\sigma}\frac{k_\sigma}{k_\beta}\right) \ll 1 \quad (3.27)$$

These extreme cases lead to the estimate

$$\left\{\frac{1 - \epsilon_\beta\left[1 + \mathbf{O}\left(\frac{\delta_\beta}{\delta_\sigma}\frac{k_\sigma}{k_\beta}\right)\right]}{\epsilon_\beta\epsilon_\sigma\left[1 + \mathbf{O}\left(\frac{\delta_\beta}{\delta_\sigma}\frac{k_\sigma}{k_\beta}\right)\right]}\right\}a_v\langle\Omega\rangle_{\beta\sigma} = \mathbf{O}\left(\frac{\epsilon_\omega}{\epsilon_\beta\epsilon_\sigma}\right)a_v\langle\Omega\rangle_{\beta\sigma} \quad (3.28)$$

where ω represents both β and σ. In addition to eqs 3.26 and 3.28, we use the standard estimates

$$\frac{\partial\langle T\rangle}{\partial t} = \mathbf{O}\left(\frac{\Delta\langle T\rangle}{t^*}\right) \quad (3.29a)$$

$$\nabla^2\langle T\rangle = \mathbf{O}\left(\frac{\Delta\langle T\rangle}{L_c^{\,2}}\right) \quad (3.29b)$$

$$\langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T\rangle = \mathbf{O}\left(\frac{\langle \mathbf{v}_\beta\rangle^\beta\Delta\langle T\rangle}{L_{\rho c_p}}\right) \quad (3.29c)$$

in order to estimate the right-and side of eq 3.20 as

$$\mathrm{RHS} = \mathbf{O}\{[(\rho c_p)_\beta - (\rho c_p)_\sigma]\Delta\langle T\rangle/t^*\} + \mathbf{O}\{(\rho c_p)_\beta\langle \mathbf{v}_\beta\rangle^\beta\Delta\langle T\rangle/L_{\rho c_p}\} + \mathbf{O}\left\{\frac{(k_\beta - k_\sigma)\Delta\langle T\rangle}{L_c^{\,2}}\right\} + \mathbf{O}\left\{\left(\frac{\epsilon_\omega}{\epsilon_\beta\epsilon_\sigma}\right)a_v\langle\Omega\rangle_{\beta\sigma}\right\} + \mathbf{O}\{\langle\Phi_\sigma\rangle^\sigma\} \quad (3.30)$$

Here we have neglected dispersive transport relative to convective transport. When this result is used in eq 3.20 along with eq 3.24, we obtain the following estimate for $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$:

$$\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma = \Lambda\Delta\langle T\rangle \quad (3.31)$$

where Λ is given by

$$\Lambda = \mathbf{O}\left\{\left[\frac{(\rho c_p)_\beta - (\rho c_p)_\sigma}{(\rho c_p)_{\beta\sigma}}\right]\frac{d_p^2}{\alpha_{\beta\sigma}t^*} + \mathbf{O}\left[\left(\frac{k_\beta}{k_{\beta\sigma}}\right)\left(\frac{d_p}{L_{\rho c_p}}\right)Pe\right] + \mathbf{O}\left[\left(\frac{k_\beta - k_\sigma}{k_{\beta\sigma}}\right)\left(\frac{d_p}{L_c}\right)^2\right] + \Sigma\right\} \bigg/ \left\{\frac{d_p^2}{\alpha_{\beta\sigma}t^*} + \mathbf{O}\left[\epsilon_\sigma\left(\frac{k_\beta}{k_{\beta\sigma}}\right)\left(\frac{d_p}{L_{\rho c_p}}\right)Pe\right] + \mathbf{O}\left(\frac{d_p}{L_c}\right)^2 + \Theta\right\} \quad (3.32)$$

The parameter Σ represents the contribution owing to the thermal sources

$$\Sigma = \mathbf{O}\left[\left(\frac{\epsilon_\omega}{\epsilon_\beta\epsilon_\sigma}\right)\frac{a_v\langle\Omega\rangle_{\beta\sigma}d_p^2}{k_{\beta\sigma}\Delta\langle T\rangle}\right] + \mathbf{O}\left[\frac{\langle\Phi_\sigma\rangle^\sigma d_p^2}{k_{\beta\sigma}\Delta\langle T\rangle}\right] \quad (3.33)$$

while Θ is a parameter defined by

$$\Theta = \mathbf{O}\left[\frac{d_p a_v}{\epsilon_\beta\epsilon_\sigma\left(\frac{k_{\beta\sigma}}{d_p}\right)\left(\frac{\delta_\beta}{k_\beta} + \frac{\delta_\sigma}{k_\sigma}\right)}\right] \quad (3.34)$$

Since d_p, a_v^{-1}, δ_β, and δ_σ will generally be on the same order of magnitude, Θ can never be too different from $(\epsilon_\beta\epsilon_\sigma)^{-1}$ and we express this idea as

$$\Theta = \mathbf{O}[(\epsilon_\beta\epsilon_\sigma)^{-1}] \quad (3.35)$$

One must keep in mind that we do not know the sign (positive or negative) of the estimates that appear in eqs 3.32–3.34. This certainly limits the usefulness of this type of analysis, since two terms of the same order of magnitude may combine to yield a result of the same order of magnitude or a result that is much less than the order of magnitude of the original two terms. Clearly one must use eqs 3.31–3.35 judiciously.

We are now in a position to return to the restrictions given by eqs 3.11–3.13 and make use of eqs 3.23, 3.29, and 3.31 to obtain the following constraints.

$$\left\{\frac{\epsilon_\beta\epsilon_\sigma[(\rho c_p)_\beta - (\rho c_p)_\sigma]L_c^2}{(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)t^*}\right\}\Lambda \ll 1 \quad (3.36)$$

$$\left\{\epsilon_\beta\epsilon_\sigma Pe\left(\frac{L_c}{d_p}\right)\left(\frac{L_c}{L_{\rho c_p}}\right)\left(\frac{k_\beta}{\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma}\right)\right\}\Lambda \ll 1 \quad (3.37)$$

$$\left\{\frac{\epsilon_\beta\epsilon_\sigma(k_\beta - k_\sigma)}{(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)}\right\}\Lambda \ll 1 \quad (3.38)$$

Earlier we noted that Φ_σ and Ω played no *direct* role in the restrictions given by eqs 3.11–3.13; however, we now see that these two thermal sources do appear in the constraints given by eqs 3.36–3.38 since $\langle\Phi_\sigma\rangle^\sigma$ and $\langle\Omega\rangle_{\beta\sigma}$ appear in the term Λ.

Once again we note that eqs 3.36–3.40 are *automatically satisfied* when the conditions given by eq 3.6 are imposed, and we also note that this is not the case for the constraints originally presented by Whitaker (Section 3.3, 1980; 1986a). Those original constraints were based on eqs 3.4 and 3.5 as opposed to the less severe (but acceptable) constaints given by eqs 3.7–3.9.

The general transient form of Λ is quite complex, and it would seem best to develop specific values of Λ for the study of transient processes. However, one can consider the special case $t^* \to 0$ with $\Sigma = 0$ in order to extract the following simple forms of eqs 3.36–3.38:

$$\left\{\frac{\epsilon_\beta\epsilon_\sigma[(\rho c_p)^\beta - (\rho c_p)_\sigma]L_c^2}{(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)t^*}\right\}\left[\frac{(\rho c_p)_\beta - (\rho c_p)_\sigma}{(\rho c_p)_{\beta\sigma}}\right] \ll 1 \quad (3.39)$$

$$\left\{\epsilon_\beta\epsilon_\sigma Pe\left(\frac{L_c}{d_p}\right)\left(\frac{L_c}{L_{\rho c_p}}\right)\left(\frac{k_\beta}{\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma}\right)\right\} \times \left[\frac{(\rho c_p)_\beta - (\rho c_p)_\sigma}{(\rho c_p)_{\beta\sigma}}\right] \ll 1 \quad (3.40)$$

$$\left\{\frac{\epsilon_\beta\epsilon_\sigma(k_\beta - k_\sigma)}{\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma}\right\}\left[\frac{(\rho c_p)_\beta - (\rho c_p)_\sigma}{(\rho c_p)_{\beta\sigma}}\right] \ll 1 \quad (3.41)$$

Here one should keep in mine that L_c and $L_{\rho c_p}$ may depend on t^*.

The *long-time* or steady-state form of Λ can be extracted by letting t^* become arbitrarily large. This leads to

$$\Lambda = \frac{\mathbf{O}\left[\epsilon_\sigma\left(\frac{k_\beta}{k_{\beta\sigma}}\right)\left(\frac{d_p}{L_{\rho c_p}}\right)Pe\right] + \mathbf{O}\left[\left(\frac{k_\beta - k_\sigma}{k_{\beta\sigma}}\right)\left(\frac{d_p}{L_c}\right)^2\right] + \Sigma}{\mathbf{O}\left[\epsilon_\sigma\left(\frac{k_\beta}{k_{\beta\sigma}}\right)\left(\frac{d_p}{L_{\rho c_p}}\right)Pe\right] + \mathbf{O}\left(\frac{d_p}{L_c}\right)^2 + \Theta} \quad (3.42)$$

and from this result we can see that $\Lambda \to 1$ when *convective effects dominate*. Under these circumstances the constraint given by eq 3.37 may not be satisfied; however, one must be very careful to note that the phrase *convective effects* refers primarily to the quantity $Pe/L_{\rho c_p}$ in both eq 3.42 and eq 3.37. If we return to eq 2.17, and consider the case in which convective and conductive effects are the same order of magnitude

$$\epsilon_\beta(\rho c_p)_\beta\langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T\rangle \sim \nabla\cdot[(\mathbf{K}_{\text{eff}} + \mathbf{K}_D)\cdot\nabla\langle T\rangle] \quad (3.43)$$

we can develop the following estimate

$$Pe\left(\frac{d_p}{L_{\rho c_p}}\right) = \mathbf{O}\left\{\left(\frac{\mathbf{K}_{\text{eff}} + \mathbf{K}_D}{\epsilon_\beta k_\beta}\right)\left(\frac{d_p}{L_c}\right)^2\right] \quad (3.44)$$

From this it becomes clear that the constraint given by eq 3.37 does not automatically fail at large values of the Peclet number.

