On Models for Evaporation of a Multicomponent Droplet

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In a recent paper Newbold and Amundson (1973) propose a model for evaporation of a multicomponent droplet into a stagnant gas and claim that the model has the properties: "the transport of one component can be augmented by the bulk (Stefan) flow of the other components, and that the droplet can never exceed its boiling point, a property not realized by previous models." The purpose of this note is to point out that the models recommended for calculating multicomponent evaporation presented in standard textbooks on heat and mass transfer, for example, Bird, Stewart, and Lightfoot (1960) and Spalding (1963) do have the properties claimed as new by Newbold and Amundson. Furthermore it will be shown that (1) for evaporation into a stagnant gas the textbook models are almost identical to the proposed model, and (2) the textbook models have important additional virtues in as much as they also can be directly applied to more realistic engineering problems where the droplet is moving relative to the gas, where the assumptions of uniform concentrations and temperature within the droplet are inaccurate and where thermal radiation cannot be neglected in the droplet energy balance.

Bird et al. (1960) give the necessary analysis and formulae required to apply film theory to multicomponent mass transfer. Since this textbook is so familiar to most chemical engineers, it seems worthwhile to take this opportunity to further acquaint chemical engineers with Spalding's essentially equivalent, but somewhat more general, analysis of multicomponent mass transfer. The treatment presented here follows most closely Spalding (1963) though some may find Spalding (1960) or Kays (1966) more palatable. The equations in Spalding's theory corresponding to the final flux expressions Equations (35) and (47) of Newbold and Amundson are

$$\dot{m}'' = g^*_{m,i} \ln(1 + \mathcal{B}_{m,i}) = g^*_h \ln(1 + \mathcal{B}_h) \qquad i = 1, \ldots, (n-1), I \quad (1)$$

where

$$\mathcal{B}_{m,i} \equiv \frac{m_{i,e} - m_{i,s}}{m_{i,s} - m_{i,t}}$$

$$\mathcal{B}_h \equiv \frac{h_e - h_s}{h_s - h_t} = \frac{C_{pe}(T_e - T_s)}{\sum_{i=1}^{n-1} m_{i,t}\lambda_i + \dot{q}_u''/\dot{m}''}$$

$$g^*_{m,i} = \frac{\rho \mathcal{D}_{im}}{D} Nu^*_m; \quad g^*_h = \frac{k}{C_p D} Nu^*_h$$

and for evaporation into a stagnant gas these Nusselt numbers are equal to 2. The mass fractions in the gas phase adjacent to the interface $m_{i,s}$ are related to the liquid phase concentrations through Raoult's law, as in the Newbold and Amundson model. Equations (1) are $(n + 1)$ equations in the $(n + 1)$ unknowns $\dot{m}''$, $m_{i,t}$ and $\dot{q}_u''$; the precise solution scheme would depend on the numerical method chosen to solve the coupled droplet mass species and energy balances.

The theory presented above invokes only one assumption additional to those made by Newbold and Amundson; for the gaseous species either the Lewis numbers Le_i are unity, or the specific heats C_{pi} are equal. However, both this theory and that of Newbold and Amundson already include the assumptions of effective binary diffusion and constant thermodynamic and transport properties: it is not at all certain that the additional assumption will result in an answer further from the truth. Furthermore this assumption can be easily removed, as will be discussed below. In other respects the Spalding result is a mass-basis equivalent of the result of Newbold and Amundson. The Stefan flow augmentation is given by the nonlinear dependence of mass transfer rate $\dot{m}''$ on the driving forces $\mathcal{B}$; that the boiling point cannot be exceeded is guaranteed by the fact that as $T \rightarrow T_{\mathrm{B.P.}}$, $m_{i,s} \rightarrow m_{i,t}$, and so $\dot{m}'' \rightarrow \infty$.

