LETTERS IN HEAT AND MASS TRANSFER
Vol. 3, pp. 173 - 182, 1976

Pergamon Press
Printed in the United States

DETERMINATION OF INTERFACIAL MASS AND ENERGY TRANSFER RATES FOR MULTICOMPONENT VAPOUR-LIQUID SYSTEMS

R. Krishna and G.L. Standart

Department of Chemcial Engineering
University of Manchester Institute of Science and Technology
Sackville Street, Manchester M60 1QD, England

(Communicated by J.H. Whitelaw)

ABSTRACT

This paper presents a local analysis of simultaneous mass and energy transfer processes in vapour-liquid systems, with n components in either phase. Using a simple one-dimensional interphase transport model, a general procedure for determining the interfacial state, given information on the parameters in the bulk fluid phases, is obtained. The calculation of the interfacial 'total' mass and energy transport rates from knowledge of the 'diffusive' fluxes is discussed and the final results presented in compact matrix notation.

Two specific examples of condensation of mixed vapours and multicomponent distillation are examined in light of the general analysis and the validity of some classical assumptions questioned.

Introduction

Simultaneous mass and energy transport phenomena in vapour-liquid systems are common in many operations of engineering interest such as condensation, evaporation, distillation and absorption etc. Most published treatments of the transport processes are restricted to simple two-component (binary) systems A general discussion of n-component systems without restriction to one or other processing operation does not seem to be available. In this paper we attempt a general analysis of the problem as applied to a differential section of the vapour-liquid contacting operation. We use a simple one-dimensional interphase model and restrict discussions to non-reacting systems in the absence of electric, magnetic and centrifugal force fields.

Interfacial Mass and Energy Fluxes

Consider a vapour-liquid system; let 'y' denote the vapour phase and 'x', the liquid phase. It is easy to show by a material balance that if N_i is the normal constituent material flux in a given position at the interface and with respect to it, we must have

$$N_i^y = N_i^x = N_i, \qquad i = 1,2,\ldots n \qquad (1)$$

The only assumptions required are that no surface reaction is occurring and there are no constituent adsorptions at the interface. The flux N_i is thus a phase invariant. If we further assume that (i) the average state of each phase can be characterized by the bulk phase properties (denoted by subscript b), (ii) the transport rates in the interfacial region in directions tangent to the interface are negligible compared to the normal interfacial transport rates and (iii) that under unsteady state conditions, the rate of accumulation in the interfacial region is negligible compared to the normal interphase transport rate (or at least that the average rate of accumulation is negligible), we can similarly show that

$$N_{ib}^y = N_i = N_{ib}^x, \qquad i = 1,2,\ldots n \qquad (2)$$

In addition to these 'total' transport fluxes, it is also convenient to define normal constituent material diffusion fluxes J_i. Many definitions for the diffusion fluxes are possible but the simplest for our purposes is the diffusion flux defined with respect to the total mixture material transport flux, N_t, defined as

$$N_t = \sum_{i=1}^{n} N_i = N_t^y = N_t^x \qquad (3)$$

Thus for the vapour phase we have

$$J_i^y \equiv N_i - y_i N_t, \qquad i = 1,2,\ldots n \qquad (4)$$

with an analogous definition for the liquid phase,

$$J_i^x \equiv N_i - x_i N_t, \qquad i = 1,2,\ldots n \qquad (5)$$

The mole fractions y_i, x_i are not all independent for we have

$$\sum_{i=1}^{n} y_i = 1; \quad \sum_{i=1}^{n} x_i = 1 \qquad (6)$$

From equations (3) - (6) we see that the n diffusion fluxes in either phase are not all independent for we have

$$\sum_{i=1}^{n} J_i^y = 0; \quad \sum_{i=1}^{n} J_i^x = 0 \tag{7}$$

and therefore only n-1 of the diffusion fluxes J_i can be independent. These diffusion fluxes are not phase invariants and indeed in view of equations (4) and (5), we see that due to the variation of the compositions along the direction of transfer, they vary even within a phase from the bulk phase to the interface value. For a particular phase, given the compositions at the ends of the transfer path: at the interface and in the bulk, and the mass transport coefficients, it is possible to calculate these diffusion fluxes. For n-component systems the appropriate rate relations are:

$$J_i^y = \sum_{j=1}^{n-1} k^{\bullet}_{yij}(y_{jb} - y_{jI}); \quad J_i^x = \sum_{j=1}^{n-1} k^{\bullet}_{xij}(x_{jI} - x_{jb}), \quad i = 1,2,\dots n-1 \tag{8}$$

where $[k^{\bullet}_y]$ and $[k^{\bullet}_x]$ are the partial matrices of multicomponent mass transfer coefficients, of dimension $n-1 \times n-1$, in the vapour and liquid phases respectively. Methods for estimating the elements of these matrices are discussed in [1,2,3,4].

