

Reply:

Taylor, Baur and Krishna¹ reviewed the literature on residue curves that attempt to incorporate mass transfer effects. The article of Silva et al.² was shown to be fundamentally wrong. In their letter to the editor Silva et al. have questioned some of our arguments. Below is our response to their letter.

There are so many inconsistencies in the model described in their article (and in their letter to the editor) that it is hard to know where to begin and end with our comments.

Silva et al. state that we used “an argument from Doherty and Malone where it is stated that ‘the vapors are removed from contact from the liquid as soon as it is form’, that is, at infinite velocity, which requires a very high-pressure difference across the film to say the least.”

The latter part of this sentence is nonsense. In the model used by Doherty and Malone³ (and scores of others) there is no pressure difference across the film because there is no vapor film — because there is no vapor (Silva et al. must have forgotten that the vapor is instantly removed)!

The authors go on to say that “the correct question is: would the film theory model apply to films where bulk motion occurs?” They state that the answer is yes, and provide a mathematical solution of the diffusion equations to make their point.

Unfortunately, the solution presented in their letter (their Eq. 2) is wrong because it does not satisfy the boundary conditions specified in their Eq. 1.

However, their question is not without merit. It is most certainly true that the film model applies when there is bulk flow. The simplest approach to mass transfer (not always meaningful for multicomponent systems) is to say that the

molar fluxes in the vapor phase at a phase interface may be written as

$$N_i^V = c_i^V k_i^V (y_i^V - y_i^I) + y_i^I N_t^V \quad (1)$$

c_i^V is the molar density of the super-scripted phase, y_i^V is the mole fraction in the bulk vapor phase, and y_i^I are the mole fractions of species i at the phase interface. N_t^V is the total molar flux in phase p . k_i^V are the mass-transfer coefficients for the vapor phase (with units of velocity). The first term on the righthand side is the diffusion flux; the second term is the convective flux (due to bulk motion). The total flux is defined by $N_t^V = c_t^V u^V$ where u^V is the velocity of the vapor phase through the film.

Normally, in applications of the film model the convective velocity included in the diffusion equations is normal to the bulk flow velocity (see, for example, the classic text of Bird et al. for a comprehensive treatment of the film model for binary mass transfer in the presence of convection). In the application of convective mass transfer theory by Silva et al., in the article in question, the velocity through the film is in the same direction as the flow out of the batch still (the vapor is evolved at the boiling liquid surface, passes through a vapor film, and continues in the same direction until it leaves the equipment). Thus, theirs is a decidedly nonstandard application of the film model. Furthermore, their approach requires the total molar flux through the vapor film be directly proportional to the vapor flow rate out of the still. Specifically: $q = c_t^V u^V a = N_t^V a$ where a is the area of the interface.

It is important to note that the *mass-transfer rate equation used in the model of Silva et al. does not include a “drift” term* to account for the convective contribution introduced in their Eq. 1. Their rate equation is valid only in the limit that the fluxes are very low, and the total flux approaches zero (clearly a contradiction with their requirement of flow out of the equipment). What they have done (in effect) is to drop (for no stated reason) the convective term on the righthand side of Eq. 1, change the mole fraction driving

force in Eq.1 into a partial-pressure difference, and that driving force into one that includes the total pressures at the interface, and in the bulk vapor in order to be able to perform any calculations that lead to results that have the appearance of physical sense. The second term on the righthand side of Eq. 1 can be dropped only if the total flux is identically zero, or for those components whose bulk phase mole fraction is very low indeed. The former is not satisfied here since all nonzero fluxes have the same sign. The latter possibility cannot be satisfied by all components in a mixture; at least one species must be present in significant relative amounts. Thus, this dilute solution approximation also is not appropriate here. To the best of our knowledge, the mass-transfer rate relation used by Silva et al. has never before appeared in the entire literature on mass transfer. Were their equations to be correct, then every article and every text on mass transfer in gases would be wrong.

Silva et al. state that the mass-transfer coefficients are not related by Eq. A10 in our article, and refer to an alternative in their own (Eq. A8 in our article). Equation A10 is derived from fundamentally sound relationships for mass and energy transfer, together with some simplifying assumptions, such as those leading to Eq. 1 given earlier. It is important to emphasize once more that not all of Eq. 1 are independent. If we write Eq. 1 for all species in the mixture and, in addition, impose values of the mass-transfer coefficients that are not all equal, then it is completely certain that we will violate the fundamental principle of mass conservation. Silva et al. cannot circumvent this problem simply by insisting that Eq. A10 does not apply. They need to demonstrate that their relationship does not violate fundamental conservation relationships.

We shall mention just one more problem here (this is in addition to the issues documented earlier, and in our article). Silva et al. may well be correct in saying (in their letter) that a pressure gradient is needed for the vapor to leave the equipment, *but there is no such pressure gra-*

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dient in their model. In their model the bulk pressure difference exists only over the thickness of the film. This particular inconsistency could be avoided by assuming that there is no bulk vapor phase, only a vapor film, but that is surely not their intention (see Figure 1 of their article).

It is important for Silva et al. to recognize that we are talking about a model. The standard model of residue curves does not ask us to worry about how the vapor is removed from contact with the liquid, only that it is. With this assumption we showed that the standard model is completely consistent with itself. This does not mean that the standard model is completely consistent

with physical reality. It is only important that the model sufficiently reflects reality in order to be useful. The vast literature on residue curves (including experimental studies) suggests that there can be no doubt at all that the standard model is useful. There should also be no doubt that the standard model lacks realism in some ways. Silva et al. attempted to develop a model of a simple distillation process that is more realistic. Their calculations (and findings) are wrong because their model is completely without meaning.

Literature Cited

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To the Editor:

I would like to inform you that there are some typographical errors in an article entitled "Swelling and Erosion Affecting Flavor Release from Glassy Particles in Water" by Bouquerand et al. (pp. 3257-3270, Dec. 2004). These errors appeared in Eqs. 1, 2, 4, and 7, and the correct form of them are as follows, respectively

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$$\frac{\partial \phi}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D(\phi) \frac{\partial \phi}{\partial r} \right] \quad (1)$$

$$\frac{\partial \theta}{\partial \tau} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left[\rho^2 \Delta(\theta) \frac{\partial \theta}{\partial \rho} \right] \quad (2)$$

$$\frac{\partial}{\partial \rho} \left[\rho^2 \Delta(\theta) \frac{\partial \theta}{\partial \rho} \right] = 0 \quad (4)$$

$$\frac{dr}{d\tau} = \frac{\phi_1 - \phi_0}{1 - \phi_1} [\Gamma(1) - \Gamma(\theta_w)] \frac{R_0^2}{r^2 \left(\frac{1}{s} - \frac{1}{r} \right)} \quad (7)$$

$$\frac{ds}{d\tau} = - \frac{\Gamma(1) - \Gamma(\theta_w)}{\theta_w} \frac{R_0^2}{s^2 \left(\frac{1}{s} - \frac{1}{r} \right)}$$

where ϕ is the volume fraction of water in particle.

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Reply:

Thanks to the reviewer for his judicious remarks concerning the Eqs. 1, 2 and 4. These remarks are justified when the whole particle is considered as it is the case.

I am more doubtful about the introduction of R_0^2 in Eq. 7. However, this does not imply conceptual nor numerical modifications in the result section of the article as Eq. 7 was resolved for $Ro = 1$. The article should gain in rigor with the reviewer comments.

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