The Interaction Between Mass and Heat Transfer in the Rectification of Mixtures

ELI RUCKENSTEIN

Polytechnic Institute, Bucharest, Romania

The adiabatic rectification process is generally considered diffusional. If the boiling points of the components are close enough, such an assumption is a natural one, because the heat fluxes in the two phases due to thermal conductivity are very small. If the boiling points are very different, it is possible that the heat flux from the interface towards the bulk of the liquid is large. Are there cases in which this heat flux affects the rate of mass transfer between the two phases? The answer to this question represents the main aim of this communication.

The interaction between heat and mass transfer was first considered in the thermal theory of rectification by using the two-film model (*1, 2*). This theory was proposed to explain the experimental observation that for mixtures having sufficiently different boiling points, the performance of a distillation column depends on concentration and has a maximum (*3* to *5*). It takes into account the effect of the heat transfer on the mass transfer and assumes, besides, that for large values of the heat flux directed from the interface toward the bulk of the liquid, a vaporization in the bulk occurs. It is necessary to notice that the dependence of the performance on concentration (however not the occurrence of a maximum) was explained also by means of the classical diffusional theory by taking into account only the dependence of the slope of the equilibrium curve on concentration (*6, 7*).

The interaction between heat and mass transfer will be examined in the framework of a more realistic model, namely, the penetration-renewal model. Only the situation in which vaporization in the bulk does not occur will be analyzed in a quantitative manner, the other owing to prohibitive complication in a qualitative manner.

BASIC EQUATIONS

Let us consider the transfer processes in the liquid phase and write for each component the corresponding equation valid in the penetration-renewal model. Because the heat transfer from the interface towards the bulk of the liquid is taken into account, and also because one considers that the molar vaporization heats are different, there exists no equal molar counterflow of the fluxes of the two components, and consequently the velocity component along the normal to the interface differs from zero. The usual penetration theory must be replaced by the variant due to Arnold (*8*), which takes into account the effect of this velocity too.

For the concentration field, one may write

$$\frac{\partial n_A}{\partial \theta} + \frac{\partial N_A}{\partial z} = 0, \quad \frac{\partial n_B}{\partial \theta} + \frac{\partial N_B}{\partial z} = 0 \tag{1}$$

where

$$N_A = un_A - D\frac{\partial n_A}{\partial z} \quad \text{and} \quad N_B = un_B - D\frac{\partial n_B}{\partial z} \tag{2}$$

and for the temperature field

$$\frac{\partial (n_A c_{pA} + n_B c_{pB})\, t}{\partial \theta} + \frac{\partial Q}{\partial z} = 0 \tag{3}$$

where

$$Q = N_A H_A + N_B H_B - k\frac{\partial t}{\partial z} \tag{4}$$

Assuming that

$$H_A = c_{pA} t \quad \text{and} \quad H_B = c_{pB} t \tag{5}$$

and taking into account Equations (1), one obtains

$$(n_A c_{pA} + n_B c_{pB})\frac{\partial t}{\partial \theta} + (c_{pA} N_A + c_{pB} N_B)\frac{\partial t}{\partial z} = k\frac{\partial^2 t}{\partial z^2} \tag{6}$$

For simplicitiy, it will be considered that

$$c_{pA} = c_{pB} = c_p \tag{7}$$

Equation (6) becomes, finally

$$n_t\, c_p \frac{\partial t}{\partial \theta} + c_p\,(N_A + N_B)\frac{\partial t}{\partial z} = k\frac{\partial^2 t}{\partial z^2} \tag{8}$$

By considering that $n_A + n_B = n_t =$ const., Equations (2) lead to

$$u = \frac{N_A + N_B}{n_t}$$

Because from Equations (1) $\dfrac{\partial (N_A + N_B)}{\partial z} = 0$, one may conclude that u depends only on time; consequently

$$u = \frac{N_{A0} + N_{B0}}{n_t} \tag{9}$$

An equation for u is supplied by a thermal balance at the interface. Indeed, at the vapor-liquid interface, one may write

$$Q_{V,0} = Q_{L,0} \tag{10}$$

which, by neglecting the heat transfered by thermal conductivity in the vapor phase, becomes

$$N_{A,0}(H_{AV} - H_{AL}) + N_{B0}(H_{BV} - H_{BL}) + k\left(\frac{\partial t}{\partial z}\right)_{z=0} = 0$$

