

The unexpected weirdness of rate-based simulation of some high-pressure column operations

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Abstract. Diffusion is the process by which molecules move. One way to model multicomponent diffusion is with a version of Fick's law: $(J) = -[D] d(c)/dz$ where $[D]$ is a matrix of multicomponent diffusion coefficients. $[D]$ is the product of two other matrices, one of which involves partial derivatives of the fugacity or activity coefficients. It is usually the case that all of the elements on the main diagonal of $[D]$ have a positive value. Wambui-Mutoru and Firoozabadi¹ showed that CO₂-rich and N₂-rich hydrocarbon systems could have main diagonal elements of $[D]$ that are negative. Using rate-based column simulations, we have found that these negative main diffusion coefficients readily occur in some high-pressure distillation operations. We investigate these processes in more detail and explore the consequences for the design and operation of columns in which this phenomenon is predicted to occur.

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Introduction and Motivation

Rate-based column simulation models have become a viable alternative to the industry-standard equilibrium stage models and Seader²⁻⁴ has provided convenient descriptions of this class of model. There are at least ten organizations involved with process simulation that provide both equilibrium stage and rate-based column models in commercially available simulation systems (see Doherty et al.⁵ for a partial list). A complete description of a non-equilibrium model (also known as a rate-based model) is not given here as such are widely available.²⁻⁷ The essential point is that the actual separation depends on the mass transfer rates between the vapor and liquid phases, which, in turn, depend on the degree to which the vapor and liquid phases are not in equilibrium.

Mass transfer in multicomponent systems is complicated; the mass transfer rates of all compounds depend on the driving forces (mole fraction or, more generally, chemical potential gradients) of *all* of the components present in the mixture. This can lead to compounds diffusing in the direction opposite to that suggested by their own mole fraction gradient. There are two ways in wide use for modeling multicomponent mass transfer; the first is via a matrix generalization of Fick's Law:⁷

$$(J) = -c_t[D](\nabla x)$$

where (J) is a column matrix of molar diffusion fluxes, (∇x) is a column matrix of composition gradients (driving forces), and the matrix $[D]$ is the matrix of Fick diffusion coefficients matrix with dimension $n - 1 \times n - 1$. In general, the matrix $[D]$ is not symmetric ($D_{ij} \neq D_{ji}$), and the off-diagonal elements D_{ij} ($i \neq j = 1, 2, \dots, n - 1$) are nonzero.

The alternative approach, the generalized Maxwell-Stefan equation for multicomponent systems is⁷

$$d_i = - \sum_{j=1}^n \frac{(x_i J_j - x_j J_i)}{c_t \mathfrak{D}_{ij}}$$

where d_i are the generalized driving forces for diffusion, and the $\mathfrak{D}_{ij}$ are the binary pair Maxwell-Stefan diffusion coefficients.

These two formulations of the mass transfer rate equations are closely related and the matrix of multicomponent diffusion coefficients that appears in the generalized Fick's law can be obtained by using the Maxwell-Stefan formulation⁷

$$[D] = [B]^{-1}[\Gamma]$$

where $[B]$ is a square matrix of order $n - 1$, with elements given by

$$B_{ii} = \frac{x_i}{\mathfrak{D}_{in}} + \sum_{k=1, k \neq i}^n \frac{x_k}{\mathfrak{D}_{ik}} \quad B_{ij} = -x_i \left(\frac{1}{\mathfrak{D}_{ij}} - \frac{1}{\mathfrak{D}_{in}} \right)$$

and where Γ_{ij} is a matrix of thermodynamic factors, and can be expressed as below if fugacity coefficients are used.

$$\Gamma_{ij} = \delta_{ij} + x_i \left. \frac{\partial \ln \phi_i}{\partial x_j} \right|_{T, P, x_k, k \neq j=1 \dots n-1}$$

It is now clear that thermodynamics enters into rate-based column simulations in two ways. First, via the inclusion of these partial derivative terms in the mass transfer rate equations and, second, via a key assumption of all rate-based models, that the phase interface is an equilibrium state. Thus, the central importance of thermodynamic equilibrium properties is in no way diminished by the use of a non-equilibrium model.

The matrix of Fick diffusion coefficients has been shown to be positive definite.⁷ This does not, however, require the main diagonal elements to be positive, but, with the aid of the kinetic theory of gases, it can be shown that the main diagonal coefficients are, in fact, individually positive. That would be true if the mixture were ideal in the thermodynamic sense; but what if a system of interest is not ideal; a non-ideal liquid or a gas mixture at high pressure, for example?

