Int. J. Heat Mass Transfer. Vol. 19, pp. 323–333. Pergamon Press 1976. Printed in Great Britain

FILM CONDENSATION FROM A TERNARY MIXTURE OF VAPORS UPON A VERTICAL SURFACE

F. E. SAGE
Continental Oil Company, Ponca City, Oklahoma 74601, U.S.A.

and

JOSEPH ESTRIN†
Chemical Engineering Department, Clarkson College of Technology, Potsdam, New York 13676, U.S.A.

(*Received* 4 *November* 1974 *and in revised form* 28 *May* 1975)

Abstract—An analytical study of the condensation of a vapor in the presence of noncondensable gases is presented. The bulk mixture is considered quiescent, and the only flow is that induced by the condensate flowing down the wall and the accompanying free convection effects. A full predictive, constant physical property, boundary-layer condensation model is used to describe the system.

In a ternary system fractionation is shown to occur between the two noncondensables as the interface is approached. The fractionation is dependent on the difference between the linearized Schmidt numbers.

The gas–vapor boundary layer is shown to be supersaturated in the condensation from a saturated mixture with a Lewis number greater than one. Supersaturation can also be obtained in systems with Lewis numbers less than one but only at larger driving forces as measured by the difference between bulk and wall temperatures.

NOMENCLATURE

A_i,	defined by equation (25);
c,	defined, $\dfrac{g\left(1-\dfrac{\rho_\infty}{\rho_i}\right)^{1/4}}{\nu}$ or $\left(\dfrac{N_{Gr_x}}{4x^3}\right)^{1/4}$, by equation (21);
C_p,	specific heat at constant pressure;
$\mathbf{D}_{ij}$,	binary diffusion coefficient for species $i-j$;
D_i,	eigenvalue of multicomponent diffusion coefficient matrix;
D_{ij},	multicomponent diffusion coefficients;
f,	dimensionless stream function, equation (16);
g,	acceleration due to gravity;
$\mathbf{j}_i$,	mass diffusion flux of component i relative to the mass velocity;
k,	thermal conductivity;
M,	molecular weight (average molecular weight without subscript);
n,	number of components;
N_{Gr_x},	local Grashof number $\dfrac{x^3 g(1-\rho_\infty/\rho_i)}{\nu^2}$;
N_{Le},	Lewis number (N_{Sc}/N_{Pr});
N_{Pr},	Prandtl number $(C_p\mu/k)$;
N_{Sc},	Schmidt number $(\mu/\rho\mathbf{D}_{ij})$;
N_{Sc_i},	Schmidt number for linear combination i $(\mu/\rho D_i)$;
P,	pressure;
q,	local heat flux;
S,	defined in equation (9);
T,	temperature (absolute);
u,	longitudinal velocity;
u_g,	interfacial longitudinal velocity;
v,	normal velocity;
w,	local mass flux;
w_i,	mass fraction of component i;
y_i,	mole fraction of component i;
Y_i,	ratio of mole fraction of component i to the total mole fraction of noncondensable.

Greek symbols

α,	thermal diffusivity, $\dfrac{k}{\rho C_p}$;
β,	variable defined by equation (23);
γ,	dimensionless temperature, equation (19);
δ,	condensate film thickness;
η,	similarity variable, equation (20);
λ,	latent heat of vaporization;
μ,	absolute viscosity;
ν,	kinematic viscosity, μ/ρ;
ρ,	density;
ϕ_i,	mass fraction difference, equations (17) and (18);
ψ,	stream function.

ubscripts

1, 2,	noncondensable components;
3,	condensable component;
a,	reference state conditions;
g,	noncondensable gas;
i,	interface, $y = \delta$;
L,	liquid;
sat,	saturated;
w,	wall, $y = 0$;
∞,	bulk.

Superscripts

$*$,	equilibrium quantity.

---

†This manuscript was prepared while J. Estrin was on Sabbatical leave at the National Center for Atmospheric Research, Boulder, Colorado. The National Center for Atmospheric Research is sponsored by the National Science Foundation.

1. INTRODUCTION

Mass transfer in multicomponent gaseous mixtures

Multicomponent systems are of great practical interest. Most industrial processes and separation schemes involve multicomponent mixtures. In many cases the multicomponent nature of the process is neglected; the system is treated as a pseudo-binary mixture. The limitations of this approach have been pointed out by Toor [23].

Here we apply the analytical methods for treating multicomponent systems to the condensation of a condensable component from its mixture with two non-condensables. The binary problem has been thoroughly analysed [9, 12, 18] and recent experiments confirm the theoretical approach [1]. The multicomponent problem has been applied to the consideration of fission product removal from contaminated vapors [11] and also to condensation from mixed vapors [22]. In the former reference the contaminant was considered to be in trace quantities and justifiable simplification resulted. The work reported upon here is similar to that of Taitel and Tamir [22], but the computational procedure and particular results discussed are different.

The formulation of equations to calculate multicomponent mass-transfer rates must involve the introduction of a diffusion law into continuity equations. Stefan and Maxwell [7, 19] derived the expression from simple kinetic theory and intuitive observations for ideal gases at constant pressure and temperature. The more rigorous kinetic theory models of Hirschfelder, Curtiss and Bird [4] under conditions of constant pressure and temperature reduce to their relationship.

In 1945, Onsager [10] suggested a generalization of Fick's law to multicomponent systems for liquids. He stated that the diffusion flux of a component is linearly related to the concentration gradients of all the components, or mathematically

$$\mathbf{J}_i = -\sum_{j=1}^{n} D_{ij}^{*}\nabla C_j \qquad i = 1, \ldots, n.$$

In this expression, the D_{ij}^{*} are multicomponent diffusion coefficients which are functions of the binary diffusion coefficients and component concentrations. $\mathbf{J}_i$ is the molar flux relative to the molar-average velocity and is related to $\mathbf{N}_i$ by

$$\mathbf{J}_i = \mathbf{N}_i - y_i \sum_{j=1}^{n} N_j.$$

Hirschfelder, Curtiss and Bird [4] have shown the two diffusion laws are equivalent. Reference [15] gives further discussion of these two laws and details on inversion between the laws in mass units for use in boundary-layer theory.

Toor [24] and Stewart and Prober [21] proposed a linearization of Onsager's form of the diffusion law. With this technique the basic nature of multicomponent diffusion is maintained. The multicomponent diffusion coefficients are evaluated at a reference state and their concentration dependences neglected. Since

$$\sum_{i=1}^{n} \nabla y_i = 0 \quad \text{and} \quad \sum_{i=1}^{n} \mathbf{J}_i = 0$$

the Onsager form can be written in matrix notation as

$$(\mathbf{J}) = -C[D](\nabla y)$$

in which $(\mathbf{J})$ and (∇y) are column vectors with elements $J_1, J_2, \ldots, J_{n-1}$ and $\nabla y_1, \nabla y_2, \ldots, \nabla y_{n-1}$, respectively. $[D]$ is a $(n-1)$ by $(n-1)$ matrix with elements of the multicomponent diffusion coefficients computed at the reference state.

