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CONDENSATION OF A BINARY VAPOUR MIXTURE IN THE PRESENCE OF AN INERT GAS

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Abstract—The simultaneous heat and mass transfer process during condensation of a binary vapour mixture in the presence of a non-condensable gas is analysed using matrix formulations of the interfacial mass transfer rate relations A film model for multicomponent mass transfer based on an exact solution to the Maxwell–Stefan equations is used to calculate the mass transfer coefficients in the ternary vapour phase With the aid of a computational example involving condensation of methanol and water vapours in the presence of air, it is demonstrated that diffusional interactions can significantly affect condensation rates

INTRODUCTION

Condensation of mixed vapours is an operation of great industrial significance In many cases, the condensation process takes place in the presence of a non-condensable, or inert, gas Most published analyses of the simultaneous heat and mass transfer process involved in the condensation of binary vapour mixtures, either condensation of a single vapour in the presence of an inert gas or condensation of a mixture of two vapours, follow the classic treatments of Ackermann[1] and Colburn and Drew[2] Published extensions of the Ackermann–Colburn and Drew analysis to multicomponent vapour condensation (e g Schrodt[3]) assume negligible diffusional interactions in the vapour phase and use uncoupled binary type mass transfer rate relations

It is now well appreciated that the mass transfer characteristics of systems with three or more species (i e multicomponent systems) are completely different from that exhibited by a simple two-component system Thus, as discussed in detail by Toor[4], it is possible in a multicomponent system to experience the three interaction phenomena *osmotic diffusion* (diffusion of a species in the absence of its constituent driving force), *diffusion barrier* (no transfer of a species even though a constituent driving force exists for its transfer) and *reverse diffusion* (diffusion of a species in a direction opposite to that dictated by its constituent driving force) These interaction phenomena have been observed experimentally for diffusion in gaseous mixtures[5] and for interphase mass transfer in liquid–liquid systems[6] For interphase transfer between a ternary vapour–gas mixture (consisting of acetone and benzene and either nitrogen or helium) and a falling liquid film (consisting of acetone and benzene) in a wetted wall column, Toor and Sebulsky[7] and Modine[8] observed that diffusional interactions were significant, especially for runs involving rich vapour mixtures These authors used a vapour phase mass transfer formulation based on an approximate method of solution to the Maxwell–Stefan equations developed earlier by Toor[4]

Recently Krishna and Standart[9] have developed a multicomponent film model based on an exact matrix method of solution the Maxwell–Stefan equations Their film model can be readily incorporated into design procedures for separation equipment It is the object of this paper to develop a proper treatment of heat and mass transfer processes involved during condensation of multicomponent vapour–gas mixtures allowing for diffusional interactions in the vapour phase according to the model described in reference [9] The simplest case of condensation of a binary vapour mixture in the presence of an inert non-condensable gas is considered in detail, extension of the analysis to more complicated cases is straightforward The condensed liquid phase is considered to be totally miscible For definiteness, condensation of a downflowing vapour inside a single vertical tube is considered, the coolant is assumed to flow in a direction counter-current to the condensate

MATERIAL BALANCES AND MASS TRASFER RATE RELATIONS

The differential molar material balance for each of the condensing species i in the vapour phase takes the form

$$\frac{dG_i}{d\xi} = -N_i\pi dZ, \quad i = 1, 2 \tag{1}$$

For the inert non-condensable gas we have

$$\frac{dG_3}{d\xi} = -N_3\pi dZ = 0 \tag{2}$$

Relation (2) arises from the requirement that the inert species be insoluble in the liquid condensate film, i e

$$N_3 = 0 \tag{3}$$

The molar rates of transfer of species 1 and 2 in the vapour phase can be written as a sum of the diffusive and

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convective contributions as

$$N_i = J_{ib} + y_{ib}N_t, \quad i = 1, 2 \tag{4}$$

where N_t is the mixture condensation flux

$$N_t = N_1 + N_2 \tag{5}$$

In view of eqns (3) and (5) we may write eqns (4) in two dimensional matrix notation as

$$(N) = [\beta](J_b) \tag{6}$$

where the elements of the matrix $[\beta]$ are given by

$$\beta_{ij} = \delta_{ij} + y_{ib}/y_{3b}, \quad i,j = 1, 2 \tag{7}$$

The constitutive relations for mass transfer in the vapour phase are properly written in terms of the bulk diffusion fluxes J_{ib} In two dimensional matrix notation, these rate relations take the form

$$(J_b) = [k_y^\bullet](y_b - y_I) \tag{8}$$

where $[k_y^\bullet]$ is a 2×2 matrix of mass transfer coefficients in the vapour phase defined in terms of the partial vapour phase composition driving forces $(y_{ib} - y_{iI})$ The superscript black dot ● on the mass transfer coefficients serves to remind us that these mass transfer coefficients are functions of the interfacial mass transfer rates N_i