Ten years ago, Wambui-Mutoru and Firoozabadi¹ showed that CO₂-rich and N₂-rich hydrocarbon systems could have main diagonal elements of $[D]$ that are negative. Since $[B]$ is positive definite with positive diagonal elements the most likely way for negative entries on the main diagonal of $[D]$ to occur is if the matrix $[\Gamma]$ has “large” negative entries on its main diagonal. This necessarily calls into question the thermodynamic stability of the fluid. A binary fluid will be unstable if the thermodynamic factor Γ is negative. The situation is less clear cut for multicomponent systems, but negative elements on the main diagonal of $[\Gamma]$ are not, in general, expected, and could have interesting and unexpected implications for column operations in which that occurs, if in fact, it does!

This intriguing finding of Wambui-Mutoru and Firoozabadi leads us to pose these questions:

1. Can we reproduce the results of Wambui-Mutoru and Firoozabadi¹?
2. Can we encounter negative diagonal entries in $[\Gamma]$ in a rate-based column simulation?
3. Do negative diagonal entries in $[\Gamma]$ lead to reverse diffusion in high pressure column simulations?
4. What influences the occurrence of negative diagonal entries in $[\Gamma]$?
5. Does this say anything about the models we use to model high pressure operations?
6. Does any of this make a difference in process simulation?

In the remainder of this paper we provide some answers to these questions.

1. Can we reproduce the results of Wambui-Mutoru and Firoozabadi?

We have reproduced the calculations done by Wambui-Mutoru and Firoozabadi and can confirm their finding of negative entries on the main diagonal of the matrix $[\Gamma]$ in CO₂ and N₂ rich systems. However, we submit that the Binary Interaction Parameters (BIPs) used by Wambui-Mutoru are not realistic. That said, we found negative main diagonal elements of $[D]$ with several alternative more realistic sets of BIPs. Thus, surprising as it was to us, Wambui-Mutoru’s main finding – that $[D]$ can have negative main diagonal elements – is confirmed.

However, we were not able to confirm their claim that the mixtures they studied are thermodynamically stable; our calculations with their system hint at instability. This leads us to wonder if it is possible to find mixtures that have negative entries on the main diagonal of $[\Gamma]$ and that are thermodynamically stable? The answer to this question is yes! Limitations on space preclude us from presenting all of the evidence in support of both conclusions; that will have to wait for the full-length version of this paper.

2. Can we encounter negative diagonal entries in $[\Gamma]$ in rate-based column simulations?

Negative diagonal entries in $[\Gamma]$ are not found at “low” pressure (whatever “low” means). Thus, in order to see if they occurred in rate-based column simulations we looked at some high pressure column operations. We have long had an

interest in demethanizers and nitrogen rejection units; nitrogen is likely or certain to be found in both. Ghorbani, Hamed, Mehrpooya and their various coworkers, both separately as well together, as well as others have published extensively on the simulation of liquefied natural gas (LNG) processes and nitrogen rejection units (NRU); see, for example, references 8-15 that we have used as the inspiration for the column simulations used for this study. The NRU described by Hamed et al¹² makes for a good starting point for this study because their column is quite simple and contains only two compounds, nitrogen and methane. This is unrepresentative of an actual NRU. We have, therefore, based our calculations on simulations of the Hamed column to which we added many other heavier components with very low feed fractions; as we shall see, the presence of additional heavier compounds is important here. The Peng-Robinson EOS was used for all of the simulations carried out for this work.

During the normal course of a rate-based simulation the matrix of thermodynamic factors is calculated for each phase on all stages on every iteration. We ask the simulation program to report if negative main diagonal elements of the matrix $[\Gamma]$ are encountered. Of most interest are those simulations that report the occurrence of any negative elements for the final, fully converged, column state. As already implied, we have found that these negative elements occur rather frequently in both demethanizers and NRU. We do not rule out the possibility that such entries can occur also in other high pressure columns (e.g. de-ethanizers) but we have not explicitly searched for such occurrences.

