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Short Communication

Highlighting multiplicity in the Gilliland solution to the Maxwell-Stefan equations describing diffusion distillation



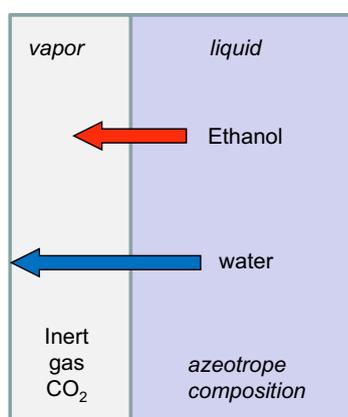
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HIGHLIGHTS

- Alcohol/water mixtures can be separated by diffusion through inert gas.
- The efficacy of separation improves with higher molar mass of inert gas.
- The Gilliland equations yield three different solution sets, only one is realistic.
- The Prigogine minimum entropy production principle identifies the physically correct solution.
- If porous barriers are used, the pore diameter should be large enough to ensure bulk diffusion.

GRAPHICAL ABSTRACT



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ABSTRACT

This article investigates the separation of ethanol/water, and 2-propanol/water liquid mixtures of azeotropic composition by allowing diffusion through six different inert gases: helium, nitrogen, air, argon, CO₂, and xenon. The Maxwell-Stefan (M-S) equations afford a rigorous quantification of the achievable separation. For steady-state transfer, analytic solutions to the M-S formulation were obtained in parametric form by Gilliland. For each investigated system in this study, the Gilliland approach yields three different solution sets for the transfer fluxes of alcohol and water; only one of these is physically realizable in practice. The physically realistic solution can be identified by invoking the Prigogine principle of minimum entropy production. Robust computational algorithms are essential for modeling and development of diffusion distillation technology; these are indicated.

The efficacy of diffusion distillation depends on differences in alcohol-inert and water-inert friction in the vapor phase; such differences increase with increasing molar mass of the inert component. Inert gases such as CO₂ and Xe are more effective than lighter inerts such as air, nitrogen or helium. Some of the strategies in the published literature, involve interposing porous barriers between the vapor and liquid phases; the choice of the pore diameter influences the efficacy of diffusion distillation. For alcohol/water mixtures, it is preferable to choose the pore diameter such that “bulk” diffusion, rather than Knudsen diffusion regime prevails inside the pores.

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Nomenclature

c_t	total molar concentration of mixture, mol m ⁻³
d_p	diameter of pore, m
\mathcal{D}_{ij}	M-S binary pair diffusivity, m ² s ⁻¹
$D_{i,Kn}$	Knudsen diffusivity of species i , m ² s ⁻¹
$[D]$	diffusivity matrix, m ² s ⁻¹
$[I]$	identity matrix, dimensionless
M_i	molar mass of species i , kg mol ⁻¹
N_i	molar flux of species i , mol m ⁻² s ⁻¹
p_i	partial pressure, Pa
p_t	total pressure, Pa
P_i^0	vapor pressure, Pa
R	gas constant, 8.314 J mol ⁻¹ K ⁻¹
t	time, s
T	absolute temperature, K
x_i	mole fraction of component i in liquid phase, dimensionless
y_i	mole fraction of component i in vapor phase, dimensionless

z direction coordinate, m

Greek letters

γ_i	activity coefficient of component i , dimensionless
δ	film thickness, m
δ_{ij}	Kronecker delta, dimensionless
η	dimensionless distance in diffusion layer, dimensionless
λ_i	eigenvalues of $[\Phi]$, dimensionless
σ	rate of entropy production, J m ⁻³ s ⁻¹ K ⁻¹
Φ_{ij}	dimensionless mass transfer rate factors, dimensionless

Subscripts

0	referring to position, $z = 0$
δ	referring to position, $z = \delta$
1	component 1
2	component 2
3	component 3

1. Introduction

For a binary alcohol(1)/water(2) mixture, the vapor-liquid equilibrium is described by $y_i = \gamma_i x_i P_i^0 / p_t$; at the azeotropic composition, we have $y_i = x_i$. Binary mixtures of azeotropic composition cannot be separated by conventional distillation because there is no driving force for transfer from liquid to vapor phase, and vice versa. The addition of an entrainer (species 3) is a common strategy employed in azeotropic and extractive distillation processes; the addition of the entrainer serves to alter the phase equilibrium thermodynamics in such a manner as to allow complete separation of species 1, and 2. Such processes are energy-intensive because of the need for solvent recovery in an additional distillation column. There is considerable research on developing energy-efficient alternatives to azeotropic and extractive distillation processes. One such alternative involves the introduction of an “inert” gas as species 3 (Fullarton and Schlünder, 1986). The separation principle is based on the differences in the interfacial mass transfer fluxes (N_1 , and N_2) of components 1 and 2 in the ternary mixture (1, 2, and 3). Essentially, the separation relies on maintaining conditions such that the ratio of fluxes N_1/N_2 is significantly different from the corresponding ratio of mole fractions of the azeotrope, x_1/x_2 . In the absence of the third component, we must have $N_1/N_2 = x_1/x_2 = y_1/y_2$, as there is no driving force during condensation or evaporation for each of the components of a mixture with azeotropic composition. When an inert non-condensable, is introduced into the vapor phase, this allows mixtures of azeotropic composition to be separated because the vapor compositions are altered and driving forces for component transfers are “created”.