The mathematical technique to uncouple these expressions is to find the modal matrices $[P]$ and $[P]^{-1}$ which will diagonalize the diffusion coefficient matrix $[D]$.

$$[P]^{-1}[D][P] = \begin{bmatrix} D_1 & & & \\ & D_2 & & \\ & & \ddots & \\ & & & D_{n-1} \end{bmatrix}.$$

Then operating on the Onsager form with $[P]^{-1}$ gives

$$(\bar{\mathbf{J}}) = -C \begin{bmatrix} D_1 & & & \\ & D_2 & & \\ & & \ddots & \\ & & & D_{n-1} \end{bmatrix} (\nabla \bar{y})$$

where the over bars indicate linear combinations of the variables. Frequently the result gives uncoupled expressions which are the same as the binary expressions but involves linear expressions of the flux and of the concentration of a component rather than the flux and concentration *per se* [21, 24]. In this work the momentum equation and the mass conservation equations are coupled and an uncoupling of these does not result from the use of the method. Rather a simplification of the numerical results and their interpretation are effected. Taitel and Tamir [22] did not make use of this linearization technique; they directly employed the equations for diffusion in multi-component gases [2].

2. ANALYTICAL MODEL

Objectives

We had two primary objectives in the development of the analytical model for this research.

(1) Extension of the fully predictive boundary-layer condensation model to include multicomponent gas–vapor systems and thereby determine the effects of various third components on a given binary condensation system.

(2) Application of this condensation system as a possible approach to water mist formation experiments by predicting the extent of supersaturation in the vapor phase boundary layer.

The reference state, constant property approach is very attractive [15, 22]. The effort (machine time) required to solve a variable properties problem is much more than the constant property analysis. Further, for many systems the accuracy of physical properties and of the variation in physical properties with temperature, pressure and composition are not well established, and it would appear to be hardly justified to even attempt their consideration.

Mathematical model

The process studied in this report involves the steady-state condensation of a single component from a mixture of two or three components. Taitel and Tamir [22] studied the influence of multicomponents upon the condensation rate; they included two and three condensible components in three component systems. Condensation occurs upon a vertical, isothermal surface upon which the condensate is in stable laminar flow. The bulk vapor is uniform in concentration and temperature and has no vertical component of velocity. This two-dimensional configuration is shown in Fig. 1.

Making the same assumptions for describing the liquid condensate layer as Sparrow and Lin [18], viz., that it is well described by the Nusselt model, the pertinent equation for heat transfer at position x is:

$$\frac{qx}{\lambda\mu_L} = \left[\frac{C_{PL}(T_i - T_w)}{\lambda N_{Pr_L}}\right]^{3/4}\left(\frac{gx^3}{4v_L^2}\right)^{1/4} \tag{1}$$

condensate film thickness:

$$\frac{\delta}{x} = \left[\frac{C_{PL}(T_i - T_w)}{\lambda N_{Pr_L}}\right]^{1/4}\left(\frac{gx^3}{4v_L^2}\right)^{-1/4} \tag{2}$$

vertical velocity of the interface:

$$\frac{u_\delta x}{v_L} = 2\left[\frac{C_{PL}(T_i - T_w)}{\lambda N_{Pr_L}}\right]^{1/2}\left(\frac{gx^3}{4v_L^2}\right)^{1/2} \tag{3}$$

condensate flux at x:

$$w = q/\lambda. \tag{4}$$

In equations (1)–(4), the liquid physical properties are evaluated at an appropriate reference temperature [9].

The vapor phase diffusion expressions are based on the Onsager [10] extension of Fick's Law. As used here the diffusion law states that the diffusion flux, $\mathbf{j}_i$, is linearly related to the concentration gradients, ∇w_i, of the components, that is

$$\mathbf{j}_i = -\rho \sum_{j=1}^{n-1} D_{ij}\nabla w_j, \quad i = 1, \ldots, n-1 \tag{5}$$

where D_{ij} are the multicomponent diffusion coefficients.

For a three-component vapor system, the boundary layer equations for the conservation of individual species are:

$$u\frac{\partial w_1}{\partial x} + v\frac{\partial w_1}{\partial y} = D_{11}\bigg|_a \frac{\partial^2 w_1}{\partial y^2} + D_{12}\bigg|_a \frac{\partial^2 w_2}{\partial y^2} \tag{6}$$

$$u\frac{\partial w_2}{\partial x} + v\frac{\partial w_2}{\partial y} = D_{21}\bigg|_a \frac{\partial^2 w_2}{\partial y^2} + D_{22}\bigg|_a \frac{\partial^2 w_2}{\partial y^2} \tag{7}$$

where subscripts 1 and 2 refer to the noncondensables and 3 to the condensable component as given in Fig. 1. Analytical expressions for the multicomponent diffusion coefficients are:

$$D_{11} = \frac{\mathbf{D}_{13}[(1-w_1)M_1\mathbf{D}_{12} + w_1 M_3 \mathbf{D}_{23}]\left[w_1\left(\frac{1}{M_1 M_3} - \frac{1}{M_1^2}\right) + \frac{1}{MM_1}\right] + w_1\mathbf{D}_{23}(M_3\mathbf{D}_{13} - M_2\mathbf{D}_{12})\frac{w_2}{M_2}\left(\frac{1}{M_3} - \frac{1}{M_1}\right)}{S} \tag{8A}$$

$$D_{12} = \frac{\mathbf{D}_{13}[(1-w_1)M_1\mathbf{D}_{12} + w_1 M_3 \mathbf{D}_{23}]\left[\frac{w_1}{M_1}\left(\frac{1}{M_3} - \frac{1}{M_2}\right)\right] + w_1\mathbf{D}_{23}(M_3\mathbf{D}_{13} - M_2\mathbf{D}_{12})\left[w_2\left(\frac{1}{M_2 M_3} - \frac{1}{M_2^2}\right) + \frac{1}{MM_2}\right]}{S} \tag{8B}$$

where $$S = \frac{w_1}{M_1}\mathbf{D}_{23} + \frac{w_2}{M_2}\mathbf{D}_{13} + \frac{w_3}{M_3}\mathbf{D}_{12} \tag{9}$$

Expressions for D_{21} and D_{22} are derived from the above equations by replacing the subscript 1 by 2 in all subscripted members except $\mathbf{D}_{12}$ which is unchanged. The a subscript indicates evaluation of the physical property at reference state a. (For example, a may refer to average conditions of temperature, pressure and concentration.)

