Chapter 9

BALANCE EQUATIONS OF THE EQUIPMENT
FOR MULTICOMPONENT AND BINARY SYSTEMS

9.1. INTRODUCTION

In Chapter 4 balance equations for momentum, energy and mass were formulated with special emphasis on mass balance. The balance which describes the law of the conservation of mass was formulated taking into account a differential volume dxdydz in which only one fluid phase was contained. The mass balance consisted of three basic terms: accumulation of a component, flow of a component, and its production as a result of chemical reactions (equation 4-4). The flow of a component was divided into convective and diffusive parts (equation 4-5). In Chapter 5 it was stated that an exact description of mass transfer in turbulent flow is very difficult because the instantaneous velocity profile of the flowing fluid is not known. Therefore, it is impossible to use equations (4-4) and (4-5) in the calculation of mass transfer in turbulent flow and some simplification in the process description is necessary. This can be done by introducing mass transfer models in which some ideal flow types are assumed. The most popular and widely applicable is the film model in which plug flow of phases is assumed and mass transfer between phases takes place by diffusion at the surface of gas and liquid films. Substitution of these simplifications requires, in turn, a modification of the mass balance equations. However, a new problem arises. The authors of the film model pointed out that the total mass transfer resistance is located in the films and accumulation takes place only in the phase bulk which they considered as one of the main advantages of their model. The phase bulk moves at a constant velocity that is equal to the mean fluid velocity and a thin film is treated as stagnant. This is why

formally the differential mass balance equation is formulated not for the whole differential volume of a phase but only for its bulk. As for the physical absorption of one or many gases, the formulation of balances for the whole phase or for its bulk only leads to the same results because fluxes entering a given phase are equal to the fluxes entering the bulk (Fig. 9-1a). For chemical
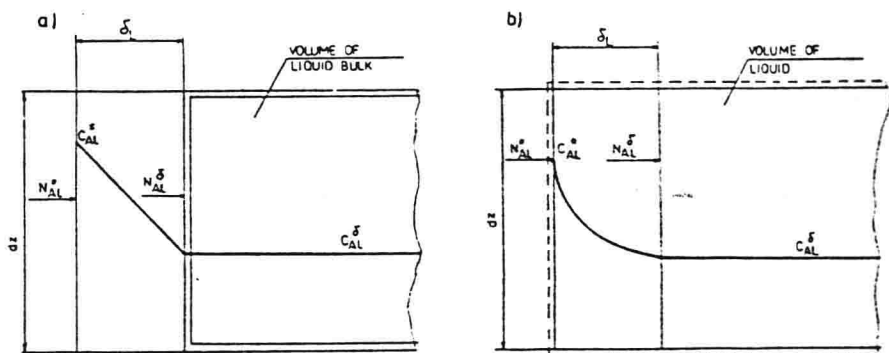

Fig. 9-1. Mass balance of differential volume of equipment

absorption this has far-reaching consequences, since both fluxes are not equal (Fg. 9-1b). Part of the diffusing component (components) reacts in the film and the flux N_{iL}^{δ} entering the bulk is not equal to the flux N_{iL}^{*} entering the liquid phase. As a result, in the liquid phase balances a flux (N_{iL}^{δ} or n_{iL}^{δ}) at the film-bulk boundary will occur.

Absorption is most often a two-phase process involving gas and liquid phases. Depending on the type of equipment, each phase can constitute either a continuous or disperse phase in the system. For example, in packed columns the liquid and the gas are continuous phases, and in bubble columns the liquid is a continuous phase and the gas is a disperse phase. Uneven distribution of the disperse phase in the equipment, different values and shapes of particular elements, as well as the complex character of continuous phase flow make an exact mathematical description of the two-phase flow practically impossible. The presence of a solid body in the form of an additional disperse phase (e.g. stagnant or moving packing) gives a further complication in the description of phase flow in the unit. This leads to the use of substitute models of flow. Hence, besides the mass transfer models an additional simplification is introduced, i.e. a flow model. One of the simplest and, at the same time, most widely applied is the

