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Effects of a small amount of noncondensable gas on film condensation of multicomponent mixtures

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Abstract—The effects of a small amount of noncondensable gas on film condensation of multicomponent vapor mixtures are analytically studied. The governing equations of mass transfer and phase equilibrium of multicomponent species at the liquid–vapor interface are solved with perturbation due to the addition of a small amount of noncondensable gas to the main vapor mixture to obtain its behavior in the process of film condensation. Generally, the overall condensation rate is not always to be decreased with introducing the noncondensable gas into the multicomponent mixture. For small temperature difference across the condensate layer, the condensation rate decreases proportionally to the mole fraction of noncondensable gas accumulated at the interface. The results are applied for two binary systems of condensable and condensable species as well as condensable and noncondensable species with a numerical example.

INTRODUCTION

In the process of film condensation of multicomponent mixtures, the more volatile components are accumulated in the vapor phase at the liquid–vapor interface because of the difference of phase-equilibrium between the liquid and vapor phases. Thus, the removal mechanism of these species accumulated in the vapor phase is to control the overall process of film condensation. When a noncondensable gas is involved in the system, it should be noted that even a small amount of the gas could have a considerable effect on the condensation process. The boundary between condensable and noncondensable species is somewhat arbitrary because it depends on the range of temperature under consideration. The noncondensable gas can be considered to have a very low boiling temperature compared with other species, that is, as being a highly volatile component. In this respect, noncondensable gases may be expected to dominate considerably the condensation process.

In the unary system of one-component vapor, there are a number of engineering experiments reported of the effects of noncondensable gases on the condensation process. There have been a number of theoretical and experimental studies on the effects and considerable progress has been made towards understanding the relevant problem [1–12]. In these cases, the noncondensable gas always acts to deteriorate the condensation process. However, in cases of two or more component systems, it is not true since the noncondensable gas does not always promote accumulation of the volatile components at the interface.

In principle, condensation of condensable vapors with noncondensable gas is the matter of a multicomponent system consisting of chemical species having widely different boiling points. In the present paper, the effect of a small amount of noncondensable gas on film condensation is studied for the multicomponent system as well as for the binary system [13–18].

FILM CONDENSATION OF MULTICOMPONENT MIXTURES

A multicomponent system of condensable vapors of n species and a small amount of noncondensable gas (the $(n+1)$th species) is considered condensing onto a cooled wall and flowing down in a thin film in the gravity direction. By taking the coordinates as shown in Fig. 1 and assuming a thin film flow of condensate, the equations of continuity, motion and energy give the relationships of the condensation rate $\dot{m}$ to the film

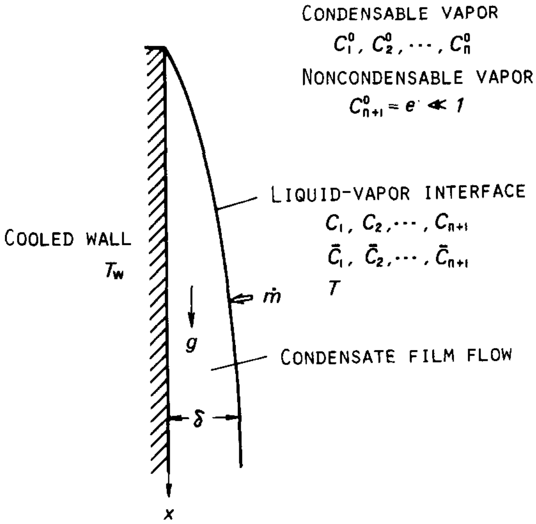

FIG. 1. Film condensation of multicomponent vapor mixture with a noncondensable gas.

NOMENCLATURE

C_i	mass fraction of species i
h_i	mass transfer coefficient of species i, equation (4)
k	thermal conductivity
M_i	molecular weight of species i
$\dot{m}$	condensation rate per unit interface area
n	the total number of species
n_i	mole concentration of species i
p	pressure
p_i	vapor pressure of species i
p_i^s	saturation vapor pressure of species i
R	gas constant
T	interfacial temperature
T_w	wall temperature
T_i	equation (25)
x_i	mole fraction of species i.

Greek symbols

α_x	fraction changed of quantity x at the interface, equation (9)
β	mole fraction of noncondensable gas at the interface, equation (11)
γ	activity coefficient, equation (6)
δ	condensate film thickness
ε	mass fraction of noncondensable gas, equation (8)
λ	latent heat of vaporzation
ν	kinematic viscosity
ρ_i	density of species i.

Subscripts

i	species
0	without noncondensable gas introduced, $\varepsilon = 0$
t	interfacial temperature
m	condensation rate
δ	condensate film thickness.

Superscripts

o	main stream
s	saturation vapor
$-$	condensate.

thickness δ and the temperature difference $(T-T_w)$ of the condensate [18]:

$$\dot{m} = \frac{\partial}{\partial x}\left(\frac{1}{3}\frac{\bar{\rho}g}{\bar{\nu}}\delta^3\right), \tag{1}$$

$$\lambda\dot{m} = \bar{k}\frac{T-T_w}{\delta}, \tag{2}$$

where $\dot{m}$ is the rate of the condensate mass per unit time and unit interfacial surface area, δ the condensate film thickness, g the gravitational acceleration, ρ the density, ν the kinematic viscosity, k the heat conductivity, λ the latent heat of vaporization, T the interfacial temperature, T_w the wall temperature, and the superior bar means the condensate.