The remaining conservation equations for the gas phase boundary layer are continuity:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{10}$$

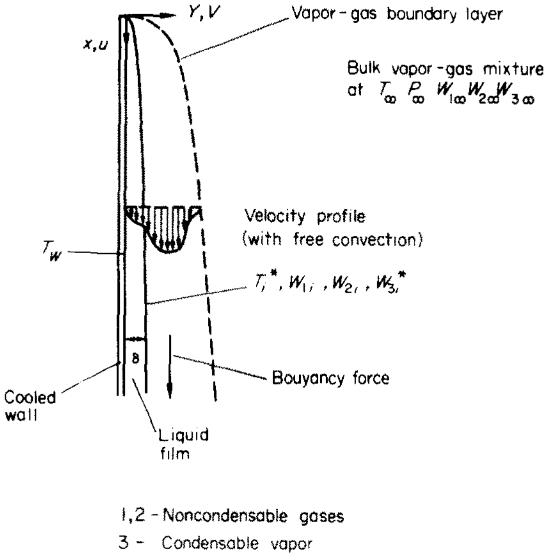

FIG. 1. Physical model of filmwise condensation in the presence of noncondensables.

momentum:

$$u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}=g\left(1-\frac{\rho_\infty}{\rho}\right)+\nu\Big|_a\frac{\partial^2 u}{\partial y^2} \qquad (11)$$

energy:

$$u\frac{\partial T}{\partial x}+v\frac{\partial T}{\partial y}=\alpha\Big|_a\frac{\partial^2 T}{\partial y^2}. \qquad (12)$$

We have used the energy equation—it has significance in the interpretation of some of our results. In earlier reported work [18, 22] the energy equation was not of importance and was neglected.

As is common in free convection problems, all physical properties in the above boundary-layer equations are considered constant except for the density in the buoyancy term of the momentum equation. The boundary-layer assumption of neglecting longitudinal diffusion of mass, energy and momentum is completely accepted in these equations. The boundary conditions associated with the above equations (6, 7, 10–12) are:

at $y=\infty$: $u=0,\ T=T_\infty,\ w_1=w_{1\infty},\ w_2=w_{2\infty}$ (13)

at $x=0$: $u=0,\ T=T_\infty,\ w_1=w_{1\infty},\ w_2=w_{2\infty}$ (14)

at $y=\delta$: $u=u_\delta,\ w=\rho u\dfrac{\mathrm{d}\delta}{\mathrm{d}x}-\rho v$ (mass conservation)

$T=T^*(w_{1i},w_{2i}),\ j_1=ww_{1i},\ j_2=ww_{2i}$ (15)

(interface impermeable to noncondensables).

Equations (6, 7, 10–15) are reduced to total differential equations with unique boundary conditions by the following definitions of dimensionless variables and the similarity variable, η.

(a) Dimensionless stream function:

$$f(\eta)=\Psi\Bigg/\left(4\nu\left(\frac{N_{Gr_x}}{4}\right)^{1/4}\right) \qquad (16)$$

(b) Mass fractions:

$$\phi_1(\eta)=w_1-w_{1\infty} \qquad (17)$$

$$\phi_2(\eta)=w_2-w_{2\infty} \qquad (18)$$

(c) Temperature:

$$\gamma(\eta)=\frac{T_\infty-T}{T_\infty}. \qquad (19)$$

(d) Similarity variable:

$$\eta=\frac{y-\delta}{x}\left(\frac{N_{Gr_x}}{4}\right)^{1/4} \qquad (20)$$

or

$$\eta=\frac{c(y-\delta)}{x^{1/4}}$$

where

$$N_{Gr_x}=\frac{gx^3(1-\rho_\infty/\rho_i)}{\nu^2} \qquad (21)$$

$$c=\left(\frac{g(1-\rho_\infty/\rho_i)}{4\nu^2}\right)^{1/4}.$$

Substitution of these variables into the boundary-layer equations gives

$$f'''+3ff''-2(f')^2+\beta=0 \qquad (22)$$

where

$$\beta=(1-\rho_\infty/\rho)/(1-\rho_\infty/\rho_i). \qquad (23)$$

Applying the ideal gas law and rearranging in terms of the present variables, β becomes

$$\beta=\left[\gamma\left(1-\sum_{j=1}^{n-1}A_j\phi_j\right)+\sum_{j=1}^{n-1}A_j\phi_j\right]\Bigg/\left[\gamma\left(1-\sum_{j=1}^{n-1}A_j\phi_j\right)+\sum_{j=1}^{n-1}A_j\phi_j\right]_i. \qquad (24)$$

The subscript, i, in the denominator indicates evaluations are made at the interfacial conditions and the A_j are defined

$$A_j=\frac{\dfrac{1}{M_3}-\dfrac{1}{M_j}}{\dfrac{1}{M_3}-\left(\dfrac{1}{M_3}-\dfrac{1}{M_1}\right)w_{1\infty}-\left(\dfrac{1}{M_3}-\dfrac{1}{M_2}\right)w_{2\infty}},$$

$$j=1,2 \qquad (25)$$

$$\bar{\phi}_1''+3N_{Sc_1}f\bar{\phi}_1'=0 \qquad (26)$$

$$\bar{\phi}_2''+3N_{Sc_2}f\bar{\phi}_2'=0 \qquad (27)$$

$$\gamma''+3N_{Pr}f\gamma'=0 \qquad (28)$$

where only the concentration dependence of the buoyancy term has been included. Overlines (¯) in equations (26) and (27) indicate linear combinations of variables ϕ_1 and ϕ_2 based upon the method of Toor [24] and Stewart and Prober [21] for multicomponent systems. The N_{Sc_1} are the Schmidt numbers of the linearized components.

Transformaion of the boundary conditions in equations (13–15) to the new variables give:

$$f'(0)=\tfrac{1}{2}(1-\rho_\infty/\rho_i)^{-1/2}\left[\frac{C_{p_L}(T_i-T_w)}{N_{Pr_L}\lambda}\right]^{1/2} \qquad (29)$$

Mass conservation of the interface,

$$f(0)=\tfrac{1}{3}\left[\frac{(\rho\mu)_L}{(\rho\mu)_a}\right]^{1/2}(1-\rho_\infty/\rho_i)^{-1/4}\left[\frac{C_{p_L}(T_i-T_w)}{N_{Pr_L}\lambda}\right]^{1/4}. \qquad (30)$$

Vanishing longitudinal velocity in the bulk,

$$f'\to 0 \quad \text{as} \quad \eta\to\infty. \qquad (31)$$

Interface impermeable to noncondensable gases,

$$\bar{\phi}_1'(0)/[\bar{\phi}_1(0)+w_{1\infty}]=-3f(0)N_{Sc_1} \qquad (32)$$

$$\bar{\phi}_2'(0)/[\bar{\phi}_2(0)+w_{2\infty}]=-3f(0)N_{Sc_2}. \qquad (33)$$

Equilibrium at the interface,

$$\gamma(0)=\gamma^*(\phi_1(0),\phi_2(0)). \qquad (34)$$

Prescribed bulk conditions,

$$\gamma\to 0 \quad \text{as} \quad \eta\to\infty \qquad (35)$$

$$\phi_1\to 0 \quad \text{as} \quad \eta\to\infty \qquad (36)$$

$$\phi_2\to 0 \quad \text{as} \quad \eta\to\infty. \qquad (37)$$

The overlines in boundary conditions (32) and (33) represent linear combinations as before in equations (26) and (27).