pseudo-homogeneous-phase model in which it is assumed that all phases co-exist in defined proportions in an arbitrarily small volume dV of the equipment (Fig. 9-2). A measure of the concentration of a given phase is a local phase hold-up expressed as a share of the volume of this phase in the considered element dV of the equipment. If α denotes gas hold-up, β denotes liquid hold-up and ε denotes bed voidage, then the volumes of these phases in the element dV are α dV for the gas, β dV for the liquid and $(1-\varepsilon)$dV for the solid, respectively.
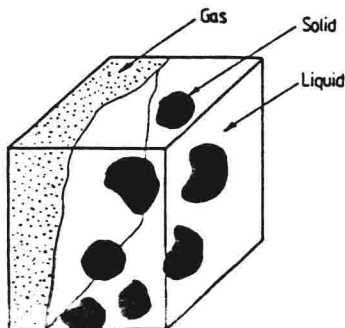

Fig. 9-2. Element of differential volume of equipment

In the pseudo-homogeneous-phase model each phase is treated as continuous, with parameters such as composition, temperature, pressure and flow rate change continuous through in the entire volume. Using the above assumptions it is possible to apply differential equations of mass and heat balances for the calculation of absorbers.

A complete description of an absorber should include the equations of motion, continuity for each of the components and energy formulated for two phases. As mentioned above, because of the complex character of flow in multicomponent systems, the applicability of the momentum balance is limited. Therefore, the general form of the momentum balance is not presented here.

As in Chapter 4, assume that the gas and liquid phases are n-component systems (components $A_1,...,A_n$). In the liquid phase r-homogeneous chemical reactions occur. They are represented by the equations

$$\sum_{i=1}^{n} \upsilon_{ij} A_i = 0 \quad (j = 1,...,r) \tag{4-1}$$

In a further consideration a_m denotes the gas-liquid mass transfer area in unit volume of the equipment. The interfacial area in the element dV is a_m dV.

Further on in this Chapter balance equations expressed by mass and molar quanitites will be presented. First of all, multicomponent systems will be considered.

9.2. MASS BALANCES

9.2.1. Mass Balances of Gas Phase for Multicomponent Mixtures

The mass balance of component i in an element of the absorber of differential volume dV = dxdydz in differential time dt consists of the following items:

a) accumulation of component i

$$\left[\frac{\partial \rho_{iG}}{\partial t} dt \right] \alpha\ dx\ dy\ dz$$

b) inflow of the component

$$\left[w_{iG}^{(\alpha)} \right]_x \left[\alpha\ dy\ dz \right] dt + \left[w_{iG}^{(\alpha)} \right]_y \left[\alpha\ dx\ dz \right] dt$$

$$+ \left[w_{iG}^{(\alpha)} \right]_z \left[\alpha\ dx\ dy \right] dt$$

c) outflow of the component

$$\left[w_{iG}^{(\alpha)} \right]_x \left[\alpha\ dy\ dz \right] dt + \left[\frac{\partial w_{iG}^{(\alpha)}}{\partial x} dx \right] \left[\alpha\ dy\ dz \right] dt$$

$$+ \left[w_{iG}^{(\alpha)} \right]_y \left[\alpha\ dx\ dz \right] dt + \left[\frac{\partial w_{iG}^{(\alpha)}}{\partial y} dy \right] \left[\alpha\ dx\ dz \right] dt$$

$$+ \left[w_{iG}^{(\alpha)} \right]_z \left[\alpha\ dx\ dy \right] dt + \left[\frac{\partial w_{iG}^{(\alpha)}}{\partial z} dz \right] \left[\alpha\ dx\ dy \right] dt$$

d) outflow of the component to the liquid phase through mass transfer (in the gas phase the equality $n^{\delta}_{iG} = n_{iG}$ is satisfied)

$$n_{iG} \left[a_m \text{ dx dy dz} \right] \text{ dt}$$

Balancing the above components gives the differential equation

$$\alpha \, \frac{\partial \rho_{iG}}{\partial t} = - \alpha \text{ div } w^{(\alpha)}_{iG} - a_m n_{iG} \qquad (i = 1,...,n) \tag{9-1}$$

The vector

$$w^{(\alpha)}_{iG} = \left[\left(w^{(\alpha)}_{iG} \right)_x, \left(w^{(\alpha)}_{iG} \right)_y, \left(w^{(\alpha)}_{iG} \right)_z \right] = \rho_{iG} u^{(\alpha)}_{iG}$$

$$(i = 1,...,n) \tag{9-2}$$

occurring in the balance equation represents the mass flow velocity of component i in the gas phase. The modulus of vector $w^{(\alpha)}_{iG}$ determines the mass of component i flowing in unit time through a unit surface perpendicular to the linear velocity vector of component $u^{(\alpha)}_{iG}$ in this phase. In equation (9-1) the first term on the right-hand side denotes the difference between the inflow and outflow of component i, and the other term represents the transfer of component i from the gas phase through the interfacial area. The left-hand side illustrates mass accumulation in the gas phase.