Characteristic Lengths. We have already commented on the characteristic lengths identified by $L_{\rho c_p}$ and L_c, and we need to say something about δ_σ and δ_β before completing this section. The characteristic lengths, δ_σ and δ_β, are defined by the order of magnitude estimates given by eqs 3.19. Because these are only *estimates*, they do not provide precise values of δ_σ and δ_β; however, we do have some knowledge of these lengths from the solution of special boundary value problems. For example, during the early stages of a transient process we could estimate δ_σ according to

$$\delta_\sigma = \mathbf{O}[(\alpha_\sigma t)^{1/2}] \quad (3.45)$$

provided δ_σ was less than ℓ_σ. When eq 3.45 is a valid estimate of δ_σ, it seems certain that the constraint given by eq 3.36 would fail. For steady-state processes, or characteristic times such that $(\alpha_\sigma t^*)^{1/2} > \ell_\sigma$, we take δ_σ to be on the order of ℓ_σ and this leads to

$$\delta_\sigma \sim \ell_\sigma \sim a_v^{-1} \sim d_p \tag{3.46}$$

In the β-phase, the steady-state value of δ_β would be the smallest of either the *thermal boundary layer thickness* or ℓ_β. Since ℓ_β will be the same order as d_p, we can estimate the steady-state value of δ_β as

$$\delta_\beta = \mathbf{O}(d_p), \quad Re^{1/2}Pr^{1/3} < 1 \tag{3.47a}$$

$$\delta_\beta = \mathbf{O}(d_p/Re^{1/2}Pr^{1/3}), \quad Re^{1/2}Pr^{1/3} > 1 \tag{3.47b}$$

Here the Reynolds number and the Prandtl number are defined by

$$Re = \langle v_\beta \rangle^\beta d_p/\nu_\beta, \quad Pr = \mu_\beta/\alpha_\beta \tag{3.48}$$

These representations of δ_σ and δ_β can be used to estimate the value of Θ as given by eq 3.34; however, one should remember that eq 3.35 provides a reasonable reliable estimate of Θ.

Thermal Sources. Since a knowledge of Λ is crucial to our understanding of the conditions of local thermal equilibrium, it is apparent that we need to know $\langle \Omega \rangle_{\beta\sigma}$, $\langle \Phi_\sigma \rangle^\sigma$, and $\Delta\langle T \rangle$ if we are to determine Λ. This suggests that we need to solve eq 2.17 for specified values of $\langle \Omega \rangle_{\beta\sigma}$ and $\langle \Phi_\sigma \rangle^\sigma$ in order to determine $\Delta\langle T \rangle$; however, at this point we are not certain that the closure representations given by eqs 2.16 are valid and this means that we have not yet established the range of validity of eq 2.17. To explore this matter, we need to examine the closure problem for $\tilde{T}_\sigma$ and $\tilde{T}_\beta$ and this is done in the next section.

4. Closure

On the basis of the restrictions given by eqs 3.7–3.9 and the associated constraints given by eqs 3.36–3.38, we conclude that eq 2.13 can be simplified to eq 2.15. However, we do not know whether the closure representations given by eqs 2.16 are valid, and exploring their validity is the objective of this section.

In order to develop the closure problem for $\tilde{T}_\beta$ and $\tilde{T}_\sigma$, we return to the boundary value problem given by eqs 2.1–2.4 and make use of the decompositions given by

$$T_\beta = \langle T_\beta \rangle^\beta - \tilde{T}_\beta, \quad T_\sigma = \langle T_\sigma \rangle^\sigma + \tilde{T}_\sigma \tag{4.1}$$

Following the method of Crapiste et al. (1986), we use the decompositions in eqs 2.1 and 2.4 and express the results as

$$(\rho c_p)_\beta \left(\frac{\partial \tilde{T}_\beta}{\partial t} + \mathbf{v}_\beta \cdot \tilde{T}_\beta + \tilde{\mathbf{v}}_\beta \cdot \nabla \langle T_\beta \rangle^\beta \right) - \nabla \cdot (k_\beta \nabla \tilde{T}_\beta) = -(\rho c_p)_\beta \left(\frac{\partial \langle T_\beta \rangle^\beta}{\partial t} + \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle T_\beta \rangle^\beta \right) + \nabla \cdot (k_\beta \nabla \langle T_\beta \rangle^\beta) \tag{4.2}$$

B.C.1 $\quad \tilde{T}_\beta = \tilde{T}_\sigma + \langle T_\sigma \rangle^\sigma - \langle T_\beta \rangle^\beta, \quad \text{at } \mathcal{A}_{\beta\sigma} \quad (4.3)$

B.C.2 $\quad \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \tilde{T}_\beta = \mathbf{n}_{\beta\sigma} \cdot k_\sigma \nabla \tilde{T}_\sigma + \mathbf{n}_{\beta\sigma} \cdot k_\sigma \nabla \langle T_\sigma \rangle^\sigma - \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \langle T_\beta \rangle^\beta + \langle \Omega \rangle_{\beta\sigma} + \tilde{\Omega}, \quad \text{at } \mathcal{A}_{\beta\sigma} \quad (4.4)$

$$(\rho c_p)_\sigma \frac{\partial \tilde{T}_\sigma}{\partial t} - \nabla \cdot (k_\sigma \nabla \tilde{T}_\sigma) - \tilde{\Phi}_\sigma = -(\rho c_p)_\sigma \frac{\partial \langle T_\sigma \rangle^\sigma}{\partial t} + \nabla \cdot (k_\sigma \nabla \langle T_\sigma \rangle^\sigma) + \langle \Phi_\sigma \rangle^\sigma \tag{4.5}$$

In addition to eqs 4.1 we have also used the decompositions

$$\Phi_\sigma = \langle \Phi_\sigma \rangle^\sigma + \tilde{\Phi}_\sigma, \quad \Omega = \langle \Omega \rangle_{\beta\sigma} + \tilde{\Omega} \tag{4.6}$$

and we have been careful to place all the averaged quantities on the right-hand side of the governing differential equations. Carbonell and Whitaker (1984) have shown that averaged quantities (such as the right-hand side of eq 4.2) can be treated as constants with respect to integration over the averaging volume when the following length-scale constraint is satisfied:

$$(r_0/L)^2 \ll 1 \tag{4.7}$$

This allows us to express eq 4.2 as (Crapiste et al., 1986)

$$(\rho c_p)_\beta \left(\frac{\partial \tilde{T}_\beta}{\partial t} + \mathbf{v}_\beta \cdot \nabla \tilde{T}_\beta + \tilde{\mathbf{v}}_\beta \cdot \nabla \langle T_\beta \rangle^\beta \right) - \nabla \cdot (k_\beta \nabla \tilde{T}_\beta) = (\rho c_p)_\beta \left\{ \frac{1}{V_\beta} \int_{V_\beta} \left(\frac{\partial \tilde{T}_\beta}{\partial t} + \mathbf{v}_\beta \cdot \nabla \tilde{T}_\beta + \tilde{\mathbf{v}}_\beta \cdot \nabla \langle T_\beta \rangle^\beta \right) \mathrm{d}V \right\} - \frac{1}{V_\beta} \int_{V_\beta} \nabla \cdot (k_\beta \nabla \tilde{T}_\beta) \, \mathrm{d}A \tag{4.8}$$

It is relatively easy (Carbonell and Whitaker, 1984) to develop arguments in favor of the inequalities

$$\frac{\partial \langle \tilde{T}_\beta \rangle^\beta}{\partial t} \ll \frac{\partial \tilde{T}_\beta}{\partial t}, \quad \langle \tilde{\mathbf{v}}_\beta \cdot \nabla \langle T_\beta \rangle^\beta \rangle^\beta \ll \tilde{\mathbf{v}}_\beta \cdot \nabla \langle T_\beta \rangle^\beta \tag{4.9}$$

thus eq 4.8 can be simplified to

$$(\rho c_p)^\beta \left(\frac{\partial \tilde{T}_\beta}{\partial t} + \mathbf{v}_\beta \cdot \nabla \tilde{T}_\beta + \tilde{\mathbf{v}}_\beta \cdot \nabla \langle T_\beta \rangle^\beta \right) - \nabla \cdot (k_\beta \nabla \tilde{T}_\beta) = (\rho c_p)_\beta \left\{ \frac{1}{V_\beta} \int_{V_\beta} \mathbf{v}_\beta \cdot \nabla \tilde{T}_\beta \, \mathrm{d}V \right\} - \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \tilde{T}_\beta \, \mathrm{d}A - \frac{1}{V_\beta} \int_{A_{\beta e}} \mathbf{n}_{\beta e} \cdot k_\beta \nabla \tilde{T}_\beta \, \mathrm{d}A \tag{4.10}$$

Here we have used the divergence theorem to represent the volume integral of $\nabla \cdot (k_\beta \nabla \tilde{T}_\beta)$ in terms of the area integrals over $A_{\beta\sigma}$ and $A_{\beta e}$. For an incompressible flow we can use the continuity equation

$$\nabla \cdot \mathbf{v}_\beta = 0 \tag{4.11}$$

and the divergence theorem to express the right-hand side of eq 4.10 entirely in terms of area integrals. This provides

$$(\rho c_p)_\beta \left(\frac{\partial \tilde{T}_\beta}{\partial t} + \mathbf{v}_\beta \cdot \nabla \tilde{T}_\beta + \tilde{\mathbf{v}}_\beta \cdot \nabla \langle T_\beta \rangle^\beta \right) - \nabla \cdot (k_\beta \nabla \tilde{T}_\beta) = (\rho c_p)_\beta \left\{ \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mathbf{v}_\beta \tilde{T}_\beta \, \mathrm{d}A \right\} + (\rho c_p)_\beta \left\{ \frac{1}{V_\beta} \times \int_{A_{\beta e}} \mathbf{n}_{\beta e} \cdot \mathbf{v}_\beta \tilde{T}_\beta \, \mathrm{d}A \right\} - \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mathbf{k}_\beta \nabla \tilde{T}_\beta \, \mathrm{d}A - \frac{1}{V_\beta} \int_{A_{\beta e}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \tilde{T}_\beta \mathrm{d}A \tag{4.12}$$