For engineering calculations it is sufficiently accurate to use a film model to describe the mass transfer in the vapour phase, this film model forms the basis of the Ackermann–Colburn and Drew treatment Thus we assume that there exists a thin film of gas next to the condensate within which all the composition changes occur Outside this film the gas composition has a uniform value y_{ib} at any position ξ The transition from the bulk gas phase composition y_{ib} to the interface composition y_{iI} takes place by molecular transport mechanism within the film of thickness δ

If the temperature differences in the vapour phase are assumed not to interact with the mass transport process and if suitably averaged properties are used, then the molecular diffusion process across the film are properly described by the Maxwell–Stefan equations

$$\frac{dy_i}{dz} = \sum_{\substack{j=1 \\ j \neq i}}^{3} \frac{y_i N_j - y_j N_i}{c\mathscr{D}_{ij}}, \quad i = 1, 2 \tag{9}$$

Only two eqns (9) are considered because the three composition gradients dy_i/dz sum to zero

By defining the following

(i) Binary zero flux mass transfer coefficients

$$\kappa_{ij} = c\mathscr{D}_{ij}/\delta, \quad i,j = 12, 13, 23 \tag{10}$$

(ii) Matrix of dimensionless rate factors $[\Phi]$ with elements

$$\Phi_{11} = \frac{N_1}{\kappa_{13}} + \frac{N_2}{\kappa_{12}}, \quad \Phi_{12} = -N_1(1/\kappa_{12} - 1/\kappa_{13})$$
$$\Phi_{21} = -N_2(1/\kappa_{12} - 1/\kappa_{23}), \quad \Phi_{22} = \frac{N_1}{\kappa_{12}} + \frac{N_2}{\kappa_{23}} \tag{11}$$

(iii) A matrix of zero flux multicomponent mass transfer coefficients $[k_y]$ with elements given by

$$\begin{aligned} k_{y11} &= \kappa_{13}(y_{1b}\kappa_{23} + (1 - y_{1b})\kappa_{12})/S \\ k_{y12} &= y_{1b}\kappa_{23}(\kappa_{13} - \kappa_{12})/S \\ k_{y21} &= y_{2b}\kappa_{13}(\kappa_{23} - \kappa_{12})/S \\ k_{y22} &= \kappa_{23}(y_{2b}\kappa_{13} + (1 - y_{2b})\kappa_{12})/S \end{aligned} \tag{12}$$

where

$$S = y_{1b}\kappa_{23} + y_{2b}\kappa_{13} + y_{3b}\kappa_{12} \tag{13}$$

the set of two linear differential equations (9) can be solved to yield the expression for calculating the finite flux matrix of mass transfer coefficients $[k_y^\bullet]$ as [9]

$$[k_y^\bullet] = [k_y][\Phi]\{\exp[\Phi] - [I]\}^{-1} \tag{14}$$

Combining eqns (6), (8) and (14) we get the working expression for calculation of the interfacial fluxes

$$(N) = [\beta][k_y][\Phi]\{\exp[\Phi] - [I]\}^{-1}(y_b - y_I) \tag{15}$$

It is clear from eqns (11) that the calculation of the matrix of correction factors defined as

$$[\Xi] \equiv [\Phi]\{\exp[\Phi] - [I]\}^{-1} \tag{15'}$$

requires prior knowledge of the transfer fluxes N_i and therefore a trial procedure is involved in the calculation of eqn (15) Stable convergence is assured if iterations are started assuming that the matrix $[\Xi]$ is the identity matrix The zero flux binary mass transfer coefficients κ_{ij} can be calculated from an appropriate mass transfer correlation for example of the j factor type

The differential material balance for the liquid condensate film takes the form

$$\frac{dL_i}{d\xi} = N_i^x \pi dZ, \quad i = 1, 2 \tag{16}$$

where N_i^x is the molar flux of species i into the liquid condensate phase, for steady state transfer this flux must equal the condensation flux N_i in the vapour phase Now if it is assumed that the composition of condensate liquid at the interface x_{iI} is determined by the ratio of the condensation rates, we have

$$x_{iI} = N_i/(N_1 + N_2), \quad i = 1, 2 \tag{17}$$

If equilibrium is assumed to prevail at the interface then the composition of the vapour at the interface may be obtained from

$$y_{iI} = \frac{\gamma_i x_{iI} p_i^0(T_I)}{p_t}, \quad i = 1, 2 \tag{18}$$

and

$$y_{3I} = 1 - y_{1I} - y_{2I} \tag{19}$$

In eqn (18), $p_i^0(T_I)$ is the vapour pressure of component i at the interface temperature T_I, γ_i is the activity coefficient of species i in the binary condensed liquid phase and is a function of x_{iI} and T_I, p_t is the total system pressure. The determination of the interface vapour composition y_{iI}, required in the calculation of N_i, thus requires knowledge of the interface temperature T_I, this information is obtained from an energy balance.