The sum of the mass flow velocities of all the components is called the mass velocity of the gas phase in the equipment

$$w^{(\alpha)}_G = \sum_{i=1}^{n} w^{(\alpha)}_{iG} \qquad (i = 1,...,n) \tag{9-3}$$

To take into account the deviations of the gas phase from plug flow, the mass velocity of component i is written as a sum of two components

$$w^{(\alpha)}_{iG} = j^{\blacktriangledown}_{D,iG} + b_{iG} w^{(\alpha)}_G \qquad (i = 1,...,n) \tag{9-4}$$

where the first one, $j^{\blacktriangledown}_{D,iG}$, denotes the dispersive constituent of mass velocity $w^{(\alpha)}_{iG}$, and the second one, $b_{iG} w^{(\alpha)}_G$, denotes its

convective constituent. The pheonomenon of dispersion will be discussed in detail in Chapter 10. Dispersion is described by equations that are formally similar to Fick's diffusion equations. Their detailed form will be given in balancing the gas phase in molar terms.

Substitution of equation (9-4) to equation (9-1) provides a final form for the balance of component i in the gas phase

$$\alpha \frac{\partial \rho_{iG}}{\partial t} + \alpha \operatorname{div} \mathbf{j}_{D,iG}^{\blacktriangledown} = - \alpha \operatorname{div} \left[b_{iG} \mathbf{w}_{iG}^{(\alpha)} \right] - a_m n_{iG}$$

$$(i = 1,...,n) \qquad (9-5)$$

The general mass balance of the gas phase is obtained upon summing up of the component balances (9-1) and taking into account equations (2-1), (3-8) and (9-3)

$$\alpha \frac{\partial \rho_G}{\partial t} = - \alpha \operatorname{div} \mathbf{w}_G^{(\alpha)} - a_m n_{tG} \qquad (9-6)$$

The molar balance of component i in the gas phase is obtained by dividing the equation of mass balance (9-1) by the molecular weight M_i

$$\alpha \frac{\partial C_{iG}}{\partial t} = - \alpha \operatorname{div} \mathbf{W}_{iG}^{(\alpha)} - a_m N_{iG} \qquad (i = 1,...,n) \qquad (9-7)$$

In this equation, the vector

$$\mathbf{W}_{iG}^{(\alpha)} = \left[\left[\mathbf{W}_{iG}^{(\alpha)} \right]_x, \left[\mathbf{W}_{iG}^{(\alpha)} \right]_y, \left[\mathbf{W}_{iG}^{(\alpha)} \right]_z \right] = C_{iG} \mathbf{u}_{iG}^{(\alpha)}$$

$$(i = 1,...,n) \qquad (9-8)$$

denotes the molar velocity of component i in the gas phase and can be written as the sum

$$\mathbf{W}_{iG}^{(\alpha)} = \mathbf{J}_{D,iG}^{\blacktriangledown} + y_i \mathbf{W}_G^{(\alpha)} \qquad (i = 1,...,n) \qquad (9-9)$$

where

$$\mathbf{W}_G^{(\alpha)} = \sum_{i=1}^{n} \mathbf{W}_{iG}^{(\alpha)} \qquad (9-10)$$

The dispersive component $\mathbf{J}_{D,iG}^{\blacktriangledown}$ of the molar velocity $\mathbf{W}_{iG}^{(\alpha)}$ can be described by the equation

$$\mathbf{J}_{D,iG}^{\blacktriangledown} = - C_G \hat{D}_{DG} \operatorname{grad} y_i \qquad (i = 1,...,n) \qquad (9-11)$$

where $\hat{D}_{DG}$ is the tensor whose constituents are the dispersion coefficients common to all components in different directions of the eqipment.