Figure 1 shows some results from a simulation of a Nitrogen Rejection Unit; specifically, we show the thermodynamic factor for nitrogen, Γ_{N_2,N_2} , the multicomponent Fick diffusion coefficients, D_{N_2,N_2} and D_{N_2,CH_4} , and the ratio $D_{N_2,CH_4}/D_{N_2,N_2}$. We show these quantities only for that part of the column where $\Gamma_{N_2,N_2} < 0$. This is just one of many simulations that exhibit similar behavior.

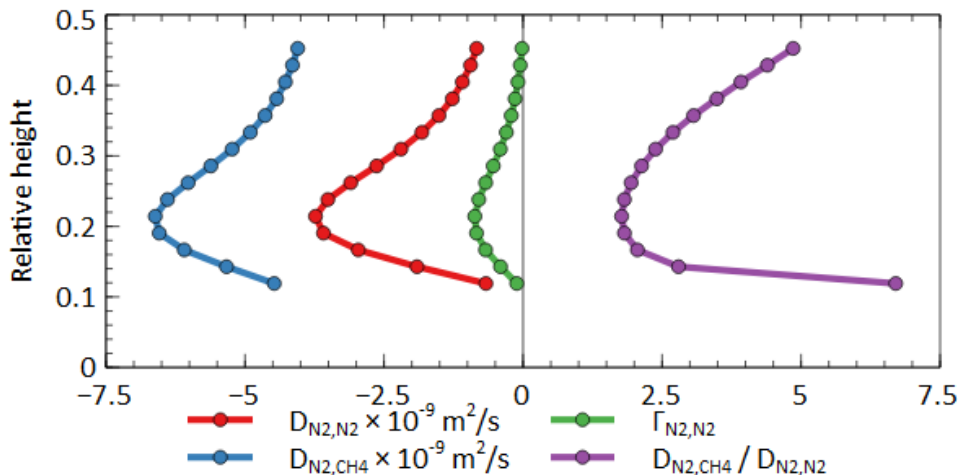


Fig. 1. Thermodynamic factor, Γ_{N_2,N_2} , multicomponent Fick diffusion coefficients D_{N_2,N_2} and D_{N_2,CH_4} and the ratio $D_{N_2,CH_4}/D_{N_2,N_2}$ from a simulation of a Nitrogen Rejection Unit. Profiles shown only for that part of the column where $\Gamma_{N_2,N_2} < 0$.

It should be noted that the occurrence of negative entries on the diagonals of $[\Gamma]$ and, hence, of $[D]$ depends on the sequence in which the components are ordered. This is an inevitable consequence of the definitions of these matrices. Thus, to some extent the, the existence of these negative diagonal elements in the multicomponent Fick's law formulation has a degree of arbitrariness. (There are many systems – most perhaps – for which negative diagonal elements can never be observed, no matter the component order. Thus, their potential existence is meaningful.) It is also true that the fluxes (what actually matters in a process simulation) are independent of the component ordering (as, of course, must be the case). This leads directly to Question 3.

3. Do negative diagonal entries in $[\Gamma]$ lead to reverse diffusion in high pressure column simulations?

Under the right circumstances they must! Of course, whether or not reverse diffusion will occur in any given process will depend on *all* of the local driving forces, and *all* of the coefficients, diagonal as well as non-diagonal, on the same row of $[D]$ on which the negative element is found, but, if there are negative entries on the main diagonal of the Fick matrix it must be possible for circumstances to exist in which a compound goes from low concentration to high, exactly

the opposite of what we generally expect to happen. This could be of considerable importance if the components with negative main diffusion coefficients are key to the desired separation as is the case in our NRU where the key components are nitrogen and methane. In the relevant section of our hypothetical NRU the mole fraction driving forces of species other than these two are negligibly small and we can expand the generalized Fick's law to give the diffusion flux of nitrogen as

$$J_{N_2} = -c_t \left(D_{N_2, N_2} \times \frac{\Delta x_{N_2}}{\delta} + D_{N_2, CH_4} \times \frac{\Delta x_{CH_4}}{\delta} \right)$$

where $\Delta x_{N_2}/\delta$ is a difference approximation to the mole fraction gradient (think of Δx_i as the mole fraction difference over the liquid side film for mass transfer and δ as the liquid phase film thickness). In this specific case, the driving force of methane is essentially equal in magnitude and opposite in sign to that of nitrogen. Thus, to a very close approximation, the diffusion flux of nitrogen is given by

$$\frac{J_{N_2}}{-c_t \times \Delta x_{N_2}/\delta} = D_{N_2, N_2} - D_{N_2, CH_4} > 0$$

From Fig. 1 we see that $D_{N_2, CH_4} < D_{N_2, N_2} < 0$. Thus, at least for this case and all similar ones that we have investigated, the term on the right hand side of the equation above is always positive, which means that reverse diffusion of nitrogen does not occur (in these cases). Put another way, in these simulations the flux of nitrogen actually depends much more strongly on the driving force of methane than it does on its own driving force! The negative Γ_{N_2, N_2} is working here to suppress the importance of the driving force of nitrogen!