ENERGY BALANCES AND HEAT TRANSFER RATE RELATIONS

The variation of the bulk vapour temperature is described by the differential energy balance relation

$$G_t \bar{C}_p \frac{\mathrm{d}T_b}{\mathrm{d}\xi} = -q_b \pi d Z \tag{20}$$

where the conductive heat flux in the vapour phase is given by

$$q_b = h_y^\bullet (T_b - T_I) \tag{21}$$

The superscript black dot on the vapour phase heat transfer coefficient emphasises the fact that the heat transfer coefficient $h_y^\bullet$ is dependent on the condensation rates. From the classic Ackermann–Colburn and Drew analysis we obtain the coefficient $h_y^\bullet$ in terms of the zero flux coefficient h_y as

$$h_y^\bullet = h_y \frac{\theta}{\exp \theta - 1} \tag{22}$$

where θ is the dimensionless heat transfer rate factor defined by

$$\theta = \frac{N_1 C_{p1} + N_2 C_{p2}}{h_y} \tag{23}$$

The zero flux heat transfer coefficient h_y can be calculated from standard correlations say of the j_H factor type. The rate factor θ plays a role in heat transfer exactly analogous to that played by the matrix $[\Phi]$ for mass transfer in the ternary vapour phase.

The temperature of the coolant increases as it passes up the tube as heat is transferred through the tube wall. The variation of the coolant temperature is described by

$$L_c C_{pc} \frac{\mathrm{d}T_c}{\mathrm{d}\xi} = -q_w \pi d Z \tag{24}$$

where q_w is the conductive heat flux through the tube wall. In writing eqn (24) we ignore the small differences in the heat transfer areas available for transfer in the vapour phase, across the liquid film and the tube wall. If we denote h_0 as the heat transfer coefficient which includes the heat transfer resistances of the condensed liquid film, wall, coolant and dirt films present on either side of the tube surface, then we may write

$$q_w = h_0(T_I - T_C) \tag{25}$$

If we assume negligible liquid subcooling and heats of mixing, then the heat flux through the wall into the coolant may also be written as

$$q_w = q_b + \sum_{i=1}^{2} N_i(\bar{H}_i^y - \bar{H}_i^x) \tag{26}$$

where $\bar{H}_i^y$ and $\bar{H}_i^x$ represent the partial molar enthalpies of species i in the vapour and liquid phases respectively. If the vapour phase is assumed to be thermodynamically ideal we may also write equation (26) in the form

$$q_w = q_b + \sum_{i=1}^{2} N_i C_{pi}(T_b - T_I) + \sum_{i=1}^{2} N_i \Delta H_{vi} \tag{27}$$

where ΔH_{vi} is the heat of vapourization of component i.

The interfacial state (x_{iI}, y_{iI}, T_I) must be such that the eqn (27) is satisfied. Once the interfacial variables are determined the partial composition driving forces ($y_{ib} - y_{iI}$) and the temperature driving force ($T_b - T_I$) can be found and the differential eqns (1), (16), (20) and (24) can be integrated along the tube length by using finite difference approximations.

COMPUTATIONAL RESULTS AND DISCUSSION

In order to demonstrate the significance of the cross coefficients of the matrix $[k_y^\bullet]$ in the calculation of the mass and heat transfer rates during condensation, computations were carried out for condensation of methanol and water vapours in the presence of air. The composition of the vapours entering the top of the single vertical tube (inside diameter $d = 0.0254$ m, length of tube $Z = 2.12$ m) is $y_1 = 0.7$, $y_2 = 0.2$, $y_3 = 0.1$. The vapour gas mixture enters the condenser tube at the rate of 0.0001841 kmol/s and at a temperature of 360.0 K. The total system pressure is 1.0135 bar. The coolant flow is 0.04376 kg/s and leaves the condenser at a temperature of 308.15 K.