In many practical problems the dispersive component is often neglected and equation (9-9) simplifies to the form

$$W_{iG}^{(\alpha)} = y_i \, W_G^{(\alpha)} \qquad (i = 1,...,n) \qquad (9\text{-}12)$$

The general molar balance of the gas phase is formed similarly as the corresponding mass balance

$$\alpha \, \frac{\partial C_G}{\partial t} = - \alpha \, \text{div} \, W_G^{(\alpha)} - a_m N_{tG} \qquad (9\text{-}13)$$

9.2.2. Mass Balances of the Liquid Phase
for Multicomponent Mixtures

The liquid phase balances for the element of an absorber with the differential volume dV are formed in the same way as the gas phase balances. The first four balancing components remain very similar, while the constituent referring to the transfer of component i to the bulk liquid is equal to $a_m \, n_{iL}^{\delta}$ dx dy dz dt.

Additional balancing of the constituent is connected with formation of component i in chemical reactions in the liquid bulk

$$\beta \, M_i \sum_{j=1}^{r} \upsilon_{ij} R_j \; dx \; dy \; dz \; dt$$

The differential mass balance of component i is expressed by the equation

$$\beta \, \frac{\partial \rho_{iL}}{\partial t} = - \beta \, \text{div} \, w_{iL}^{(\beta)} + a_m n_{iL}^{\delta} + \beta \, M_i \sum_{j=1}^{r} \upsilon_{ij} R_j \quad (i = 1,...,n)$$

$$(9\text{-}14)$$

and the general mass balance of the liquid phase is described by the equation

$$\beta \, \frac{\partial \rho_L}{\partial t} = - \beta \, \text{div} \, w_L^{(\beta)} + a_m n_{tL}^{\delta} \qquad (9\text{-}15)$$

The above balances written in molar terms are expressed by means of the equations

$$\beta \frac{\partial C_{iL}}{\partial t} = -\beta \operatorname{div} \mathbf{W}_{iL}^{(\beta)} + a_m N_{iL}^{\delta} + \beta \sum_{j=1}^{r} v_{ij} R_j \qquad (i = 1, \ldots, n)$$

$$(9\text{-}16)$$

$$\beta \frac{\partial C_L}{\partial t} = -\beta \operatorname{div} \mathbf{W}_L^{(\beta)} + a_m N_{tL}^{\delta} + \beta \sum_{j=1}^{r} \left[R_j \sum_{i=1}^{n} v_{ij} \right] \qquad (9\text{-}17)$$

The mass velocities $w_{iL}^{(\beta)}$ and $w_L^{(\beta)}$ and molar velocities $\mathbf{W}_{iL}^{(\beta)}$ and $\mathbf{W}_L^{(\beta)}$ are defined as for the gas phase.

9.2.3. Mass Balances of the Equipment for Binary Mixtures

Most cases of either physical or chemical absorption are multicomponent systems. However, from the didactic point of view it is useful to present methods of calculation of absorbers for binary systems. Hence, it is necessary to formulate particular mass balances for binary mixtures. For binary systems in the liquid phase the following reaction can take place

$$A = v_B B \qquad (9\text{-}18)$$

The reaction rate R denotes the number of kilomoles of component A which is formed in time unit and in unit liquid volume.

For the gas phase the respective balances have the forms

$$\alpha \frac{\partial \rho_{AG}}{\partial t} = -\alpha \operatorname{div} w_{AG}^{(\alpha)} - a_m n_{AG} \qquad (9\text{-}19)$$

$$\alpha \frac{\partial \rho_G}{\partial t} = -\alpha \operatorname{div} w_G^{(\alpha)} - a_m n_{tG} \qquad (9\text{-}20)$$

$$w_G^{(\alpha)} = w_{AG}^{(\alpha)} + w_{BG}^{(\alpha)} \qquad (9\text{-}21)$$

$$n_{tG} = n_{AG} + n_{BG} \qquad (9\text{-}22)$$

or, using the molar values

$$\alpha \frac{\partial C_{AG}}{\partial t} = -\alpha \operatorname{div} \mathbf{W}_{AG}^{(\alpha)} - a_m N_{AG} \qquad (9\text{-}23)$$