Numerical solution

The solution of equations (22)–(28) with boundary conditions (29)–(37) have been obtained numerically. The following general procedure was employed: one chooses the system to be studied and the bulk conditions of temperature, pressure and concentrations. Another parameter must also be fixed to completely define the problem.

A convenient method involves specifying the temperature drop across the liquid layer. Fixing this quantity is essentially the same as fixing the heat flux; determination of the wall temperature occurred after the solution of the equations was obtained. Once the values of the above parameters were decided upon, the solution involved estimating the interfacial conditions ($\phi_i(0)$'s) which allows computation of the physical properties of the liquid phase and the gas phase at appropriate reference states. $f''(0)$ and $\lambda'(0)$ were then estimated and the equations integrated by the Runge–Kutta method to determine if the infinity conditions were satisfied. Improved values of the interfacial conditions were obtained using the Zeh–Gill [26] technique until a desired degree of convergence was obtained at this reference state. Complete equations for the technique are in [15]. The reference states for the liquid and the gas phases were improved using a Newton–Raphson scheme and the above procedure repeated until the overall desired degree of convergence was obtained. This procedure determines the velocity, temperature and concentration profiles, wall temperature and heat transfer rate. These profiles were then used to determine supersaturation profiles in the boundary layer.

An alternative method of solution involves the choosing of the wall temperature, in place of the temperature drop across the liquid phase, to determine the problem. In this case, the temperature drop, which appears in equations (29) and (30), was treated as an unknown "physical property" and determined at the same time as the reference state physical properties since it was fixed when interfacial concentrations were guessed. Once this quantity was obtained, the procedure was the same as that in the above case of constant temperature drop except that the new temperature drop was computed when improved interfacial concentrations were obtained from the Newton–Raphson scheme. This technique offered many advantages since comparison of various parameters and results could be made at the same wall temperature; however, numerical instability, apparently inherent in this approach, makes it difficult to use on new systems for which good preliminary estimates are not known.

Limitations imposed on the model

An assumption which is implicit in both the boundary-layer formulation of the problem and in the use of a similarity transformation is that everywhere in the region of the condensate surface the net body forces must be directed downward. This requirement limits the model to binary systems in which the condensable component is lighter than the noncondensable [12]. In a multicomponent system the requirement can be met even if one or more of the noncondensables are lighter than the condensable component. The requirement is that an increase in density be realized as the interface is approached.

A further restriction upon the laminar flow assumption is that the Grashof number be sufficiently low so that the flow is in fact laminar. If this free convection boundary layer is considered to be analogous to that of a heated or cooled stationary vertical surface, then the dependence of flow characteristics on the Grashof number in the free convection system can be extended to the condensing system; that is, the system is in laminar flow for

$$N_{Gr_x} < 2 \times 10^9.$$

For the condensation process we might anticipate much larger values of the Grashof number before the flow regimes change. The condensation process acts upon the boundary layer in a manner similar to suction in flow over a porous wall, for which it has a stabilizing influence [14]. Thus, the criterion for laminar flow might be extended significantly for the condensation process.

A further limitation is imposed on the model since condensation is only accounted for at the interface. The investigation of supersaturation in the boundary layer is of interest in this research. It is well known that supersaturation may exist without the generation of an aerosol so long as the presence of condensation nuclei are avoided. Homogeneous nucleation will occur only at very high levels of supersaturation ratio, about 3·3 for water at 300°K [5].

Three types of comparisons of variable property solution with reference state solutions have been made. A comparison of overall transport results is purely superficial, but a necessary requirement. Shapes of the local profiles most accurately reflect the importance of variable properties. Changes in the physical properties and parameters across the boundary layer indicate the importance of variable properties. Each type of comparison has been carried out and discussed in [15]. These comparisons involved the variable property solutions of Mincowyz [9] for the air–water system.

The film reference state [24] was used throughout these comparisons. That is,.the physical properties are computed at the average boundary-layer composition and temperature. The condition may not actually exist in the boundary layer. Bulk and interfacial reference states gave very poor results. It was noted that despite the variations in physical property parameters across the boundary layer overall transport results are acceptable especially when $w_{g\infty} > 0{\cdot}1$ per cent, say. This is consistent with the observations of Rose [12] who compared his approximate solutions with the numerical solutions of Mincowycz.

Results for binary systems

Three binary systems were studied with the main emphasis on differences in molecular weight. The condensable was water and the noncondensables, nitrogen, Freon 12, and neon.

Overall heat-transfer reductions from the Nusselt model for binary systems have been discussed previously [1, 18]. We summarize our results briefly in what follows. Freon, on a weight percent basis, does not reduce the heat transfer as much as nitrogen does. On a mole or volume percent basis the opposite is true. Two effects are seen here. The weight percent of the noncondensable affects the velocity profile by changing the buoyancy forces. The mole or volume percent represents the number of molecules for the noncondensable. Since Freon has a higher molecular weight, 121, than nitrogen, 28, small amounts contribute more to the sweeping effect of the free convection boundary layer. The Schmidt number for the Freon–water system is about 1·5, whereas it is about 0·55 for the nitrogen–water system. The higher Schmidt number of the Freon–water system means that more molecules will accumulate at the interface because of the higher resistance to diffusion. Thus, even with the increased sweeping ability of the Freon, the increased number of molecules represented by the mole percent will force a greater buildup at the interface and, consequently, a greater reduction in heat transfer.

The neon–water system has a high Schmidt number, about 1·1, but the molecular weight of neon is only 20. The natural convection effects are less than exist with nitrogen, and the diffusional resistance is greater. A comparison of these systems shows that on both a weight and mole basis the heat transferred is reduced more significantly by neon than by nitrogen.

Multicomponent systems

Three multicomponent systems were studied—nitrogen–neon–water, nitrogen–Freon 12–water, and nitrogen–methane–water. The nitrogen–methane–water is the only system in which a noncondensable has a molecular weight less than that of the condensable. The reduction in heat transfer because of the presence of noncondensables is shown in Fig. 2. The nitrogen–water system with neon and Freon as third components fall distinctly between the binary cases. Nitrogen–methane and water actually show a greater reduction in heat transfer than shown by the same weight percent mixture of nitrogen–neon and water. The methane has a lower molecular weight than neon and the system exhibits decreased convective effects. Even though this low Schmidt number methane system offers less resistance due to molecular diffusion, the heat transfer is decreased.