The continuity of mass transfer of species i at the liquid–vapor interface can be written by

$$\dot{m}\bar{C}_i = \dot{m}C_i - q_i \quad (i = 1,2,\ldots,n,n+1), \tag{3}$$

where C_i and $\bar{C}_i$ are the mass fraction of species i in the vapor and liquid phases, respectively, at the interface, and q_i is the mass transfer rate of vapor of species i from the interface to the bulk due to molecular diffusion. The total mass transfer rate summed over the whole species should be zero; there is no net mass transfer rate due to molecular diffusion. Thus, the number of the independent equations (3) is to be n including the species introduced as the noncondensable gas, $i = 1,2,\ldots,n-1,n+1$. The mass transfer through the condensate is ignored because of its negligible effect. The mass transfer rate due to molecular diffusion q_i can be expressed in the form of

$$q_i = h_i(C_i - C_i^o) \quad (i = 1,2,\ldots,n,n+1), \tag{4}$$

where C_i^o is the mass fraction of species i in the main stream and h_i means an effective mass transfer coefficient of species i determined by the flow and molecular diffusion conditions. Thus, the mass transfer relation (3) with (4) leads to

$$\dot{m} = h_i\frac{C_i - C_i^o}{C_i - \bar{C}_i} \quad (i = 1,2,\ldots,n-1,n+1). \tag{5}$$

The relationships of phase equilibrium at the interface is given by

$$p_i = \bar{X}_i\gamma_i(\bar{X}_i, T)p_i^s(T) \quad (i = 1,2,\ldots,n,n+1), \tag{6}$$

where p_i is the partial pressure of species i in the vapor phase, $\bar{X}_i$ the mole fraction of species i in the liquid phase, γ_i the activity coefficient, and p_i^s the saturation vapor pressure of species i. The condensable gas can be considered to have a very high saturation pressure and its phase equilibrium can also be expressed by equation (6). The vapors are assumed to be an ideal gas:

$$p_i = n_iRT, \quad p = \sum_{i=1}^{n+1} p_i \quad (i = 1,2,\ldots,n,n+1), \tag{7}$$

where n_i is the mole concentration of species i and R the gas constant.

EFFECT OF NONCONDENSABLE GAS

A small amount of noncondensable gas in the mass concentration, ε, is introduced into the main stream of multicomponent vapors. The mass fraction of species in the main stream is then

$$\begin{aligned} C_i^o &= C_{i0}^o(1-\varepsilon) \quad (i = 1,2,\ldots,n), \\ C_{n+1}^o &= \varepsilon, \end{aligned} \tag{8}$$

where the subscript 0 means the state before introducing the noncondensable gas, $\varepsilon = 0$. Due to the introduction of noncondensable gas, changes in the mass concentration of species i, the temperature at the interface, the film thickness and the condensation rate are associated with and expressed in the form of:

$$\begin{aligned}
&\rho_i = \rho_{i0}(1+\alpha_i\varepsilon) \quad (i = 1,2,\ldots,n), \quad \rho_{n+1} = \rho_0\alpha_{n+1}\varepsilon,\\
&\bar{\rho}_i = \bar{\rho}_{i0}(1+\bar{\alpha}_i\varepsilon) \quad (i = 1,2,\ldots,n), \quad \bar{\rho}_{n+1} = 0,\\
&T = T_0(1+\alpha_t\varepsilon),\\
&\delta = \delta_0(1+\alpha_\delta\varepsilon),\\
&\dot{m} = \dot{m}_0(1+\alpha_m\varepsilon).
\end{aligned} \tag{9}$$

It should be noted that the above expansion of the flow variables around $\varepsilon = 0$ is only possible for the multicomponent vapors of $n \geqslant 2$, because equation (3) cannot hold for condensation of pure vapor. In the expression of mass fraction, $C_i = \rho_i/\sum_{j=1}^{n+1}\rho_j$, and mole fraction, $X_i = \rho_i/M_i/\sum_{j=1}^{n+1}(\rho_j/M_j)$, they are written as follows:

$$C_i = C_{i0}\left\{1+\left(\alpha_i-\sum_{j=1}^{n} C_{j0}\alpha_j-\alpha_{n+1}\right)\varepsilon\right\} \quad (i = 1,2,\ldots,n),$$

$$C_{n+1} = \alpha_{n+1}\varepsilon, \tag{10a}$$

$$\bar{C}_i = \bar{C}_{i0}\left\{1+\left(\bar{\alpha}_i-\sum_{j=1}^{n} \bar{C}_{j0}\bar{\alpha}_j\right)\varepsilon\right\} \quad (i = 1,2,\ldots,n),$$

$$X_i = X_{i0}\left\{1+\left(\alpha_i-\sum_{j=1}^{n} X_{j0}\alpha_j-\beta\right)\varepsilon\right\} \quad (i = 1,2,\ldots,n),$$

$$X_{n+1} = \beta\varepsilon, \tag{10b}$$

$$\bar{X}_i = \bar{X}_{i0}\left\{1+\left(\bar{\alpha}_i-\sum_{j=1}^{n} \bar{X}_{j0}\bar{\alpha}_j\right)\varepsilon\right\} \quad (i = 1,2,\ldots,n),$$

where in the liquid phase no fraction of the species of noncondensable gas introduced is assumed and $\beta\varepsilon$ is the mole fraction of the noncondensable gas at the interface.

$$\beta = \frac{\alpha_{n+1}}{M_{n+1}\sum_{j=1}^{n}\frac{C_{j0}}{M_j}}, \tag{11}$$

where M_i is the molecular weight of species i.

