Composition at the interface between multicomponent nonequilibrium fluid phases

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The computation of mass transfer between two nonequilibrium phases requires interfacial composition. For a system with a total of \( M \) components, the assumption of local thermodynamic equilibrium provides only \( M \) equations while the number of unknown interfacial compositions is \( 2(M-1) \). In binary systems \((M=2)\), the number of equations matches the number of unknowns and the interfacial composition is readily computed at any temperature and pressure. In multicomponent systems \((M\geq3)\), the number of unknowns exceeds the number of equations and additional constraints are required. To the best of our knowledge, a general solution to the problem of computing interfacial composition in multicomponent systems has not been presented in the past, despite its fundamental importance. In this work we present a general and consistent method of computing interfacial composition where the additional constraints are obtained from mass balance across the interface. The derivations reveal that in multicomponent systems interfacial composition depends on the diffusion coefficients in the two bulk phases. This is a fundamental difference from binary systems. The differences are demonstrated by comparing examples of mixing of nonequilibrium phases in binary and ternary \((M=3)\) systems. © 2009 American Institute of Physics. [DOI: 10.1063/1.3072793]

I. INTRODUCTION

When two nonequilibrium fluid phases are brought into contact with one another, thermodynamic equilibrium will establish at their interface. As a consequence, interfacial composition on either side of the interface differs from the bulk compositions. The resulting composition and density gradients trigger diffusive and convective mass transport. In other words, diffusion and convection lead to complete or partial mixing of the two phases, and the ability to determine interfacial composition is essential to model the process.

Modeling the mixing of two nonequilibrium multicomponent fluid phases is of great interest in a large number of problems. Evaporation of multicomponent droplets is a fundamental problem in the description of sprays and aerosols which have a wide range of applications in combustion, meteorology, and pharmaceutics.\textsuperscript{1,2} Another example comes from the petroleum industry. For decades, gas has been injected into oil reservoirs to maintain the pressure and thus, improve oil recovery.\textsuperscript{3} Depending on the conditions, a substantial amount of the injected gas may dissolve in the oil phase. Upon dissolution, fluid properties such as viscosity, density, and surface tension may change significantly. As a result, the oil phase may flow faster through the reservoir, increasing production further. These secondary recovery mechanisms are particularly important in fractured hydrocarbon reservoirs.\textsuperscript{4}

An accurate description of the mixing of nonequilibrium phases is also important in CO\textsubscript{2}-sequestration projects.\textsuperscript{5} CO\textsubscript{2}-emissions associated with the world’s ever increasing consumption of fossil fuels lead to global warming and there is an increasing concern of the consequences. While the eventual solution to the problem is to switch to alternative, clean energy sources, such a switch is unlikely to happen in the near future. In the meantime, the most feasible way of achieving a significant reduction in CO\textsubscript{2}-emissions to the atmosphere is perhaps through storage in geological formations. The technology for large scale injection into the subsurface is already developed. Moreover, CO\textsubscript{2}-injection is a hot candidate for improved oil recovery projects. Thus, CO\textsubscript{2}-storage offers both financial and environmental incentives. Depleted oil reservoirs and saline aquifers are identified as promising storage formations. However, assessing the storage potential of a given formation requires a way to model the mixing of the injected CO\textsubscript{2} (gas or supercritical) and the formation fluid (brine or oil). Numerical simulations can then help optimizing injection rates and locations, ensuring safe and efficient operation.

Evaporation of volatile liquids from an open container is a classical problem and has been analyzed in detail.\textsuperscript{6,7} Pure and saturated binary liquids have received the most attention. In such liquids the composition remains uniform and the analysis simplifies to a mass transport problem in the gas phase. The main complicating factor is the moving gas-liquid interface. Slattery\textsuperscript{7} extended the analysis to unsaturated binary liquids, indicating that diffusion and convection takes place in both phases. In his analysis, the gas phase may be ternary \((M=3)\) provided one of the components does not condense. The literature on mass transfer between multicomponent phases is largely focusing on modeling evaporating...
fuel droplets. Frequently, the composition of the droplet is assumed uniform implying that the composition on the liquid side of the interface is known. Alternatively, the gas is assumed to always be saturated at the interface and Raoult’s law is used to find the composition on the liquid side.