Figures 1 and 2 give the results of the calculation of the

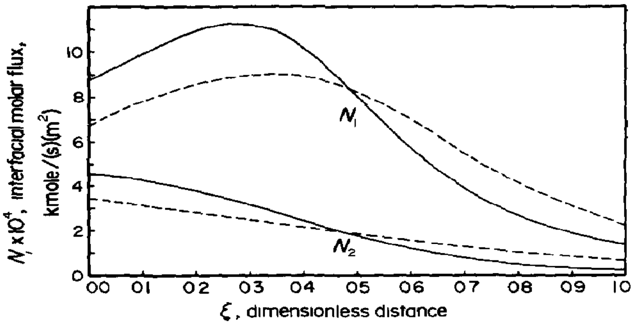

Fig. 1. Variations of interfacial molar transfer rates N_1 and N_2 along condenser tube length ——, interacting model, ----, non-interacting model.

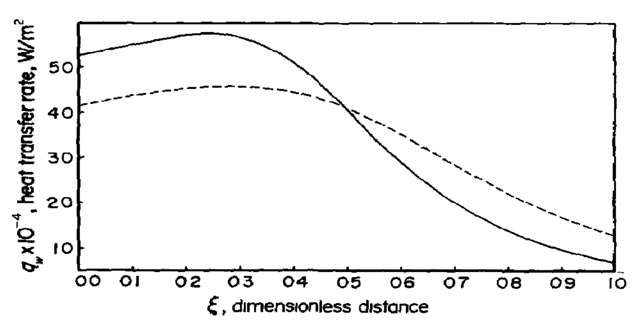

Fig. 2. Variation of heat transfer rate q_w along condenser tube length ——, interacting model, – – –, non-interacting model.

mass and heat transfer fluxes along the condenser length for the above conditions. In the computations, the physical and transport properties were taken from standard sources such as Perry's Handbook, 5th Edn. The vapour phase diffusivities $\mathcal{D}_{ij}$ were estimated using the method given by Fuller, Schettler and Giddings[10].

The vapour phase zero flux mass and heat transfer coefficients were estimated from the Chilton–Colburn analogy

$$j_H = \frac{h_y A}{G_t C_p}(Pr)^{2/3} = j_M = \frac{k_{ij} A}{G_t}(Sc_{ij})^{2/3} = 0.023 Re^{-0.17} \tag{28}$$

The coefficient h_0 was taken to be constant along the condenser and equal to 1700 W/(m^2)(K).

In Figs. 1 and 2 are also included calculations using simpler binary type mass transfer relations

$$J_{ib} = k_{yieff}(y_{ib} - y_{iI}), \quad i = 1, 2 \tag{29}$$

with the effective mass transfer coefficient evaluated from eqn (28) using the effective diffusivity $\mathcal{D}_{yieff}$ as defined by Wilke[11]

$$\mathcal{D}_{yieff} = \frac{1 - y_{ib}}{\sum\limits_{\substack{k=1\\k\neq i}}^{3} y_{kb}/\mathcal{D}_{ik}}, \quad i = 1, 2 \tag{30}$$

The results of the calculations show that the simple mass transfer model described by eqn (29) gives rise to large errors. For the conditions existing at the top of the condenser, the elements of the matrix of zero flux mass transfer coefficients are calculated from eqns (12) and (13) to be (units kmol/(s)(m^2)(mole fraction))

$$\begin{aligned} k_{y11} &= 0.002187, & k_{y12} &= -0.00008266 \\ k_{y21} &= 0.0001198, & k_{y22} &= 0.0024614 \end{aligned} \tag{31}$$

The bulk and interface compositions for the conditions prevailing at the top of the condenser are obtained as

$$\begin{aligned} y_{1b} &= 0.700, & y_{1I} &= 0.7317, & y_{1b} - y_{1I} &= -0.0317 \\ y_{2b} &= 0.200, & y_{2I} &= 0.0944, & y_{2b} - y_{2I} &= 0.1056 \end{aligned} \tag{32}$$

Since the driving force for transfer of component 2 is about $3\frac{1}{2}$ times the magnitude of the driving force for component 1, it is clear from eqns (15) and (31) that diffusional interaction effects will be much more important for component 1 than for component 2. This is borne out in Fig. 1 which shows that the differences between the interacting and non-interacting model predictions for the fluxes are greater for component 1.

As condensation proceeds the vapours get leaner and the interaction effects decrease because the cross coefficients k_{y12} and k_{y21} decrease in magnitude (see eqn 12). The predictions of the two models in Figs. 1 and 2 become closer to each other as we proceed down the tube.