Since $H_{AV} - H_{AL} = \lambda_A$, and $H_{BV} - H_{BL} = \lambda_B$, one gets

$$N_{A0}\lambda_A + N_{B0}\lambda_B + k\left(\frac{\partial t}{\partial z}\right)_{z=0} = 0 \tag{11}$$

Eliminating from (9) N_{B0} by means of (11), and taking into account that

$$N_{A0} = un_{A0} - D\left(\frac{\partial n_A}{\partial z}\right)_{z=0}$$

one obtains

$$u = \frac{-D\left(\frac{\partial n_A}{\partial z}\right)_{z=0}\left(1-\frac{\lambda_A}{\lambda_B}\right) - \frac{k}{\lambda_B}\left(\frac{\partial t}{\partial z}\right)_{z=0}}{n_t - n_{A,0}\left(1-\frac{\lambda_A}{\lambda_B}\right)} \tag{12}$$

Therefore, we have to solve the equations

$$\frac{\partial n_A}{\partial \theta} + u\frac{\partial n_A}{\partial z} = D\frac{\partial^2 n_A}{\partial z^2} \tag{13}$$

and

$$\frac{\partial t}{\partial \theta} + u\frac{\partial t}{\partial z} = a\frac{\partial t^2}{\partial z^2} \tag{14}$$

where u is given by Equation (12) for the boundary conditions

$$\begin{aligned} n_A &= n_{A,0}, & t &= t_0 & \text{for} \quad & z = 0 \\ n_A &= n_{A,\infty}, & t &= t_\infty & \text{for} \quad & z \to \infty \\ n_A &= n_{A,\infty}, & t &= t_\infty & \text{for} \quad & t = 0 \end{aligned} \tag{15}$$

THE SOLUTION OF THE EQUATIONS

The changes of variables

$$\eta = \frac{z}{(4D\theta)^{1/2}} \tag{16}$$

$$\mu = \frac{z}{(4a\theta)^{1/2}} \tag{17}$$

allow the transformation of Equations (13) and (14) into

$$\frac{d^2 n_A}{d\eta^2} + 2[\eta - \phi]\frac{dn_A}{d\eta} = 0 \tag{18}$$

$$\frac{d^2 t}{d\mu^2} + 2[\mu - \Phi]\frac{dt}{d\mu} = 0 \tag{19}$$

where

$$\phi = -\frac{f}{2}\,\frac{1}{n_t - n_{A0}f}\left(\frac{dn_A}{d\eta}\right)_{\eta=0} - \frac{k}{2\lambda_B\,(n_t - n_{A0}f)}\,\frac{1}{a^{1/2}\,D^{1/2}}\left(\frac{dt}{d\mu}\right)_{\mu=0} \tag{20}$$

and

$$\Phi = \left(\frac{a}{D}\right)^{-1/2}\phi \tag{21}$$

The solutions of Equations (18) and (19) for the boundary conditions (15) have the form

$$\frac{n_A - n_{A\infty}}{n_{A0} - n_{A\infty}} = \frac{\operatorname{erfc}\,(\eta - \phi)}{1 + \operatorname{erf}\phi} \tag{22}$$

and

$$\frac{t - t_\infty}{t_0 - t_\infty} = \frac{\operatorname{erfc}\,(\mu - \Phi)}{1 + \operatorname{erf}\Phi} \tag{23}$$

Using Equations (22) and (23), one obtains for ϕ the equation

$$\phi = \frac{f}{\sqrt{\pi}}\,\frac{n_{A0} - n_{A\infty}}{n_t - n_{A0}f}\,\frac{1}{(1 + \operatorname{erf}\phi)e^{\phi^2}} + \left(\frac{a}{D}\right)^{1/2}\frac{1}{\sqrt{\pi}}\,\frac{n_t c_p\,(t_0 - t_\infty)}{\lambda_B\,(n_t - n_{A0}f)}\,\frac{1}{(1 + \operatorname{erf}\phi)e^{\Phi^2}} \tag{24}$$