In the petroleum literature there are a number of laboratory-scale experiments of the mixing occurring when hydrocarbon liquids are exposed to gases such as methane and carbon dioxide. In the modeling of the experiments, multicomponent mixtures are treated as pseudobinaries. To the best of our knowledge, the literature provides no analysis of the mixing of nonequilibrium phases of more than two components when all components may transfer across the interface.

In binary mixtures, the composition at the interface between two phases is uniquely determined by thermodynamic equilibrium. In other words, interfacial composition is only a function of temperature and pressure. However, this is not the case for multicomponent mixtures where more information is necessary to find a unique solution. Uniform composition in one of the phases and nonvolatility and/or nonsolvency of some components provide additional constraints, but these assumptions are only applicable in special cases. In this work, we present a general and consistent approach to determine the composition on both sides of the interface between two nonequilibrium phases with an arbitrary number of components. The derivations are based on the concept of local thermodynamic equilibrium and the additional constraints are obtained from local mass balance. The resulting set of equations are solved numerically and can be used in simulations of various evaporation and condensation phenomena. A simulation of a laboratory-scale mixing experiment is included as an illustration.

II. THEORY

The fundamental assumption behind our derivations is that the two fluid phases are in thermal, mechanical, and chemical equilibria at their interface. In other words, the time it takes to establish local thermodynamic equilibrium is negligible compared to the time scales of diffusive and convective mass transports. The assumption may be more applicable to gas-liquid than liquid-liquid interfaces. Limiting the analysis to flat interfaces, local thermodynamic equilibrium implies that temperature \( T \), pressure \( P \), and chemical potential \( \mu_i \) of each component \( i \) are continuous across the interface. A generalization to curved interfaces is readily derived by using the Young–Laplace equation to account for the pressure jump.

The interface is modeled as a discontinuity between two phases, implying that composition is allowed to change abruptly at interface. Thus, the interface is characterized by two different sets of mole fractions, i.e., one on each side. One set of mole fractions represents interfacial composition as seen by the heavier phase. The other set of mole fractions represents interfacial composition as seen by the lighter phase. As the interface is assumed to have zero thickness, the two compositions coexist at the same spatial coordinates. The proposed model is adequate in the absence of surfactants.

A. Problem formulation

Consider a horizontal interface between two nonequilibrium phases. For clarity, we use a gas-liquid interface in the derivations, but the results are valid whenever the condition of local equilibrium is met. Local chemical equilibrium implies that the jump in composition across the interface is restricted by

\[
\mu_i^G(n_j^G, T, P) = \mu_i^L(n_j^L, T, P), \quad z = 0, \quad i, j = 1, \ldots, M. \tag{1}
\]

Here, \( \mu_i \) is the chemical potential of component \( i \), \( n_j \) is the mole fraction of component \( j \), \( M \) is the total number of components, and \( G \) and \( L \) denote the gas and liquid phases, respectively. The coordinate system \( z \) is centered on and moving with the interface. Note that for an \( M \)-component mixture, Eq. (1) provides \( M \) equations while there are \( 2(M−1) \) independent mole fractions to solve for. For a binary mixture (\( M=2 \)), this is sufficient to find a unique solution, implying that interfacial composition is determined by temperature and pressure only. However, for multicomponent mixtures (\( M \geq 3 \)) there are more unknowns than equations, and additional information is required to find a unique solution. At global equilibrium, composition is uniform within each phase, and standard phase-split calculations solve the problem by using global mass balance. This approach cannot be applied when the two phases are not in equilibrium because composition is no longer uniform. Instead, the additional constraints on interfacial composition comes from local mass balance. As mass is not created nor destroyed, the mass flux of each component must be continuous everywhere, including across the interface,

\[
c^G n_j^G v_z^G + J_z^G = c^L n_j^L v_z^L + J_z^L, \quad z = 0, \quad i = 1, \ldots, M. \tag{2}
\]