At the interface between the porous catalyst pellets and the fluid phase, convective transport will be negligible compared to conductive transport (Plumb and Whitaker, 1990a, Section V). This allows us to impose the inequality

$$(\rho c_p)_\beta \left\{ \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mathbf{v}_\beta \tilde{T}_\beta \, \mathrm{d}A \right\} \ll \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mathbf{k}_\beta \nabla \tilde{T}_\beta \, \mathrm{d}A \tag{4.13}$$

and thus simplify eq 4.12. In addition, it is plausible to suppose that $\mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \tilde{T}_\beta$ is the same order of magnitude as $\mathbf{n}_{\beta e} \cdot k_\beta \nabla \tilde{T}_\beta$ and this leads to

$$\frac{1}{V_\beta} \int_{A_{\beta e}} \mathbf{n}_{\beta e} \cdot k_\beta \nabla \tilde{T}_\beta \, \mathrm{d}A \ll \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \tilde{T}_\beta \, \mathrm{d}A \tag{4.14}$$

since $A_{\beta e}$ is much less than $A_{\beta\sigma}$ on the basis of the length-scale constraint given by eq 2.10. Given eqs 4.13 and 4.14, we can simplify eq 4.12 to

$$(\rho c_p)_\beta\left(\frac{\partial \tilde{T}_\beta}{\partial t} + \mathbf{v}_\beta\cdot\nabla\tilde{T}_\beta + \tilde{\mathbf{v}}_\beta\cdot\nabla\langle T_\beta\rangle^\beta\right) - \nabla\cdot(k_\beta\nabla\tilde{T}_\beta) = (\rho c_p)_\beta\left\{\frac{1}{V_\beta}\int_{A_{\beta e}}\mathbf{n}_{\beta e}\cdot\mathbf{v}_\beta\tilde{T}_\beta\,dA\right\} - \frac{1}{V_\beta}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta\,dA \tag{4.15}$$

At this point we can use the averaging theorem and the divergence theorem to obtain

$$(\rho c_p)_\beta\left\{\frac{1}{V_\beta}\int_{A_{\beta e}}\mathbf{n}_{\beta e}\cdot\mathbf{v}_\beta\tilde{T}_\beta\,dA\right\} = \epsilon_\beta^{-1}(\rho c_p)_\beta\nabla\cdot\langle\mathbf{v}_\beta\tilde{T}_\beta\rangle \tag{4.16}$$

and we can also express the convective flux term on the left-hand side of eq 4.15 as

$$(\rho c_p)_\beta\mathbf{v}_\beta\cdot\nabla\tilde{T}_\beta = (\rho c_p)_\beta\nabla\cdot(\mathbf{v}_\beta\tilde{T}_\beta) \tag{4.17}$$

The inequality

$$\nabla\cdot\langle\mathbf{v}_\beta\tilde{T}_\beta\rangle \ll \nabla\cdot(\mathbf{v}_\beta\tilde{T}_\beta) \tag{4.18}$$

is based on the idea that the characteristic length for $\langle\mathbf{v}_\beta\tilde{T}_\beta\rangle$ is L while characteristic length for $\mathbf{v}_\beta\tilde{T}_\beta$ is ℓ_β. Since the latter is much, much smaller than the former, the inequality given by eq 4.18 results. In terms of eq 4.15, this means that the following inequality can be imposed in order to simplify the governing differential equation for $\tilde{T}_\beta$.

$$(\rho c_p)_\beta\left\{\frac{1}{V_\beta}\int_{A_{\beta e}}\mathbf{n}_{\beta e}\cdot\mathbf{v}_\beta\tilde{T}_\beta\,dA\right\} \ll (\rho c_p)_\beta\mathbf{v}_\beta\cdot\nabla\tilde{T}_\beta \tag{4.19}$$

When eq 4.19 is used in eq 4.15, and the analysis given by eqs 4.8–4.19 is applied to eq 4.5, we can express the closure problem as

$$(\rho c_p)_\beta\left(\frac{\partial \tilde{T}_\beta}{\partial t} + \mathbf{v}_\beta\cdot\nabla\tilde{T}_\beta + \tilde{\mathbf{v}}_\beta\cdot\nabla\langle T_\beta\rangle^\beta\right) = \nabla\cdot(k_\beta\nabla\tilde{T}_\beta) - \frac{1}{V_\beta}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta\,dA \tag{4.20}$$

B.C.1 $\quad \tilde{T}_\beta = \tilde{T}_\sigma + \langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta, \quad \mathcal{A}_{\beta\sigma} \qquad (4.21)$

B.C.2 $\quad \mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta = \mathbf{n}_{\beta\sigma}\cdot k_\sigma\nabla\tilde{T}_\sigma + \mathbf{n}_{\beta\sigma}\cdot k_\sigma\nabla\langle T_\sigma\rangle^\sigma - \mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\langle T_\beta\rangle^\beta + \langle\Omega\rangle_{\beta\sigma} + \tilde{\Omega}, \quad \text{at } \mathcal{A}_{\beta\sigma} \qquad (4.22)$

$$(\rho c_p)_\sigma\frac{\partial\tilde{T}_\sigma}{\partial t} = \nabla\cdot(k_\sigma\nabla\tilde{T}_\sigma) + \tilde{\Phi}_\sigma - \frac{1}{V_\sigma}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\tilde{T}_\sigma\,dA \tag{4.23}$$

Levec and Carbonell (1985) have considered this heat-transfer process in the absence of thermal sources, and their result is essentially identical with eqs 4.20–4.23 when Φ_σ and Ω are zero. In addition, this closure problem has the same structure as that for mass transport and adsorption in a porous medium composed of porous particles (Plumb and Whitaker, 1990b, Section 7).

The term $\tilde{\Phi}_\sigma$ poses somewhat of a problem unless it is negligible relative to the other terms in eq 4.23. Since $\tilde{\Phi}_\sigma$ will be a function of both $\tilde{T}_\sigma$ and $\tilde{c}_A$ (Whitaker, 1989, eq 281) the $\tilde{T}_\sigma$ equation will be coupled to the $\tilde{c}_A$ equation and therefore coupled to $\nabla\langle c_A\rangle^\sigma$. Under these circumstances the closure representations given by eqs 2.16 will not be complete and the one-equation model given by eq 2.17 will contain additional terms related to $\nabla\langle c_A\rangle^\sigma$ and $\nabla^2\langle c_A\rangle^\sigma$.

If the homogeneous thermal source depends on the temperature and the concentration of only one species

$$\Phi_\sigma = \Phi_\sigma(T_\sigma, c_A) \tag{4.24}$$

it can be shown (Whitaker, 1987, 1988b, 1989) that $\tilde{\Phi}_\sigma$ takes the form

$$\tilde{\Phi}_\sigma = \left(\frac{\partial\Phi_\sigma}{\partial T_\sigma}\right)\tilde{T}_\sigma + \left(\frac{\partial\Phi_\sigma}{\partial c_A}\right)\tilde{c}_A \tag{4.25}$$

Under these circumstances, eq 4.23 takes the form

$$(\rho c_p)_\sigma\frac{\partial\tilde{T}_\sigma}{\partial t} = \nabla\cdot(k_\sigma\nabla\tilde{T}_\sigma) + \left(\frac{\partial\Phi_\sigma}{\partial T_\sigma}\right)\tilde{T}_\sigma + \left(\frac{\partial\Phi_\sigma}{\partial c_A}\right)\tilde{c}_A - \frac{1}{V_\sigma}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\tilde{T}_\sigma\,dA \tag{4.26}$$

Here we can clearly see the coupling between $\tilde{T}_\sigma$ and $\tilde{c}_A$ that we discussed in section 2, and if the one-equation model is to be valid this coupling must be negligible.

Our objective at this point is to determine under what circumstances $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ will be linear functions of $\nabla\langle T\rangle$. To accomplish this, we first make use of eqs 2.11 in order to express the closure problem as

$$(\rho c_p)_\beta\left(\frac{\partial \tilde{T}_\beta}{\partial t} + \mathbf{v}_\beta\cdot\nabla\tilde{T}_\beta + \tilde{\mathbf{v}}_\beta\cdot\nabla\langle T\rangle + \tilde{\mathbf{v}}_\beta\cdot\nabla\hat{T}_\beta\right) = \nabla\cdot(k_\beta\nabla\tilde{T}_\beta) - \frac{1}{V_\beta}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta\,dA \tag{4.27}$$

B.C.1 $\quad \tilde{T}_\beta = \tilde{T}_\sigma + \langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta, \quad \text{at } \mathcal{A}_{\beta\sigma} \qquad (4.28)$

B.C.2 $\quad \mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta = \mathbf{n}_{\beta\sigma}\cdot k_\sigma\nabla\tilde{T}_\sigma + \mathbf{n}_{\beta\sigma}\cdot(k_\sigma - k_\beta)\nabla\langle T\rangle + \mathbf{n}_{\beta\sigma}\cdot(k_\sigma\nabla\hat{T}_\sigma - k_\beta\nabla\hat{T}_\beta) + \langle\Omega\rangle_{\beta\sigma} + \tilde{\Omega}, \quad \text{at } \mathcal{A}_{\beta\sigma} \qquad (4.29)$

$$(\rho c_p)_\sigma\frac{\partial\tilde{T}_\sigma}{\partial t} = \nabla\cdot(k_\sigma\nabla\tilde{T}_\sigma) + \left(\frac{\partial\Phi_\sigma}{\partial T_\sigma}\right)\tilde{T}_\sigma + \left(\frac{\partial\Phi_\sigma}{\partial c_A}\right)\tilde{c}_A - \frac{1}{V_\sigma}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\tilde{T}_\sigma\,dA \tag{4.30}$$

In order that $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ depend only on $\nabla\langle T\rangle$, as suggested by eqs 2.16, it would appear that we must be able to neglect the following terms in eqs 4.27–4.30:

$$\tilde{\mathbf{v}}_\beta\cdot\nabla\hat{T}_\beta, \quad \langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta, \quad \mathbf{n}_{\beta\sigma}\cdot(k_\sigma\nabla\hat{T}_\sigma - k_\beta\nabla\hat{T}_\beta), \quad \tilde{\Omega}, \quad (\partial\Phi_\sigma/\partial c_A)\tilde{c}_A$$

The restrictions that one can propose to form the basis for neglecting these terms are not unique; however, there are some guidelines available to us in terms of the *sources* that serve as the generators of the $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ fields. If the five terms listed above are discarded, the sources that remain in the closure problem are given in the next section.