The relationships of phase equilibrium, equation (6) is perturbated as

$$\frac{\mathrm{d}X_i}{X_i} = \frac{\mathrm{d}\bar{X}_i}{\bar{X}_i}+\frac{1}{\gamma_i}\left\{\sum_{j=1}^{n}\frac{\partial\gamma_i}{\partial\bar{X}_j}\,\mathrm{d}\bar{X}_j+\frac{\partial\gamma_i}{\partial T}\,\mathrm{d}T\right\} + \frac{1}{p_i^{\mathrm{s}}}\frac{\partial p_i^{\mathrm{s}}}{\partial T}\,\mathrm{d}T \quad (i = 1,2,\ldots,n,n+1). \tag{12}$$

Equations (9) and (10) give the following perturbation of the mole fraction of species and the temperature:

$$\begin{aligned}
&\frac{\mathrm{d}X_i}{X_i} = \left(\alpha_i-\sum_{j=1}^{n} X_j\alpha_j-\beta\right)\varepsilon \quad (i = 1,2,\ldots,n),\\
&\frac{\mathrm{d}\bar{X}_i}{\bar{X}_i} = \left(\bar{\alpha}_i-\sum_{j=1}^{n} \bar{X}_j\bar{\alpha}_j\right)\varepsilon \quad (i = 1,2,\ldots,n,),\\
&\frac{\mathrm{d}T}{T} = \alpha_t\varepsilon,
\end{aligned} \tag{13}$$

where for brevity the subscript 0 is omitted in the right-hand side. By using these relationships, equation (12) of phase equilibrium is reduced to

$$\alpha_i-\sum_{j=1}^{n} X_j\alpha_j-\beta = \bar{\alpha}_i-\sum_{j=1}^{n}\bar{X}_j\bar{\alpha}_j+\sum_{j=1}^{n}\frac{\partial\ln\gamma_i}{\partial\ln\bar{X}_j} \times\left(\bar{\alpha}_j-\sum_{k=1}^{n}\bar{X}_k\bar{\alpha}_k\right)+\frac{\partial\ln\gamma_i p_i^{\mathrm{s}}}{\partial\ln T}\alpha_t \quad (i = 1,2,\ldots,n). \tag{14}$$

The mass transfer coefficient, h_i, is generally a function of species concentrations of vapor and other flow properties. The flow conditions are hardly changed with introducing a small amount of noncondensable gas and the effect of change in species concentrations on the coefficient may also be considered to be small, except for the special case of azeotrope mixtures being very close to the azeotropic point where $h_i \to 0$. By assuming $\mathrm{d}h_i = 0$, the mass continuity at the interface, equation (5), is reduced to

$$\frac{\mathrm{d}\dot{m}}{\dot{m}} = \left(\frac{1}{C_i-C_i^{\mathrm{o}}}-\frac{1}{C_i-\bar{C}_i}\right)\mathrm{d}C_i+\frac{\mathrm{d}\bar{C}_i}{C_i-\bar{C}_i}-\frac{\mathrm{d}C_i^{\mathrm{o}}}{C_i-C_i^{\mathrm{o}}} \quad (i = 1,2,\ldots,n-1), \tag{15}$$

which gives

$$\alpha_{\mathrm{m}} = \left(\frac{C_i}{C_i-C_i^{\mathrm{o}}}-\frac{C_i}{C_i-\bar{C}_i}\right)\left(\alpha_i-\sum_{j=1}^{n} C_j\alpha_j-\alpha_{n+1}\right) + \frac{\bar{C}_i}{C_i-\bar{C}_i}\left(\bar{\alpha}_i-\sum_{j=1}^{n}\bar{C}_j\bar{\alpha}_j\right)+\frac{C_i^{\mathrm{o}}}{C_i-C_i^{\mathrm{o}}} \quad (i = 1,2,\ldots,n-1). \tag{16}$$

Equation (5) for noncondensable gas ($i = n+1$) gives

$$\alpha_{n+1} = \frac{1}{1-\dfrac{\dot{m}}{h_{n+1}}}. \tag{17}$$

The relationship of the condensation rate to the film thickness and the temperature gradient of the condensate, equations (1) and (2), give

$$\alpha_{\mathrm{m}} = \frac{3}{4}\frac{T}{T-T_{\mathrm{w}}}\alpha_t, \quad \alpha_\delta = \frac{1}{4}\frac{T}{T-T_{\mathrm{w}}}\alpha_t. \tag{18}$$

It implies that changes in the film thickness and the condensation rate should be proportional to that in the interfacial temperature. When the noncondensable gas acts as to decrease the interfacial temperature, the net rate of condensation tends to be decreased. The equation of state of ideal gas for the vapors (7) gives

$$\sum_{i=1}^{n+1} \mathrm{d}n_i + \frac{\mathrm{d}T}{T} \sum_{i=1}^{n+1} n_i = 0, \tag{19}$$

which is rewritten by equation (13) as

$$\sum_{i=1}^{n} X_i \alpha_i + \beta + \alpha_\mathrm{t} = 0. \tag{20}$$

The density of the condensate can be assumed as a function of the temperature only. This gives

$$\frac{\partial \ln \bar{\rho}}{\partial \ln T} \alpha_\mathrm{t} = \sum_{i=1}^{n} \bar{C}_i \bar{\alpha}_i. \tag{21}$$

In summary, equations (14), (16), (20) and (21) can be solved for $(2n+1)$ unknowns of

$$\alpha_1, \alpha_2, \ldots, \alpha_n, \quad \bar{\alpha}_1, \bar{\alpha}_2, \ldots, \bar{\alpha}_n, \alpha_\mathrm{t}.$$

Equation (14) is rewritten by equation (20) as

$$\alpha_i = \bar{\alpha}_i - \sum_{j=1}^{n} \bar{\alpha}_j \bar{X}_j \left(1 - \sum_{k=1}^{n} \bar{X}_k \frac{\partial \ln \gamma_i}{\partial \bar{X}_{j-k}}\right) + \left(\frac{\partial \ln \gamma_i \mathrm{p}_i^\mathrm{s}}{\partial \ln T} - 1\right)\alpha_\mathrm{t} \quad (i = 1, , \ldots, n), \tag{22}$$

where

$$\frac{\partial}{\partial \bar{X}_{j-k}} \equiv \frac{\partial}{\partial \bar{X}_j} - \frac{\partial}{\partial \bar{X}_k}.$$