Here, \( c \) is molar density, \( v_z \) is mole-averaged vertical velocity, and \( J_z \) is vertical diffusive molar flux of component \( i \). Note that Eq. (2) introduces two additional unknowns, i.e., vertical velocity at either side of the interface. The diffusive fluxes are not unknowns, but relate to composition through Fick’s law. Thus, Eqs. (1) and (2) provide the number of equations necessary to determine interfacial composition. Clearly, the interfacial composition between multicomponent phases depends on nonequilibrium properties (i.e., molecular diffusion coefficients). This is fundamentally different from binary mixtures where interfacial composition depends on equilibrium properties (\( T \) and \( P \)) only.

B. Influence of diffusion on interfacial composition

Taking advantage of the fact that there is no net diffusive flux and that there are only \( M−1 \) independent mole fractions in each phase, net mass balance at the interface is readily obtained by summing Eq. (2) over all components,
\[ c^G \dot{u}^G_z = c^L \dot{u}^L_z, \quad z = 0. \]  
(3)

It is convenient to let the expression for net mass balance replace the \( M \)th component balance expression,

\[ c^G n_i^G \dot{u}^G_z + \dot{J}^G_z = c^L n_i^L \dot{u}^L_z + \dot{J}^L_z, \quad z = 0, \quad i = 1, \ldots, M - 1. \]  
(4)

In order to proceed, the diffusive fluxes must be expressed by a constitutive law. Multicomponent diffusive flux can be expressed by

\[ \dot{J}_i = -c \sum_{j=1}^{M-1} D_{ij} \nabla n_j, \quad i = 1, \ldots, M - 1, \]  
(5)

where \( D_{ij} \) are the molecular diffusion coefficients. Equation (5) is known as a generalized Fick’s law and can be derived from either irreversible thermodynamics or from momentum balance. The final expression for component balance across the interface is obtained by combining Eqs. (4) and (5),

\[ c^G n_i^G \dot{u}^G_z - c^G \sum_{j=1}^{M-1} D_{ij}^G \frac{\partial n_j^G}{\partial z} = c^L n_i^L \dot{u}^L_z - c^L \sum_{j=1}^{M-1} D_{ij}^L \frac{\partial n_j^L}{\partial z}, \]

\[ z = 0, \quad i = 1, \ldots, M - 1. \]  
(6)

Although calculating the interfacial composition between nonequilibrium multicomponent phases requires knowing the diffusion coefficients, the space of possible solutions can be explored by quantifying the discontinuities at the interface. Eliminating the bulk velocities between Eqs. (3) and (4) relates the discontinuities in composition and diffusive flux at the interface,

\[ \beta_{ij} = \frac{n_i^G - n_i^L}{n_i^G - n_i^L} = \frac{\dot{J}_i^G - \dot{J}_i^L}{\dot{J}_i^G - \dot{J}_i^L}. \]  
(7)

In other words, the ratio of the jumps in composition of components \( i \) and \( j \) equals the ratio of the jumps in diffusive flux of the same two components. The parameters \( \beta_{ij} \) will be referred to as jump ratios. One can readily show that only \( M - 2 \) of the jump ratios are independent. Thus, for any given set of jump ratios, interfacial composition is uniquely determined from the chemical equilibrium conditions in Eq. (1).