$$\alpha \frac{\partial C_G}{\partial t} = -\alpha \operatorname{div} \mathbf{W}_G^{(\alpha)} - a_m N_{tG} \qquad (9\text{-}24)$$

$$W_G^{(\alpha)} = W_{AG}^{(\alpha)} + W_{BG}^{(\alpha)} \tag{9-25}$$

$$N_{tG} = N_{AG} + N_{BG} \tag{9-26}$$

Similarly, for the liquid phase we have

$$\beta \frac{\partial \rho_{AL}}{\partial t} = -\beta \, \text{div} \, w_{AL}^{(\beta)} + a_m n_{AL}^{\delta} - \beta \, M_A R \tag{9-27}$$

$$\beta \frac{\partial \rho_L}{\partial t} = -\beta \, \text{div} \, w_L^{(\beta)} + a_m n_{tL}^{\delta} \tag{9-28}$$

where

$$w_L^{(\beta)} = w_{AL}^{(\beta)} + w_{BL}^{(\beta)} \tag{9-29}$$

and

$$n_{tL} = n_{AL}^{\delta} + n_{BL}^{\delta} \tag{9-30}$$

or in the form

$$\beta \frac{\partial C_{AL}}{\partial t} = -\beta \, \text{div} \, W_{AL}^{(\beta)} + a_m N_{AL}^{\delta} - \beta \, R \tag{9-31}$$

$$\beta \frac{\partial C_L}{\partial t} = -\beta \, \text{div} \, W_L^{(\beta)} + a_m N_{tL}^{\delta} + \beta \left[-1 + v_B \right] R \tag{9-32}$$

where

$$W_L^{(\beta)} = W_{AL}^{(\beta)} + W_{BL}^{(\beta)} \tag{9-33}$$

$$N_{tL} = N_{AL}^{\delta} + N_{BL}^{\delta} \tag{9-34}$$

It is useful to give a definition of a binary system. A binary system is a system in which there are only two components both in the gas and liquid phases (Fig. 9-3). A typical example is absorption of pure ammonia in water. Frequently, however, the notion of the binary system in engineering calculations can be extended to systems in which the above condition is not fulfilled exactly. So, if two components occur in the gas phase, only one being absorbed, and in the liquid phase it can be assumed that the solvent is not volatile, then such a system can be treated as a binary one (Fig. 9-4a). An example of this system is absorption of NH_3 from nitrogen in water, assuming that the nitrogen is not
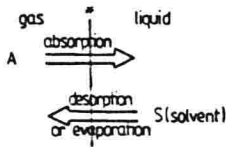
Fig. 9-3. Typical binary system

absorbed and water does not evaporate to the gas phase. This system can be additionally extended to cases where many components occur in the gas phase, only one of them being active in absorption (Fig. 9-4b). If in the liquid phase the reaction between component A and a nonvolatile reagent present in large excess takes place, the case can be treated in a simplified way and the formulae for binary systems can be used (Fig. 9-4c). Another case refers to the absorption of component A and its reaction with component B in the liquid phase in the presence of a large excess of a nonvolatile solvent.

In all of these cases, although the system is multicomponent, in the calculation of absorbers the relations quoted in Chapter 9.2.3. for binary systems after some small modification can be used.
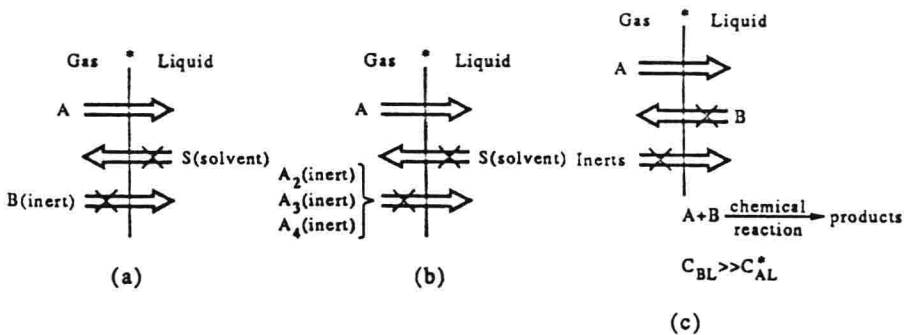

Fig. 9-4. Pseudo-binary system

9.3. ENERGY BALANCES

The energy balances for both phases are formulated using the notion of enthalpy. The following assumptions are used:
a) there is constant pressure in the absorber,
b) energy dissipation due to viscous friction of fluids is negligibly small,
c) no external forces other than gravitation act upon the system.