Sources.

$$\tilde{\mathbf{v}}_\beta\cdot\nabla\langle T\rangle, \quad \mathbf{n}_{\beta\sigma}\cdot(k_\sigma - k_\beta)\nabla\langle T\rangle, \quad \langle\Omega\rangle_{\beta\sigma}$$

These three sources (or nonhomogeneous terms) will be the generators of the $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ fields; thus one could argue that various terms in eqs 4.27–4.30 could be neglected if they were small compared to these sources. On the other hand, the homogeneous terms in the boundary value problem will be on the order of the source terms; thus one could argue that various terms in eqs 4.27–4.30 could be neglected if they are small compared to the homogeneous terms. Our situation is much more complex than the situation we encountered in the simplification of eq 2.13. There we were dealing with a single equation and no boundary conditions and it seemed reasonable to develop the restrictions on the basis of the smallest but nonzero term in the energy-transport equation. In this case we are dealing with two equations that are coupled through the boundary conditions given by eqs 4.28 and 4.29, and our choice of constraints is based largely on the comparison of like terms since this introduces a minimum of error into the order of magnitude estimates.

Our first restriction is given by

$$\tilde{\mathbf{v}}_\beta\cdot\nabla\hat{T}_\beta \ll \tilde{\mathbf{v}}_\beta\cdot\nabla\langle T\rangle \quad (4.31)$$

and this choice is motivated by the fact that $\tilde{\mathbf{v}}_\beta\cdot\nabla\langle T\rangle$ is a source of the same form as $\tilde{\mathbf{v}}_\beta\cdot\nabla\hat{T}_\beta$. Our second restriction is given by

$$\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta \ll \tilde{T}_\beta \quad (4.32)$$

and this choice is motivated by the fact that $\tilde{T}_\beta$ and $\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta$ are similar forms and they both appear in the boundary condition given by eq 4.28. This same type of reasoning leads to

$$k_\sigma\nabla\hat{T}_\sigma - k_\beta\nabla\hat{T}_\beta \ll k_\beta\nabla\tilde{T}_\beta \quad (4.33)$$

This latter restriction could be set up to neglect $k_\sigma\nabla\hat{T}_\sigma - k_\beta\nabla\hat{T}_\beta$ relative to $(k_\sigma - k_\beta)\nabla\langle T\rangle$ or relative to $\langle\Omega\rangle_{\beta\sigma}$; however, we must keep in mind that the $\tilde{T}_\beta$ field is influenced by all three of the sources listed above and by neglecting $k_\sigma\nabla\hat{T}_\sigma - k_\beta\nabla\hat{T}_\beta$ relative to $k_\beta\nabla\tilde{T}_\beta$ we capture the influence of all three sources.

It seems obvious that we should discard the deviation source terms according to

$$\tilde{\Omega} \ll \langle\Omega\rangle_{\beta\sigma} \quad (4.34)$$

$$\left(\frac{\partial\Phi_\sigma}{\partial c_{\mathrm{A}}}\right)\tilde{c}_{\mathrm{A}} \ll \left(\frac{\partial\Phi_\sigma}{\partial T_\sigma}\right)\tilde{T}_\sigma \quad (4.35)$$

The first of these does not present a problem since the spatial deviation of Ω will generally be very small compared to its area average (Whitaker, 1987, 1988b). The restriction given by eq 4.35 may be difficult to satisfy under some circumstances, and if it is not satisfied eq 4.30 (and therefore eq 4.27) will be coupled to $\nabla\langle c_{\mathrm{A}}\rangle^\sigma$ by the closure problem for $\tilde{c}_{\mathrm{A}}$. Under these circumstances the closure representations given by eqs 2.16 will not be complete.

The restriction given by eq 4.31 can be expressed as

$$\tilde{\mathbf{v}}_\beta\frac{\Delta\hat{T}_\beta}{L} \ll \tilde{\mathbf{v}}_\beta\frac{\Delta\langle T\rangle}{L} \quad (4.36)$$

and use of eq 3.10a along with the idea that $\Delta\hat{T}_\beta$ is the same order as $\hat{T}_\beta$ leads to

$$\epsilon_\sigma(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma) \ll \Delta\langle T\rangle \quad (4.37)$$

Here we have ignored any variation in ϵ_σ since we seek only to develop a constraint based on the order of magnitude estimate of $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$. This is available to us through eq 3.31 and it allows us to express eq 4.37 as

$$\epsilon_\sigma\Lambda \ll 1 \quad (4.38)$$

This constraint must be added to those given earlier by eqs 3.36–3.38; however, for most practical cases this constraint is comparable to eq 3.38.

Moving onto the second restriction in the closure problem, we note that the idea behind eq 4.32 is that $\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta$ should be small compared to $\tilde{T}_\beta$ so that this *source* can be discarded from the boundary condition B.C.1. If this source can be discarded from the boundary condition, it cannot influence the $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ fields and this means that it cannot influence the area integrals in eq 2.15. Concerning these area integrals, we should note that they act as *filters* for the information contained in the closure problem; i.e., not all the information associated with the $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ fields can pass through the area integrals in eq 2.15. Later we will show how eq 4.32 can be replaced by a *filtered* constraint; thus we ignore eq 4.32 for the present and move on to the restriction given by eq 4.33. In order to replace that restriction with a constraint (Whitaker, 1988a), we need to develop an estimate of $\tilde{T}_\beta$. To do so, we turn our attention to the three nonnegligible sources in eqs 4.27 and 4.29 and we propose the following:

$$\nabla\cdot(k_\beta\nabla\tilde{T}_\beta) \sim (\rho c_p)_\beta\tilde{\mathbf{v}}_\beta\cdot\nabla\langle T\rangle \quad (4.39a)$$

$$k_\beta\nabla\tilde{T}_\beta \sim (k_\sigma - k_\beta)\nabla\langle T\rangle \quad (4.39b)$$

$$k_\beta\nabla\tilde{T}_\beta \sim \langle\Omega\rangle_{\beta\sigma} \quad (4.39c)$$

Given that the characteristic length for the $\tilde{T}_\beta$ field is ℓ_β, eqs 4.39 lead to the following estimate:

$$\tilde{T}_\beta = \mathbf{O}\left[Pe\left(\frac{\ell_\beta}{L}\right)\Delta\langle T\rangle\right] + \mathbf{O}\left[\left(\frac{k_\sigma - k_\beta}{k_\beta}\right)\left(\frac{\ell_\beta}{L_c}\right)\Delta\langle T\rangle\right] + \mathbf{O}\left(\frac{\langle\Omega\rangle_{\beta\sigma}\ell_\beta}{k_\beta}\right) \quad (4.40)$$

Use of eqs 4.40, 3.10, and 3.31 in eq 4.33 leads to the following constraint:

$$\Lambda \ll \left\{\mathbf{O}\left[Pe\left(\frac{k_\beta}{\epsilon_\sigma k_\beta + \epsilon_\beta k_\sigma}\right)\right] + \mathbf{O}\left(\frac{k_\sigma - k_\beta}{\epsilon_\sigma k_\beta + \epsilon_\beta k_\sigma}\right) + \mathbf{O}\left[\frac{\langle\Omega\rangle_{\beta\sigma}L_c}{(\epsilon_\sigma k_\beta + \epsilon_\beta k_\sigma)\Delta\langle T\rangle}\right]\right\} \quad (4.41)$$

When this result is compared with eq 3.42, we see that it will be satisfied without difficulty, provided the homogeneous thermal source hidden in the definition of Σ

$$\Sigma = \mathbf{O}\left[\left(\frac{\epsilon_\omega}{\epsilon_\beta\epsilon_\sigma}\right)\frac{a_{\mathrm{v}}\langle\Omega\rangle_{\beta\sigma}d_{\mathrm{p}}^2}{k_{\beta\sigma}\Delta\langle T\rangle}\right] + \mathbf{O}\left[\frac{\langle\Phi_\sigma\rangle^\sigma d_{\mathrm{p}}^2}{k_{\beta\sigma}\Delta\langle T\rangle}\right] \quad (4.42)$$

does not create a problem. The influence of the thermal sources is discussed in detail in the next section. To summarize our development of constraints for the closure problem, we note that eq 4.31 has been replaced by eq 4.38 and that eq 4.33 has been replaced by eq 4.41. For the present we will ignore eq 4.32 since the subsequent development will show that it can be replaced by a *filtered constraint*.