Substituting equation (22) into equation (20) gives

$$\alpha_\mathrm{t} = \frac{\sum_{i=1}^{n} \bar{\alpha}_i \left\{(X_i - \bar{X}_i) + \bar{X}_i \sum_{j,k=1} X_j \bar{X}_k \frac{\partial \ln \gamma_i}{\partial \bar{X}_{i-k}}\right\} + \beta}{-\sum_{j=1}^{n} X_j \frac{\partial \ln \gamma_j p_j^\mathrm{s}}{\partial \ln T}}. \tag{23}$$

Equation (16) with equations (18) and (22) gives

$$\begin{aligned}\frac{3}{4}\frac{T}{T-T_\mathrm{w}}\alpha_\mathrm{t} = {} & \left(\frac{C_i}{C_i - C_i^\mathrm{o}} - \frac{C_i}{C_i - \bar{C}_i}\right)\left\{\bar{\alpha}_i - \sum_{j=1}^{n} C_j \bar{\alpha}_j \right. \\ & + \sum_{j,k,l=1}^{n} \bar{\alpha}_j \bar{X}_j \bar{X}_k C_l \frac{\partial}{\partial \bar{X}_{j-k}} \ln\left(\frac{\gamma_i}{\gamma_l}\right) \\ & \left. + \sum_{j=1}^{n} C_j \frac{\partial}{\partial \ln T}\left(\frac{\gamma_i p_i^\mathrm{s}}{\gamma_j p_j^\mathrm{s}}\right)\alpha_\mathrm{t} - \alpha_{n+1}\right\} \\ & + \frac{\bar{C}_i}{C_i - \bar{C}_i}\left(\bar{\alpha}_i - \frac{\partial \ln \bar{\rho}}{\partial \ln T}\alpha_\mathrm{t}\right) + \frac{C_i^\mathrm{o}}{C_i - C_i^\mathrm{o}} \\ & (i = 1, 2, \ldots, n-1).\end{aligned} \tag{24}$$

Further, equation (24) with (23) is expressed in the form

$$\sum_{j=1}^{n} a_{ij} \bar{\alpha}_j = b_i \quad (i = 1, 2, \ldots, n-1), \tag{25}$$

where

$$\begin{aligned} a_{ij} = {} & \frac{C_i^\mathrm{o}}{C_i - C_i^\mathrm{o}}\delta_{ij} + \left(\frac{C_i}{C_i - C_i^\mathrm{o}} - \frac{C_i}{C_i - \bar{C}_i}\right) \\ & \times \left\{-C_j + \bar{X}_j \sum_{k,l=1}^{n} \bar{X}_k C_l \frac{\partial}{\partial \bar{X}_{j-k}} \ln\left(\frac{\gamma_i}{\gamma_l}\right)\right\} \\ & + T_i \left\{(X_j - \bar{X}_j) + \bar{X}_j \sum_{k,l=1}^{n} X_k \bar{X}_l \frac{\partial \ln \gamma_k}{\partial \bar{X}_{j-l}}\right\}, \end{aligned}$$

$$b_i = \left(\frac{C_i}{C_i - C_i^\mathrm{o}} - \frac{C_i}{C_i - \bar{C}_i}\right)\alpha_{n+1} - \frac{C_i^\mathrm{o}}{C_i - C_i^\mathrm{o}} - T_i \beta,$$

$$\begin{aligned} T_i = {} & \left(\sum_{j=1}^{n} X_j \frac{\partial \ln \gamma_j p_j^\mathrm{s}}{\partial T}\right)^{-1}\left\{\frac{3}{4}\frac{1}{T-T_\mathrm{w}}\right. \\ & - \left(\frac{C_i}{C_i - C_i^\mathrm{o}} - \frac{C_i}{C_i - \bar{C}_i}\right)\sum_{j=1}^{n} C_j \frac{\partial}{\partial T} \ln\left(\frac{\gamma_i p_i^\mathrm{s}}{\gamma_j p_j^\mathrm{s}}\right) \\ & \left. + \frac{\bar{C}_i}{C_i - \bar{C}_i}\frac{\partial \ln \bar{\rho}}{\partial T}\right\}. \end{aligned}$$

One remaining equation for $\bar{\alpha}_i$ is given by equation (21) with (23) as,

$$\sum_{j=1}^{n} (\bar{C}_j + d_j)\bar{\alpha}_j = d_0, \tag{26a}$$

where

$$d_0 = -\beta \frac{\partial \ln \bar{\rho}}{\partial \ln T}\left(\sum_{k=1}^{n} X_k \frac{\partial \ln \gamma_k p_k^\mathrm{s}}{\partial \ln T}\right)^{-1}$$

$$d_j = -\frac{d_0}{\beta}\left\{(X_j - \bar{X}_j) + \bar{X}_j \sum_{k,l=1}^{n} X_k \bar{X}_l \frac{\partial \ln \gamma_k}{\partial \bar{X}_{j-l}}\right\}.$$

For usual cases of condensate liquids, the temperature dependence of the density is much less than that of the saturation pressure. Thus, equation (26a) is further rewritten as

$$\sum_{j=1}^{n} \bar{\alpha}_j \bar{C}_j = 0. \tag{26b}$$

By equations (25) and (26), the amounts of the mass fraction of liquid species increased at the liquid–vapor interface $\bar{\alpha}_i$ can be obtained, and those of vapor species by equation (22). The changes in the interfacial temperature and the condensation rate, α_t and α_m, are given by equations (23) and (18), respectively.