Turning now to the more realistic engineering problem where the gas is moving relative to the droplet, we rewrite Equations (1) in their more general form

$$\dot{m}'' = g_{m,i}\mathcal{B}_{m,i} = g_h \mathcal{B}_h \quad (2)$$

Equations (1) are obtained from Equations (2) by introducing the relations

$$\frac{g_{m,i}}{g^*_{m,i}} = \frac{\ln(1 + \mathcal{B}_{m,i})}{\mathcal{B}_{m,i}}; \quad \frac{g_h}{g^*_h} = \frac{\ln(1 + \mathcal{B}_h)}{\mathcal{B}_h} \quad (3)$$

derived from film theory, and which are exact for the stagnant gas problem. For the forced convection problem Nusselt numbers are now obtained from standard correlations, for example, Edwards et al. (1973) give

$$Nu^*_h = 2 + 0.37 Re_D^{0.6} Pr^{0.33} \quad (4)$$

and for Nu^*_m, Pr is replaced by Sc. As a first approximation the effect of finite mass transfer rates can be accounted for through the film theory relations, Equations (3). For a more accurate estimate relations based on analyses of laminar stagnation point flows with foreign gas injection may be used; for example, following Mills and Wortman (1972) we can replace $\mathcal{B}$ in Equations (3) with $a\mathcal{B}$ where

$$a_{m,i} = 1.65 \left(\frac{M_{\mathrm{air}}}{M_i}\right)^{5/6}; \quad a_{h,i} = 1.3 \left(\frac{M_{\mathrm{air}}}{M_i}\right) \left[\frac{C_{pi}}{\frac{5}{2}\frac{\mathcal{R}}{M_i}}\right]^{1/2} \quad (5)$$

where M_i and C_{pi} are average values for the evaporating species. Relations of a similar form which in addition account for multicomponent diffusion have been given by Gomez, Mills, and Curry (1970). Film theory analysis for unequal specific heats has been presented by Knuth (1963) and can be used for the stagnant gas problem.

The effect of nonuniform concentrations within the liquid droplet could be investigated, at least in the earlier stages of droplet evaporation, by assuming a penetration model for mass transfer. In addition to Equations (1) or

(2) we would then have

$$\dot{m}'' = g^{l*}_{m,i}\mathcal{B}^{l}_{m,i} \quad i = 1, 2 \ldots, (n-1) \qquad (6)$$

where

$$\mathcal{B}^{l}_{m,i} = \frac{m_{i,0} - m_{i,u}}{m_{i,u} - m_{i,t}}$$

Now the mass fractions in the liquid phase just adjacent to the interface $m_{i,u}$ are related to the $m_{i,s}$ through Raoult's law while $m_{i,0}$ the initial liquid composition is specified. The conductance $g^{l*}_{m,i}$ is given by Edwards et al. (1973) as

$$g^{l*}_{m,i} = \rho\left(\frac{\mathcal{D}^{l}_{im}}{\pi t}\right)^{1/2} \qquad (7)$$

or $g^{l}_{m,i}$ could be obtained from finite transfer rate penetration theory. Equations (6) add $(n-1)$ equations in the $(n-1)$ additional unknown mass fractions $m_{i,u}$ to the original sets, Equations (1) or (2); again the precise solution scheme would depend on the numerical method chosen to solve the coupled droplet balances.

For combustion calculations the heat transfer model may be refined to include thermal radiation exchange by generalizing $\mathcal{B}_h$ to read

$$\mathcal{B}_h = \frac{C_{pe}(T_e - T_s)}{\sum_{i=1}^{n-1} m_{i,t}\lambda_i + \dot{q}_u''/\dot{m}'' - \dot{q}_r''/\dot{m}''} \qquad (8)$$

where $\dot{q}_r''$ is the net radiation received by the droplet. Here absorption of radiation by the vapor has been neglected; the shielding of the droplet by the vapor has probably little effect on the net heat transfer rate as most of the absorbed heat will be conducted to the droplet anyway. Finally, the effect of conduction into the droplet can be included by evaluating the term $\dot{q}_u''$ in the denominator of Equation (8); again in the earlier stages of evaporation, a penetration model could be used for this purpose.