Diffusional effects have been exploited to separate alcohol/water mixtures of azeotropic composition by distillation in the presence of an inert gas such as helium, nitrogen, air, argon, and CO₂ (Fullarton and Schlünder, 1986; Singh and Prasad, 2011). Experimental verification of the efficacy of the diffusion distillation concept has been established in wetted-wall columns (Fullarton and Schlünder, 1986; Singh and Prasad, 2011, 2015; Ziobrowski et al., 2009). The same separation principle prevails in other constructs in which a porous barrier, or membrane, is interposed between the liquid and vapor/gas phases; such separations have been variously termed “sweep-gas distillation”, or “frictional distillation” (Banat et al., 1999a, 1999b; Breure et al., 2008).

It must be remarked that the concept of deliberate addition of a third component to enable diffusion-selective separation was

already developed in the 1950s (Cichelli et al., 1951; Keyes and Pigford, 1957). These early research activities were focused on the separation of gaseous isotopes by diffusing through a third component in the form of a condensable vapor. The following quote from Keyes and Pigford (1957) is both illuminating and instructive *partial separation of the components of a binary gas mixture can be effected by diffusion at constant total pressure through a third gas or vapor, provided there exists a difference in diffusivities of the components with respect to the vapor. The third component is commonly called the separating agent.*

Diffusion distillation, and indeed all sweep diffusion processes, place heavy reliance on the proper description of molecular diffusion phenomena in the gaseous phase. Rigorous models to describe the diffusion of three-component gas mixtures are required, and it is therefore no real surprise that the earliest practical applications of the Maxwell-Stefan (M-S) diffusion formulations are to be found in the analysis of sweep diffusion processes for separating gaseous isotopes (Cichelli et al., 1951; Keyes and Pigford, 1957).

For diffusion of a binary mixture (components 1, and 2) in the presence of an inert, non-transferring component (3), at constant pressure and temperature, the M-S equations take the form (detailed derivations are provided in the Supplementary material accompanying this publication)

$$\begin{aligned} -c_t \frac{dy_1}{dz} &= \frac{y_2 N_1 - y_1 N_2}{D_{12}} + \frac{y_3 N_1}{D_{13}}; \\ -c_t \frac{dy_2}{dz} &= \frac{y_1 N_2 - y_2 N_1}{D_{12}} + \frac{y_3 N_2}{D_{23}} \end{aligned} \quad (1)$$

For separations operating at steady-state, we need to determine the transfer fluxes, N_1 , and N_2 , by solving the set of two independent Eqs. (1) together with the boundary conditions

$$\begin{aligned} z = 0; \quad (y) &= (y_0) \\ z = \delta; \quad (y) &= (y_\delta) \end{aligned} \quad (2)$$

At first sight, the task of determining the fluxes N_1 , and N_2 seems simple and straightforward; it is neither. The earliest published solution to Maxwell-Stefan equations (1) should be credited to Edwin Richard Gilliland, one of the pioneering founders of the chemical engineering profession. Gilliland developed an analytic solution in the parametric form of Eqs. (3) and (4) below:

$$\frac{N_1}{D_{13}} + \frac{N_2}{D_{23}} = \frac{c_t}{\delta} \ln \left(\frac{y_{3\delta}}{y_{30}} \right) \quad (3)$$

and

$$\frac{N_1 + N_2}{D_{12}} = \frac{c_t}{\delta} \ln \left(\frac{y_{1\delta} \frac{N_1 + N_2}{N_1} - \left(\frac{1}{D_{12}} - \frac{1}{D_{13}} \right) \frac{N_1 + N_2}{N_2} y_{2\delta} - \left(\frac{1}{D_{13}} - \frac{1}{D_{23}} \right)}{y_{10} \frac{N_1 + N_2}{N_1} - \left(\frac{1}{D_{12}} - \frac{1}{D_{13}} \right) \frac{N_1 + N_2}{N_2} y_{20} - \left(\frac{1}{D_{13}} - \frac{1}{D_{23}} \right)} \right) \quad (4)$$

Eqs. (3) and (4) were published in the 1st edition of *Absorption and Extraction*, authored by Thomas Kilgore Sherwood (Sherwood, 1937), another pioneer in mass transfer. Eqs. (3) and (4) are also available in the classic paper of Herbert Lawrence Toor (Toor, 1957). The fluxes N_1 and N_2 may be determined with say the Excel solver, using starting guess values. Sherwood (1937) demonstrated the utility of the Gilliland solution by means of an illustrative example for absorption of NH_3 (1) and water vapor (2) from air (3) into water. For a chosen set of conditions, three distinct sets of solutions for the fluxes N_1 and N_2 were obtained, depending on the starting guess values. On the basis of physical arguments, only one of these sets was considered to be physically realizable in practice. Later editions of the classic 1937 book of Sherwood, do not contain any discussions of Maxwell–Stefan equations, and the Gilliland solutions are omitted (Sherwood et al., 1975). Readers who do not have access to the 1937 edition of Sherwood's book, will find the discussions of the multiple solutions for $\text{NH}_3(1)/\text{H}_2\text{O}(2)/\text{Air}(3)$ diffusion in the Supplementary material accompanying this paper; see also (Krishna, 1977). The use of the Gilliland equations for flux calculations is also illustrated by the work of Bröcker and Schulze (1991).