When the restrictions indicated by eqs 4.31 and 4.33–4.35 are satisfied, the closure problem given by eqs 4.27–4.30 simplies to

$$(\rho c_p)_\beta\left(\frac{\partial\tilde{T}_\beta}{\partial t} + \mathbf{v}_\beta\cdot\nabla\tilde{T}_\beta + \tilde{\mathbf{v}}_\beta\cdot\nabla\langle T\rangle\right) = \nabla\cdot(k_\beta\nabla\tilde{T}_\beta) - \frac{1}{V_\beta}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta\,dA \quad (4.43)$$

B.C.1 $\quad \tilde{T}_\beta = \tilde{T}_\beta + \langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta, \quad \text{at } \mathcal{A}_{\beta\sigma} \quad (4.44)$

B.C.2 $\quad \mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta = \mathbf{n}_{\beta\sigma}\cdot k_\sigma\nabla\tilde{T}_\sigma + \mathbf{n}_{\beta\sigma}\cdot(k_\sigma - k_\beta)\nabla\langle T\rangle + \langle\Omega\rangle_{\beta\sigma}, \quad \text{at } \mathcal{A}_{\beta\sigma} \quad (4.45)$

$$(\rho c_p)_\sigma\frac{\partial\tilde{T}_\sigma}{\partial t} = \nabla\cdot(k_\sigma\nabla\tilde{T}_\sigma) + \left(\frac{\partial\Phi_\sigma}{\partial T_\sigma}\right)\tilde{T}_\sigma - \frac{1}{V_\sigma}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\tilde{T}_\sigma\,dA \quad (4.46)$$

The present form of the closure problem can be treated as quasi-steady when the following time-scale constraints are satisfied.

$$\frac{\alpha_\beta t^*}{\ell_\beta^2} \gg 1, \quad \frac{\alpha_\sigma t^*}{\ell_\sigma^2} \gg 1 \tag{4.47}$$

On the basis of eq 3.39, which we write here in the form

$$\frac{[(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)/(\rho c_p)_{\beta\sigma}]t^*}{L_c^2} \gg \epsilon_\beta\epsilon_\sigma\left[\frac{(\rho c_p)_\beta - (\rho c_p)_\sigma}{(\rho c_p)_{\beta\sigma}}\right]^2 \tag{4.48}$$

we see that eqs 4.47 will almost always be satisfied when the one-equation model is valid. The exception to this would be the special case in which $(\rho c_p)_\beta$ is equal to $(\rho c_p)_\sigma$.

In order to deal with the term $\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta$ in the quasi-steady form of the closure problem, we define two new deviation temperatures given by

$$\tilde{R}_\beta = \tilde{T}_\beta - \frac{1}{2}(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta),$$
$$\tilde{R}_\sigma = \tilde{T}_\sigma + \frac{1}{2}(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta) \tag{4.49}$$

In addition, we impose the restrictions

$$\nabla(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta) \ll \nabla\tilde{T}_\beta, \quad \nabla(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta) \ll \nabla\tilde{T}_\sigma \tag{4.50}$$

so that the quasi-steady closure problem takes the form

$$(\rho c_p)_\beta(\mathbf{v}_\beta\cdot\nabla\tilde{R}_\beta + \tilde{\mathbf{v}}_\beta\cdot\nabla\langle T\rangle) = \nabla\cdot(k_\beta\nabla\tilde{R}_\beta) - \frac{1}{V_\beta}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{R}_\beta\,dA \tag{4.51}$$

B.C.1
$$\tilde{R}_\beta = \tilde{R}_\sigma \tag{4.52}$$

B.C.2
$$\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{R}_\beta = \mathbf{n}_{\beta\sigma}\cdot k_\sigma\nabla\tilde{R}_\sigma + \mathbf{n}_{\beta\sigma}\cdot(k_\sigma - k_\beta)\nabla\langle T\rangle + \langle\Omega\rangle_{\beta\sigma}, \quad \text{at } \mathcal{A}_{\beta\sigma} \tag{4.53}$$

$$0 = \nabla\cdot(k_\sigma\nabla\tilde{R}_\sigma) + \left(\frac{\partial\Phi_\sigma}{\partial T_\sigma}\right)\tilde{R}_\sigma - \frac{1}{V_\sigma}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\tilde{R}_\sigma\,dA - \frac{1}{2}\left(\frac{\partial\Phi_\sigma}{\partial T_\sigma}\right)(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta) \tag{4.54}$$

Here we can see that the transformation given by eqs 4.49 and the constraints given by eqs 4.50 have generated a new source term in the governing equation for $\tilde{T}_\sigma$. To discard this term it will be sufficient to impose

$$\left(\frac{\partial\Phi_\sigma}{\partial T_\sigma}\right)(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta) \ll \nabla\cdot(k_\sigma\nabla\tilde{R}_\sigma) \tag{4.55}$$

along with eqs 4.50. We already have estimates of $\tilde{T}_\beta$ and $\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta$ from eqs 4.4 and 3.36. To develop an estimate of $\tilde{T}_\sigma$, we follow the procedure indicated by eqs 4.39 and propose

$$k_\sigma\nabla\tilde{T}_\sigma \sim (k_\sigma - k_\beta)\nabla\langle T\rangle \tag{4.56a}$$

$$k_\sigma\nabla\tilde{T}_\sigma \sim \langle\Omega\rangle_{\beta\sigma} \tag{4.56b}$$

This leads to an estimate of $\tilde{T}_\sigma$ analogous to eq 4.40.

$$\tilde{T}_\sigma = \mathbf{O}\left[\left(\frac{k_\sigma - k_\beta}{k_\sigma}\right)\left(\frac{\ell_\sigma}{L_c}\right)\Delta\langle T\rangle\right] + \mathbf{O}\left(\frac{\langle\Omega\rangle_{\beta\sigma}\ell_\sigma}{k_\sigma}\right) \tag{4.57}$$

We can now represent the constraints associated with the restrictions given by eqs 4.50 and 4.55 as

$$\Lambda \ll \left\{\mathbf{O}(Pe) + \mathbf{O}\left(\frac{k_\sigma - k_\beta}{k_\beta}\right) + \mathbf{O}\left(\frac{\langle\Omega\rangle_{\beta\sigma}L_c}{k_\beta\Delta\langle T\rangle}\right)\right\} \tag{4.58a}$$

$$\Lambda \ll \left\{\mathbf{O}\left(\frac{k_\sigma - k_\beta}{k_\beta}\right) + \mathbf{O}\left(\frac{\langle\Omega\rangle_{\beta\sigma}L_c}{k_\beta\Delta\langle T\rangle}\right)\right\} \tag{4.58b}$$

$$\left(\frac{\partial\Phi_\sigma}{\partial T_\sigma}\right)\Lambda \ll \left\{\mathbf{O}\left(\frac{k_\sigma - k_\beta}{\ell_\sigma L_c}\right) + \mathbf{O}\left(\frac{\langle\Omega\rangle_{\beta\sigma}}{\ell_\sigma\Delta\langle T\rangle}\right)\right\} \tag{4.58c}$$

The first two of these three constraints will be no more difficult to satisfy than eq 4.41, which resulted from the restriction given by eq 4.33. The last of these three constraints may be difficult to satisfy if the rate of chemical reaction is a strong function of the temperature.

On the basis of eq 4.58 our closure problem at last takes the simplified form given by

$$(\rho c_p)_\beta(\mathbf{v}_\beta\cdot\nabla\tilde{R}_\beta + \tilde{\mathbf{v}}_\beta\cdot\nabla\langle T\rangle) = \nabla\cdot(k_\beta\nabla\tilde{R}_\beta) - \frac{1}{V_\beta}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{R}_\beta\,dA \tag{4.59}$$

B.C.1
$$\tilde{R}_\beta = \tilde{R}_\sigma, \quad \text{at } \mathcal{A}_{\beta\sigma} \tag{4.60}$$

B.C.2
$$\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{R}_\beta = \mathbf{n}_{\beta\sigma}\cdot k_\sigma\nabla\tilde{R}_\sigma + \mathbf{n}_{\beta\sigma}\cdot(k_\sigma - k_\beta)\nabla\langle T\rangle + \langle\Omega\rangle_{\beta\sigma}, \quad \text{at } \mathcal{A}_{\beta\sigma} \tag{4.61}$$

$$0 = \nabla\cdot(k_\sigma\nabla\tilde{R}_\sigma) + \left(\frac{\partial\Phi_\sigma}{\partial T_\sigma}\right)\tilde{R}_\sigma - \frac{1}{V_\sigma}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\tilde{R}_\sigma\,dA \tag{4.62}$$

At this point we follow the procedure suggested by Ryan et al. (1981) and discussed in more detail by Whitaker (1986b). This consists of representations for $\tilde{R}_\beta$ and $\tilde{R}_\sigma$ of the form

$$\tilde{R}_\beta = \mathbf{f}\cdot\nabla\langle T\rangle + h_\beta\langle\Omega\rangle_{\beta\sigma} + \psi \tag{4.63}$$

$$\tilde{R}_\sigma = \mathbf{g}\cdot\nabla\langle T\rangle + h_\sigma\langle\Omega\rangle_{\beta\sigma} + \xi \tag{4.64}$$

The functions ψ and ξ are considered to be arbitrary; thus we are free to express the *closure variables* $\mathbf{f}$, $\mathbf{g}$, h_β, and h_σ in terms of the following two boundary value problems:

problem I

$$(\rho c_p)_\beta(\mathbf{v}_\beta\cdot\nabla\mathbf{f} + \tilde{\mathbf{v}}_\beta) = \nabla\cdot(k_\beta\nabla\mathbf{f}) - \frac{1}{V_\beta}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\mathbf{f}\,dA \tag{4.65}$$

B.C.1
$$\mathbf{f} = \mathbf{g}, \quad \text{at } \mathcal{A}_{\beta\sigma} \tag{4.66}$$

B.C.2
$$\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\mathbf{f} = \mathbf{n}_{\beta\sigma}\cdot k_\sigma\nabla\mathbf{g} + \mathbf{n}_{\beta\sigma}(k_\sigma - k_\beta), \quad \text{at } \mathcal{A}_{\beta\sigma} \tag{4.67}$$

$$0 = \nabla\cdot(k_\sigma\nabla\mathbf{g}) + \left(\frac{\partial\Phi_\sigma}{\partial T_\sigma}\right)\mathbf{g} - \frac{1}{V_\sigma}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\mathbf{g}\,dA \tag{4.68}$$

problem II

$$(\rho c_p)_\beta(\mathbf{v}_\beta\cdot\nabla h_\beta) = \nabla\cdot(k_\beta\nabla h_\beta) - \frac{1}{V_\sigma}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla h_\beta\,dA \tag{4.69}$$

B.C.1
$$h_\beta = h_\sigma, \quad \text{at } \mathcal{A}_{\beta\sigma} \tag{4.70}$$

B.C.2
$$\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla h_\beta = \mathbf{n}_{\beta\sigma}\cdot k_\sigma\nabla h_\sigma + 1, \quad \text{at } \mathcal{A}_{\beta\sigma} \tag{4.71}$$

$$0 = \nabla\cdot(k_\sigma\nabla h_\sigma) + \left(\frac{\partial\Phi_\sigma}{\partial T_\sigma}\right)h_\sigma - \frac{1}{V_\sigma}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla h_\sigma\,dA \tag{4.72}$$

When the closure variables are determined by these two problems, one can use eqs 4.59–4.62 to develop estimates of ψ and ξ. These estimates indicate that ψ and ξ make negligible contributions to $\tilde{R}_\beta$ and $\tilde{R}_\sigma$ when the length-scale constraint given by eq 2.10 is valid.