Whether or not this precise set of circumstances exist in all nitrogen rejection units as well as in other units we cannot yet say; many more simulations remain to be done to see how often these circumstances occur.

4. What influences the occurrence of negative diagonal elements in $[\Gamma]$?

In this section we discuss those factors that we have found to influence the presence/absence of these negative numbers.

Binary Interaction Parameters (BIPs): Phase equilibrium models in wide use depend crucially on the numerical values assigned to the binary interaction parameters that are an essential part of these models. Phase equilibrium predictions are exceptionally sensitive to the values given to these BIPs. We considered multiple sets of BIPs in this work:

- (a) All BIPs set equal to zero
- (b) BIPs taken from three different process simulation packages available commercially
- (c) BIPs predicted by the PPR78 model^{16,17}

We have found that negative main diagonal thermodynamic factors occur for all of these different sets of BIPs. To be sure, the exact circumstances (temperature, pressure, composition) leading to negative $\Gamma_{i,i}$ are not the same for all sets of BIPs. That all sets of BIPs can lead to negative $\Gamma_{i,i}$ is, however, important because it rules out the possibility that this occurrence can be said to be an artifact created by a particular set of BIPs.

Pressure: Negative $\Gamma_{i,i}$ can occur only if the pressure is sufficiently high. "High" is, of course, a relative term; we are not able to provide a value of pressure above which this phenomenon occurs and below which it does not. All we can state with certainty is that for a given mixture composition there exists a pressure above which negative $\Gamma_{i,i}$ may be found (it was 268 kPa for the NRU discussed here). It is essential to recognize that some mixture compositions can never lead to negative $\Gamma_{i,i}$. That negative $\Gamma_{i,i}$ can be found at pressures of importance in real demethanizers and NRUs can also be asserted (we found negative $\Gamma_{i,i}$ at every pressure at which we ran our hypothetical demethanizer; this includes pressures far below the practical range).

Components present: Negative $\Gamma_{i,i}$ can, apparently, occur only if there are compounds in the mixture with a molecular weight sufficiently high. More precisely, we have not (yet) found negative $\Gamma_{i,i}$ when there are "too few" compounds in the mixture. For this investigation we added many higher molecular weight hydrocarbons (which were assigned feed mole fractions at sub-ppm levels, as expected in demethanizers and NRUs) to the binary mixture in reference 12 that served as the basis for our calculations. Compounds were then systematically eliminated from the bottom of the list (those same heavier species) and the simulation re-run to see if the presence or absence of that compound was important. We did not observe negative $\Gamma_{i,i}$ once we had eliminated all compounds heavier than propane.

Phase stability: It had been our expectation that negative $\Gamma_{i,i}$ could be found only for mixtures that are thermodynamically unstable; in other words, the fluid mixture of interest should “want” to split into two (or potentially more) distinct phases. As already noted, our investigation of the mixtures discussed by Wambui-Mutoru and Firoozabadi¹ had suggested to us that these mixtures were not stable (this in contradiction to the claims in their paper). We carried out thermodynamic stability tests for each mixture in our column simulations for which we had observed negative $\Gamma_{i,i}$. We used our own stability test code as part of the column simulations (and, for additional certainty, ran each test with many different initial guesses). We also used the independent stability test in the SPLIT thermodynamic software by AmsterCHEM, version 1.0.0.30 (www.amsterchem.com). None of the mixtures in our column simulations has been found to be thermodynamically unstable. We will admit to being surprised by this finding.

5. Does this say anything about the models we use to model high pressure operations?

The original finding by Wambui-Mutoru and Firoozabadi¹ – that the matrix of multicomponent Fick diffusion coefficients as well as the matrix of thermodynamic factors could have negative elements on the main diagonal – was a surprise to us when it was published. They say, correctly, that this is due to the non-ideality of these high-pressure mixtures. This paper confirms their essential findings but we cannot say whether or not this is a non-physical artifact created by our choice of thermodynamic model.