The objectives of the current investigation of diffusion distillation are four-fold. The first objective is to investigate the multiplicity of fluxes that result from use of Eqs. (3) and (4) when applied to diffusion distillation. We address the question of determining the physically realistic set of fluxes by invoking the Prigogine principle of minimum entropy production (Prigogine, 1961). The second objective is to elucidate the choice of the inert gas on the separation performance. Specifically, we aim to rationalize the experiments of Singh and Prasad (2011, 2015) in which the separation selectivity was found to be strongly dependent on the choice of the inert gas: helium, air, or argon. The third objective is to investigate the role of the porous barrier that is often interposed between the vapor and liquid phases. Is the porous barrier essential, and are there fundamental guidelines for choice of the pore sizes of such barriers? The fourth, and final objective is to apply the Prigogine entropy concepts in analyzing steady-state multiplicity in multicomponent diffusion with heterogeneous catalyzed reaction; the analysis is relevant in the context of reactive distillation (Higler et al., 1999; Taylor and Krishna, 2000).

The Supplementary material accompanying this publication, available for download in the online version of this article, provides detailed derivations of model equations, numerical solution methodology used, and data inputs.

2. Multiplicity of Gilliland solutions in diffusion distillation

Consider mass transfer between the liquid and vapor phase for ethanol(1)/water(2)/ CO_2 (3). The mass transfer resistance is assumed to be restricted to the vapor phase, and the effective film thickness of the gas phase resistance is $\delta = 1$ mm. Assume that the liquid phase is the binary mixture ethanol(1)/water(2) at $T = 343.15$ K. The azeotropic composition at this temperature can be calculated as $x_1 = 0.87$, $x_2 = 0.13$. Let us bring this liquid mixture in contact with an inert gas phase consisting of the CO_2 (=species 3). The vapor pressure of ethanol at 343.15 K is 71.2 kPa, and the

vapor pressure of water at 343.15 K is 31.2 kPa. The total gas phase pressure $p_t = 101.3$ kPa. The composition of the vapor phase at the gas/liquid interface in equilibrium with the liquid mixture can be calculated from $y_i = \gamma_i x_i P_i^0 / p_t$. This yields $y_{1\delta} = 0.6177$, $y_{2\delta} = 0.09264$, $y_{3\delta} = 0.2897$. The bulk vapor composition is taken to be: $y_{10} = 0.0$, $y_{20} = 0.0$, $y_{30} = 1.0$. The driving forces are $\Delta y_1 = y_{10} - y_{1\delta} = -0.6177$, and $\Delta y_2 = y_{20} - y_{2\delta} = -0.09264$. Both driving forces are directed from liquid to the vapor phase.

The values of the vapor phase M-S diffusivities of the three binary pairs at 343.15 K, calculated using the (Fuller et al., 1966) method, are $D_{12} = 2.05$; $D_{13} = 1.27$; $D_{23} = 2.67 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$; these diffusivities are independent of composition.

Depending on the starting guess used in any equation solver, there are three distinct sets of solutions to Eqs. (3) and (4), called Gilliland sets A, B, and C. Our solutions are based on the Given-Find solve block of MathCad 15 (PTC, 2013).

Good starting guess values for the transfer fluxes can be obtained using a simplified linearized solution to Eqs. (1), as proposed by (Krishna, 1981)

$$\begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = \frac{c_t}{\delta} [D] \begin{pmatrix} y_{10} - y_{1\delta} \\ y_{20} - y_{2\delta} \end{pmatrix} \quad (5)$$

in which the diffusivity matrix

$$[D] = \begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} = \frac{\begin{bmatrix} \frac{y_1}{D_{12}} + \frac{y_2}{D_{23}} & \frac{y_1}{D_{12}} \\ \frac{y_2}{D_{12}} & \frac{y_2}{D_{12}} + \frac{y_3}{D_{13}} \end{bmatrix}}{\left(\frac{y_1 y_3}{D_{12} D_{13}} + \frac{y_2 y_3}{D_{12} D_{23}} + \frac{y_3 y_2}{D_{13} D_{23}} \right)} \quad (6)$$

is evaluated at the arithmetic average vapor compositions $y_{i,av} = (y_{i0} + y_{i\delta})/2$. With this simplification, the fluxes can be evaluated explicitly as follows $N_1 = -0.446$; $N_2 = -0.11 \text{ mol m}^{-2} \text{ s}^{-1}$. Using these values at starting guesses, the Gilliland A solution set is obtained: $N_1 = -0.506$; $N_2 = -0.14$; both fluxes are directed from the liquid to the vapor phase. The ratio of the flux of water to that of ethanol is $N_2/N_1 = 0.225$; this ratio is higher than the ratio of the compositions in the liquid phase $x_2/x_1 = 0.15$. Diffusional evaporation leads to a relatively higher proportion of water in the vapor phase, causing separation of the azeotrope.

If the starting guess values are chosen as $N_1 = -0.3$; $N_2 = -0.27$, the Gilliland B solution set is obtained: $N_1 = -0.2476$; $N_2 = -0.6546$, yielding a flux ratio $N_2/N_1 = 2.64$. Remarkably, in this case, the flux of water is significantly higher than the flux of ethanol. There is no fundamental physical reasoning that allows us to discount, a priori, the set of fluxes obtained in the Gilliland set B.

If the starting guess values are chosen to be $N_1 = -0.3$; $N_2 = 0.1$, we obtain the Gilliland C solution set: $N_1 = -1.073$; $N_2 = 1.073$, yielding a flux ratio $N_2/N_1 = -1$. Indeed it is easy to check that $N_1 + N_2 = 0$ always satisfies Eq. (4), as also pointed out by Toor (1957).

