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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

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, CO$_2$, 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 CO$_2$ 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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1. Introduction

For a binary alcohol(1)/water(2) mixture, the vapor-liquid equilibrium is described by \( y_i = \frac{\gamma_i x_i P}{\rho_i / \rho} \). 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.

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The vapor pressure of water at 343.15 K is 31.2 kPa. The total gas phase pressure \( p_g = 101.3 \) kPa. The composition of the vapor phase at the gas/liquid interface in equilibrium with the liquid mixture can be calculated from 
\[ y_i = \frac{y_i P_i^g}{p_g}. \]
This yields \( y_{1a} = 0.6177 \), \( y_{2a} = 0.09264 \), \( y_{3a} = 0.2897 \). The bulk vapor composition is taken to be: \( y_{1b} = 0.0, \ y_{2b} = 0.0, \ y_{3b} = 1.0 \). The driving forces are \( \Delta y_1 = y_{1a} - y_{1b} = -0.6177 \), and \( \Delta y_2 = y_{2b} - y_{2a} = -0.09264 \). 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 \( D_{12} = 2.05 \), \( D_{13} = 1.27 \), \( D_{23} = 2.67 \times 10^{-5} \) m\(^2\) 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 (PFC, 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)
\[
\begin{align*}
N_1/N_2 &= \frac{c_s}{\delta} [y_{10} - y_{1a}] \\
N_1/N_2 &= \frac{c_s}{\delta} [y_{20} - y_{2a}]
\end{align*}
\]
in which the diffusivity matrix
\[
[D] = \begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} = \begin{bmatrix} y_1^2 & y_1 y_2 \\ y_1 y_2 & y_2^2 \end{bmatrix}
\]
is evaluated at the arithmetic average vapor compositions \( y_{1a} = (y_{10} + y_{1b})/2 \). With this simplification, the fluxes can be evaluated explicitly as follows \( N_1 = -0.446 \), \( N_2 = -0.11 \) mol m\(^{-2}\) 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 \( x_3/x_1 = 0.15 \). Diffusional evaporation leads to a relatively higher proportion of water in the vapor phase, causing separation of the azetrope.

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 \( D_i \). The M-S diffusivity \( D_i \) is inversely proportional to the square root of the mean molar mass of the pairs \( \sqrt{M_i} \). We should therefore expect the ratio of fluxes to depend on the square root of the molar mass of the inert gas, \( \sqrt{M_i} \). 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.
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 into 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 $p_2 = 101.3$ kPa. The composition of the vapor phase at the gas/liquid interface in equilibrium with the liquid mixture can be calculated from $y_1 = \gamma_1 x_1 p_2 / p_1$. This yields $y_1 = 0.09836$, $y_2 = 0.05963$, $y_3 = 0.84201$. The bulk vapor composition is taken to be: $y_{10} = 0.0$, $y_{20} = 0.0$, $y_{30} = 1.0$. The driving forces are $\Delta y_1 = y_{10} - y_1 = -0.09836$, and $\Delta y_2 = y_{20} - y_2 = -0.05963$. 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 $N_1/N_2$ 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 $y_1 = 1 - y_1 - y_2$, and re-cast Eqs. (1) using matrix notation

$$\begin{pmatrix} \frac{dy_1}{d\eta} \\ \frac{dy_2}{d\eta} \end{pmatrix} = \Phi \begin{pmatrix} y_1 \\ y_2 \end{pmatrix} - \frac{\delta}{C_1} \begin{pmatrix} \frac{N_1}{m_1} \\ \frac{N_2}{m_2} \end{pmatrix}$$

(7)

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

$$\Phi = \frac{\delta}{C_1} \begin{pmatrix} \frac{N_1}{m_1} + \frac{N_2}{m_2} \\ -N_1 \left( \frac{1}{m_1} - \frac{1}{m_2} \right) \end{pmatrix}$$

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

$$y_1 - y_{10} = -[\exp[\Phi] \eta - [I] \exp[\Phi] - [I]]^{-1} (y_0 - y_1)$$

(9)