In order to compute values for the closure variables, one needs a specific model of a porous medium and a set of boundary conditions at the entrances and exits of the β- and σ-phases. This is not necessary for our purposes, and we only need to know that $\tilde{R}_\beta$ and $\tilde{R}_\sigma$ can be expressed as

$$\tilde{R}_\beta = \mathbf{f}\cdot\nabla\langle T\rangle + h_\beta\langle\Omega\rangle_{\beta\sigma} \tag{4.73}$$

$$\tilde{R}_\sigma = \mathbf{g}\cdot\nabla\langle T\rangle + h_\sigma\langle\Omega\rangle_{\beta\sigma} \tag{4.74}$$

This means that $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ take the form

$$\tilde{T}_\beta = \mathbf{f}\cdot\nabla\langle T\rangle + h_\beta\langle\Omega\rangle_{\beta\sigma} + \frac{1}{2}(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta) \tag{4.75}$$

$$\tilde{T}_\sigma = \mathbf{g}\cdot\nabla\langle T\rangle + h_\sigma\langle\Omega\rangle_{\beta\sigma} - \frac{1}{2}(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta) \tag{4.76}$$

and when these results are used in eq 2.15 we find

$$\langle\rho\rangle C_p\frac{\partial\langle T\rangle}{\partial t} + \epsilon_\beta(\rho c_p)_\beta\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T\rangle = \nabla\cdot\left[(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)\nabla\langle T\rangle + \left(\frac{k_\beta - k_\sigma}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\mathbf{f}\,\mathrm{d}A\right) + \frac{1}{2}\left(\frac{k_\beta + k_\sigma}{\mathcal{V}}\right)\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta)\,\mathrm{d}A\right] - (\rho c_p)_\beta\nabla\cdot(\langle\tilde{\mathbf{v}}_\beta\mathbf{f}\rangle\cdot\nabla\langle T\rangle) + \epsilon_\sigma\langle\Phi_\sigma\rangle^\sigma + a_\mathrm{v}\langle\Omega\rangle_{\beta\sigma} + \nabla\cdot\left[\left(\frac{k_\beta - k_\sigma}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}h_\beta\,\mathrm{d}A\right)\langle\Omega\rangle_{\beta\sigma}\right] - (\rho c_p)_\beta\nabla\cdot\left[\langle\tilde{\mathbf{v}}_\beta\rangle\frac{1}{2}(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta)\right] - (\rho c_p)_\beta\nabla\cdot(\langle\tilde{\mathbf{v}}_\beta h_\beta\rangle\langle\Omega\rangle_{\beta\sigma}) \tag{4.77}$$

We are now in a position to *define* the effective thermal conductivity as

$$\boldsymbol{K}_\mathrm{eff} = (\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)\boldsymbol{I} + \frac{k_\beta - k_\sigma}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\mathbf{f}\,\mathrm{d}A \tag{4.78}$$

and the thermal dispersion tensor as

$$\boldsymbol{K}_\mathrm{D} = -(\rho c_p)_\beta\langle\tilde{\mathbf{v}}_\beta\mathbf{f}\rangle \tag{4.79}$$

With these definitions we can express eq 4.77 as

$$\langle\rho\rangle C_p\frac{\partial\langle T\rangle}{\partial t} + \epsilon_\beta(\rho c_p)_\beta\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T\rangle = \nabla\cdot\left[(\boldsymbol{K}_\mathrm{eff} + \boldsymbol{K}_\mathrm{D})\cdot\nabla\langle T\rangle + \frac{1}{2}\left(\frac{k_\beta + k_\sigma}{\mathcal{V}}\right)\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta)\,\mathrm{d}A\right] + \epsilon_\sigma\langle\Phi_\sigma\rangle^\sigma + a_\mathrm{v}\langle\Omega\rangle_{\beta\sigma} + \nabla\cdot\left[\left(\frac{k_\beta - k_\sigma}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}h_\beta\,\mathrm{d}A\right)\langle\Omega\rangle_{\beta\sigma}\right] - (\rho c_p)_\beta\nabla\cdot\left[\langle\tilde{\mathbf{v}}_\beta\rangle\frac{1}{2}(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta)\right] - (\rho c_p)_\beta\nabla\cdot(\langle\tilde{\mathbf{v}}_\beta h_\beta\rangle\langle\Omega\rangle_{\beta\sigma}) \tag{4.80}$$

We can now see how the *filtered* restriction suggested by eq 4.32 can be replaced by the *unfiltered* constraint associated with the simplification of eq 4.80.

On the basis of the length-scale constraint given by eq 4.7 we can remove $\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta$ from the area integral over $A_{\beta\sigma}$, and this leads to

$$\frac{1}{2}\left(\frac{k_\beta + k_\sigma}{\mathcal{V}}\right)\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta)\,\mathrm{d}A = \left\{\frac{1}{2}\left(\frac{k_\beta + k_\sigma}{\mathcal{V}}\right)\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\,\mathrm{d}A\right\}(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta) \tag{4.81}$$

The spatial averaging theorem provides the result

$$\frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\,\mathrm{d}A = -\nabla\epsilon_\beta \tag{4.82}$$

and this allows us to express eq 4.81 as

$$\frac{1}{2}\left(\frac{k_\beta + k_\sigma}{\mathcal{V}}\right)\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta)\,\mathrm{d}A = -\frac{1}{2}(k_\beta + k_\sigma)\nabla\epsilon_\beta(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta) \tag{4.83}$$

We can now simplify eq 4.80 by imposing the restriction

$$\frac{1}{2}\left(\frac{k_\beta + k_\sigma}{\mathcal{V}}\right)\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta)\,\mathrm{d}A \ll \boldsymbol{K}_\mathrm{eff}\cdot\nabla\langle T\rangle \tag{4.84}$$

and when we make use of eqs 4.81, 4.82, and 3.31 we can develop the constraint given by

$$L_\mathrm{c}\nabla\epsilon_\beta\Lambda \ll \boldsymbol{K}_\mathrm{eff}/(k_\beta + k_\sigma) \tag{4.85}$$

For a homogeneous porous medium this *filtered* constraint is automatically satisfied and in general eq 4.85 will be easier to satisfy than eq 4.38, which originated from the restriction given by eq 4.31.

At this point it is important to return to eq 4.32 and to see how that restriction compares with eq 4.85. If we make use of eq 4.40 in eq 4.32, we find the following *unfiltered* constraint

$$\Lambda \ll \left\{\mathbf{O}\left[Pe\left(\frac{\ell_\beta}{L}\right)\right] + \mathbf{O}\left[\left(\frac{k_\sigma - k_\mathrm{b}}{k_\beta}\right)\frac{\ell_\beta}{L_\mathrm{c}}\right] + \mathbf{O}\left(\frac{\langle\Omega\rangle_{\beta\sigma}\ell_\beta}{k_\beta\Delta\langle T\rangle}\right)\right\} \tag{4.86}$$

In general, this *unfiltered* constraint, imposed directly on the boundary value problem for $\tilde{T}_\beta$ and $\tilde{T}_\sigma$, will be more difficult to satisfy than the *filtered* constraint given by eq 4.85. However, it *does not need* to be satisfied since eq 4.32 was not used to simplify the closure problem.

Since problem II for the closure variables h_β and h_σ contains only a single source term in the flux boundary condition given by eq 4.71, we can develop a conservative estimate (an overestimate) of h_β and h_σ according to

$$h_\omega = \mathbf{O}(\delta_\omega/k_\omega) \tag{4.87}$$

Here one can think of δ_ω/k_ω as the larger of either δ_β/k_β or δ_σ/k_σ. This can be used to produce the estimate

$$\nabla\cdot\left[\left(\frac{k_\beta - k_\sigma}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}h_\beta\,\mathrm{d}A\right)\langle\Omega\rangle_{\beta\sigma}\right] = \mathbf{O}\left[\left(\frac{\delta_\omega}{L}\right)\left(\frac{k_\beta - k_\sigma}{k_\omega}\right)a_\mathrm{v}\langle\Omega\rangle_{\beta\sigma}\right] \tag{4.88}$$

From this it is clear that the following inequality

$$\nabla\cdot\left[\left(\frac{k_\beta - k_\sigma}{\mathcal{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}h_\beta\,\mathrm{d}A\right)\langle\Omega\rangle_{\beta\sigma}\right] \ll a_\mathrm{v}\langle\Omega\rangle_{\beta\sigma} \tag{4.89}$$

is always satisfied and eq 4.80 can be simplified accordingly.