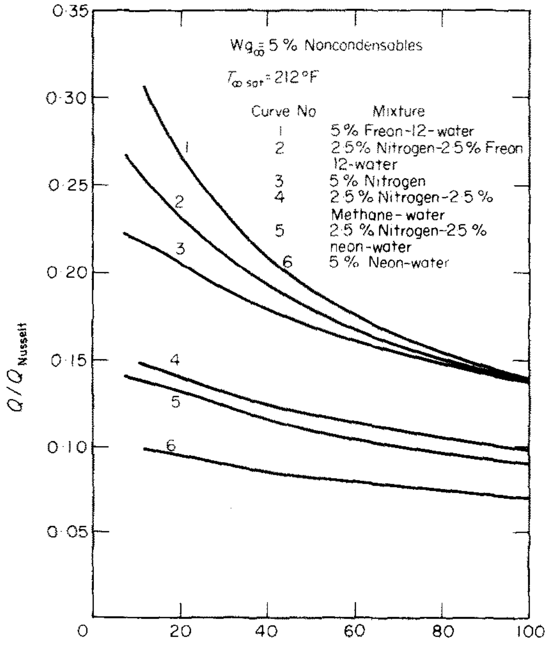

FIG. 2. Effect of various noncondensables on filmwise condensation of water vapor.

The nitrogen–methane–water system offers the opportunity for study of the conditions in which the boundary layer assumptions become invalid. No solution exists for the methane–water system. The buoyancy forces are opposed to the liquid flow. However, mixtures of methane with nitrogen give solutions of the boundary-layer equation. Figure 3 shows the velocity profiles in one such case. The total amount of noncondensable is held constant at 5 wt%, and the amount of methane in the mixture is increased. The free convection velocity profile disappears for concentrations of methane greater than about 4 per cent of the total 5 per cent noncondensables. The Grashof number goes to zero and changes sign in this frame of reference.

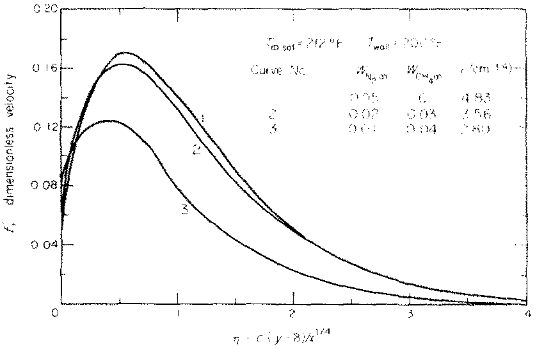

FIG. 3. Dimensionless velocity profile in the nitrogen–methane–water system at 5 per cent noncondensable.

Fractionation of noncondensables in multicomponent systems

In a ternary system in which the diffusive properties of one noncondensable are different from the other, the relative concentration of one component over the other will occur in the region of the interface, i.e. a fractionation of the noncondensables occurs as the interface is approached. The one-dimensional sweep diffusion process example of Cichelli *et al.* [3] is a solution of the film model using Maxwell–Stefan diffusion expressions. The notions of boundary layer skimming, as recently described by Lee and Lightfoot [6] and Shaw *et al.* [16], are conceivably applicable here. In the multicomponent concept used here, a difference in the linearized Schmidt numbers indicates the degree of separation. The nitrogen–Freon–water system has widely different

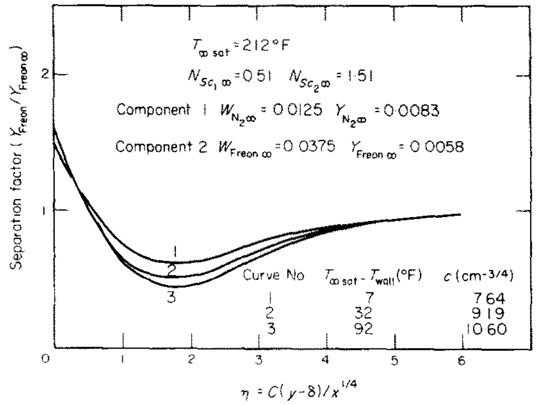

FIG. 4. Effect of temperature difference on the separation factor in nitrogen–Freon–water (high concentration of Freon).

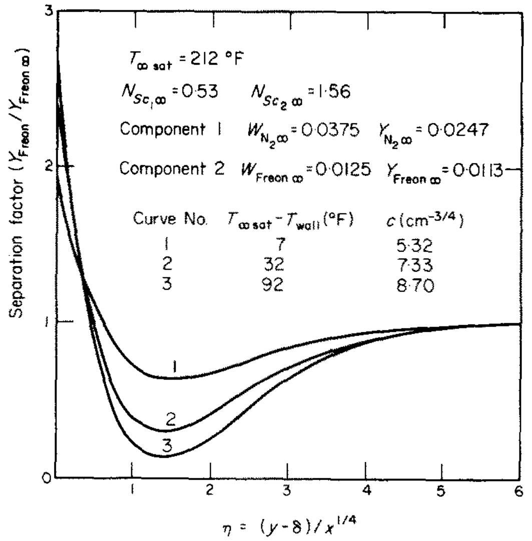

FIG. 5. Effect of temperature difference on the separation factor in nitrogen–Freon–water (high concentration of nitrogen).

linearized Schmidt numbers. The result is a buildup of Freon at the interface. When the concentration of Freon in the mixture is high, the increase in relative concentration shown by the separation factor in Fig. 4 is 1·5 and almost independent of the driving force. Figure 5 shows the effect when the Freon is diluted. Here the separation factor is as high as 2·75 for the same driving force and more strongly dependent on the condensation rate. Similarly a separation occurs in the ternary system of nitrogen–neon–water. Figures 6 and 7 summarize these results. The linearized Schmidt numbers in the nitrogen–methane–water system are about the same and no appreciable separation occurs. For other noncondensable systems in which a separation is desired, a condensable component which gives different linearized Schmidt numbers should be sought. The separation can be tested experimentally.

Figures 8 and 9 summarize qualitatively the effect of driving force and bulk concentration on the separation factor. These are not profiles as in the previous figures

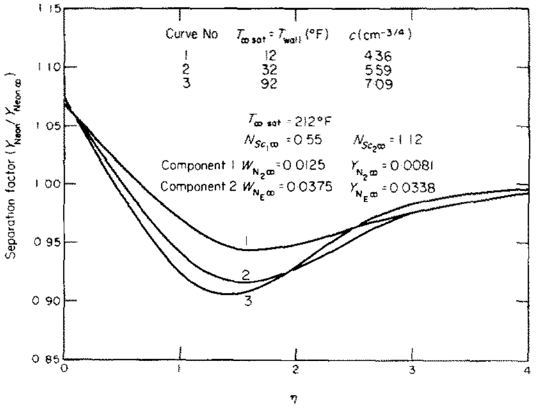

FIG. 6. Effect of temperature difference on the separation factor in neon–nitrogen–water system (high concentration of neon).