9.3.1. Gas Phase Energy Balance for Multicomponent Mixtures

The energy balance of the gas phase for an element of the absorber with differential volume dV in terms of enthalpy consists of the following items:

a) energy accumulation

$$\left[\frac{\partial(h_G \rho_G)}{\partial t} \, dt \right] \alpha \; dx \; dy \; dz$$

b) energy inflow

$$\left[\sum_{i=1}^{n} \tilde{h}_{iG} \, w_{iG}^{(\alpha)} \right]_x \left[\alpha \; dy \; dz \right] dt + \left[\sum_{i=1}^{n} \tilde{h}_{iG} \, w_{iG}^{(\alpha)} \right]_y \left[\alpha \; dx \; dz \right] dt$$

$$+ \left[\sum_{i=1}^{n} \tilde{h}_{iG} \, w_{iG}^{(\alpha)} \right]_z \left[\alpha \; dx \; dy \right] dt$$

c) energy outflow

$$\left[\sum_{i=1}^{n} \tilde{h}_{iG} w_{iG}^{(\alpha)} \right]_x \left[\alpha dy dz \right] dt + \left[\frac{\partial(\sum_{i=1}^{n} \tilde{h}_{iG} w_{iG}^{(\alpha)})_x}{\partial x} \, dx \right] \left[\alpha dy dz \right] dt$$

$$+ \left[\sum_{i=1}^{n} \tilde{h}_{iG} w_{iG}^{(\alpha)} \right]_y \left[\alpha dx dz \right] dt + \left[\frac{\partial(\sum_{i=1}^{n} \tilde{h}_{iG} w_{iG}^{(\alpha)})_y}{\partial y} \, dy \right] \left[\alpha dx dz \right] dt$$

$$+ \left[\sum_{i=1}^{n} \tilde{h}_{iG} w_{iG}^{(\alpha)} \right]_z \left[\alpha dx dy \right] dt + \left[\frac{\partial(\sum_{i=1}^{n} \tilde{h}_{iG} w_{iG}^{(\alpha)})_z}{\partial z} \, dz \right] \left[\alpha dx dy \right] dt$$

d) heat flow due to conduction

$$- \lambda_G \frac{\partial T_G}{\partial x} \left[\alpha \; dy \; dz \right] dt - \lambda_G \frac{\partial T_G}{\partial y} \left[\alpha \; dx \; dz \right] dt$$

$$- \lambda_G \frac{\partial T_G}{\partial z} \left[\alpha \; dx \; dy \right] dt$$

e) heat outflow due to conduction

$$- \lambda_G \frac{\partial T_G}{\partial x} \left[\alpha \; dy \; dz \right] \; dt - \left[\frac{\partial}{\partial x} \left[\lambda_G \frac{\partial T_G}{\partial x} \right] dx \right] \left[\alpha \; dy \; dz \right] \; dt$$

$$- \lambda_G \frac{\partial T_G}{\partial y} \left[\alpha \; dx \; dz \right] \; dt - \left[\frac{\partial}{\partial y} \left[\lambda_G \frac{\partial T_G}{\partial y} \right] dy \right] \left[\alpha \; dx \; dz \right] \; dt$$

$$- \lambda_G \frac{\partial T_G}{\partial z} \left[\alpha \; dx \; dy \right] \; dt - \left[\frac{\partial}{\partial z} \left[\lambda_G \frac{\partial T_G}{\partial z} \right] dz \right] \left[\alpha \; dx \; dy \right] \; dt$$

f) under the assumption that the heat transfer area is equal to the mass transfer area, heat transfer to the liquid phase is

$$q_G^\delta \left[a_m \; dx \; dy \; dz \right] \; dt$$

g) heat outflow to the liquid phase carried out with the mass flux

$$\sum_{i=1}^{n} \tilde{h}_{iG} n_{iG} \left[a_m \; dx \; dy \; dz \right] \; dt$$