For cases when the temperature difference across the condensate layer is so small that

$$\frac{T}{T-T_\mathrm{w}} \gg \frac{\partial \ln p^\mathrm{s}}{\partial \ln T},$$

the quantity T_i can be approximated by

$$T_i \simeq \left(\sum_{j=1}^{n} X_j \frac{\partial \ln \gamma_j p_j^\mathrm{s}}{\partial \ln T}\right)^{-1} \frac{3}{4}\frac{T}{T-T_\mathrm{w}} \equiv T_\mathrm{m} \gg 1,$$

and b_i is approximately equal to $-T_\mathrm{m}\beta$. Equations (25) and (26) then show that $\bar{\alpha}_i \propto -T_\mathrm{m}\beta$; hence $\alpha_\mathrm{t}, \alpha_\mathrm{m} \propto -\beta$. It implies that for small temperature difference across the condensate layer the decrease in the condensation rate should be proportional to the mole fraction of the noncondensable gas accumulated at the interface. For larger values of the temperature difference, the change in the condensation rate should not always be linearly dependent on the mole fraction of the noncondensable gas, β.

Ideal solutions

When the condensate is an ideal solution, $\gamma_i = 1$, the equations to be solved are simplified as follows. Equations (25) and (26b) are

$$\sum_{j=1}^{n} \bar{\alpha}_j \left\{ \left(\frac{C_i^{\circ}}{C_i - C_i^{\circ}} \delta_{ij} - \left(\frac{C_i}{C_i - C_i^{\circ}} - \frac{C_i}{C_i - \bar{C}_i} \right) C_j \right. \right. \\ \left. + T_i (X_j - \bar{X}_j) \right\} = \left(\frac{C_i}{C_i - C_i^{\circ}} - \frac{C_i}{C_i - \bar{C}_i} \right) \alpha_{n+1} \\ - \frac{C_i^{\circ}}{C_i - C_i^{\circ}} - T_i \beta \quad (i = 1, 2, \ldots, n-1), \tag{27}$$

$$\sum_{j=1}^{n} \bar{\alpha}_j \bar{C}_j = 0, \tag{28}$$

where

$$T_i = \left(\sum_{j=1}^{n} X_j \frac{\partial \ln \gamma_j p_j^{\mathrm{s}}}{\partial \ln T} \right)^{-1} \left\{ \frac{3}{4} \frac{T}{T - T_{\mathrm{w}}} \right. \\ \left. - \left(\frac{C_i}{C_i - C_i^{\circ}} - \frac{C_i}{C_i - \bar{C}_i} \right) \sum_{j=1}^{n} C_j \frac{\partial}{\partial \ln T} \left(\frac{p_i^{\mathrm{s}}}{p_j^{\mathrm{s}}} \right) \right\}.$$

α_i and α_{t} are then given by

$$\alpha_i = \bar{\alpha}_i - \sum_{j=1}^{n} \bar{X}_j \bar{\alpha}_j + \left(\frac{\partial \ln p_i^{\mathrm{s}}}{\partial \ln T} - 1 \right) \alpha_{\mathrm{t}} \quad (i = 1, 2, \ldots, n) \tag{29}$$

$$\alpha_{\mathrm{t}} = - \left(\sum_{i=1}^{n} X_i \frac{\partial \ln p_i^{\mathrm{s}}}{\partial \ln T} \right)^{-1} \left\{ \sum_{i=1}^{n} (X_i - \bar{X}_i) \bar{\alpha}_i + \beta \right\}. \tag{30}$$

Since usually $\partial p_i^{\mathrm{s}} / \partial T > 0$, α_{t} decreases or increases depending on the sign of the term in the brackets { } of equation (30). If the term takes a negative value, adding the condensable gas tends to promote the condensation process.

Equations (27) and (28) are easily solved as

$$\bar{\alpha}_i = \frac{1}{a_i} (b_i + a_i' A - T_i B) \quad (i = 1, 2, \ldots, n-1), \\ \bar{\alpha}_n = - \frac{1}{\bar{C}_n} \sum_{i=1}^{n-1} \frac{\bar{C}_i}{a_i} (b_i + a_i' A - T_i B), \tag{31}$$

$$a_i = \frac{C_i^{\circ}}{C_i - C_i^{\circ}}, \quad a_i' = \frac{C_i}{C_i - C_i^{\circ}} - \frac{C_i}{C_i - \bar{C}_i},$$

$$A = \frac{1}{C} \left\{ \sum_{i=1}^{n-1} C_i' \frac{b_i}{a_i} \left(1 + \sum_{j=1}^{n-1} X_j' \frac{T_j}{a_j} \right) \right. \\ \left. - \sum_{i=1}^{n-1} X_i' \frac{b_i}{a_i} \sum_{j=1}^{n-1} C_j' \frac{T_j}{a_j} \right\},$$

$$B = \frac{1}{C} \left\{ \sum_{i=1}^{n-1} X_i' \frac{b_i}{a_i} \left(1 - \sum_{j=1}^{n-1} C_j' \frac{a_j'}{a_j} \right) \right. \\ \left. + \sum_{i=1}^{n-1} C_i' \frac{b_i}{a_i} \sum_{j=1}^{n-1} X_j' \frac{a_j'}{a_j} \right\},$$

$$C = \left(1 - \sum_{i=1}^{n-1} C_i' \frac{a_i'}{a_i} \right) \left(1 + \sum_{j=1}^{n-1} X_j' \frac{T_j}{a_j} \right) \\ + \sum_{i=1}^{n-1} C_i' \frac{T_i}{a_i} \sum_{j=1}^{n-1} X_j' \frac{a_j'}{a_j},$$

$$C_i' = C_i - \frac{C_n}{\bar{C}_n} \bar{C}_i, \quad X_i' = (X_i - \bar{X}_i) - (X_n - \bar{X}_n) \frac{\bar{C}_i}{\bar{C}_n}.$$