The bulk fluid compositions are determined by the overall material balances along the flow path and are considered known in the present analysis. Two problems still remain: (i) determination of the interfacial state and (ii) determination of the total molar fluxes N_i. It is clear from equations (4), (5) and (8) that even if the diffusion fluxes J_i can be calculated from equations (8), the determination of the total fluxes N_i requires an additional piece of information. This information is provided by an energy balance at the interface.

With assumptions parallel to those given below equation (1) we find that an energy balance at the interface leads to

$$E_b^y = E^y = E_b^x = E^x = E \tag{9}$$

which shows that the 'total' energy flux E is a phase invariant. In many engineering operations we can neglect the terms in the normal energy flux expressing the rate of transfer of kinetic energy and the rate of doing work by the surface frictional stresses. With this simplification, the invariant energy flux may be written as

$$E^y = q^y + \sum_{i=1}^{n} \overline{H}_i^y N_i = E^x = q^x + \sum_{i=1}^{n} \overline{H}_i^x N_i \tag{10}$$

q^y and q^x are the 'diffusive' (or conductive) heat fluxes in the vapour and liquid phases respectively. They are analogous to the diffusion fluxes, J_i, and are not phase invariants but must be considered to give a more intrinsic expression of the thermal transport behaviour of the particular phase than the total energy flux E. It is usual to relate these diffusive heat fluxes to the temperature driving forces by use of appropriate heat transfer coefficients. Thus we have

$$q^y = h_y^\bullet (T_b^y - T_I); \quad q^x = h_x^\bullet (T_I - T_b^x) \tag{11}$$

where the bulk vapour and liquid temperatures, T_b^y and T_b^x, will be determined by overall energy balances along the vapour-liquid contactor and are considered to be known for the purposes of the present analysis.

Determination of the Interfacial State

Under normal conditions of interphase mass and energy transfer we may safely assume that the two bulk phase pressures are equal to the interface pressure, which is thus known. If we assume that equilibrium prevails at the interface, we have *n-1* unknown intensive state conditions. It is convenient to take the *n-1* liquid phase compositions at the interface, x_{iI}, as the unknowns. Alternatively, *n-2* of the interface liquid compositions together with the interface temperature T_I may be taken as the unknown parameters to be determined. For the determination of the *n-1* unknown interfacial parameters, we need *n-1* independent equations; these equations are obtained as follows.

Equations (4) and (5) may be combined to give for each of the *n-1* independent species

$$N_t = - \frac{J_i^x - J_i^y}{x_i - y_i}, \qquad i = 1,2,\ldots n-1 \tag{12}$$

Also, equation (10) may be re-written in view of equations (4) and (5) as

$$\begin{aligned} q^x - q^y &= \sum_{i=1}^{n} (\bar{H}_i^y - \bar{H}_i^x) N_i = \sum_{i=1}^{n} \lambda_i N_i = \\ &= \sum_{i=1}^{n} \lambda_i J_i^y + \sum_{i=1}^{n} \lambda_i y_i N_t = \sum_{i=1}^{n} \lambda_i J_i^x + \sum_{i=1}^{n} \lambda_i x_i N_t \\ &= \sum_{i=1}^{n-1} (\lambda_i - \lambda_n) J_i^y + \bar{\lambda}_y N_t = \sum_{i=1}^{n-1} (\lambda_i - \lambda_n) J_i^x + \bar{\lambda}_x N_t \end{aligned} \tag{13}$$

where we define

$$\bar{\lambda}_y = \sum_{i=1}^{n} \lambda_i y_i; \quad \bar{\lambda}_x = \sum_{i=1}^{n} \lambda_i x_i \tag{14}$$

Equations (12) and (13) may be combined to give *n-1* independent relations which will determine the interfacial state:

$$-\frac{J_i^x - J_i^y}{x_i - y_i} = \frac{q^x - q^y}{\bar{\lambda}_y} - \frac{\sum_{k=1}^{n-1}(\lambda_k - \lambda_n)J_k^y}{\bar{\lambda}_y} = N_t, \quad i = 1,2,\ldots n-1 \tag{15}$$

In equations (15) we use the vapour phase diffusion fluxes. Alternatively we may use the liquid phase diffusion fluxes to obtain

$$-\frac{J_i^x - J_i^y}{x_i - y_i} = \frac{q^x - q^y}{\bar{\lambda}_x} - \frac{\sum_{k=1}^{n-1}(\lambda_k - \lambda_n)J_k^x}{\bar{\lambda}_x} = N_t, \quad i = 1,2,\ldots n-1 \tag{16}$$

Equations (15) or (16) allow the calculation of the n-1 unknown interfacial parameters. With this information, the composition and temperature driving forces in the vapour and liquid phases may be calculated; this allows the calculation of the diffusive mass and heat fluxes from equations (8) and (11). The final problem is the calculation of the total mass and energy fluxes.