Upon balancing components a)- g), the differential equation is obtained

$$\alpha \frac{\partial(h_G \rho_G)}{\partial t} = - \alpha \; \mathrm{div} \left[\sum_{i=1}^{n} \tilde{h}_{iG} \; w_{iG}^{(\alpha)} \right] + \alpha \; \mathrm{div} \left[\lambda_G \mathrm{grad} \; T_G \right]$$

$$- a_m q_G^\delta - a_m \sum_{i=1}^{n} \tilde{h}_{iG} n_{iG} \qquad\qquad (9\text{-}35)$$

or in the equivalent form

$$\alpha \frac{\partial(H_G C_G)}{\partial t} = - \alpha \; \mathrm{div} \left[\sum_{i=1}^{n} \tilde{H}_{iG} \; W_{iG}^{(\alpha)} \right] + \alpha \; \mathrm{div} \left[\lambda_G \mathrm{grad} \; T_G \right]$$

$$- a_m q_G^\delta - a_m \sum_{i=1}^{n} \tilde{H}_{iG} N_{iG} \qquad\qquad (9\text{-}36)$$

Substitution of the molar balances (9-7), equation (9-9), (9-13), and the formula for the complete differential of molar enthalpy for P = constant into equation (9-36) leads to the gas phase energy balance in terms of temperature

$$\alpha\, C_{pG}\left[C_G\frac{\partial T_G}{\partial t} + W_G^{(\alpha)}\ \text{grad}\ T_G\right] = -\,\alpha \sum_{i=1}^{n} J_{D,iG}^{\blacktriangledown}\ \text{grad}\ \hat{\tilde{H}}_{iG}$$

$$+\ \alpha\ \text{div}\left[\lambda_G\ \text{grad}\ T_G\right] - a_m q_G^{\delta} \tag{9-37}$$

The sum of the first and second components on the right-hand side of this equation describes heat transfer resulting from transport due to dispersion and molecular conduction. Generally, this transport can be described by the formula

$$Q_G^{ef} = -\,\chi_G^{ef}\ \text{grad}\ T_G \tag{9-38}$$

where χ_G^{ef} is the tensor of the effective heat transfer coefficient.

9.3.2. Liquid Phase Energy Balance for Multicomponent Mixtures

The enthalpy balance of the liquid phase is formed analogously to the process in the gas phase balance. Only the term referring to the heat transported by the mass flux is changed

$$\sum_{i=1}^{n} \tilde{\tilde{h}}_{iL} n_{iL}^{\delta}\ \left[a_m\ dx\ dy\ dz\right]\ dt$$

The differential energy balance will therefore be expressed by the formula

$$\beta\ \frac{\partial(h_L \rho_L)}{\partial t} = -\,\beta\ \text{div}\left[\sum_{i=1}^{n} \tilde{\tilde{h}}_{iL}\ w_{iL}^{(\beta)}\right] + \beta\ \text{div}\left[\lambda_L \text{grad}\ T_L\right]$$

$$+\ a_m\, q_L^{\delta} + a_m \sum_{i=1}^{n} \tilde{\tilde{h}}_{iL}\ n_{iL}^{\delta} \tag{9-39}$$

or in the equivalent form

$$\beta\ \frac{\partial(H_L C_L)}{\partial t} = -\,\beta\ \text{div}\left[\sum_{i=1}^{n} \hat{\tilde{H}}_{iL}\ w_{iL}^{(\beta)}\right] + \beta\ \text{div}\left[\lambda_L \text{grad}\ T_L\right]$$

$$+\ a_m\, q_L^{\delta} + a_m \sum_{i=1}^{n} \hat{\tilde{H}}_{iL}\ N_{iL}^{\delta} \tag{9-40}$$

Substitution of molar balances (9-16) and (9-17), equation (9-9) referring to the liquid phase and the formula for the complete differential of molar enthalpy for P = constant gives the energy balance equations in terms of the liquid temperature

$$\beta \ C_{pL}\left[C_L\frac{\partial T_L}{\partial t} + W_L^{(\beta)} \ \text{grad} \ T_L\right] = -\beta \sum_{i=1}^{n} J_{D,iL}^{\blacktriangledown} \ \text{grad} \ \hat{H}_{iL}$$

$$+ \ \beta \ \text{div}\left[\lambda_L \text{grad} \ T_L\right] + a_m q_L^{\delta} + \beta \sum_{j=1}^{r}\left[-\Delta H_{rj}\right] R_j \qquad (9\text{-}41)$$

where the molar heat of the j-th chemical reaction is given by the formula

$$\left[-\Delta H_{rj}\right] = \sum_{i=1}^{n} \upsilon_{ij} \ \hat{H}_{iL} \qquad (j = 1,...,r) \qquad (9\text{-}42)$$

By analogy to the gas phase

$$Q_L^{ef} = -\chi_L^{ef} \ \text{grad} \ T_L \qquad (9\text{-}43)$$

The differential balance equations presented above hold for most absorber types.