Three different solution sets are also realized by choosing the inert gas to be helium, nitrogen, air, argon, and xenon; plots of the flux ratios N_2/N_1 for Gilliland A, B, C solution sets are presented in Fig. 1a as a function of the square root of the molar mass of the inert gas. The choice of the inert gas influences the relative values of 1–3 friction and 1–2 friction. The friction is inversely proportional to the corresponding M-S diffusivity pairs D_{ij} . The M-S diffusivity D_{ij} is inversely proportional to the square root of the mean molar mass of the pairs $\sqrt{M_{ij}}$. We should therefore expect the ratio of fluxes to depend on the square root of the molar mass of the inert gas, $\sqrt{M_3}$. Also plotted in Fig. 1a are the flux calculations using the linearized Eq. (5); the flux ratios are above 10% higher than those of Gilliland A set of values.

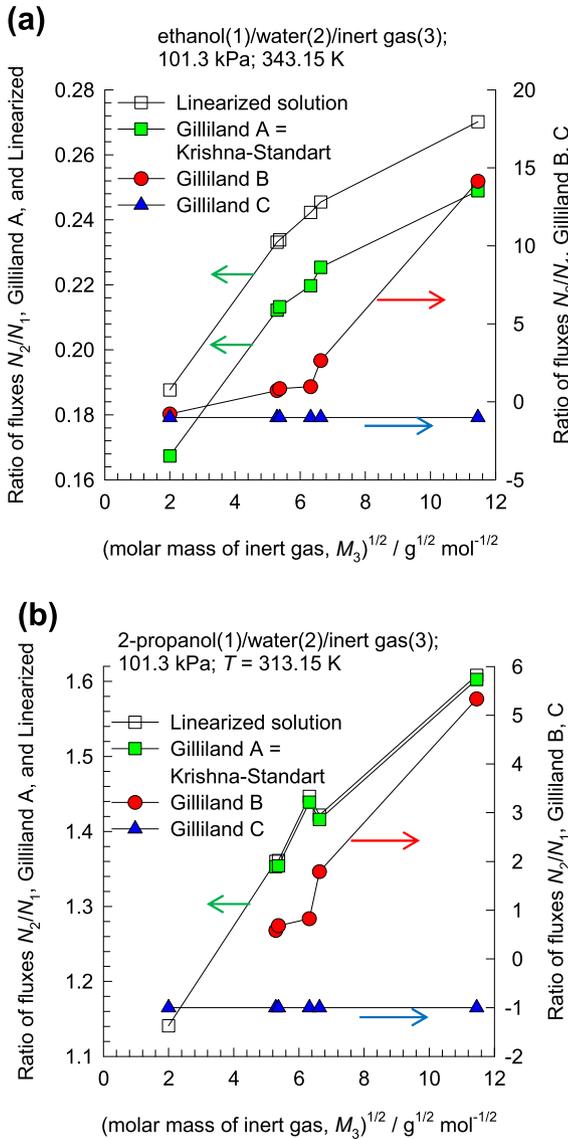


Fig. 1. Comparison of ratio of steady-state fluxes N_2/N_1 for diffusional evaporation of (a) ethanol/water, and (b) 2-propanol/water into vapor phase containing inert gas. The flux ratios are obtained using six different inert gases as component 3: helium, nitrogen, air, argon, CO_2 , and xenon as inert gas. The x-axis is the square root of the molecular weight of the inert gas $\sqrt{M_3}$.

For 2-propanol(1)/water(2) mixtures the azeotrope composition at 313.15 K is $x_1 = 0.62258$, $x_2 = 0.37742$; the ratio of the mole fraction of water to that of propanol is $x_2/x_1 = 0.60624$. Let us bring this liquid mixture in contact with an inert gas phase. The vapor pressure of ethanol at 313.15 K is 13.6 kPa, and the vapor pressure of water at 313.15 K is 7.36 kPa. The total gas phase pressure $p_t = 101.3$ kPa. The composition of the vapor phase at the gas/liquid interface in equilibrium with the liquid mixture can be calculated from $y_i = \gamma_i x_i P_i^0 / p_t$. This yields $y_{1\delta} = 0.09836$, $y_{2\delta} = 0.05963$, $y_{3\delta} = 0.84201$. The bulk vapor composition is taken to be: $y_{10} = 0.0$, $y_{20} = 0.0$, $y_{30} = 1.0$. The driving forces are $\Delta y_1 = y_{10} - y_{1\delta} = -0.09836$, and $\Delta y_2 = y_{20} - y_{2\delta} = -0.05963$. Both driving forces are directed from liquid to the vapor phase. Depending on the starting guess values for the fluxes, Eqs. (3) and (4) yields multiple solutions; plots of the flux ratios N_2/N_1 for Gilliland A, B, C solution sets are presented in Fig. 1b as a function of the square root of the molar mass of the inert gas.