Determination of Interfacial 'Total' Transport Fluxes

We may combine n-1 of the equations (4) with equations (15) to give

$$N_i = (1 - \Lambda_i y_i)J_i^y - y_i \sum_{\substack{k=1\\k\neq i}}^{n-1} \Lambda_k J_k^y + y_i \frac{\Delta q}{\bar{\lambda}_y}, \quad i = 1,2,\ldots n-1 \tag{17}$$

where we have defined the parameters

$$\Lambda_k = (\lambda_k - \lambda_n)/\bar{\lambda}_y; \quad \Delta q = q^x - q^y \tag{17'}$$

Equation (17) may be re-written in neat matrix notation (n-1 dimensional) as

$$(N) = [B^y](J^y) + (y)\frac{\Delta q}{\bar{\lambda}_y} \tag{18}$$

where the matrix $[B^y]$ which may be termed the bootstrap solution matrix has the elements

$$B_{ik}^y = \delta_{ik} - y_i \Lambda_k, \quad i,k = 1,2,\ldots n-1 \tag{19}$$

An expression analogous to (18) may be written in terms of the liquid phase mass diffusion fluxes. Thus

$$(N) = [B^x](J^x) + (x)\frac{\Delta q}{\bar{\lambda}_x} \tag{20}$$

Equation (18) or (20) may be used to determine the n-1 total fluxes, N_i, i = 1,2,...n-1. The nth total flux is determined from

$$N_n = N_t - \sum_{i=1}^{n-1} N_i \tag{21}$$

and the total energy flux obtained from equation (10).

Analysis of Special Cases

Condensation of Mixed Vapours

The classic Colburn and Drew analysis [5] forms the basis of many design procedures for condensation of binary vapour mixtures on vertical or horizontal surfaces. Employing essentially a 'film' model for the simultaneous mass and energy transfer process in the vapour phase, Colburn and Drew derived an expression for the total rate of condensation of the binary vapour mixture (with components 1 and 2) as

$$N_t = k_y \ln\left\{\frac{1 - y_{1I}/z_1}{1 - y_{1b}/z_1}\right\} \tag{22}$$

where k_y is the vapour phase binary mass transfer coefficient and z_1 represents the ratio of the rate of condensation of species 1 to the total rate of condensation of the mixture, i.e.

$$z_1 = N_1/N_t = N_1/(N_1 + N_2) = 1 - z_2 \tag{23}$$

When a binary vapour mixture is just brought into contact with a cold surface, say at the top of a vertical condenser, the composition of the liquid condensate formed may be identified with this ratio z_1, i.e.

$$x_{1I} = z_1 \tag{24}$$

The special relationship (24) will be strictly valid for the case where the condensed liquid film is just being formed for it implies (cf. equations (5), (23) and (24))

$$J_1^x = 0 \tag{25}$$

which can only arise with a vanishing mass transfer coefficient in the liquid phase. For a vertical condenser, relation (24) will not be valid for conditions prevailing further down the surface where there will be a build-up of condensed liquid and the mass transfer coefficient in the liquid phase cannot vanish in the general case. For processes involving condensation of some components whilst other components in the mixture are evaporating, relationships such as

$$x_{iI} = z_i = N_i/N_t \tag{26}$$

will clearly not hold for it would mean negative interface liquid compositions for the evaporating components.

Multicomponent Distillation

In the treatment of transport processes during distillation, most textbook treatments [e.g. 6] assume that conditions of equimolar counter diffusion, i.e

$$N_t = 0 \tag{27}$$

hold. It is clear from equations (15) that the requirement (27) will be realized if the following two conditions are satisfied:

$$\text{(i)} \quad \Delta q \equiv q^x - q^y = h^\bullet_x(T_I - T^x_b) - h^\bullet_y(T^y_b - T_I) = 0 \tag{28}$$

and

$$\text{(ii)} \quad \lambda_k = \lambda_n, \qquad i = 1,2,\ldots n-1 \tag{29}$$

Let us consider the first condition (i). The difference between the conductive heat fluxes in the liquid and vapour phases can only vanish if these fluxes fortuitously cancel each other; we cannot expect (28) to represent a general, even common, result.