As an approximation, the average of a spatial deviation is often taken to be zero, and if we follow that tradition the next to the last term in eq 4.77 can be immediately discarded. An estimate of $\langle\tilde{\mathbf{v}}_\beta\rangle$ is available from Carbonell and Whitaker (1984, Section 2) and reliable values of $\boldsymbol{K}_\mathrm{D}$ are available from Levec and Carbonell (1985). These can be used to support the idea that

$$(\rho c_p)_\beta\nabla\cdot\left[\langle\tilde{\mathbf{v}}_\beta\rangle\frac{1}{2}(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta)\right] \ll \nabla\cdot[(\boldsymbol{K}_\mathrm{eff} + \boldsymbol{K}_\mathrm{D})\cdot\nabla\langle T\rangle] \quad (4.90)$$

This allows us to simplify eq 4.80 to

$$\langle\rho\rangle C_p\frac{\partial\langle T\rangle}{\partial t} + \epsilon_\beta(\rho c_p)_\beta\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T\rangle = \nabla\cdot[(\boldsymbol{K}_\mathrm{eff} + \boldsymbol{K}_\mathrm{D})\cdot\nabla\langle T\rangle] + \epsilon_\sigma\langle\Phi_\sigma\rangle^\sigma + a_\mathrm{v}\langle\Omega\rangle_{\beta\sigma} - (\rho c_p)_\beta\nabla\cdot(\langle\tilde{\mathbf{v}}_\beta h_\beta\rangle\langle\Omega\rangle_{\beta\sigma}) \quad (4.91)$$

Often transport coefficients that are determined by closure problems or by experiments are assumed to be constant. If we were to make this assumption concerning the last term in eq 4.91, we could express it as

$$-(\rho c_p)_\beta\nabla\cdot(\langle\tilde{\mathbf{v}}_\beta h_\beta\rangle\langle\Omega\rangle_{\beta\sigma}) = -(\rho c_p)_\beta\langle\tilde{\mathbf{v}}_\beta h_\beta\rangle\cdot\nabla\langle\Omega\rangle_{\beta\sigma} \quad (4.92)$$

The heterogeneous thermal source will depend on the temperature and the concentration of the reactants at the β–σ interface. If both the temperature *and* concentration fields can be described by one-equation models, the functional dependence of $\langle\Omega\rangle_{\beta\sigma}$ can be described by

$$\langle\Omega\rangle_{\beta\sigma} = \mathcal{F}(\langle T\rangle,\langle c_\mathrm{A}\rangle^\beta) \quad (4.93)$$

Here we consider only a single reactant as we did in eq 4.24. On the basis of eq 4.93 we can express the gradient of $\langle\Omega\rangle_{\beta\sigma}$ as

$$\nabla\langle\Omega\rangle_{\beta\sigma} = \left(\frac{\partial\langle\Omega\rangle_{\beta\sigma}}{\partial\langle T\rangle}\right)\nabla\langle T\rangle + \left(\frac{\partial\langle\Omega\rangle_{\beta\sigma}}{\partial\langle c_\mathrm{A}\rangle^\beta}\right)\nabla\langle c_\mathrm{A}\rangle^\beta \quad (4.94)$$

Use of this result in eq 4.92, along with the estimate

$$-(\rho c_p)_\beta\langle\tilde{\mathbf{v}}_\beta h_\beta\rangle = \mathrm{O}\left[Pe\left(\frac{\delta_\omega}{d_\mathrm{p}}\right)\left(\frac{k_\beta}{k_\omega}\right)\right] \quad (4.95)$$

allows us to express eq 4.92 as

$$-(\rho c_p)_\beta\nabla\cdot(\langle\tilde{\mathbf{v}}_\beta h_\beta\rangle\langle\Omega\rangle_{\beta\sigma}) = \mathrm{O}\left[Pe\left(\frac{\delta_\omega}{d_\mathrm{p}}\right)\left(\frac{k_\beta}{k_\omega}\right)\left(\frac{\partial\langle\Omega\rangle_{\beta\sigma}}{\partial\langle T\rangle}\right)\right]\cdot\nabla\langle T\rangle + \mathrm{O}\left[Pe\left(\frac{\delta_\omega}{d_\mathrm{p}}\right)\left(\frac{k_\beta}{k_\omega}\right)\left(\frac{\partial\langle\Omega\rangle_{\beta\sigma}}{\partial\langle c_\mathrm{A}\rangle^\beta}\right)\right]\cdot\nabla\langle c_\alpha\rangle^\beta \quad (4.96)$$

This means that we can think of the last term in eq 4.91 as generating both a convective thermal transport term and a convective mass transport term. The thermal transport term can be neglected when

$$Pe\left(\frac{\delta_\omega}{d_\mathrm{p}}\right)\left(\frac{k_\beta}{k_\omega}\right)\frac{\partial\langle\Omega\rangle_{\beta\sigma}}{\partial\langle T\rangle} \ll (\rho c_p)_\beta\epsilon_\beta\langle\mathbf{v}_\beta\rangle^\beta \quad (4.97)$$

and a little thought will indicate that this constraint can be expressed

$$\frac{\delta_\omega}{k_\omega}\frac{\partial\langle\Omega\rangle_{\beta\sigma}}{\partial\langle T\rangle} \ll 1 \quad (4.98)$$

The idea of a heterogeneous source giving rise to a convective transport term is not new, and Paine et al. (1983) found a similar result for the problem of mass transport in a capillary tube with a heterogeneous reaction.

We expect the thermal source terms in eq 4.91 to depend on both $\langle T\rangle$ and $\langle c_\mathrm{A}\rangle$; however, the convective transport term suggested by eq 4.96 is something different. The appropriate constraint to impose in order that this convective mass transport term be negligible is given by

$$\left[Pe\left(\frac{\delta_\omega}{d_\mathrm{p}}\right)\left(\frac{k_\beta}{k_\omega}\right)\left(\frac{\partial\langle\Omega\rangle_{\beta\sigma}}{\partial\langle c_\mathrm{A}\rangle^\beta}\right)\right]\nabla\langle c_\mathrm{A}\rangle^\beta \ll a_\mathrm{v}\langle\Omega\rangle_{\beta\sigma} \quad (4.99)$$

and when this constraint is satisfied our one-equation model for thermal energy transport reduces to

$$\langle\rho\rangle C_p\frac{\partial\langle T\rangle}{\partial t} + \epsilon_\beta(\rho c_p)_\beta\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T\rangle = \nabla\cdot[(\boldsymbol{K}_\mathrm{eff} + \boldsymbol{K}_\mathrm{D})\cdot\nabla\langle T\rangle] + \epsilon_\sigma\langle\Phi_\sigma\rangle^\sigma + a_\mathrm{v}\langle\Omega\rangle_{\beta\sigma} \quad (4.100)$$

This result is, of course, identical with that given earlier by eq 2.17. One should remember that eq 2.17 was obtained from eq 2.13 on the basis of the constraints given by eqs 3.36–3.38 and the constitutive relations given by eqs 2.16. In this section we have seen that the derivation of eqs 2.16 is not a trivial matter.

5. Role of the Thermal Sources

In the development of the constraints that were required for the simplification of eq 2.13 to eq 2.17 we found two source terms of the form $\langle\Omega\rangle_{\beta\sigma}/\Delta\langle T\rangle$ and $\langle\Phi_\sigma\rangle^\sigma/\Delta\langle T\rangle$. For any given problem, it is possible that these quantities are not known a priori; thus estimates of these quantities would be extremely useful. To develop these constraints, we return to eq 2.17 and use that result to estimate the value of $\Delta\langle T\rangle$ that would be generated by the thermal sources. This has been done elsewhere (Whitaker, 1986a, Section 4) and we list the results as

$$\frac{\epsilon_\sigma\langle\Phi_\sigma\rangle^\sigma}{\Delta\langle T\rangle}, \frac{a_\mathrm{v}\langle\Omega\rangle_{\beta\sigma}}{\Delta\langle T\rangle} = \left\{\mathrm{O}\left(\frac{\langle\rho\rangle C_p}{t^*}\right) + \mathrm{O}\left[\frac{\epsilon_\beta(\rho c_p)_\beta\langle\mathbf{v}_\beta\rangle^\beta}{L_{\rho c_p}}\right] + \mathrm{O}\left(\frac{\boldsymbol{K}_\mathrm{eff} + \boldsymbol{K}_\mathrm{D}}{L_\mathrm{c}^2}\right)\right\} \quad (5.1)$$

One must be careful to note that the estimate of $\Delta\langle T\rangle$ in eqs 5.1 is based solely on the effect of the individual thermal sources. It does not take into account the influence of boundary conditions which can generate finite values of $\Delta\langle T\rangle$ even when Φ_σ and Ω are zero. This means that the estimates given by eqs 5.1 may be overestimates and they should be used with care.

In order to understand how the thermal sources influence the constraints that we have developed, we make use of eqs 5.1 in eq 3.32 to produce a new representation for Λ given by

$$\Lambda = \frac{\mathcal{A} + \mathcal{B} + \mathcal{C}}{\left\{\dfrac{d_\mathrm{p}^2}{\alpha_{\beta\sigma}t^*} + \mathrm{O}\left[\epsilon_\sigma\left(\dfrac{k_\beta}{k_{\beta\sigma}}\right)\left(\dfrac{d_\mathrm{p}}{L_{\rho c_p}}\right)Pe\right] + \mathrm{O}\left(\dfrac{d_\mathrm{p}}{L_\mathrm{c}}\right)^2 + \Theta\right\}} \quad (5.2)$$

Here $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ are defined according to

$$\mathcal{A} = \left\{\mathrm{O}\left[\frac{(\rho c_p)_\beta - (\rho c_p)_\sigma}{(\rho c_p)_{\beta\sigma}}\right] + \mathrm{O}\left[\frac{\epsilon_\omega}{\epsilon_\beta\epsilon_\sigma}\frac{\langle\rho\rangle C_p}{(\rho c_p)_{\beta\sigma}}\right] + \mathrm{O}\left[\frac{1}{\epsilon_\sigma}\frac{\langle\rho\rangle C_p}{(\rho c_p)_{\beta\sigma}}\right]\right\}\frac{d_\mathrm{p}^2}{\alpha_{\beta\sigma}t^*} \quad (5.3)$$

$$\mathscr{B} = \left\{\mathrm{O}(\epsilon_\sigma) + \mathrm{O}\left(\frac{\epsilon_\omega}{\epsilon_\sigma}\right) + \mathrm{O}\left(\frac{\epsilon_\beta}{\epsilon_\sigma}\right)\right\}\left(\frac{k_\beta}{k_{\beta\sigma}}\right)\left(\frac{d_p}{L_{\rho c_p}}\right)Pe \quad (5.4)$$

$$\mathscr{C} = \left\{\mathrm{O}\left(\frac{k_\beta - k_\sigma}{k_{\beta\sigma}}\right) + \mathrm{O}\left[\frac{\epsilon_\omega}{\epsilon_\beta\epsilon_\sigma}\left(\frac{\boldsymbol{K}_{\mathrm{eff}} + \boldsymbol{K}_{\mathrm{D}}}{k_{\beta\sigma}}\right)\right] + \mathrm{O}\left[\frac{1}{\epsilon_\sigma}\left(\frac{\boldsymbol{K}_{\mathrm{eff}} + \boldsymbol{K}_{\mathrm{D}}}{k_{\beta\sigma}}\right)\right]\right\}\left(\frac{d_p}{L_c}\right)^2 \quad (5.5)$$

The general constraints associated with the simplification of eq 2.13 to eq 2.15 are given by eqs 3.36–3.38. When $\langle\Phi_\sigma\rangle^\sigma$ and $\langle\Omega\rangle_{\beta\sigma}$ represent the main source of nonzero values of $\Delta\langle T\rangle$, one should use eq 5.2 to determine Λ in eqs 3.36–3.38. It is very important to keep in mind that eqs 5.1–5.5 *should not be used* when $\langle\Phi_\sigma\rangle^\sigma$ and $\langle\Omega\rangle_{\beta\sigma}$ are zero.