As an illustration, consider a nitrogen-methane-decane mixture at \( T=120^\circ C \) and \( P=137 \) bar. Nitrogen is labeled as component 1, methane as component 2, and decane is the reference component. The chemical potentials are calculated from the Peng–Robinson equation of state. Note that because nitrogen and methane are more volatile than decane, the jump ratio \( \beta_{12} \) cannot be negative. Figure 1 shows interfacial composition as a function of \( \beta_{12} \) on the gas and liquid side, respectively. Extremely small and large jump ratios only occur when there is a negligible amount of nitrogen or methane present in either phase, i.e., when the mixture is essentially a binary. When an appreciable amount of each component is present, interfacial composition is significantly influenced by variations in the jump ratio.

C. Calculating interfacial composition

Provided chemical potentials \( \mu_i \) and molar density \( c \) are available from an equation of state and all diffusion coefficients are available from measurements or from a correlation, interfacial composition can be found from the nonlinear set of equations given by Eqs. (1), (3), and (6). In the numerical solution procedure all mole fractions in each phase are treated as independent variables. The resulting increase in number of unknowns is matched by adding the restrictions

\[ \sum_{i=1}^{M} n_i^G = \sum_{i=1}^{M} n_i^L = 1 \]  
(8)

to the set of equations to be solved. The complete set of equations is, therefore,

\[ \mu_i^G(n_i^G, T, P) = \mu_i^L(n_i^L, T, P), \quad i = 1, \ldots, M. \]  
(9a)

\[ c^G n_i^G \dot{u}^G_z - c^G \sum_{j=1}^{M-1} D_{ij}^G \frac{\partial n_j^G}{\partial z} = c^L n_i^L \dot{u}^L_z - c^L \sum_{j=1}^{M-1} D_{ij}^L \frac{\partial n_j^L}{\partial z}, \]

\[ i = 1, \ldots, M - 1, \]  
(9b)

\[ c^G \dot{u}^G_z = c^L \dot{u}^L_z, \]  
(9c)

\[ \sum_{i=1}^{M} n_i^G = 1, \]  
(9d)

\[ \sum_{i=1}^{M} n_i^L = 1, \]  
(9e)

where all \( 2M+2 \) equations are to be evaluated at the interface \( z=0 \). The procedure of solving these equations for mole fractions \( n_i \) and vertical bulk velocity \( u_z \) on either side of the interface will be referred to as interfacial flash. Any numerically
Visible content:

Nitrogen, methane, and possible fluids. An extension to multicomponent mixtures is not analyses of mixing experiments with binary and pseudobin- samples for compositional analysis and experiments can be fact that interfacial composition in binary mixtures only de- mines diffusion coefficients from the time evolution of bulk process is available, the experiments can be used to deter- mions have to change as the two phases equilibrate. In our simulations, we keep $V$ and $N_i$ fixed, implying that $P$ will evolve with time. Although the total volume is fixed, the phase volumes may change during the mixing process. Consequently, the liquid level $h$ is also a function of time.

### III. SIMULATING MIXING OF MULTICOMPONENT PHASES

Laboratory-scale experiments provide a way of studying the mixing of two nonequilibrium phases in a controlled en-vironment. Provided an adequate description of the mixing process is available, the experiments can be used to determine diffusion coefficients from the time evolution of bulk properties such as pressure or phase volumes. One advantage with this approach is that there is no need to remove samples for compositional analysis and experiments can be conducted at elevated pressures and temperatures.

To the best of our knowledge, literature only provides analyses of mixing experiments with binary and pseudobinary fluids. An extension to multicomponent mixtures is not possible without knowing how to determine the composition at the interface. In the following, we show how the interfacial flash routine presented in this paper can be implemented in simulations of multicomponent mixing experiments.