Equation (29) requires the molar latent heats of vapourization of the constituent species to be identical. In practice, molar latent heats of many compounds are close to one another but the differences will not be zero. Typically we may expect the term Λ_i, defined in equation (17') to be of the order of magnitude 0.1.; the sign of Λ_i can be either positive or negative. Let us examine the effect of such small differences in the latent heats on the interfacial rates of transfer.

For a three component system, equations (18) may be written explicitly as

$$N_1 = (1 - y_1\Lambda_1)J^y_1 - y_1\Lambda_2 J^y_2 + y_1 \Delta q/ \bar{\lambda}_y \tag{30}$$

and

$$N_2 = - y_2\Lambda_1 J^y_1 + (1 - y_2\Lambda_2)J^y_2 + y_2 \Delta q/ \bar{\lambda}_y \tag{31}$$

The diffusion fluxes J^y_1 and J^y_2 need not have the same magnitude for non-ideal ternary mixtures. It is quite possible to have a situation in which we have

$$J^y_2 = 5\, J^y_1 \tag{32}$$

Further, let us suppose that the following values hold

$$y_1 \Lambda_1 = + 0.05; \quad y_1 \Lambda_2 = + 0.05 \tag{33}$$

Equation (30) will then give in view of values in (32) and (33),

$$N_1 \simeq 0.70\, J^y_1 \tag{34}$$

The assumption of equimolar counter transfer (27) will of course give $N_1 = J_1^y$, 30% in error. In multicomponent systems it is quite feasible to have the diffusion fluxes differ by a factor of five as assumed for the purposes of illustration above. Therefore extremely small cross coefficients in the matrix $[B^y]$ can give rise to large deviations from the condition (27). Such effects are not present to such a dramatic extent for binary systems because for this case we must necessarily have (cf. equation (7))

$$J_1^y = - J_2^y \tag{35}$$

and there will be no enhancement of the differences in latent heats. For binary systems (27) represents a good approximation and this explains its enshrinement in so many texts. However, for systems with three or more species large deviations from the equimolar counter transfer condition may be experienced, thus underlining the fundamental differences between the transport characteristics of binary and multicomponent systems.

Nomenclature

$[B]$	bootstrap solution matrix, with elements given by equations (19)
E	phase invariant total energy flux
$h^\bullet$	heat transfer coefficient
$\bar{H}_i^y$	partial molar enthalpy of species in vapour mixture
$\bar{H}_i^x$	partial molar enthalpy of species in liquid mixture
J_i	molar diffusion flux of species i
$k^\bullet_{yij}$	multicomponent mass transfer coefficients in the vapour phase
$k^\bullet_{xij}$	multicomponent mass transfer coefficients in the liquid phase
$\mathcal{k}_y$	vapour phase binary mass transfer coefficient
N_i	total molar flux of species i
N_t	total mixture molar flux
q	conductive heat flux
T	absolute temperature
x_i	mole fraction of species i in liquid mixture
y_i	mole fraction of species i in vapour mixture
z_i	ratio of total molar flux of species i to mixture total flux

Greek Letters

δ_{ik}	Kronecker delta
λ_i	$\equiv \bar{H}_i^y - \bar{H}_i^x$, differences in the partial molar enthalpies of the vapour and liquid phases

Greek Letters (cont'd)

$\Lambda_i \equiv (\lambda_i - \lambda_n)/\bar{\lambda}$

Matrix Notation

( )	column matrix of dimension $n-1$
[ ]	square matrix of dimension $n-1 \times n-1$

Subscripts

b	bulk phase property or parameter
i	species i
I	interfacial property
j,k	indices
x	liquid phase property or parameter
y	vapour phase property or parameter

Superscripts

x	liquid phase property or parameter
y	vapour phase property or parameter
$\bullet$	transfer coefficient corresponding to finite rates of mass transfer

References

1. R. Krishna and G.L. Standart, "A multicomponent film model incorporating a general matrix method of solution to the Maxwell-Stefan equations", A.I.Ch.E. J., in press

2. W.E. Stewart and R. Prober, Ind. Eng. Chem. Fundamentals, 3, 224 (1964)

3. W.E. Stewart, A.I.Ch.E. J., 19, 398 (1964)

4. H.L. Toor, A.I.Ch.E. J., 10, 460 (1964)

5. A.P. Colburn and T.B. Drew, Trans. Am. Inst. Chem. Engrs., 33, 197 (1937)

6. T.K. Sherwood, R.L. Pigford and C.R. Wilke, Mass Transfer, McGraw-Hill, New York (1975)