For a small temperature difference across the condensate layer, $b_i \simeq - T_{\mathrm{m}} \beta$, the solution is

$$\bar{\alpha}_i = \frac{- T_{\mathrm{m}} \beta}{1 + T_{\mathrm{m}} K} \frac{1}{a_i} \simeq - \frac{\beta}{K a_i}, \\ \bar{\alpha}_n = \frac{T_{\mathrm{m}} \beta}{1 + T_{\mathrm{m}} K} \sum_{i=1}^{n-1} \frac{\bar{C}_i}{\bar{C}_n} \frac{1}{a_i} \simeq \frac{\beta}{K} \sum_{i=1}^{n-1} \frac{\bar{C}_i}{\bar{C}_n} \frac{1}{a_i}, \tag{31'}$$

where

$$K = \sum_{i=1}^{n-1} \left\{ (X_i - \bar{X}_i) - (X_n - \bar{X}_n) \frac{\bar{C}_i}{\bar{C}_n} \right\} \frac{1}{a_i}.$$

Changes in the interfacial temperature and the condensation rate are then

$$\alpha_{\mathrm{t}} \simeq - \left(\sum_{i=1}^{n} X_i \frac{\partial \ln p_i^{\mathrm{s}}}{\partial \ln T} \right)^{-1} \frac{\beta}{T_{\mathrm{m}} K} = \\ - \left(\frac{3}{4} \frac{T}{T - T_{\mathrm{w}}} \right)^{-1} \frac{\beta}{K}, \\ \alpha_{\mathrm{m}} \simeq - \frac{\beta}{K}. \tag{32}$$

The change in the condensation rate is proportional to the mole fraction of noncondensable gas at the interface divided by the factor K. The condensation rate should not always be decreased by introducing the noncondensable gas, being decreased or increased by depending on the sign of the value K.

CONDENSATION OF BINARY MIXTURES

The results obtained in the preceding section cannot be applied for the purely unary system as mentioned before. However, there is no restriction in their application for the binary system of a condensable and a noncondensable vapor as well as for two-component condensable vapors (condensable and condensable vapors).

Condensable and noncondensable vapor mixtures

The condensate always consists of only one component species, say $\bar{C}_1 = 1$ and $\bar{C}_2 = 0$ where the subscripts 1 and 2 denote the condensable and noncondensable species, respectively. Hence, there is no change in the condensate concentration, $\bar{\alpha}_1 = \bar{\alpha}_2 = 0$. From equations (23), the change in the interfacial temperature is

$$\alpha_{\mathrm{t}} = - \left(X_1 \frac{\partial \ln p_1^{\mathrm{s}}}{\partial \ln T} + X_2 \frac{\partial \ln p_2^{\mathrm{s}}}{\partial \ln T} \right)^{-1} \beta \simeq - \frac{RT}{\lambda} \beta, \tag{33}$$

where the Clausius–Clapeyron relation is assumed for the saturation vapor pressure of both species and $\lambda = \lambda_1 X_1 + \lambda_2 X_2 \simeq \lambda_1 X_1$.

The change in the condensation rate is given as

$$\alpha_m = -\frac{3}{4}\frac{T}{T-T_w}\frac{RT}{\lambda}\beta. \tag{34}$$

It is noted that the decrease in the condensation rate is proportional to $\beta(\propto M_3^{-1})$ and RT/λ. As the molecular weight of noncondensable vapor and/or the latent heat of the condensable vapor take smaller values, the effects of the noncondensable vapor addition are to be magnified.

Condensable and condensable vapor mixtures

For the two component system of condensable vapor, equations (25) and (26) are

$$\begin{gathered} a_{11}\bar{\alpha}_1 + a_{12}\bar{\alpha}_2 = b_1, \\ (\bar{C}_1 + d_1)\bar{\alpha}_1 + (\bar{C}_2 + d_2)\bar{\alpha}_2 = d_0, \end{gathered} \tag{35}$$

which give

$$\begin{gathered} \bar{\alpha}_1 = \frac{1}{a}\{(\bar{C}_2 + d_2)b_1 - a_{12}d_0\} \simeq \frac{b_1}{a}\bar{C}_2, \\ \bar{\alpha}_2 = \frac{1}{a}\{a_{11}d_0 - (\bar{C}_1 + d_1)b_1\} \simeq -\frac{b_1}{a}\bar{C}_1, \end{gathered} \tag{36}$$

where

$$a = a_{11}(\bar{C}_2 + d_2) - a_{12}(\bar{C}_1 + d_1), \quad b_1 = 1 - T_1\beta,$$

$$\begin{aligned} a_{11} = {} & \frac{C_1^o}{C_1 - C_1^o} + \left(\frac{C_1}{C_1 - C_1^o} - \frac{C_1}{C_1 - \bar{C}_1}\right) \\ & \times \left\{-C_1 + C_2 \frac{\partial}{\partial \ln \bar{X}_1} \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right\} \\ & + T_1\left(X_1 - \bar{X}_1 + X_1 \frac{\partial \ln \gamma_1}{\partial \ln \bar{X}_1} \right. \\ & \left. + X_2 \frac{\partial \ln \gamma_2}{\partial \ln \bar{X}_1}\right), \end{aligned}$$

$$\begin{aligned} a_{12} = {} & \left(\frac{C_1}{C_1 - C_1^o} - \frac{C_1}{C_1 - \bar{C}_1}\right)\left\{-C_2 + C_2 \frac{\partial}{\partial \ln \bar{X}_2} \right. \\ & \left. \times \ln\left(\frac{\gamma_1}{\gamma_2}\right)\right\} + T_1\left(X_2 - \bar{X}_2 + X_1 \frac{\partial \ln \gamma_1}{\partial \ln \bar{X}_2} \right. \\ & \left. + X_2 \frac{\partial \ln \gamma_2}{\partial \ln \bar{X}_2}\right), \end{aligned}$$