3. The Krishna-Standart analytic solution for diffusion distillation

The solution method of Krishna and Standart (1976) will now be applied to calculate the fluxes in diffusion distillation. We define a dimensionless distance: $\eta = z/\delta$, introduce the equality $y_3 = 1 - y_1 - y_2$, and re-cast Eqs. (1) using matrix notation

$$\begin{pmatrix} \frac{dy_1}{d\eta} \\ \frac{dy_2}{d\eta} \end{pmatrix} = [\Phi] \begin{pmatrix} y_1 \\ y_2 \end{pmatrix} - \frac{\delta}{c_t} \begin{pmatrix} \frac{N_1}{D_{13}} \\ \frac{N_2}{D_{23}} \end{pmatrix} \quad (7)$$

where we define a two-dimensional square matrix of dimensionless fluxes, that are η -invariant

$$[\Phi] = \frac{\delta}{c_t} \begin{bmatrix} \frac{N_1}{D_{13}} + \frac{N_2}{D_{12}} & -N_1 \left(\frac{1}{D_{12}} - \frac{1}{D_{13}} \right) \\ -N_2 \left(\frac{1}{D_{12}} - \frac{1}{D_{23}} \right) & \frac{N_2}{D_{23}} + \frac{N_1}{D_{12}} \end{bmatrix} \quad (8)$$

Eq. (7) represents a system of coupled ordinary differential equations with constant coefficients. The system of equations can be solved analytically to obtain the mole fraction profiles within the diffusion layer

$$(y_\eta - y_0) = -[\exp[\Phi]\eta - [I]][\exp[\Phi] - [I]]^{-1}(y_0 - y_\delta) \quad (9)$$

In Eq. (9), $[I]$ is the identity matrix with Kronecker delta δ_{ik} as elements. The composition gradient at the position $\eta = z/\delta$ can be obtained by differentiation of Eq. (9); we get

$$\frac{d(y_\eta)}{d\eta} = -[\Phi][\exp[\Phi]\eta][\exp[\Phi] - [I]]^{-1}(y_0 - y_\delta) \quad (10)$$

The steady-state transfer fluxes of components 1, and 2 can be determined by combining Eqs. (1) and (10)

$$\begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = -\frac{c_t}{\delta} [D_\eta] \frac{d(y_\eta)}{d\eta} = \frac{c_t}{\delta} [D_\eta][\Phi][\exp[\Phi]\eta][\exp[\Phi] - [I]]^{-1}(y_0 - y_\delta) \quad (11)$$

The diffusivity matrix $[D_\eta]$ can be evaluated from Eq. (6) using the appropriate gas phase mole fractions. Without loss of generality, we may evaluate the diffusivity $[D_\eta]$ at position $\eta = z/\delta = 0$, and obtain

$$\begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = -\frac{c_t}{\delta} [D_{\eta=0}] \frac{d(y)}{d\eta} \Big|_{\eta=0} = \frac{c_t}{\delta} [D_{\eta=0}][\Phi][\exp[\Phi] - [I]]^{-1}(y_0 - y_\delta) \quad (12)$$

The Sylvester theorem, detailed in Appendix A of Taylor and Krishna (1993) is required for explicit calculation of $[\Phi][\exp[\Phi] - [I]]^{-1}$. Though the expression (12) appears to be explicit in the fluxes, it is to be noted that the matrix $[\Phi][\exp[\Phi] - [I]]^{-1}$ is also a function of the fluxes. In the limit of vanishingly small transfer fluxes we have the limiting behavior $[\Phi][\exp[\Phi] - [I]]^{-1} \rightarrow [I]$. In this work, the set of coupled algebraic equations (12) were solved iteratively using the Given-Find solve block of MathCad 15 (PTC, 2013) using starting guesses for the fluxes. For all mixtures investigated, the final converged values of the fluxes are identical to Gilliland A set for ethanol/water/inert, and 2-propanol/water/inert, irrespective of the starting guess values; see Fig. 1a and b.

The eigenvalues λ_1, λ_2 of $[\Phi]$ provide valuable insights into the characteristics of sets A, B, and C of the Gilliland solutions. The Gilliland set A corresponds to the case in which the eigenvalues λ_1, λ_2 are both distinct, and non-zero. The Gilliland set B corresponds to the case in which the eigenvalues λ_1, λ_2 are equal to each other. The Gilliland set C corresponds to the case in which the second eigenvalue is zero, $\lambda_2 = 0$. Details of the numerical values of λ_1, λ_2

for all mixtures investigated are provided in the [Supplementary material](#).

What fundamental principle can we employ to decide between Gilliland sets A, B, and C?

4. The Prigogine principle of minimum entropy production

The second law of thermodynamics dictates that the rate of entropy production must be positive definite, $\sigma \geq 0$; the situation $\sigma = 0$ manifests at thermodynamic equilibrium (Prigogine, 1961; Standart et al., 1979). For the ternary gas diffusion with $N_3 = 0$, the rate of entropy production is (detailed derivations in [Supplementary material](#))

$$\sigma = -R \left[N_1 \frac{1}{y_1} \frac{dy_1}{dz} + N_2 \frac{1}{y_2} \frac{dy_2}{dz} \right] \geq 0 \quad (13)$$

The Prigogine principle of minimum entropy production says that the steady state of an irreversible process, i.e., the state in which the thermodynamic variables are independent of the time, is characterized by a minimum value of the rate of entropy production (Prigogine, 1961).

We illustrate the application of the Prigogine principle by considering diffusional evaporation of 2-propanol(1)/water(2) into inert CO₂ (species 3).

Using the fluxes calculated from the linearized Eq. (6): $N_1 = -0.0384$; $N_2 = -0.0546 \text{ mol m}^{-2} \text{ s}^{-1}$, as starting guess values, Eqs. (3) and (4) yields the Gilliland A set of fluxes: $N_1 = -0.0386$; $N_2 = -0.0546 \text{ mol m}^{-2} \text{ s}^{-1}$, with $N_2/N_1 = 1.416$; the rate of entropy production is $\sigma = 1.55 \text{ kJ m}^{-3} \text{ s}^{-1} \text{ K}^{-1}$.