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

$$\frac{d(y_1)}{d\eta} = -\left[D_1 [\exp[\Phi] \eta - [I]]^{-1} y_0 - y_1 \right]$$

(10)

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

$$\begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = -\frac{C_1}{\delta} \left[D_1 [\exp[\Phi] \eta - [I]]^{-1} y_0 - y_1 \right]$$

(11)

The diffusivity matrix $[D_1]$ can be evaluated from Eq. (6) using the appropriate gas phase mole fractions. Without loss of generality, we may evaluate the diffusivity $[D_1]$ at position $\eta = z/\delta = 0$, and obtain

$$\begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = -\frac{C_1}{\delta} \left[D_{10-0} [\exp[\Phi] \eta - [I]]^{-1} y_0 - y_1 \right]$$

(12)

The Sylvester theorem, detailed in Appendix A of Taylor and Krishna (1993) is required for explicit calculation of $[\Phi] [\exp[\Phi] \eta - [I]]^{-1}$. Though the expression (12) appears to be explicit in the fluxes, it is to be noted that the matrix $[\Phi] [\exp[\Phi] \eta - [I]]^{-1}$ is also a function of the fluxes. In the limit of vanishingly small transfer fluxes we have the limiting behavior $[\Phi] [\exp[\Phi] \eta - [I]]^{-1} \rightarrow [I]$. 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 $\lambda_1$, $\lambda_2$ 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 $\lambda_1$, $\lambda_2$ are both distinct, and non-zero. The Gilliland set B corresponds to the case in which the eigenvalues $\lambda_1$, $\lambda_2$ 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 $\lambda_1$, $\lambda_2$...
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 CO$_2$ (species 3).

Using the fluxes calculated from the linearized Eq. (6):

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

- If the starting guess values are chosen to be $N_1 = -0.03$: $N_2 = -0.05$ mol m$^{-2}$ s$^{-1}$, deviating only slightly from the Gilliland A set values, we obtain the Gilliland B solution set: $N_1 = -0.0352$: $N_2 = -0.0631$ mol m$^{-2}$ s$^{-1}$, yielding a flux ratio $N_2/N_1 = 1.79$; the rate of entropy production is $\sigma = 1.63$ kJ m$^{-3}$ s$^{-1}$ 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 $N_1 = -0.04$: $N_2 = 0.05$ mol m$^{-2}$ s$^{-1}$, we obtain the Gilliland C solution set: $N_1 = -0.0997$: $N_2 = 0.0997$ mol m$^{-2}$ 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, 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.](image3.png)

![Fig. 2. Rate of entropy production, $\sigma$, for diffusional evaporation of ethanol (1)/water (2) into vapor phase containing inert gas (3).](image2.png)

![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.](image4.png)
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 \( \sqrt{M_i} \), 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)

\[
\frac{N_1}{N_2} = \frac{C_1}{C_2} \left[ \frac{\delta}{\delta^2} \left( \frac{\rho_1 + \rho_2}{\rho_1 + \rho_3} \right) + \frac{\delta}{\delta^2} \left( \frac{\rho_2 + \rho_1}{\rho_2 + \rho_3} \right) \right] \left( \frac{\rho_2}{\rho_1} \right) \left( \frac{\rho_3}{\rho_2} \right) \left( \frac{\rho_4}{\rho_3} \right) \left( \frac{\rho_5}{\rho_4} \right)
\]

(14)

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

\[
D_{kN} = \frac{d_p}{3} \sqrt{\frac{8RT}{\pi M_i}}
\]

(15)

Fig. 5. Composition profiles in the gas film external to the catalyst surface with heterogeneous chemical reactions (a, b) \( A + 2B \leftrightarrow C \), and (c) \( H_2 + C_2H_4 \leftrightarrow C_2H_6 \). 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, \( \sigma \), 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 \( A + 2B \leftrightarrow C \), 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 II 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, \( \sigma \delta^2/(c_i D_R) \), 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, \( \sigma \delta^2/(c_i D_R) \), 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 azetrotic 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 sets 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 azetrotic 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 CO2 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.ices.2017.01.060.

References