From the definitions of $\mathscr{A}$, $\mathscr{B}$, and $\mathscr{C}$ it is clear that the thermal sources have an influence on the *transient* and *conductive* part of Λ, while the *convective* part represented by eq 5.4 remains essentially unchanged except for the special case of very small values of ϵ_σ. If one is concerned with the limiting cases $\epsilon_\beta \to 0$ and $\epsilon_\sigma \to 0$, it is important to take note of eq 3.35.

6. Conclusions

In this study we have considered the constraints that must be satisfied in order that the heat-transfer process in a solid–fluid system can be described in terms of a single temperature. The three constraints associated with the simplification of the local volume averaged transport equation are given by

$$\left\{\frac{\epsilon_\beta\epsilon_\sigma[(\rho c_p)_\beta - (\rho c_p)_\sigma]L_c^2}{(\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma)t^*}\right\}\Lambda \ll 1 \quad (3.38)$$

$$\left\{\epsilon_\beta\epsilon_\sigma Pe\left(\frac{L_c}{d_p}\right)\left(\frac{L_c}{L_{\rho c_p}}\right)\left(\frac{k_\beta}{\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma}\right)\right\}\Lambda \ll 1 \quad (3.39)$$

$$\left\{\frac{\epsilon_\beta\epsilon_\sigma(k_\beta - k_\sigma)}{(\epsilon_\beta k_\beta + \epsilon_\beta k_\sigma)}\right\}\Lambda \ll 1 \quad (3.40)$$

with eqs 3.32–3.34 being complete representations of Λ. The dominant constraints associated with the *closure problem* are given by

$$\tilde{\Omega} \ll \langle\Omega\rangle_{\beta\sigma} \quad (4.34)$$

$$\left(\frac{\partial\Phi_\sigma}{\partial c_A}\right)\tilde{c}_A \ll \left(\frac{\partial\Phi_\sigma}{\partial T_\sigma}\right)\tilde{T}_\sigma \quad (4.35)$$

$$\epsilon_\sigma\Lambda \ll 1 \quad (4.38)$$

$$L_c\nabla\epsilon_\beta\Lambda \ll \boldsymbol{K}_{\mathrm{eff}}/(k_\beta + k_\sigma) \quad (4.85)$$

$$\Lambda \ll \left\{\mathrm{O}\left[Pe\left(\frac{k_\beta}{\epsilon_\sigma k_\beta + \epsilon_\beta k_\sigma}\right)\right] + \mathrm{O}\left(\frac{k_\sigma - k_\beta}{\epsilon_\sigma k_\beta + \epsilon_\beta k_\sigma}\right) + \mathrm{O}\left[\frac{\langle\Omega\rangle_{\beta\sigma}L_c}{(\epsilon_\sigma k_\beta + \epsilon_\beta k_\sigma)\Delta\langle T\rangle}\right]\right\} \quad (4.41)$$

and it is important to note that eq 4.85 represents a *filtered constraint* since it was constructed on the basis of a term neglected in the volume averaged transport equation as opposed to a term neglected in the closure problem itself. The remaining constraints associated with the closure problem represent *unfiltered constraints* and are probably overly severe. Another important constraint that is made directly in the closure problem is given by eq 4.58c, and this constraint may be difficult to satisfy when the homogeneous reaction rate is a strong function of temperature. From the closure problem we have learned that the heterogeneous thermal source can give rise to a convective transport term. The filtered constraint that must be satisfied in order that this additional convective transport term be negligible is given by eq 4.97.

In order that equations such as eq 4.41 be useful, terms such as $\langle\Omega\rangle_{\beta\sigma}/\Delta\langle T\rangle$ need to be represented in terms of quantities that are known or can be easily estimated. A method of doing this has been presented in section 5.

The constraints associated with the principle of local thermal equilibrium are based on *order of magnitude estimates*. To develop more precise forms of the constraints, results from the two-dimensional model must be generated for a wide range of the appropriate parameters for both steady and transient conditions. This will allow us to determine when $\langle T_\beta\rangle^\beta$ and $\langle T_\sigma\rangle^\sigma$ are sufficiently close so that they can be replaced by the single temperature $\langle T\rangle$.

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Nomenclature

Roman Letters

$a_v = A_{\beta\sigma}/\mathcal{V}$, interfacial area per unit volume, m^{-1}
$\mathscr{A}_{\beta\sigma}$ = area of the β–σ interface, m^2
$A_{\beta\sigma} = A_{\sigma\beta}$, area of the β–σ interface contained within the averaging volume, m^2
$A_{\beta e}$ = area of the entrances and exits of the β-phase contained within the averaging volume, m^2
$(c_p)_\omega$ = constant-pressure heat capacity in the ω-phase, kcal/(kg K)
$(\rho c_p)_{\beta\sigma} = \epsilon_\sigma(\rho c_p)_\beta + \epsilon_\beta(\rho c_p)_\sigma$
$C_p = [\epsilon_\beta(\rho c_p)_\beta + \epsilon_\sigma(\rho c_p)_\sigma]/\langle\rho\rangle$, mass fraction weighted heat capacity, kcal/(kg K)
c_A = molar concentration of species A, mol/m^3
$\langle c_A\rangle^\sigma$ = intrinsic phase average molar concentration of species A in the σ-phase, mol/m^3
$\langle c_A\rangle^\beta$ = intrinsic phase average molar concentration of species A in the β-phase, mol/m^2
d_p = effective particle diameter, m
k_ω = thermal conductivity of the ω-phase, kcal/(m s K)
$k_{\beta\sigma} = \epsilon_\sigma k_\beta + \epsilon_\beta k_\sigma$
$\boldsymbol{K}_{\mathrm{eff}}$ = one-equation model effective thermal conductivity tensor, kcal/(m s K)
$\boldsymbol{K}_{\mathrm{D}}$ = thermal dispersion tensor, kcal/(m s K)
L = characteristic length associated with local volume averaged quantities, m
L_c = characteristic length associated with $\nabla^2\langle T\rangle$, m
$L_{\rho c_p}$ = characteristic length associated with $\langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T\rangle$, m
ℓ_β = characteristic length (pore diameter) for the β-phase, m
ℓ_σ = characteristic length (particle diameter) for the σ-phase, m
$\mathbf{n}_{\beta\sigma} = -\mathbf{n}_{\sigma\beta}$, outwardly directed unit normal vector pointing from the β-phase toward the σ-phase
$\mathbf{n}_{\beta e}$ = outwardly directed unit normal vector at the entrances and exits of the β-phase contained within the averaging volume

$Pe = \langle v_\beta \rangle^\beta d_p/\alpha_\beta$, Peclet number
t = time, s
t^* = characteristic process time, s
T_ω = point temperature in the ω-phase, K
$\langle T_\omega \rangle^\omega$ = intrinsic phase average temperature for the ω-phase, K
$\tilde{T}_\omega = T_\omega - \langle T_\omega \rangle^\omega$, spatial deviation temperature in the ω-phase, K
$\langle T \rangle = \epsilon_\beta \langle T_\beta \rangle^\beta + \epsilon_\sigma \langle T_\sigma \rangle^\sigma$, spatial average temperature, K
$\hat{T}_\omega = \langle T_\omega \rangle^\omega - \langle T \rangle$, macroscopic spatial deviation temperature, K
$\mathcal{V}$ = averaging volume, m^3
$\mathbf{v}_\beta$ = point velocity in the β-phase, m/s
$\langle \mathbf{v}_\beta \rangle^\beta$ = intrinsic phase average velocity, m/s
$\tilde{\mathbf{v}}_\beta = \mathbf{v}_\beta - \langle \mathbf{v}_\beta \rangle^\beta$, spatial deviation velocity, m/s

Greek Letters

$\alpha_\omega = k_\omega/(\rho c_p)_\omega$, thermal diffusivity in the ω-phase, m^2/s
$\alpha_{\beta\sigma} = k_{\beta\sigma}/(\rho c_p)_{\beta\sigma}$
δ_ω = characteristic length for heat transfer in the ω-phase, m
ϵ_ω = volume fraction of the ω-phase
$\Lambda = (\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma)/\Delta\langle T \rangle$, dimensionless temperature difference
ν_β = kinematic viscosity of the β-phase, m^2/s
ρ_ω = density in the ω-phase, kg/m^3
$\langle \rho \rangle = \epsilon_\beta \rho_\beta + \epsilon_\sigma \rho_\sigma$, spatial average density, kg/m^3
Φ_σ = homogeneous thermal source in the σ-phase, kcal/(m^3 s)
$\langle \Phi_\sigma \rangle^\sigma$ = intrinsic phase average homogeneous thermal source, kcal/(m^3 s)
Ω = heterogeneous thermal source associated with the β–σ interface, kcal/(m^2 s)
$\langle \Omega \rangle_{\beta\sigma}$ = area averaged heterogeneous thermal source, kcal/(m^2 s)

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