#### A. Experimental setup

A gas and a liquid phase at the same temperature and pressure are brought into contact inside a cylindrical container of height $H$ (see Fig. 2). The resulting mixing process is assumed to be isothermal, implying that the rate at which heat is released or absorbed is small and only causes negligible temperature variations. Constant temperature conditions are promoted by placing the container in an isothermal bath. At a given constant temperature $T$, each experiment is characterized by pressure $P$, cell volume $V$, and total number of moles $N_i$ of each component $i$. At least one of these quantities has to change as the two phases equilibrate. In our simulations, we keep $V$ and $N_i$ fixed, implying that $P$ will evolve with time. Although the total volume is fixed, the phase volumes may change during the mixing process. Consequently, the liquid level $h$ is also a function of time.

#### B. Governing equations

In a recent paper, we have formulated the problem of the mixing of nonequilibrium phases. However, the work was limited to binary systems where interfacial composition only depends on temperature and pressure. Thus, the focus was on modeling the moving interface and accounting for bulk flow due to the fact that density changes during the mixing process. The current work relates to the mixing of multicomponent phases and focuses on the calculation of interfacial composition. For the sake of completeness, we will briefly present the governing equations for the bulk phases in a multicomponent mixture.

**Mass balance of each component is given by**

$$
\frac{\partial c}{\partial t} + \nabla \cdot (c \mathbf{v}) = 0,
$$

where $\mathbf{v}$ is the bulk velocity. The total mass balance is expressed by the continuity equation

$$
\frac{\partial n_i}{\partial t} + \nabla \cdot (\mathbf{v} n_i) = 0,
$$

and total mass balance is expressed by the continuity equation

$$
\frac{\partial c}{\partial t} + \nabla \cdot (c \mathbf{v}) = 0.
$$

In the simulated isothermal experiments, molar density $c$ is a function of pressure and composition. Using the chain rule, Eq. (11) can be expressed as

#### TABLE I. Initial and final values of pressure ($P$), liquid level ($h$), gas mole fractions ($n_i^G$), and liquid mole fractions ($n_i^L$) for the simulated mixing experiments. Nitrogen, methane, and n-decane are labeled as components 1, 2, and 3, respectively.

<table>
<thead>
<tr>
<th>Type</th>
<th>$P$ (bar)</th>
<th>$h$ (mm)</th>
<th>$n_1^G$</th>
<th>$n_2^G$</th>
<th>$n_3^G$</th>
<th>$n_1^L$</th>
<th>$n_2^L$</th>
<th>$n_3^L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ternary</td>
<td>Initial</td>
<td>137.3</td>
<td>10.0</td>
<td>0.190</td>
<td>0.810</td>
<td>1.000</td>
<td>0.987</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>132.9</td>
<td>10.2</td>
<td>0.006</td>
<td>0.374</td>
<td>0.620</td>
<td>0.026</td>
<td>0.961</td>
</tr>
<tr>
<td>Binary</td>
<td>Initial</td>
<td>137.3</td>
<td>10.0</td>
<td>0.190</td>
<td>0.810</td>
<td>1.000</td>
<td>0.987</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>Final</td>
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<td>0.620</td>
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<td>0.961</td>
</tr>
</tbody>
</table>
is more important in the gas phase while the latter dominates 
field is related to compressibility and nonideality. The former 
is one dimensional in the vertical direction. Thus, bulk ve-

equal to the rate of change in liquid level 
the velocity of the top and bottom boundaries are oppositely 
centered on and moving with the interface. This implies that 

\[ \frac{\partial c}{\partial P} \left( \frac{\partial P}{\partial t} + \bar{v} \cdot \nabla P \right) + \sum_{j=1}^{M-1} \frac{\partial c}{\partial n_i} \left( \frac{\partial n_i}{\partial t} + \bar{v} \cdot \nabla n_i \right) + c \nabla \cdot \bar{v} = 0. \]  

(12)

In laboratory-scale experiments, spatial variations in pressure 
have negligible impact on molar density and the pressure is 
assumed uniform. Combining, Eqs. (10) and (12) yields the 
final expression for total mass balance,

\[ \frac{\partial c}{\partial P} \frac{\partial P}{\partial t} - \frac{1}{c} \sum_{j=1}^{M-1} \frac{\partial c}{\partial n_i} (\nabla \cdot \bar{J}_j) + c \nabla \cdot \bar{v} = 0. \]  

(13)

Equation (13) implies that the divergence of the velocity 
field is related to compressibility and nonideality. The former 
is more important in the gas phase while the latter dominates 
in the liquid phase.

