HESS manuscript: https://doi.org/10.5194/egusphere-2024-2023

Title: Technical note: An assessment of the relative contribution of the Soret effect to open water evaporation

Authors: Roderick ML & Shakespeare CJ

Combined response to the reviews following editorial decision of “minor revision”. RC1 is at the end because it is the longest response.

General Overview of Revisions

Here we first summarise the main changes.

[Line numbers are those in the new manuscript labelled as V4]

- **(a) In response to RC5 we now refer to the Griffani et al 2024 paper in the introduction. On reflection of this comment, we have also added an additional empirical analysis for the thermal diffusion factor and this is included in new Appendix A and we have added relevant text to the manuscript (lines 144-154).**
- **(b) In response to RC1 we have changed the basic equation of the analysis (see new Eq. 9, line 211) to include the requested advective flux and the total evaporation is now split into three components. We have included the mathematical derivation in a new Appendix B. This change required additional paragraphs throughout to consider the new flux within the body of the manuscript. The inclusion of this new flux did not materially change the conclusion of the manuscript.**
- **(c) Because of (b) we decided to change our original Figure 2. The top panels from the old Figure 2 have been put into a new Appendix C. The bottom right panel of the old Figure 2 is now included in a new Figure 3. The new Figure 2 includes a plot of the three fluxes and the three relative fluxes are now shown as histograms.**
- **(d) In response to RC3 we have conducted a more extensive search and identified the 2015 Persian Gulf heatwave as an example that has been included in new Appendix E and discussed in the main text in several places.**

We believe these changes have improved the manuscript and we have noted this in the acknowledgements.

The detailed response to each reviewer comment is shown below.

Response to RC2 (Anon. Reviewer 2, 6 Sep 2024)

Review comments in italics.

Author Response in bold.

Roderick + Shakespeare

1. *This is an unusual and nicely scholarly piece of work which should be published, more or less as is.*

We thank the reviewer for the comments.

2. *It is interesting to discover that the Soret effect has received so little experimental investigation. In that regard, I note that philosopher Nancy Cartwright in her book How the Laws of Physics Lie uses the Soret effect as an established example of a coupled-flux process in discussing causal inference. Perhaps less established than she thought.*

As our references show, the Soret effect has been extensively investigated by physicists originally interested in developing/testing/refining the kinetic theory of gases primarily in the first half of the twentieth century. What the reviewer is referring to is that the Soret effect did not make it's way to other scientific disciplines (e.g. hydrology, atmospheric science, etc.).

3. *I have really only two comments. The first is to wonder if the authors might spend a little more time in discussing the boundary layer structure in evaporation: how does the temperature vary across it? ... Can we assume that there is local kinetic (thermal) equilibrium within the boundary layer? What are reasonable boundary layer thicknesses and temperature gradients? There is brief mention only in lines 170-173.*

As described in the manuscript, and implied by the equation, we have assumed the vapour is saturated at the liquid surface and is uniform above the boundary layer. Between the surface and top of the boundary layer we assume a linear profile as described in detail in the cited reference (Lim et al, 2012). This was beyond the scope of the article but we reproduce Fig. 1 from Lim et al (2012) below (see Fig. R1 below) to show that the details are available for an interested reader. A similar profile is used to model the temperature. Boundary layer thicknesses are also reported in Lim et al., and depend on the wind speed.

We have now added new text after Eqn 5 (lines 163-165) to explain this in more detail than we had originally provided.

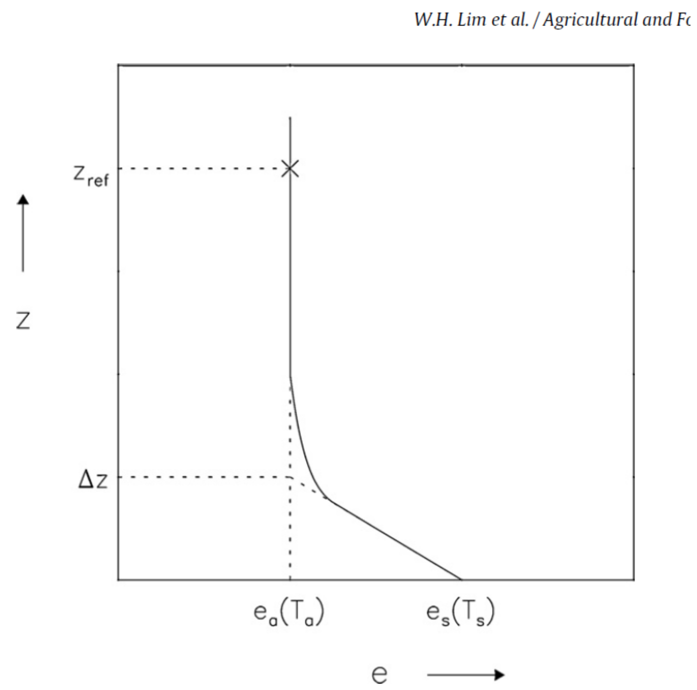


Fig. 1. A schematic diagram of the "threshold model" adopted here for the variation in vapour pressure (e) with height (z) above the evaporating surface. After Leighly (1937) and Machin (1964, 1970).

Fig. R1 Reproduced from Lim et al (2012)

4. *The second is to ask what is the connection between the the framework/ analysis set out in this paper and the description of thermal diffusion in porous media (water, liquid and vapour) originally set out by Philip and de Vries (1957) and later papers (perhaps Luikov too around the same time). Have I missed something here or should these analyses all be consistent?*

Yes, they should all be consistent.