If the starting guess values are chosen to be $N_1 = -0.03$; $N_2 = -0.05 \text{ mol m}^{-2} \text{ s}^{-1}$, deviating only slightly from the Gilliland A set values, we obtain the Gilliland B solution set: $N_1 = -0.0352$; $N_2 = -0.0631 \text{ mol m}^{-2} \text{ s}^{-1}$, yielding a flux ratio $N_2/N_1 = 1.79$; the rate of entropy production is $\sigma = 1.63 \text{ kJ m}^{-3} \text{ s}^{-1} \text{ K}^{-1}$. A further noteworthy point is that the magnitude of the flux ratios for Gilliland sets A and B are close to one another, and neither set can be discarded by subjective hand-waving.

If the starting guess values are chosen to be $N_1 = -0.04$; $N_2 = 0.05 \text{ mol m}^{-2} \text{ s}^{-1}$, we obtain the Gilliland C solution set: $N_1 = -0.0997$; $N_2 = 0.0997 \text{ mol m}^{-2} \text{ s}^{-1}$, yielding a flux ratio $N_2/N_1 = -1$; the rate of entropy production $\sigma = 0$. A null entropy production at steady-state is not a physically acceptable situation,

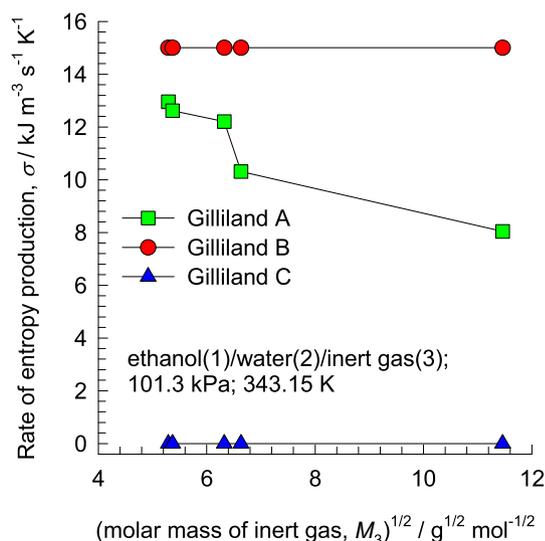


Fig. 2. Rate of entropy production, σ , for diffusional evaporation of ethanol (1)/water (2) into vapor phase containing inert gas (3).

and we conclude that Gilliland set C is not realizable in practice; counter-diffusion of alcohol and water cannot be a physically realistic solution. On the basis of the Prigogine principle, we must conclude that Gilliland set A is the one that can be realized in practice because it produces entropy at a lower rate than for the set B.

For ethanol/water/inert gas mixtures, the rates of entropy production for the solution sets A, B, and C are plotted in Fig. 2. The rate of entropy production for set C is zero, that is only possible at thermodynamic equilibrium; this set C can be discounted on the basis that equimolar counter-diffusion of ethanol/water is not a physically realistic solution. The Gilliland set A is the one that is physically realizable because it produces entropy at a lower rate.

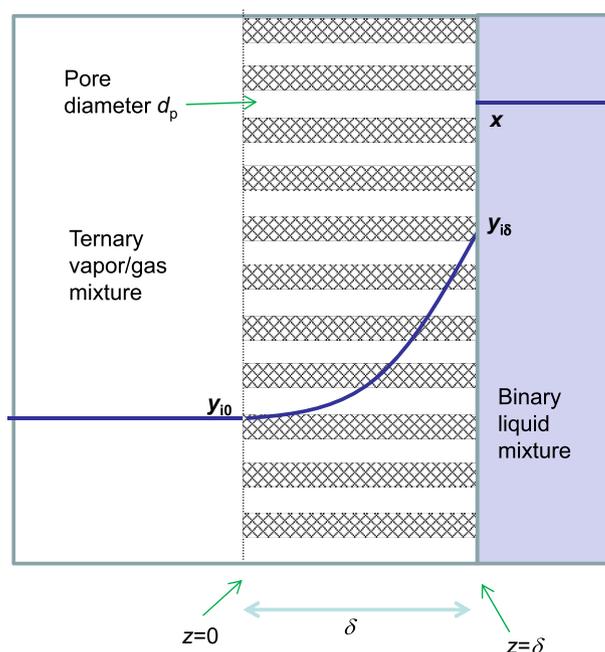


Fig. 3. Schematic showing vapor/liquid transfer across an inert porous barrier.