C. Reference frames and boundary conditions

It is convenient to solve the problem in the reference 
frame of the interface. Thus, the chosen coordinate system is 
centered on and moving with the interface. This implies that 
the velocity of the top and bottom boundaries are oppositely 
equal to the rate of change in liquid level \( \frac{dh}{dt} \). As the 
boundaries are impermeable, the same must be true for the 
bulk velocity as well, i.e.,

\[ v^G_z = - \frac{dh}{dt}, \quad z = H - h(t), \]  

(14a)

\[ v^L_z = - \frac{dh}{dt}, \quad z = -h(t). \]  

(14b)

Additionally, there is no diffusive flux through impermeable 
boundaries. Thus, according to Eq. (5), the mole fraction 
gradients must vanish,

\[ \frac{\partial n_i^G}{\partial z} = 0, \quad z = H - h(t), \quad i = 1, \ldots, M - 1, \]  

(15a)

\[ \frac{\partial n_i^L}{\partial z} = 0, \quad z = -h(t), \quad i = 1, \ldots, M - 1. \]  

(15b)

D. Bulk velocity

Assuming that the density gradient and gravity are al-
ways parallel, there is no natural convection and the problem 
is one dimensional in the vertical direction. Thus, bulk ve-
locity is strictly vertical and uniquely determined by mass 
balance. Solving Eq. (13) for the velocity gradient \( \frac{\partial v_z}{\partial z} \) 
and integrating from the top and bottom boundaries yields

\[ v^G_z = - \frac{dh}{dt} - \frac{\partial P}{\partial t} \int_{z}^{H} \frac{1}{c^G} \frac{\partial c^G}{\partial P} dz', \quad \frac{\partial h}{\partial t} \leq z \leq H - h(t), \]  

(16a)

\[ v^L_z = - \frac{dh}{dt} - \frac{\partial P}{\partial t} \int_{-h(t)}^{z} \frac{1}{c^L} \frac{\partial c^L}{\partial P} dz', \quad -h(t) \leq z \leq 0, \]  

(16b)

respectively.

E. Solution procedure

The mixing process is driven by composition differences 
between the interface and the bulk phases. Thus, the first step 
of the numerical solution algorithm is to compute the inter-
facial composition from Eq. (9). Subsequently, the rates of 
change in pressure, liquid level, and bulk composition are 
found from Eq. (10) and Eqs. (14)–(16). A brief outline of 
the numerical implementation is provided in the Appendix. A 
more detailed description is presented in Ref. 17.

IV. EXAMPLE

Consider a ternary system where a binary nitrogen-
decane liquid is exposed to a pure methane gas inside a con-
tainer of height \( H = 100 \) mm. The experiment is assumed isother-
al at temperature \( T = 120 \) °C. In order to focus on the 
effect of diffusion on interfacial composition, we seek to 
keep pressure variations small. This is achieved by choosing 
a small liquid fraction (10% of cell volume) and by allowing 
the liquid to be nearly saturated in nitrogen, initially. For 
comparison, we also simulate a binary experiment, where the 
nitrogen in the liquid phase is replaced by methane. Initial 
conditions for both mixtures as well as steady-state condi-
tions determined by constant volume phase-split calculations 
are summarized in Table I. In this work, fluid properties are 
calculated from the Peng–Robinson equation of state with
binary interaction coefficients of 0.10 between nitrogen and the other components and 0.05 between methane and decane. Additional input parameters are listed in Table II.