NUMERICAL EXAMPLE

To illustrate the use of the analysis presented above a calculation will be made for a heptane-octane fuel droplet evaporating into air at 2300°K and 1 atm. pressure. The droplet has diameter 1000 μ, temperature 360°K, and mole fractions of 0.5 heptane and 0.5 octane. Denoting heptane as species 1, octane as 2 and air as I we have

$$\lambda_1 = 3.22 \times 10^5 \text{ Ws/kg}; \quad \lambda_2 = 3.01 \times 10^5 \text{ Ws/kg}$$

$$P_{1,s} = 0.431 \text{ atm.}; \quad P_{2,s} = 0.169 \text{ atm.}$$

$$m_{1,s} = 0.585; \quad m_{2,s} = 0.257; \quad m_{I,s} = 0.158$$

$$m_{1,e} = 0; \quad m_{2,e} = 0; \quad m_{I,e} = 1$$

$$C_{pe} = 1.48 \times 10^3 \text{ Ws/kg K}$$

$$Pr = 0.705; \quad \rho = 0.271 \text{ kg/m}^3$$

$$\nu = 182 \times 10^{-6} \text{ m}^2\text{/s}; \quad Sc_i = 2.0;$$

$$\mathcal{D}_{im} = 91.0 \times 10^{-6} \text{ m}^2\text{/s}$$

where the assumed constant gas phase properties have been taken as those of air at the mean film temperature of 1340°K. Also the effective Schmidt numbers for all three species have been taken equal; as a consequence all the $g^{*}_{m,i}$ are equal, and substituting in Equations (1)

$$\frac{\dot{m}''}{g^{*}_{m,i}} = \ln\left(1 + \frac{0 - 0.585}{0.585 - m_{1,t}}\right)$$

$$= \ln\left(1 + \frac{0 - 0.257}{0.257 - m_{2,t}}\right)$$

$$= \ln\left(1 + \frac{1 - 0.158}{0.158 - 0}\right)$$

and solving gives $\dot{m}''/g^{*}_{m,i} = 1.841$; $m_{1,t} = 0.695$; $m_{2,t} = 0.305$. Now $g^{*}_{m,i} = \rho\mathcal{D}_{im}Nu^{*}_{m}/D = (0.271)(91.0 \times 10^{-6})(2)/10^{-3} = 0.0494$ kg/m²s, so that $\dot{m}'' = (1.841)(0.0494) = 0.091$ kg/m²s, the evaporation rate. Also $g^{*}_{h}/g^{*}_{m} = (k/C_p)/\rho\mathcal{D}_{im} = Sc_i/Pr = 2.84$, thus $\dot{m}''/g^{*}_{h} = 1.841/2.84 = 0.649 = \ln(1 + \mathcal{B}_h)$; solving gives $\mathcal{B}_h = 0.914$. Now solving Equation (8) for $\dot{q}_u''$,

$$\dot{q}_u'' = \frac{\dot{m}''}{\mathcal{B}_h} C_{pe}(T_e - T_s) + \dot{q}_r'' - \dot{m}''(m_{1,t}\lambda_1 + m_{2,t}\lambda_2)$$

Evaluating the terms on the right hand side,

$$\frac{\dot{m}''}{\mathcal{B}_h} C_{pe}(T_e - T_s) = \frac{(0.091)(1.482 \times 10^3)(2300 - 360)}{(0.914)}$$

$$= 287 \times 10^3 \text{ W/m}^2$$

for the radiative flux we take a volume average gas temperature of 2100°K (absorptivity × emissivity) = 0.05

$$\dot{q}_r'' \cong (0.05)(5.6697 \times 10^{-8})(2100^4 - 360^4)$$

$$= 55.3 \times 10^3 \text{ W/m}^2$$

$$\dot{m}''(m_{1,t}\lambda_1 + m_{2,t}\lambda_2) = (91 \times 10^{-3})[(0.695)(3.22 \times 10^5) + (0.305)(3.01 \times 10^5)] = 28.8 \times 10^3 \text{ W/m}^2$$

$$\dot{q}_u'' = (287 \times 10^3) + (55.3 \times 10^3) - (28.8 \times 10^3)$$

$$= 314 \times 10^3 \text{ W/m}^2$$

This is the heat flux into the droplet and is used in the droplet energy balance to determine its rate of temperature increase.