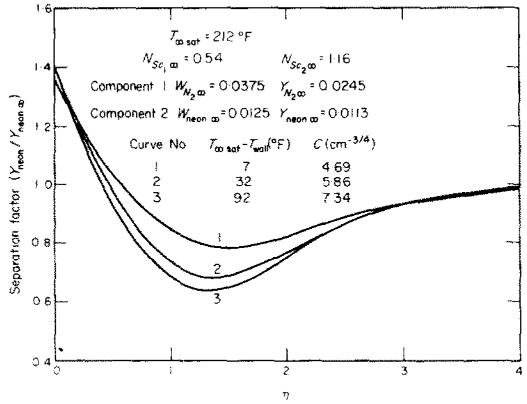

FIG. 7. Effect of temperature difference on the separation factor in neon–nitrogen–water system (high concentration of nitrogen).

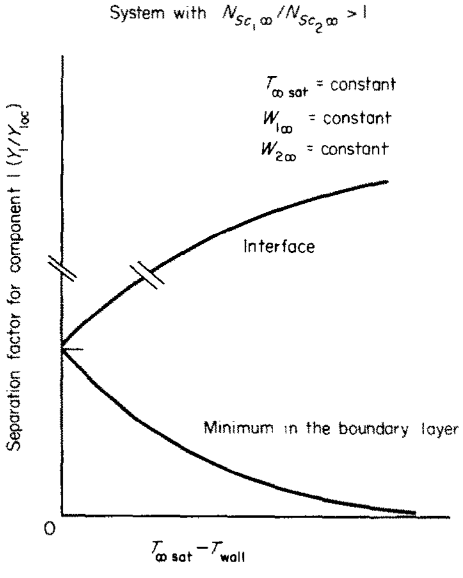

FIG. 8. Effect of temperature driving force on separation factor.

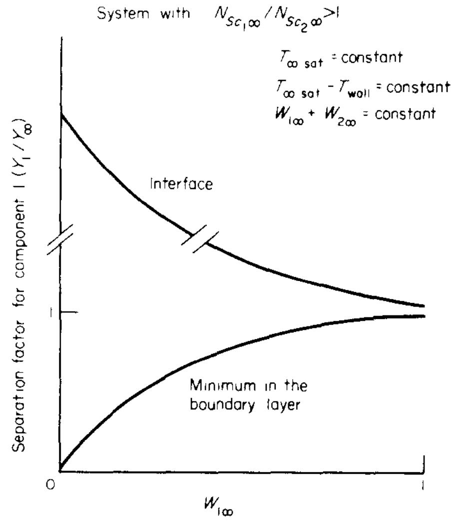

FIG. 9. Effect of weight fraction of noncondensable on separation factor.

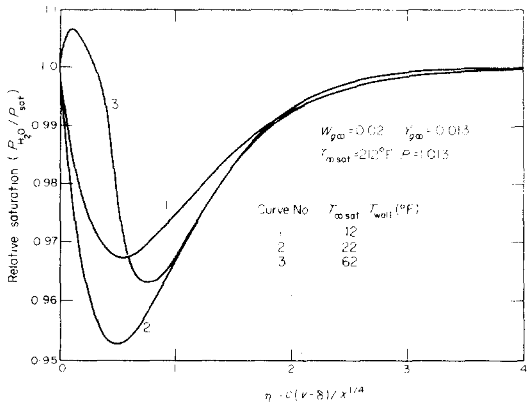

FIG. 10. Relative saturation in nitrogen–water system-effect of wall temperature.

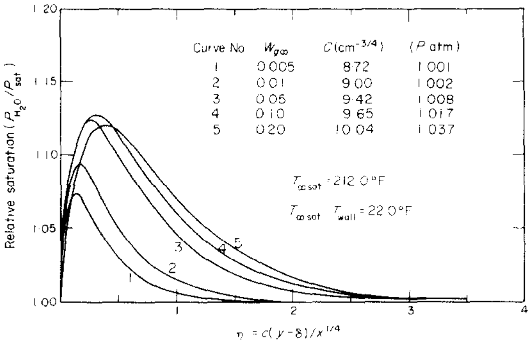

FIG. 11. Relative saturation in Freon–water system.

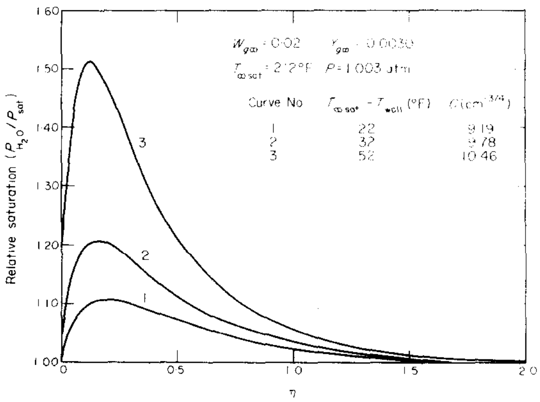

FIG. 12. Relative saturation in Freon–water system-effect of wall temperature.

but separation factors at the interface and the minimum separation factor in the boundary layer. The separation factor at the interface is the maximum in the boundary layer. For a given system in which the ratio of linearized Schmidt numbers is significantly greater than one, the component with the larger Schmidt number will concentrate at the interface and be depleted in some region in the boundary layer. The effect of the temperature driving force on the maximum and minimum separation factor (Fig. 8) is to continually increase the maximum and decrease the minimum asymptotically to zero. Figure 9 shows the effect of increasing the weight ratio of the high Schmidt number component while total weight fraction of noncondensable is held constant. Both the interface and minimum separation factors approach one as the weight ratio is increased. Thus, low concentrations of the high Schmidt number component can be highly concentrated at the interface.

Supersaturation in the vapor–gas boundary layer

Of interest in this study is the degree of supersaturation in the boundary layer and parameters which affect it. The three binary systems have been studied with this objective. The relative saturation was computed throughout the boundary layer. Supersaturation occurs in the boundary layer of the nitrogen–water system as shown in Fig. 10. The Lewis number in this system is approximately 0·55. The thermal boundary layer is smaller than the diffusion layer. Supersaturation occurs on increasing the temperature difference. Even at the large temperature difference only a small section of the boundary layer near the interface becomes supersaturated. The remainder of the boundary layer remains undersaturated. The model may not be accurate at this large temperature difference. Thus, the boundary layer may be fully undersaturated for all $N_{Le} < 1$. At higher concentrations of nitrogen, higher levels of supersaturation occur for the same temperature difference. At 10 wt% nitrogen and the same physical conditions as curve number 3 in Fig. 10, the maximum supersaturation is 1·111—an increase from 1·065 shown in the figure for 2 wt% nitrogen.