A. Pressure and liquid level evolution

In the ternary mixture there are three processes taking place: (1) methane substitutes nitrogen in the liquid, (2) additional methane dissolves in the liquid, and (3) decane evaporates into the gas phase. The first two are controlled by diffusion in the liquid phase, while the third is controlled by gas diffusion. At the high temperature and pressure conditions, diffusion coefficients are roughly one order of magnitude larger in the gas than in the liquid phase. However, due to the much smaller volume fraction, the diffusive time scale is significantly shorter in the liquid than in the gas.

Pressure and liquid level evolution in the ternary mixture are shown in Fig. 3. Initially, methane dissolution leads to a rapid decrease in pressure accompanied by an increase in liquid level. Methane-nitrogen substitution in the liquid phase occurs on the same time scale, but has negligible impact on pressure and liquid level. As the liquid phase approaches a pseudosteady state, the liquid level starts decreasing due to decane evaporation. The continuing pressure drop indicates that there is still a net flux of molecules into the liquid due to methane dissolution. However, methane molecules are much smaller than decane molecules and the liquid level decreases nevertheless.

As can be seen from Fig. 4 there is very little difference in pressure and liquid level evolution between the ternary and binary simulations. This is because methane-nitrogen substitution does not affect pressure and liquid level appreciably. The fundamental differences between the two systems are related to component fluxes.

B. Evolution of interfacial composition

Steady-state phase compositions are essentially the same for both mixtures. This is particularly true for the liquid phase. Consequently, methane flux into the liquid phase must be higher in the ternary mixture where nitrogen is being replaced than in the binary mixture where there is already a fair amount of methane present. The larger methane flux is partly countered by a flux of nitrogen leaving the liquid. In the ternary mixture, temporal changes in diffusive flux leads to variations in interfacial composition. As shown by Fig. 5, the mole fraction of nitrogen on the gas side of the interface is initially about three times greater than its steady-state value of 0.026. The evaporating nitrogen is transported into the gas phase by diffusion and the elevated interfacial concentration is necessary to generate a sufficiently large diffusive flux. At early times, the liquid-side mole fraction of nitrogen is also greater than its steady-state value (see Fig. 5). This ensures that the flux of nitrogen toward the interface matches the evaporation rate.

Interfacial composition is also influenced by the slight pressure drop occurring throughout the mixing process. However, conventional phase-split calculations performed at the final and initial pressures indicate that pressure induced variations are negligible compared to flux induced variations. In the binary mixture, interfacial composition is uniquely determined by temperature and pressure. Figure 6 shows that
the gas-side composition is virtually unaffected by the slight pressure drop. On the liquid side, methane concentration drops slightly due to a slight decrease in saturation (see Fig. 6).

C. Convective flux

Due to compressibility and nonideality, there is bulk flow in both phases and part of the mass transport is due to convection. Figure 7 shows snapshots of the diffusive, convective, and total fluxes of all components in the ternary mixture. While nitrogen flux is mainly diffusive, there are substantial convective contributions to the fluxes of methane and decane. Note that the convective fluxes do not vanish on the top and bottom boundaries, despite the fact that they are impermeable. The reason is that we are solving the problem in the reference frame of the interface where the top and bottom walls are moving with vertical velocity $-\partial h/\partial t$.

V. CONCLUDING REMARKS

The solution to the set of equations presented in Eq. (9) provides the composition at the interface between nonequilibrium phases. The derivations are valid for binary and multicomponent mixtures and they only depend on the fundamental assumptions of local thermodynamic equilibrium and mass balance across the interface. Thus, the equations are more general than previously published expressions for interfacial composition. The results show that interfacial composition in multicomponent mixtures depends on diffusive flux and consequently on diffusion coefficients. This is fundamentally different from binary mixtures where interfacial composition only depends on temperature and pressure.