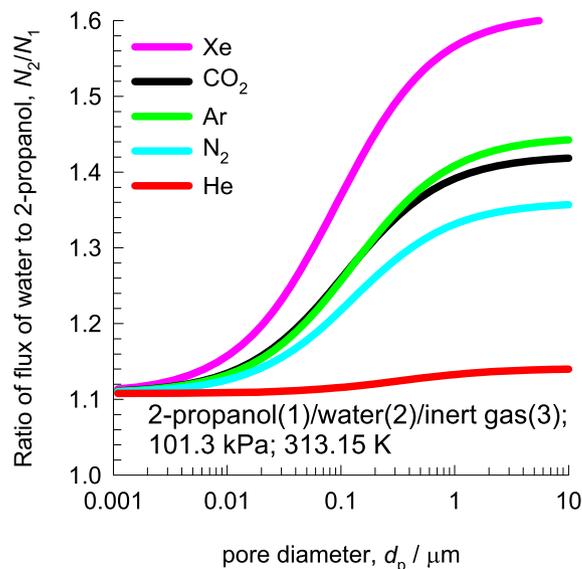
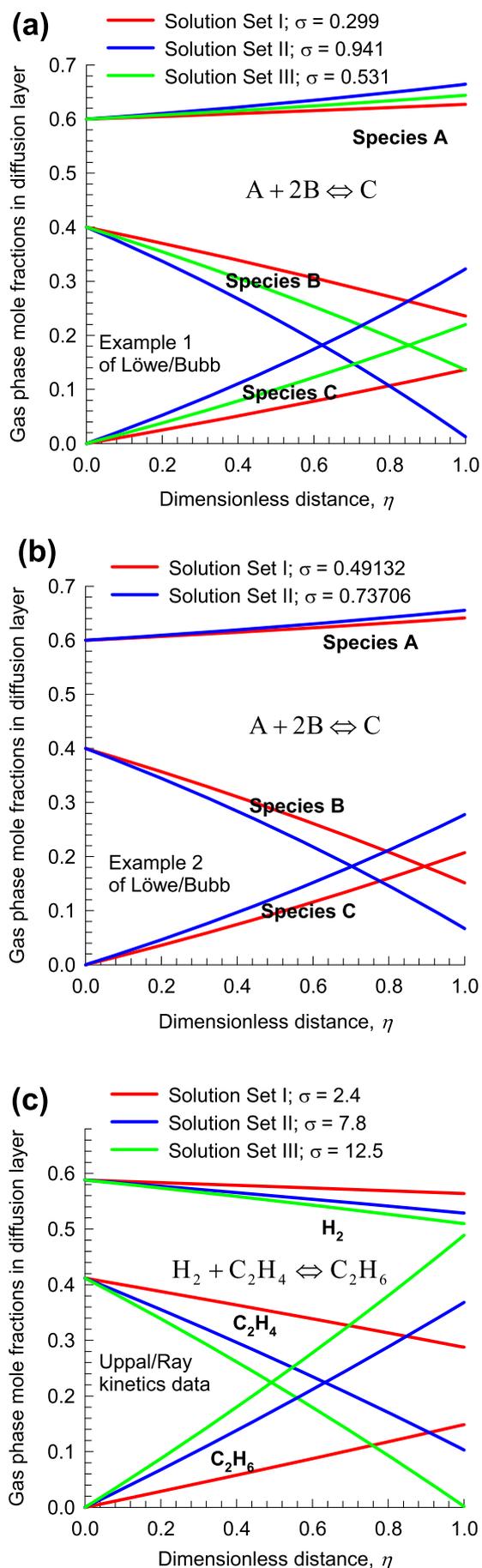


Fig. 4. Comparison of ratio of quasi-stationary fluxes N_2/N_1 for 2-propanol (1)/water (2)/inert gas (3), plotted as a function of pore diameter, d_p , of the barrier interposed between the vapor and liquid phases.



Experimental verification that the Gilliland solution set A is the physically realizable solution is provided by experimental data of Carty and Schrodt (1975) for diffusional evaporation of acetone/methanol into air. For the set of boundary conditions in their experiments, three solution sets are obtained. Of the three solution sets, only Gilliland set A yields composition profiles, and transfer fluxes, that are in agreement with the experimental data; see Fig. S4. The use of the Prigogine principle of minimum entropy production, as suggested in this work, obviates the need for using experimental data to decide on the choice of the physically realizable solution.

For steady-state equimolar diffusion in ternary gas mixtures, $N_1 + N_2 + N_3 = 0$, Toor (1957) has presented analytic solutions in parameter form, analogous to Eqs. (3) and (4); the Toor solutions also result in multiplicity of solutions. The Prigogine principle of minimum entropy production allows the selection of the physically realizable solution; see Supplementary material for detailed discussions and calculations.

From the results in Fig. 1a we must conclude that for accurate calculation of the ethanol/water fluxes, we must use Eq. (12); somewhat lower accuracy is obtained using the linearized Eq. (5). For 2-propanol/water/inert system, the linearized solution is practically identical to the results from the exact Krishna-Standart model; see Fig. 1b. This is because the 2-propanol/water/inert system was investigated at a lower temperature of 313.15 K at which the compositions of both 2-propanol and water in the gas phase are low. The separation efficacy, quantified by N_2/N_1 , appears to correlate with $\sqrt{M_3}$, broadly in agreement with the experimental results of Singh and Prasad (2011) for ethanol/water separations in a wetted-wall column using different inert gases. Simulations of transient diffusion between a liquid film and a stagnant vapor slab, more representative of wetted-wall columns, lead to the same conclusions regarding the influence of the choice of the inert gas; see Figs. S12–S16 of the Supplementary material.

5. Imposition of porous barriers between liquid and vapor phases

In view of scale-up limitations of wetted-wall columns, porous barriers are often interposed between the liquid and vapor phases (Breure et al., 2008) in experimental set-ups for diffusion distillation. Fig. 3 shows a schematic of vapor/liquid transfer across an inert porous barrier. From the conceptual point of view, the porous barrier is also to be considered as an “inert” fourth component in the quaternary system alcohol(1)/water(2)/inert gas (3)/inert barrier(component m). Extending Eq. (5), we may write for a barrier (membrane) with pore diameter, d_p (see (Krishna, 2016) for further background information)