The Lewis number for the Freon–water system is about 1·5. In this case the thermal boundary layer is larger than the diffusion boundary layer. At the same wall temperature as the nitrogen–water system discussed above, the Freon–water system boundary layer is supersaturated throughout. Increasing the concentration of Freon at the same wall temperature increases the degree and extent of supersaturation as shown in Fig. 11. Decreasing the wall temperature sharply increases the level of supersaturation. As seen in Fig. 12 a supersaturation of 1·5 is reached when the wall tem-

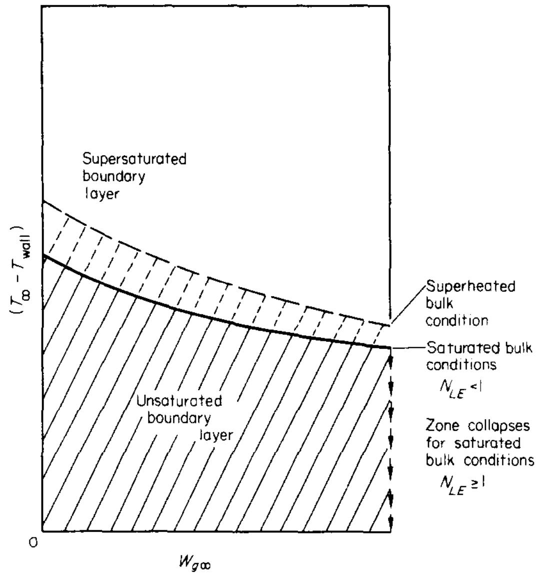

FIG. 13. Saturation condition in the vapor–gas boundary layer.

perature is 160°F. Much higher levels are obtained at higher concentrations of Freon. Critical supersaturation levels could be reached [13]. The accuracy of the model is in doubt at these large temperature differences, however, since the constant property assumption is open to serious question.

The neon–water system has a Lewis number close to one, about 1·1. As anticipated the boundary layer becomes supersaturated. In general, a vapor–gas system with a Lewis number less than one will have some temperature difference for which the boundary will become supersaturated for a particular concentration of the noncondensable. Figure 13 shows this result pictorially. For Lewis numbers greater than one and saturated bulk conditions the line is coincident with the abscissa. Superheat in the bulk will raise the curve. The formation of fog negates these profiles and new equations similar to Toor's [25] must be solved to determine the effect on the condensation heat transfer.

The effect of a third component on supersaturation is particularly important when the two noncondensable-vapor Lewis numbers can be shifted to be greater than unity and less than unity. This is the situation for nitrogen–Freon 12–water system. Figure 14 was constructed for conditions of constant driving force between the saturated bulk condition and the wall temperature. The boundary layer goes from complete undersaturation for the nitrogen–water system to complete supersaturation in the Freon–water system with consistent degrees of supersaturation for different intermediate mixtures. Similar curves can be generated for the neon–nitrogen–water, but lower levels of supersaturation are achieved. In the nitrogen–methane–water system the Lewis numbers are about 0·55 so that it takes relatively very large temperature driving forces to generate supersaturation.

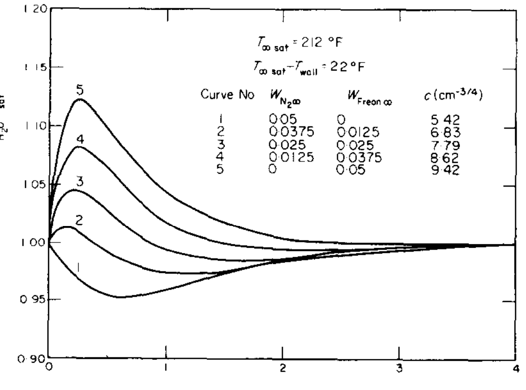

FIG. 14. Relative saturation in nitrogen–Freon–water system.

Experimental considerations

An experimental test of the validity of the model described previously is very much dependent on the order of magnitude of the thickness of the gas phase boundary layer and the length of the condensing surface for which the assumptions in the model are valid. The thermal boundary layer for the nitrogen–water system is of the order of 1 in, 6 in from the top of the condensing surface. For significant concentrations of the noncondensables, the liquid Reynolds number at 10 in from the top is less than 100.

The assumption of a laminar gas phase boundary layer must also be considered. The Grashof number indicates stability in the free convection boundary layer. Even at large temperature differences and 100°F of superheat, the boundary layer should be stable in a nitrogen–water system at 3, 6 and 10 in [15]. For the Freon–water system the result is marginal at only 12°F temperature difference and at 10 in. In the nitrogen–methane–water system the Grashof number is much lower than critical and decreases rapidly with increasing concentration of methane.

These considerations have been confirmed by the successful apparatus of Al-Diwany and Rose [1].

3. CONCLUSIONS FROM ANALYTICAL MODEL

1. The film reference state, constant property approach satisfactorily approximates the variable property solutions by Minkowycz [9] for the temperature, pressure and concentration ranges that he studied [15].

2. The free convection sweeping effect of a high molecular weight noncondensable substantially increases the heat-transfer rate even for high Schmidt number systems, for given weight fraction.

3. The Lewis number of the vapor–gas mixture determines the supersaturation in the boundary layer. For saturated bulk conditions mixtures with a Lewis number less than one in the boundary layer will be initially undersaturated as the wall temperature is decreased. A Lewis number greater than one will always give a supersaturated boundary layer from a saturated mixture.

4. In a ternary system in which the linearized Schmidt numbers of each noncondensable relative to the condensable differs, the component with the larger

Schmidt number will concentrate at the interface relative to its bulk concentration.

5. The system, nitrogen–methane–water, can be used to study the limitation on buoyancy forces of the boundary layer approach used here.

6. A physical system can be constructed which will meet the limitations imposed by the model yet be of sufficient size to permit testing of the model.