For the mass flux $N_{A,0}$, given by

$$N_{A0} = un_{A0} - D\left(\frac{\partial n_A}{\partial z}\right)_{z=0} = \frac{-D\left(\frac{\partial n_A}{\partial z}\right)_{z=0}\left(1-\frac{\lambda_A}{\lambda_B}\right) - \frac{k}{\lambda_B}\left(\frac{\partial t}{\partial z}\right)_{z=0}}{n_t - n_{A,0}\left(1-\frac{\lambda_A}{\lambda_B}\right)}\,n_{A0} - D\left(\frac{\partial n_A}{\partial z}\right)_{z=0}$$

one gets

$$N_{A0} = \frac{n_{A0}}{n_t - fn_{A0}}\left[f\left(\frac{D}{\pi\theta}\right)^{1/2}\frac{n_{A0} - n_{A\infty}}{(1 + \operatorname{erf}\phi)e^{\phi^2}} + \left(\frac{a}{\pi\theta}\right)^{1/2}\frac{c_p\,n_t(t_0 - t_\infty)}{\lambda_B(1 + \operatorname{erf}\Phi)e^{\Phi^2}}\right] + \left(\frac{D}{\pi\theta}\right)^{1/2}\frac{n_{A,0} - n_{A\infty}}{(1 + \operatorname{erf}\phi)e^{\phi^2}} \tag{25}$$

For the average value of N_{A0} taken over the time Δ of contact of the element of liquid with the interface, one obtains

$$\overline{N}_{A0} = \frac{n_{A0}}{n_t - fn_{A0}}\left[f\left(\frac{4D}{\pi\Delta}\right)^{1/2}\frac{n_{A0} - n_{A\infty}}{(1 + \operatorname{erf}\phi)e^{\phi^2}} + \left(\frac{4a}{\pi\Delta}\right)^{1/2}\frac{c_p\,n_t(t_0 - t_\infty)}{\lambda_B(1 + \operatorname{erf}\Phi)e^{\Phi^2}}\right] + \left(\frac{4D}{\pi\Delta}\right)^{1/2}\frac{n_{A0} - n_{A\infty}}{(1 + \operatorname{erf}\phi)e^{\phi^2}} \tag{26}$$

If, instead of Higbie's model, one uses Danckwert's statistical distribution, the expression of the mass flux becomes

$$\overline{N}_{A0} = \frac{n_{A0}}{n_t - fn_{A0}}\left[f(Ds)^{1/2}\frac{n_{A0} - n_{A\infty}}{(1 + \operatorname{erf}\phi)e^{\phi^2}} + (as)^{1/2}\frac{c_p\,n_t(t_0 - t_\infty)}{\lambda_B(1 + \operatorname{erf}\Phi)e^{\Phi^2}}\right] + (Ds)^{1/2}\frac{n_{A0} - n_{A\infty}}{(1 + \operatorname{erf}\phi)e^{\phi^2}} \tag{27}$$

Since, usually $\lambda_A \approx \lambda_B \equiv \lambda$, $f = 0$, Equations (27) and (24) become

$$\overline{N}_{A0} = \frac{n_{A,0}}{n_t}\,(as)^{1/2}\,\frac{c_p\,n_t(t_0 - t_\infty)}{\lambda\,(1 + \operatorname{erf}\Phi)e^{\Phi^2}}\,] + (Ds)^{1/2}\frac{n_{A0} - n_{A\infty}}{(1 + \operatorname{erf}\phi)e^{\phi^2}} \quad \text{for} \quad f = 0 \tag{28}$$

and

$$\sqrt{\pi}\,\Phi\,e^{\Phi^2}\,(1 + \operatorname{erf}\Phi) = \frac{c_p(t_0 - t_\infty)}{\lambda} \quad \text{for} \quad f = 0 \tag{29}$$

Some values of Φ as a function of $\frac{c_p(t_0 - t_\infty)}{\lambda}$ (Jakob number) are given in Table 1. Equations (28) and (29) will be discussed in what follows.

TABLE 1. Φ *vs.* $N_{Ja} \equiv \frac{c_p\,(t_0 - t_\infty)}{\lambda}$

$\frac{c_p(t_0 - t_\infty)}{\lambda}$	0	$\frac{1}{3}$	1	3	∞
Φ	0	0.156	0.358	0.662	∞

DISCUSSION

The specific heat c_p is of the order of 0.02 kcal./mole °C., while the latent vaporization heat λ of the order of 10 kcal./mole. Even if $t_0 - t_\infty$ is as large as 20°C., the Jakob number $\frac{c_p(t_0 - t_\infty)}{\lambda}$ is very small. From Equation (29), Φ is also small. In these cases, the factors $(1 + \text{erf}\,\Phi)e^{\Phi^2}$ and $(1 + \text{erf}\,\phi)e^{\phi^2}$ have values very near 1, and it is possible to approximate equation (28) by

$$\overline{N}_{A0} \approx (Ds)^{1/2}\,(n_{A0} - n_{A\infty}) \left[1 + \frac{n_{A0}}{n_t}\left(\frac{a}{D}\right)^{1/2} \frac{c_p(t_0 - t_\infty)\,n_t}{\lambda(n_{A0} - n_{A\infty})}\right]$$