$$\begin{aligned} T_1 = {} & \left(X_1 \frac{\partial \ln p_1^s}{\partial \ln T} + X_2 \frac{\partial \ln p_2^s}{\partial \ln T}\right)^{-1}\left\{\frac{3}{4}\frac{T}{T - T_w} \right. \\ & - \left(\frac{1}{C_1 - C_1^o} - \frac{1}{C_1 - \bar{C}_1}\right)C_1 C_2 \frac{\partial}{\partial \ln T} \ln\left(\frac{p_1^s}{p_2^s}\right) \\ & \left. + \frac{\bar{C}_1}{C_1 - \bar{C}_1}\frac{\partial \ln \bar{\rho}}{\partial \ln T}\right\}, \end{aligned}$$

$$d_0 \simeq 0, \quad d_1 \simeq 0, \quad d_2 \simeq 0.$$

α_t, α_1 and α_2 are then

$$\begin{aligned} \alpha_t = {} & -\left(X_1 \frac{\partial \ln p_1^s}{\partial \ln T} + X_2 \frac{\partial \ln p_2^s}{\partial \ln T}\right)^{-1}\left\{(\bar{\alpha}_1 - \bar{\alpha}_2) \right. \\ & \times (X_1 - \bar{X}_1) + \bar{\alpha}_1\left(X_1 \frac{\partial \ln \gamma_1}{\partial \ln \bar{X}_1} + X_2 \frac{\partial \ln \gamma_2}{\partial \ln \bar{X}_1}\right) \\ & \left. + \bar{\alpha}_2\left(X_1 \frac{\partial \ln \gamma_1}{\partial \ln \bar{X}_2} + X_2 \frac{\partial \ln \gamma_2}{\partial \ln \bar{X}_2}\right) + \beta\right\}, \end{aligned} \tag{37}$$

$$\begin{aligned} \alpha_1 = {} & \bar{\alpha}_1 - (\bar{\alpha}_1\bar{X}_1 + \bar{\alpha}_2\bar{X}_2) + \bar{\alpha}_1 \frac{\partial \ln \gamma_1}{\partial \ln \bar{X}_1} + \bar{\alpha}_2 \frac{\partial \ln \gamma_1}{\partial \ln \bar{X}_2} \\ & + \left(\frac{\partial \ln p_1^s}{\partial \ln T} - 1\right)\alpha_t, \end{aligned} \tag{38}$$

$$\begin{aligned} \alpha_2 = {} & \bar{\alpha}_2 - (\bar{\alpha}_1\bar{X}_1 + \bar{\alpha}_2\bar{X}_2) + \bar{\alpha}_1 \frac{\partial \ln \gamma_2}{\partial \ln \bar{X}_1} + \bar{\alpha}_2 \frac{\partial \ln \gamma_2}{\partial \ln \bar{X}_2} \\ & + \left(\frac{\partial \ln p_2^s}{\partial \ln T} - 1\right)\alpha_t. \end{aligned}$$

As mentioned before, equation (37) says that the addition of noncondensable gases could not always act as to deteriorate the condensation rate as in the case of purely one-component system. It depends on the sign of the factor in the brackets of equation (37). In the case of the ideal solution, the factor can be written as

$$\{\ \ \} = \frac{\beta + X_c}{1 + T_1 X_c} \quad X_c = \frac{(X_1 - \bar{X}_1)(C_1 - C_1^o)}{C_1^o(1 - \bar{C}_1)},$$

which always takes a positive value. Thus, the condensation rate is decreased with the noncondensable vapor addition. Nonideal solutions can hardly change this behavior. Since it is proportional to the mole fraction of noncondensable vapor at the interface, β, noncondensable vapors with heavier molecules are likely to alleviate the decrease in condensation rate. In the binary system, the condensation rate is controlled with the rate at which the volatile vapor accumulated at the liquid–vapor interface is taken away from the interface. The noncondensable vapor with heavier molecular weight is to hinder the accumulation of volatile vapor at the interface, hence to reduce the decrease in the net rate of condensation.

For an example, a system of ethanol–water is considered with the following condition [17].

$$T_w = 85.0°\text{C}, \quad T = 86.0°\text{C}$$

$$C_1^o = 0.57, \quad C_1 = 0.70, \quad \bar{C}_1 = 0.30 \quad (1\text{:ethanol}).$$

The results obtained are as follows:

$$\bar{\alpha}_1 = -6.36, \quad \bar{\alpha}_2 = 1.91, \quad \alpha_1 = -3.53, \quad \alpha_2 = -0.436$$

$$\alpha_t = -0.00946, \quad \alpha_\delta = -0.849, \quad \alpha_m = -2.55,$$

where the van Laar and Antoine equations are assumed as for the activity coefficient and the saturation vapor pressure, respectively [17], and the noncondensable gas of nitrogen is introduced.