$$\begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = \frac{c_t}{\delta} \begin{pmatrix} \frac{y_1}{D_{12}} + \frac{y_3}{D_{23}} + \frac{1}{D_{2,Kn}} \frac{y_1}{D_{12}} \\ \frac{y_2}{D_{12}} \end{pmatrix} \begin{pmatrix} \frac{y_2}{D_{12}} + \frac{y_3}{D_{13}} + \frac{1}{D_{1,Kn}} \\ \frac{y_2}{D_{23}} + \frac{1}{D_{2,Kn}} \end{pmatrix} \begin{pmatrix} y_{10} - y_{1\delta} \\ y_{20} - y_{2\delta} \end{pmatrix} \quad (14)$$

where the Knudsen diffusivity values are used to quantify the friction with the pore walls of the barrier

$$D_{i,Kn} = \frac{d_p}{3} \sqrt{\frac{8RT}{\pi M_i}} \quad (15)$$

Fig. 5. Composition profiles in the gas film external to the catalyst surface with heterogeneous chemical reactions (a, b) $A + 2B \rightleftharpoons C$, and (c) $H_2 + C_2H_4 \rightleftharpoons C_2H_6$. The calculations are all based on Eq. (9). Depending on the starting guess, different composition profiles are obtained, corresponding to one of the solution sets I, II, and III. The rates of entropy production, σ , for each solution set are also indicated. The input data and computational details are provided in the Supplementary material.

Fig. 4 presents calculations of the ratio of fluxes N_2/N_1 for 2-propanol (1)/water (2)/inert gas (3), plotted as a function of pore diameter, d_p , of the barrier interposed between the vapor and liquid phases. For each of the five inert gases investigated, increase in the pore diameter improves the separation performance; i.e. introduction of the porous barrier decreases the efficacy of separation. The results in Fig. 4 also lead to the conclusion that separations are most effective in the “bulk” diffusion regime, as compared to the “Knudsen” regime; the same conclusion has been drawn by Breure et al. (2008).

6. Applying the Prigogine principle for diffusion with heterogeneous catalytic reaction

For diffusion with heterogeneously catalyzed reversible reaction $A + 2B \rightleftharpoons C$, following Langmuir-Hinshelwood kinetics, Löwe and Bub (1976) have demonstrated the possibility of multiple solutions with the aid of Example 1 and Example 2, each with different kinetic constants. We re-trace their analysis, using the Krishna-Standart analytic solution for calculation of the steady-state fluxes in the diffusion “film”; the reaction takes place at the position $\eta = z/\delta = 1$, corresponding to the catalytic surface. The analysis is also relevant in the context of reactive distillation for which multiple steady-states are often reported (Higler et al., 1999; Taylor and Krishna, 2000).

For Example 1, depending on the starting guess values, three different solutions sets I, II, and III are obtained. The composition profiles in the “film”, calculated using Eq. (9), are shown in Fig. 5a. The obtained results are, precisely the same as those reported by Löwe and Bub (1976) as should be expected. The dimensionless rate of entropy production, $\sigma\delta^2/(c_t\dot{D}R)$, for the three sets are 0.299, 0.941, and 0.531, respectively; calculation details are provided in the Supplementary material. Invoking the Prigogine principle, we conclude that the stable steady state is Solution Set I.

For Example 2, two different solutions are obtained; the composition profiles in the “film” are shown in Fig. 5b. The dimensionless rate of entropy production, $\sigma\delta^2/(c_t\dot{D}R)$, for the two sets; the values are 0.49132, and 0.73706, respectively. Invoking the Prigogine principle, we conclude that the stable steady state is Solution Set I. Löwe and Bub (1976) present a detailed stability analysis to conclude that for both Examples 1, and 2, the Solution set I is the stable steady-state. The use of the Prigogine principle of minimum entropy production obviates the need for performing a detailed stability analysis.

Three different steady-state solutions are also realized in the analysis of diffusion and catalytic hydrogenation of ethene to produce ethane using platinum/alumina catalyst. For Langmuir-Hinshelwood kinetics and input data from Uppal and Ray (1977), the composition profiles calculated using Eq. (9), are shown in Fig. 5c. Application of the Prigogine principle leads us to conclude that the stable steady-state corresponds to solution set I, which is the low-conversion steady-state.

7. Conclusions

In this article, the Maxwell-Stefan diffusion equations have been used to investigate the strategy of introduction of an inert component for effecting the separation of azeotropic 2-propanol/water, and ethanol/water mixtures. The following major conclusions emerge from the analysis presented in this paper.

- (1) The use of the Gilliland parametric solutions to the M-S diffusion equations results in three different set of transfer fluxes, depending on the starting guess values. Of these, only

Gilliland set A solution is physically realizable, because it conforms with the Prigogine principle of minimum entropy production.

- (2) The Krishna-Standart analytic solution yields results in precise agreement with the Gilliland A set. The method is computationally robust, and converges quickly.
- (3) The linearized solution method employing Eq. (5) is of reasonable accuracy and may be used for preliminary design and screening purposes.
- (4) The efficacy of separation of alcohol(1)/water(2) mixtures of azeotropic composition by introduction of an inert gaseous component (3) essentially relies on differences in 1–2 and 2–3 friction in the vapor phase. Such differences increase with increasing molar mass of the inert component 3. Inert gases such as CO_2 and Xe are more effective than lighter inerts such as air, nitrogen or helium.
- (5) If porous barriers (membranes) are interposed between the vapor and liquid phases, the pore size of the barrier material must be chosen to be large enough to ensure that the diffusion regime within the pores corresponds to bulk diffusion. In other words, the operations should not be in the Knudsen regime.
- (6) For diffusion with heterogeneous chemical reaction, the Prigogine principle can also be gainfully employed to determine the stable steady-state.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ces.2017.01.060>.

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