Even if the Jakob number is small, the ratio

$$\frac{n_{A,0}}{n_t}\left(\frac{a}{D}\right)^{1/2} \frac{c_p(t_0 - t_\infty)n_t}{\lambda(n_{A,0} - n_{A\infty})}$$

may be important owing to the factor $(a/D)^{1/2}$ which is of the order of 10 and to the factor

$$\frac{n_{A,0}}{n_{A,0} - n_{A\infty}} > 1$$

Three cases may occur.

1. In the first, $\left|\frac{n_{A,0}}{n_t}\left(\frac{a}{D}\right)^{1/2} \frac{c_p(t_0 - t_\infty)n_t}{\lambda(n_{A0} - n_{A\infty})}\right| << 1;$

the rectification process is diffusion controlled.

2. In the second case, $\left|\frac{n_{A,0}}{n_t}\left(\frac{a}{D}\right)^{1/2} \frac{c_p(t_0 - t_\infty)n_t}{\lambda(n_{A0} - n_{A\infty})}\right|$

≈ 1, and the liquid is moderately superheated.

Such a superheating is possible because, as is known from the theory of nucleation, in a homogeneous phase the rate of nucleation is practically nil up to a certain critical superheating at which it becomes very large (*10*).

The mass flux is given in this case by Equation (27) [or by Equation (28) if $f \approx 0$]. Its dependence on composition is no longer a simple one. One of the terms of this equation has a form similar to the one valid for the diffusion controlled case. The interaction between the heat and mass transfer introduces in this term the factor $[(1 + \text{erf}\,\phi)e^{\phi^2}]^{-1}$ which depends indirectly, via the Jakob number, on the temperature at the interface and consequently on the concentration at the interface (thermodynamic equilibrium being achieved there). The other terms contain the concentration at the interface both directly and via the Jakob number. Owing to the fact that the mass flux depends on the temperature of the bulk of the liquid too, for obtaining the performance of the column the heat transfer equations must be also taken into account.

Equation (28) shows that the rate of mass transfer is decreased by the heat transfer, and consequently the performance of the column is decreased in comparison with the diffusion controlled case. This is due to the fact that a part of the heat resulting from condensation is used for heating the liquid.

It must be stressed that if the superheating is large (however smaller than the critical one mentioned above), the difference between the temperatures at the interface and in the bulk becomes small and the rate of mass transfer becomes diffusion controlled.

3. The heat transfer is very large, and the superheating of the liquid is so high that vaporization in the bulk occurs. It is possible that such a situation be achieved for the mixture ammonia-water. Indeed, for this mixture and for a pressure of 8 atm. the ratio

$$\left|\frac{n_{A,0}}{n_t}\left(\frac{a}{D}\right)^{1/2} \frac{c_p(t_0 - t_\infty)n_t}{\lambda(n_{A,0} - n_{A,\infty})}\right|$$

is of the order of 10. The evaluation was made by considering that t_∞ corresponds to the saturation. In this case, the above equations must be modified so as to take into account the vaporization in the bulk. This is, however, a very difficult task. The problem was solved previously by the author (*1, 5*) in the framework of the two-film model.

NOTATION

a = thermal diffusivity
c_p = molar specific heat
D = diffusion coefficient
f = $(1 - \lambda_A/\lambda_B)$
H = molar enthalpy
k = thermal conductivity in the liquid phase
n = molar concentration
n_t = total molar concentration ($n_t = n_A + n_B$)
N = mass flux
N_{Ja} = $c_p(t_0 - t_\infty)/\lambda$, Jakob number
Q = heat flux
s = Danckwerts' renewal frequency
t = temperature
u = velocity in the z direction
z = distance at the interface

Greek Letters

Δ = duration of contact with the interface of a liquid element
ϕ = quantity defined by Equation (20)
Φ = quantity defined by Equation (21)
η = quantity defined by Equation (16)
μ = quantity defined by Equation (17)
λ = molar vaporization heat
θ = time

Subscripts

A = component A
B = component B
0 = interface
∞ = $z \to \infty$
V = vapor phase
L = liquid phase

Superscripts

— = average quantities

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