REFERENCES

1. H. K. Al-Diwany and J. W. Rose, Free convection film condensation of steam in the presence of non-condensing gases, *Int. J. Heat Mass Transfer* **16**, 1359 (1973).
2. R. B. Bird, W. E. Stewart and E. N. Lightfoot, *Transport Phenomena*, pp. 569–570. John Wiley, New York (1960).
3. M. T. Cichelli, W. D. Weatherford and J. R. Bowman, Sweep diffusion gas separation process, *Chem. Engng Prog.* **47**, 63 (1951).
4. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*. John Wiley, New York (1954).
5. J. L. Katz and B. J. Ostermier, Diffusion cloud-chamber investigation of homogeneous nucleation, *J. Chem. Phys.* **47**, 478 (1967).
6. H-L. Lee and E. N. Lightfoot, Boundary-layer skimming: calculational curiosity or promising process? *A.I.Ch.E. Jl* **20**, 335 (1974).
7. J. C. Maxwell, *Scientific Papers*, Vol. 2. Dover, New York (1952).
8. W. H. McAdams, *Heat Transmission*, 3rd edn. McGraw-Hill, New York (1954).
9. W. J. Minkowycz, Condensation heat transfer in the presence of non-condensables, interfacial resistance, superheating, variable properties and diffusion, Ph.D. Thesis, Dept. of Mech. Eng., University of Minnesota, Minneapolis, Minnesota (1965).
10. L. A. Onsager, Theories and problems of liquid diffusion, *Proc. N.Y. Acad. Sci.* **4C**, 241 (1945).
11. N. M. Ozisik and D. Hughes, Effects of condensation on the transport of matter from vapor and noncondensable gas mixtures, *Nucl. Sci. Engng* **35**, 384 (1969).
12. J. W. Rose, Condensation of a vapour in the presence of a noncondensing gas, *Int. J. Heat Mass Transfer* **12**, 233 (1969).
13. D. E. Rosner and J. Epstein, Fog formation conditions near cool surfaces, *J. Colloid Interface Sci.* **28**, 60 (1968).
14. H. Schlichting, *Boundary Layer Theory*, 4th edn. McGraw-Hill, New York (1960).
15. F. E. Sage, Filmwise condensation on an isothermal surface from a multicomponent mixture of vapors undergoing free convection, Ph.D. Thesis, Clarkson College of Technology (1974).
16. R. A. Shaw, R. Deluca and W. N. Gill, Reverse osmosis; increased productivity by reduction of concentration polarization in laminar flow reverse osmosis using intermediate non-rejecting membrane sections, *Desalination* **11**, 189 (1972).
17. E. M. Sparrow and E. R. G. Eckert, Effects of superheated vapor and noncondensable gases on laminar film condensation, *A.I.Ch.E. Jl* **7**, 473 (1961).
18. E. M. Sparrow and S. H. Lin, Condensation heat transfer in the presence of a noncondensable gas, *J. Heat Transfer* **86**, 430 (1964).
19. J. Stefan, *Sitzber. Akad. Wiss. Wien* **63**, (Abt. II), 63 (1871).
20. D. E. Steinmeyr, Fog formation in partial condensers, *Chem. Engng Prog.* **68**, 64 (July 1972).
21. W. E. Stewart and R. Prober, Matrix calculation of multicomponent mass transfer in isothermal systems, *I/EC Fundamentals* **3**, 224 (1964).
22. Y. Taitel and A. Tamir, Film condensation of multicomponent mixtures, *Int. J. Multiphase Flow* **1**, 697 (1974).
23. H. L. Toor, Diffusion in three-component gas mixtures, *A.I.Ch.E. Jl* **3**, 198 (1957).
24. H. L. Toor, Solution of the linearized equations of multicomponent mass transfer: matrix methods, *A.I.Ch.E. Jl* **10**, 461 (1964).

15\. H. L. Toor, Fog formation in boundary value problems, *A.I.Ch.E. Jl* **17**, 5 (1971).

26\. D. W. Zeh and W. N. Gill, Convective diffusion in rotating disk systems with an imperfect semipermeable interface, *A.I.Ch.E. Jl* **14**, 715 (1968).

CONDENSATION EN FILM D'UN MELANGE TERNAIRE DE VAPEURS SUR UNE SURFACE VERTICALE

Résumé—On présente une étude analytique de la condensation d'une vapeur en présence de gaz incondensables. Le mélange est supposé globalement au repos, et le seul écoulement est celui provenant du ruissellement du condensat le long de la paroi et des effets de convection naturelle qui l'accompagnent. On a utilisé, pour décrire le système un modèle entièrement prévisionnel, et à propriétés physiques constantes.

Dans un système ternaire, on montre que le fractionnement s'effectue entre les deux incondensables lorsqu'on approche l'interface. Le fractionnement dépend de la différence entre les nombres de Schmidt linéarisés.

On montre que la couche limite gaz–vapeur est sursaturée du fait de la condensation d'un mélange saturé ayant un nombre de Lewis supérieur à un. La sursaturation peut également être obtenue dans des systèmes ayant des nombres de Lewis inférieurs à l'unité, mais seulement pour des valeurs plus élevées de la différence entre la température moyenne et la température de paroi.

FILMKONDENSATION EINES TERNÄREN DAMPFGEMISCHES AN EINER SENKRECHTEN OBERFLÄCHE

Zusammenfassung—Es wird eine analytische Untersuchung der Dampfkonzentration in Gegenwart von nichtkondensierbaren Gasen dargelegt. Das Gemisch wird als ruhend betrachtet. Strömungen werden nur verursacht durch das an der Wand abfliessende Kondensat und begleitende freie Konvektionseffekte. Zur Beschreibung des Modells wird ein Grenzschichtkondensationsmodell mit konstanten Stoffwerten benützt.

Es wird gezeigt, dass in einem ternären System eine Fraktionierung auftritt zwischen den beiden nichtkondensierbaren Gasen bei Annäherung an die Zwischenschicht. Die Fraktionierung hängt ab von den Unterschieden zwischen den linearisierten Schmidt-Zahlen.

Die Gas–Dampf-Grenzschicht erweist sich als übersättigt bei der Kondensation aus einem gesättigten Gemisch und Lewis–Zahlen grösser als 1. Übersättigung kann auch in Systemen erhalten werden, mit kleineren Lewis–Zahlen bei grösseren treibenden Kräften, die als Differenz zwischen Gemisch- und Wandtemperatur gemessen werden.

ПЛЕНОЧНАЯ КОНДЕНСАЦИЯ ПАРОВ ИЗ ТРЕХКОМПОНЕНТНОЙ СМЕСИ НА ВЕРТИКАЛЬНОЙ ПОВЕРХНОСТИ

Аннотация — Проведено аналитическое исследование конденсации пара при наличии неконденсирующихся газов. Основная масса жидкости неподвижна. Течение происходит только за счет обтекания стенки конденсатом и сопровождающихся эффектов свободной конвекции. Система описывается расчетной моделью конденсации для пограничного слоя с постоянным физическими свойствами.

Показано, что в трехкомпонентной системе происходит фракционирование между двумя неконденсирующимися газами по мере приближения к поверхности раздела. Фракционирование зависит от разности между линеаризованными числами Шмидта.

Также показано, что в случае конденсации пограничный слой газ–пар перенасыщается насыщенной смесью при $Le > 1$. Перенасыщение также достигается в системах при $Le < 1$ только при больших движущихся силах, измеряемых температурной разностью между основной массой смеси и стенкой.