CONCLUSIONS

The process of condensation of a binary vapour mixture in the presence of a non-condensable gas has been analysed using coupled mass transfer rate relations. A multicomponent film based on an exact solution to the Maxwell–Stefan diffusion equations has been used to calculate the elements of the matrix of mass transfer coefficients in the ternary vapour phase. A computational procedure has been suggested for computing the mass and heat transfer fluxes, compositions and temperatures along a single vertical condenser tube. The procedure could form the basis of a design procedure for an industrial condenser. Computations for the system methanol–water vapour–air show that diffusional interactions are very significant.

From a practical point of view we may expect diffusional interactions to be significant in partial condensers.

Though condensation of ternary vapour–gas mixture has been considered specifically in this paper, the mathematical analysis is valid with little or no modification for evaporation of a binary liquid mixture into an inert gas stream and for simultaneous condensation–evaporation process between a binary liquid and a ternary vapour–gas mixture. The treatment of the mass transport phenomena in the vapour phase should be applicable to the description of non-isothermal absorption of two soluble species from an inert gas stream into a non-volatile absorbent liquid.

NOTATION

A	cross sectional area of tube, m^2
c	molar density of gas mixture, kmol/m^3
C_{p1}	molar heat capacity of component 1, J/(kmol)(K)
C_{p2}	molar heat capacity of component 2, J/(kmol)(K)
$\bar{C}_p$	molar heat capacity of gas mixture, J/(kmol)(K)
d	inside diameter of tube, m
$\mathcal{D}_{ik}$	vapour phase diffusivity of binary gas pair $i-k$, m^2/s
$\mathcal{D}_{ieff}$	effective vapour phase diffusivity of species i through ternary vapour mixture, m^2/s
G_i	molar flow rate of species i in the vapour phase, kmol/s
G_t	molar flow rate of vapour–gas mixture, kmol/s
h_y	zero flux heat transfer coefficient in the vapour phase, W/(m^2)(K)
$h_y^{\bullet}$	finite flux heat transfer coefficient in the vapour phase, W/(m^2)(K)

h_0	overall heat transfer coefficient including resistances of condensate film, wall, coolant together with dirt resistances, W/(m^2)(K)
$\bar{H}_i$	partial molar enthalpy of species i in mixture, J/kmole
ΔH_{vi}	molar heat of vaporization of species i, J/kmole
$[I]$	identity matrix with elements δ_{ik}
j_H, j_M	Chilton–Colburn j-factors for heat and mass transfer
J_{ib}	molar diffusion flux of species i in the bulk vapour phase, kmole/(s)(m^2)
$[k_y]$	matrix of zero flux multicomponent mass transfer coefficients, kmole/(s)(m^2) (mole fraction)
$[k_y^\bullet]$	matrix of finite flux multicomponent mass transfer coefficients, kmole/(s)(m^2) (mole fraction)
$\mathscr{k}_{ik}$	mass transfer coefficient in the binary gas pair $i-k$, kmole/(s)(m^2) (mole fraction)
L_i	molar flow rate of species i in the condensed liquid film, kmole/s
L_c	mass flow rate of coolant, kg/s
N_i	molar flux of species i, kmole/(s)(m^2)
N_t	total mixture molar flux, kmole/(s)(m^2)
p_t	total system pressure, bar
p_i^0	vapour pressure of species i, bar
q_b	conductive heat flux in the bulk vapour–gas mixture, W/m^2
q_w	heat flux crossing the wall into the coolant stream, W/m^2
Re	Reynolds number of the flowing gas mixture inside tube
S	summation parameter given by eqn (13)
Sc_{ij}	Schmidt number of binary gas pair $i-j$
T	absolute temperature
x_i	mole fraction of species i in the liquid mixture
y_i	mole fraction of species i in vapour mixture
Z	total length of tube, m
z	distance measured along gas "film" from bulk gas to interface, *m*

Greek symbols

$[\beta]$	matrix with elements defined by eqn (7)
γ_i	activity coefficient of species i in solution
δ	thickness of gas "film", m
δ_{ik}	Kronecker delta
θ	dimensionless heat transfer rate factor
ξ	dimensionless distance measured along the tube from the top
$[\Xi]$	matrix of correction factors given by eqn (15′)
$[\Phi]$	matrix of dimensionless rate factors given by eqn (11)

Matrix

( )	column matrix with 2 elements
[ ]	2×2 dimensional square matrix
$[\ ]^{-1}$	inverted matrix, 2×2 dimensional

Subscripts

b	bulk fluid phase property
c	pertaining to coolant
I	interfacial property
t	pertaining to total mixture
x	liquid phase
y	vapour phase
w	pertaining to condenser wall

Superscripts

●	coefficient corresponding to finite mass transfer rates
x	liquid phase
y	vapour phase

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