9.3.3. Energy Balances for Binary Mixtures

These balances will be given only in terms of molar values. The heat balance for the gas phase in binary mixtures assumes the form

$$\alpha \ \frac{\partial(H_G C_G)}{\partial t} = -\alpha \ \text{div}\left[\hat{H}_{AG}W_{AG}^{(\alpha)} + \hat{H}_{BG}W_{BG}^{(\alpha)}\right] + \alpha \ \text{div}\left[\lambda_G \text{grad} T_G\right]$$

$$- a_m q_G^{\delta} - a_m\left[\hat{H}_{AG}N_{AG} + \hat{H}_{BG}N_{BG}\right] \qquad (9\text{-}44)$$

For the liquid phase we have

$$\beta \ \frac{\partial(H_L C_L)}{\partial t} = -\beta \ \text{div}\left[\hat{H}_{AL}W_{AL}^{(\beta)} + \hat{H}_{BL}W_{BL}^{(\beta)}\right] + \beta \ \text{div}\left[\lambda_L \text{grad} T_L\right]$$

$$+ a_m \ q_L^{\delta} - a_m\left[\hat{H}_{AL}N_{AL}^{\delta} + \hat{H}_{BL}N_{BL}^{\delta}\right] \qquad (9\text{-}45)$$

9.4. FINAL REMARKS

In the above equations the molar and mass velocities of particular components and entire phases are real velocities in the absorber. In calculations it is more convenient to use superficial velocities, i.e. the velocities referred to the cross section of the whole absorber. The superficial mass and molar flow velocities of a gas are described by the formulae (one-dimensional flow)

$$w_G = \frac{g}{S} \qquad (9\text{-}46)$$

$$W_G = \frac{G}{S} \qquad (9\text{-}47)$$

and the linear superficial velocity

$$u_G = \frac{v_G}{S} \qquad (9\text{-}48)$$

For the liquid phase these equations are respectively

$$w_L = \frac{l}{S} \qquad W_L = \frac{L}{S} \qquad u_L = \frac{v_L}{S} \qquad (9\text{-}49)$$

The superficial velocities are expressed by the product of the phase hold-up and the real velocity. For example, the superficial molar velocity of the gas and liquid phase are

$$W_G = \alpha \, W_G^{(\alpha)} \qquad (9\text{-}50)$$

$$W_L = \beta \, W_L^{(\beta)} \qquad (9\text{-}51)$$

It is easy to write the balance equations using the superficial molar or mass velocities. The equation (9-7) will be taken as an example. Using the superficial velocity the equation will take the form

$$\alpha \, \frac{\partial C_{iG}}{\partial t} = - \, \text{div} \, W_{iG} - a_m N_{iG} \qquad (i = 1,...,n) \qquad (9\text{-}52)$$

Finally, some additional assumptions made in the balances given so far should be pointed out. First of all, it was assumed that the mass and heat transfer areas are the same. This assumption is not always valid and the energy balance equations should be modified taking into account different values of both surfaces.

The other assumption is that the solid phase is inert from the point of view of mass transfer processes. This means that the solid surface does not take part in mass and heat transfer processes (it is a rather typical process that occurs in plate or packed columns). This assumption is also valid in the case when a solid body is the catalyst of a reaction that takes place in the liquid phase, the reaction being treated as a pseudo-homogeneous one (an example is slurry columns). However, an important exception is the absorption of gases with a soluble solid phase. To make a correct balance of the absorber it is necessary to formulate an additional balance of the solid phase. A similar problem appears in the absorption of oxygen from air in a bioreactor where oxygen is transported into microorganisms (a quasi-solid phase). These problems, due to the limited scope of this book, will not be discussed further.