We are using the Peng-Robinson EOS, a model that is widely used for such simulations and one that has been validated for many of the key binary mixtures in these mixtures. However, there is no data in existence that can be used to validate or invalidate the precise findings of this paper. To be clear on this point; it is not VLE data, or even ppT data, data that would be used to validate and fine tune an equation of state that is required; rather it is copious amounts of high quality diffusion data for mixtures of many components at high pressures. Such data simply does not exist. It should be noted that Wambui-Mutoru and Firoozabadi¹ cite many instances of “anomalous” diffusion data, but none covers the circumstances that occur in these high pressure column operations.

6. Does any of this make a difference in process simulation?

To what extent do these negative $\Gamma_{i,i}$ impact process simulation and, hence, column design and operation? This is the final question to which we now turn our attention.

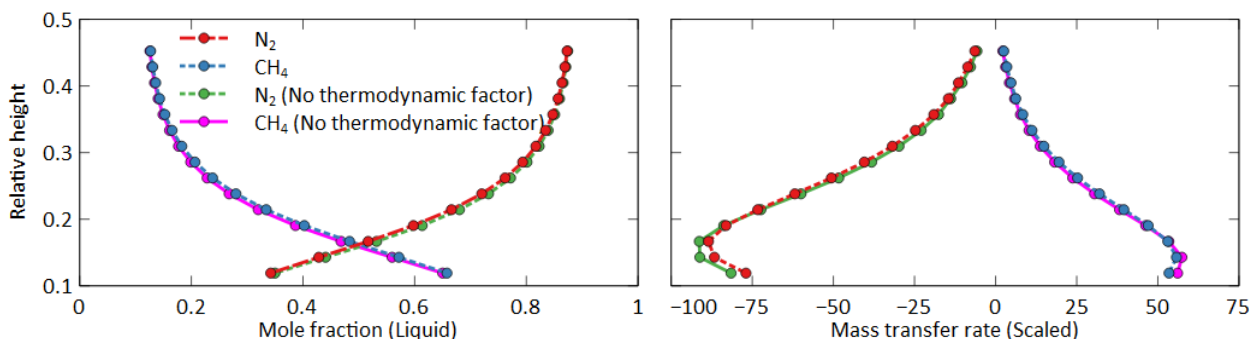


Fig. 2 Liquid phase mole fraction profiles and scaled mass transfer rates for nitrogen and methane from two simulations of a Nitrogen Rejection Unit. One simulation entirely ignores the thermodynamic factor. Positive mass transfer rates indicate transport from the gas/vapor phase to the liquid phase. Profiles cover the same section of the column seen in Fig. 1.

Figure 2 shows partial liquid phase mole fraction and corresponding mass transfer rate profiles for one of our NRU simulations. Only the profiles for nitrogen and methane are shown, but they are the key components here. Two sets of profiles are shown, one of which ignores entirely the thermodynamic factor. A quick glance suggests there is very little difference between these profiles. These results are typical of those we have obtained to date. In short, it appears that these negative $\Gamma_{i,i}$ and negative $D_{i,i}$ do not significantly impact the high pressure column simulation that we have carried out for this investigation. These results lead us to ask a new question: Is it necessary to include the matrix of thermodynamic factors in rate-based simulations of column operations involving (high pressure) non-ideal systems. That is a question to which we do not, yet, have a definitive answer.

Conclusion

We have found that the main-diagonal thermodynamic factors that are part and parcel of any rigorous model of multicomponent mass transfer can be negative. This confirms an earlier finding of Wambui-Mutoru and Firoozabadi.¹ We have found that negative thermodynamic factors readily occur in simulations of some high pressure column operations; most notably in simulations of demethanizers and nitrogen rejection units. We have not (yet) found a case where these negative thermodynamic factors have a significant impact on the important results of a column simulation.

The modest quantity of simulations carried out for this investigation so far does now allow us to conclude with certainty that the appearance of these negative coefficients has limited impact. Nor, given the contradictory results we found regarding the thermodynamic stability of the mixtures in the study by Wambui-Mutoru and Firoozabadi¹ are we willing to state that the mixture in our high pressure simulations will always be stable. Finally, there remains the possibility that there are other high pressure operations that also display this behavior. Our investigation continues.

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