It is interesting to compare the effects of the noncondensable gas between the condensable–

noncondensable and condensable–condensable systems. By denoting the change in the condensation rate in both systems as $\alpha_m^{(1)}$ and $\alpha_m^{(2)}$, respectively, the ratio of $\alpha_m^{(2)}$ to $\alpha_m^{(1)}$ is expressed by equations (33) and (37) as

$$\begin{aligned}\frac{\alpha_m^{(2)}}{\alpha_m^{(1)}} &= \frac{1}{\beta}\left\{(\bar{\alpha}_1-\bar{\alpha}_2)(X_1-\bar{X}_1)\right.\\ &\quad+\beta+\bar{\alpha}_1\left(X_1\frac{\partial \ln \gamma_1}{\partial \ln \bar{X}_1}+X_2\frac{\partial \ln \gamma_2}{\partial \ln \bar{X}_1}\right)\\ &\quad\left.+\bar{\alpha}_2\left(X_1\frac{\partial \ln \gamma_1}{\partial \ln \bar{X}_2}+X_2\frac{\partial \ln \gamma_2}{\partial \ln \bar{X}_2}\right)\right\}\\ &\simeq \frac{1}{\beta}\{(\bar{\alpha}_1-\bar{\alpha}_2)(X_1-\bar{X}_1)+\beta\},\end{aligned} \tag{39}$$

which can be further rewritten by equation (36) as

$$\simeq \frac{1}{1+T_1X_c} \simeq \frac{4}{3}\,\frac{T-T_w}{TX_c}\,\frac{\lambda}{RT}.$$

Since $T_1X_c > 0$, the ratio $\alpha_m^{(2)}/\alpha_m^{(1)}$ should be always less than unity. It means that the impurity of noncondensable gas in the binary system would be considerably less effective on the condensation process of condensable and condensable vapors compared with that of condensable and noncondensable vapors. In the case of the above example, the ratio is

$$\frac{\alpha_m^{(2)}}{\alpha_m^{(1)}} \simeq 0.0787.$$

SUMMARY

The effects of a small amount of noncondensable gas on film condensation and multicomponent vapor mixtures have been studied analytically by solving the governing equations of mass transfer and phase equilibrium at the liquid–vapor interface with the perturbation method. The changes in the mass fractions of species and the condensation rate at the liquid–vapor interface are given by equations (22) to (26) or (29) to (31) for ideal solutions. The condensation rate is not always decreased by introducing a small amount of noncondensable gas into the multicomponent vapor mixture. For small temperature differences across the condensate layer, the condensation rate decreases proportionally to the mole fraction of noncondensable gas accumulated at the interface.

The results obtained have been applied for two binary systems of condensable and noncondensable species and condensable and condensable species. For binary systems, the introduction of a small amount of noncondensable gas always leads to a decrease in the condensation rate at the interface. The decrease in the condensation rate of the condensable and condensable species is appreciably less than that of the condensable and noncondensable species.

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EFFETS D'UNE FAIBLE QUANTITE DE GAZ INCONDENSABLE SUR LA CONDENSATION EN FILM DE MELANGES DE VAPEURS

Résumé—Les effects d'une faible quantité de gaz incondensable sur la condensation en film de mélanges de vapeurs sont étudiés analytiquement. Les équations de base pour le transfert massique et l'équilibre des phases des espèces à l'interface liquide-vapeur sont résolues avec perturbation due à l'addition d'une faible quantité d'incondensable pour déterminer le comportement dans le mécanisme de condensation en film. Généralement le taux de condensation globale ne décroît pas toujours quand on introduit le gaz incondensable dans le mélange. Pour une petite différence de température à travers la couche condensée, le flux de condensat décroît proportionnellement à la fraction molaire du gaz incondensable accumulé à l'interface. Les résultats sont appliqués à deux systèmes binaires de condensables aussi bien que d'une espèce condensable avec un incondensable et on donne un exemple numérique.

DER EINFLUSS EINES GERINGEN ANTEILS AN NICHTKONDENSIERBAREM GAS AUF DIE FILMKONDENSATION VON VIELSTOFFGEMISCHEN

Zusammenfassung—Der Einfluß eines geringen Anteils an nichtkondensierbarem Gas auf die Filmkondensation von Vielstoffgemischen wurde rechnerisch untersucht. Die Bestimmungsgleichungen für Stoffübergang und Phasengleichgewicht von Vielstoffgemischen an der Grenzfläche zwischen Flüssigkeit und Dampf wurden gelöst unter Berücksichtigung von Störungen infolge eines kleinen Anteils an nichtkondensierbarem Gas im Dampfgemisch, um eine Aussage über dessen Verhalten beim Vorgang der Filmkondensation zu erhalten. Generell muß die Gesamtkondensationsrate durch den Zusatz von nichtkondensierbarem Gas im Vielkomponentengemisch nicht unbedingt abnehmen. Bei kleinen Temperaturdifferenzen innerhalb der Kondensatschicht nimmt die Kondensationsrate proportional zum Molanteil des an der Grenzfläche akkumulierten nichtkondensierbaren Gases ab. Die Ergebnisse werden in Rechenbeispielen auf zwei binäre Systeme angewandt, auf ein Stoffpaar aus kondensierbaren Stoffen sowie ein Stoffpaar aus einem kondensierbaren und einem nichtkondensierbaren Stoff.

ВЛИЯНИЕ НЕБОЛЬШОГО КОЛИЧЕСТВА НЕКОНДЕНСИРУЮЩЕГОСЯ ГАЗА НА ПЛЕНОЧНУЮ КОНДЕНСАЦИЮ МНОГОКОМПОНЕНТНЫХ СМЕСЕЙ

Аннотация—Аналитически изучается влияние небольшого количества неконденсирующегося газа на пленочную конденсацию многокомпонентных паровых смесей. Уравнения массопереноса и фазового равновесия многокомпонентной смеси на границе жидкость-пар решались с учетом возмущения, возникающего в результате добавления небольшого количества неконденсирующегося газа к основной паровой смеси, с целью определения ее свойств в процессе пленочной конденсации. Получено, что суммарная скорость конденсации не всегда уменьшается с введением неконденсирующегося газа в многокомпонентную смесь. При небольшой разности температур в слое конденсата скорость конденсации уменьшается пропорционально молярной доле неконденсирующегося газа вблизи границы раздела. В качестве числового примера рассматривается применение результатов в двух бинарных системах, в одной из которых оба газа конденсирующиеся, а в другой один неконденсирующийся.