Although constant temperature is assumed in the example, the derivations hold whenever temperature is continuous across the interface. When temperature is not constant, energy balance in the bulk phases combined with a heat flux balance across interface which properly accounts for the heat absorbed (produced) as a result of evaporation (condensation) provides the additional equation needed to determine the rate of change in temperature. Moreover, the results can be extended to curved interfaces by using the Young–Laplace equation to account for the pressure jump.

Papers in literature on mass transfer between two multicomponent phases assume one of them to be in quasisteady state and use an equation of state to find the composition on the opposite side of the interface. In contrast, the current work is applicable at all times, including the transient time before any of the phases approaches steady-state.

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APPENDIX: NUMERICAL SOLUTION PROCEDURE

In the simulations we use a finite difference scheme to find the rates of change in liquid level $\partial h/\partial t$, pressure $\partial P/\partial t$, and phase compositions $\partial n_i^G/\partial t$ and $\partial n_i^L/\partial t$. The information is used to update the state of the system and the process is repeated until convergence.

1. Discretization

The computational domain is divided into two subdomains, one for each phase. The gas and liquid subdomains are discretized by $N_G^2 + 1$ and $N_L^2 + 1$ nodes, respectively. In this paper the symbol $k$ is used as the node index. Gas nodes
The composition at all bulk nodes to be solved for in the interfacial flash routine are the mole derivatives from the previous time step. Thus, the unknowns the initial condition or has been updated based on the time node at the interface

$$z = 0.$$ The composition at the interface is determined by solving Eq. (9) where mole fraction gradients at the interface are evaluated by

$$\frac{\partial n^G_z}{\partial z} \bigg|_{z=0} = \frac{(n^G_{i,k-1} - n^G_{i,k})}{\Delta z^G},$$

$$\frac{\partial n^L_z}{\partial z} \bigg|_{z=0} = \frac{(n^L_{i,k-1} - n^L_{i,k})}{\Delta z^L}.\quad (A1a)$$

The composition at all bulk nodes ($k \neq 0$) are known from the initial condition or has been updated based on the time derivatives from the previous time step. Thus, the unknowns to be solved for in the interfacial flash routine are the mole fractions $n^G_{i,k=0}$ and $n^L_{i,k=0}$, and the bulk velocities $v^G_{i,k=0}$ and $v^L_{i,k=0}$ at the interface.

### 4. Phase properties

At this point, the composition is known everywhere. The next step is to calculate diffusion coefficients $D_{ij}$ and molar density $c$ as well as its derivatives with respect to pressure $\partial c/\partial P$ and composition $\partial c/\partial n_i$. Diffusion coefficients are computed from the correlation proposed by Leahy-Dios and Firoozabadi. The other properties are obtained from the Peng–Robinson equation of state.

### 5. Rates of change in pressure and liquid level

Using Fick’s law, the divergence of diffusive flux $\nabla \cdot \tilde{J}_i$ is now determined numerically. Subsequently, the integrals of Eq. (16) are evaluated to get expressions for bulk velocities $v^G_z$ and $v^L_z$ as functions of the rates of change in pressure $\partial P/\partial t$ and liquid level $\partial h/\partial t$. Evaluating the functions at the interface $z=0$ and comparing the results to the interfacial velocities found by interfacial flash allows us to calculate $\partial P/\partial t$ and $\partial h/\partial t$.

### 6. Rates of change in composition

Using the values of $\partial P/\partial t$ and $\partial h/\partial t$ in Eq. (16) determines the bulk velocity in both phases. This allows us to compute the rates of change in composition from the expression for local component balance in Eq. (10).

### 7. Performing a time step

As is true for all explicit finite difference schemes, the change in all quantities are found by multiplying by their time derivatives by a predetermined time step $\Delta t$. However, because we are using a dynamic mesh, the location of the...
end nodes must also be updated. As the total volume is fixed, both end nodes must move the same distance \((\partial h / \partial t)\Delta t\).


17 K. B. Haugen and A. Firoozabadi, “Mixing of two binary nonequilibrium phases in one dimension,” *AIChE J.* (to be published).