NOTATION

$\mathcal{B}$ = Spalding driving force
C_p = specific heat at constant pressure per unit mass
D = droplet diameter
$\mathcal{D}_{im}$ = effective binary diffusion coefficient of species i
g = conductance
h = enthalpy per unit mass
k = thermal conductivity of the gas phase
M = molecular weight
m = mass fraction
$\dot{m}''$ = mass transfer rate
n = absolute mass flux
Nu = Nusselt number
Pr = Prandtl number
$\dot{q}_r''$ = net radiative heat transfer
$\dot{q}_u''$ = conductive heat flux across u-surface
Re_D = Reynolds number based on diameter
$\mathcal{R}$ = gas constant per mole
Sc = Schmidt number
T = temperature
t = time
λ = latent heat of vaporization per unit mass
ρ = density

Subscripts

B.P. = boiling point
e = bulk gas
h = heat transfer
I = nonevaporating species

i = species, $i = 1, \ldots, (n-1), I$
m = mass transfer
0 = initial
s = in the gas phase, just adjacent to the interface
t = in the transferred state, for example, $m_{i,t} = n_{i,s}/\dot{m}''$
u = in the liquid phase, just adjacent to the interface

Superscripts

* = limit of zero net mass transfer ($\dot{m}'' \to 0$)
l = liquid phase

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Comments on the Note by Mills

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The authors wish to thank Professor Mills (1973) for his note pointing to the relation between our droplet model (Newbold and Amundson, 1973) and the earlier models of Spalding (1963) and Bird et al. (1960).

The exact relation between the mass transfer models can be found by substituting for $B_{m,i}$, $g^*_{m,i}$ and $m_{i,t} = n_{i,s}/\dot{m}''$ in Mills' equation (1) to get

$$\dot{m}'' = \frac{\rho D_{im}}{r} \ln\left[1 + \frac{m_{i,e} - m_{i,s}}{m_{i,s} - n_{i,s}/\dot{m}''} \right] \tag{1}$$

and then solving for $n_{i,s}$ to arrive at the expression

$$n_{i,s} = \dot{m}'' \left\{ \frac{m_{i,s} \exp\left(\dfrac{\dot{m}'' r}{\rho D_{im}} \right) - m_{i,e}}{\exp\left(\dfrac{\dot{m}'' r}{\rho D_{im}} \right) - 1} \right\} \tag{2}$$

Equation (2) is readily seen to be the mass basis equivalent of our Equation (28) [not Equation (35) as Mills suggests]:

$$J_i = \overline{J} \left\{ \frac{y_i^* \exp\left(\dfrac{\overline{J} r}{C_T D_{im}} \right) - y_{iB}}{\exp\left(\dfrac{\overline{J} r}{C_T D_{im}} \right) - 1} \right\} \tag{3}$$

Our development continues from this point to eliminate the total flux $\overline{J}$ (by assuming the flux of inert J_I equals zero), and arrives finally at an explicit expression [Equation (35) in our paper] for the flux of component i:

$$J_i = \frac{1}{r} \frac{C_T D_{Im}}{P_T} \ln(C) \left[\frac{x_i P_{Ai}^* C^{D_{Im}/D_{im}} - P_{Ai}}{C^{D_{Im}/D_{im}} - 1} \right] \tag{4}$$

where

$$C = \frac{P_T - \sum_{i=1}^{n} P_{Ai}}{P_T - \sum_{i=1}^{n} x_i P_{Ai}^*} \tag{5}$$

The advantages of this explicit formulation over Mills' implicit Equation (1) become evident when one attempts to deduce the properties of the model. For example, in order to prove, via the earlier formulation, that the boiling point cannot be exceeded, Mills finds it necessary to argue that $T \to T_{B.P.}$ implies $m_{i,s} \to m_{i,t} = n_{i,s}/\dot{m}''$. However intuitive it might seem that $m_{i,s} \to n_{i,s}/\dot{m}''$, this behavior isn't necessarily related to the model in question. (In fact, if we were willing to make an assumption of this kind we might just as well assume that the boiling point will not be exceeded.) In comparison, the boiling point property can be deduced directly from our Equations (4) and (5) above, since, by definition, the denominator of C vanishes at the boiling point.

As to Mills' assertion that the earlier formulation is advantageous because it can be applied to evaporation in flowing, as well as stagnant gases, we maintain that our formulation can be extended to this case as well. For example, if the mass transfer problem posed in our article is solved for a finite (rather than infinite) stagnant film we get

$$J_i = \frac{N_{Sh}}{2} \frac{1}{r} \frac{C_T D_{Im}}{P_T} \ln(C) \left[\frac{x_i P_{Ai}^* C^{D_{Im}/D_{im}} - P_{Ai}}{C^{D_{Im}/D_{im}} - 1} \right] \tag{6}$$

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