The Philip and de Vries (1957) work was dealing with a much more complex situation with solids as well as water in liquid and gas phases. If you look at their formulation, their original equation (reproduced here) for the mass flux of water vapor through the gas phase was,

$$q_{\mathrm{vap}} = -D_{\mathrm{atm}} \nu \alpha a \nabla \rho \qquad (1)$$

Their eqn 1 is actually based on Fick's Law (using vapor density $\nabla\rho$ as the driving force). In their Eqn 9 they used a classical 'Darcy' formulation for bulk flow of liquid.

No doubt one could reformulate the Philip and de Vries (1957) result in different ways but that is well beyond the scope of this paper. We note that the magnitude of thermodiffusion in soil (in either vapor or liquid phases) would be small as we have found here and could be ignored as Philip and de Vries have implicitly done.

Response to RC3 (Anon. Reviewer 3, 18 Sep 2024)

Review comments in italics.

Author Response in bold.

1. *This manuscript gives a detailed discussion on the relative contributions of Fickian's diffusion and Soret effect on open water evaporation, and justifies the popular practice of estimating open water evaporation through the water vapor concentration gradients. The authors prove that the Soret effect is two orders of magnitude smaller than that by concentration-dependent diffusion. I consider such kind of work is just quite rare because of limited laboratary experiments and it is valuable for us to understand the processes behind it.*

We thank the reviewer for the comments.

2. *In figure1, the thermal diffusion factor is 0.05 for N2-N2O and N2-CO2, but 0.33 for H2-CO2. It seems that even though the thermal diffusion factor of 0.33 is used for Soret effect estimation, its contribution is still much smaller compared to the concentration gradients.*

We assume the reviewer means that even if we used the (incorrect) larger value of 0.33 (instead of 0.05) the conclusions would not be materially altered. If so, we agree.

3. *In abstract, the authors mentioned that "under typical environmental conditions it is at least two orders of magnitude smaller than classical concentration-dependent mass ('Fickian') diffusion. ". From Figure1 and Figure 2, we could find that the Soret effect can be neglected in open water estimation. I 'm just wandering under what conditions in open water evaporation estimation (fresh water and saline water) the Soret effect can not be ignored? If no, please add some examples in the discussion of the manuscript.*

We have revised the text by including a new example of an extreme case (2015 Persian Gulf Heatwave, see new Appendix D) and also substantially extended the text about this point (lines 237-265) and added a new paragraph in the Discussion (lines 308-327).

4. *Further, the figure quality is not good, please make figures with good quality.*

The manuscript was prepared using 'cut and paste' to insert the figures from a PDF into a Word document and we may have inadvertently used a low resolution during that process. However, for the final printed version the figures will be high quality PDFs. We have increased the font size on the axis labels.

5. *Generally, I consider the manuscript is a good materials that can help us to understand clear the water-atmosphere interaction processes.*

We thank the reviewer for the comments.

Response to RC4 (Anon. Reviewer 4, 23 Sep 2024)

Review comments in italics.

Author Response in bold.

1. *This study quantifies the magnitude of the Soret effect on open water evaporation and demonstrate that it is typically two orders of magnitude smaller than the mass diffusion component (Fickian diffusion). This finding justifies the common practice of ignoring the Soret effect when describing evaporation in hydrological sciences.*

I believe this is an important study that should be accepted after minor corrections and clarifications. The manuscript is well-written and exhibits excellent readability. However, it may benefit from clarifications regarding the following points.

We thank the reviewer for the thoughtful comments.

Comments:

2. *C1: Multiple times throughout the manuscript, the sentences give an impression that evaporation is entirely a Fick's diffusion process (Line 26,212). However, estimation of evaporation also requires an explicit consideration of an energy term. Over open-water surfaces the gradient in the water-vapor is further strongly controlled by changes in temperature and incoming energy as reflected in the classical equilibrium energy partitioning approach (Slatyer and McIlroy, 1961).*

The energy balance approach (e.g. Slatyer & McIllroy 1961) is an alternative to the mass transfer approach (e.g. Fick's law) and this has been widely used in hydrology and agriculture (also see Yang & Roderick 2019, QJRMS, 145, 1118-1129). However, it has been held for more than 200 years (since Dalton's 1802 paper) that evaporation can be specified solely using a mass transfer approach.

Energetic constraints are needed in addition to (but do not replace) the mass transfer formulation for evaporation if one seeks to model the evolution of the system over time (e.g., in a land surface, atmosphere or ocean model). Here, however, we have direct experimental control of all key variables (air temperature/humidity and windspeed) and measure evaporation and surface temperature directly which avoids the need for such modelling.

Response to RC5 (Anon. Reviewer 5, 23 Sep 2024)

Review comments in italics.

Author Response in bold.

1. *This short technical note deals with quantifying the relative contribution of the Soret effect (i.e. thermodiffusion) compared to regular "Fickian" diffusion in the evaporation of open water bodies. The motivation behind the paper is to justify the standard practice of neglecting the Sorret effect for evaporation. For this purpose, it is based on the gas kinetic theory of Chapman and his colleagues (completed with experimental determination of the Sorret effect in binary mixtures) and on a recent dataset of evaporation rates under controlled conditions.*

   I think the paper is of general interest for people working of water vapor transport (even beyond the sole problem of open water evaporation) and is well suited for HESS. There is however one main point of concern (General Comment 1) that I would like the authors to clarify.

We thank the reviewer for the comments.

2. *General Comments 1 – It is stated at the very start of the paper that the evaporation rate of an open water body is controlled by the ability of water vapor to diffuse in the air. From what I understand this is clearly the case when the air above the water is still (in this case, diffusion in the limiting factor, effectively setting its rate for the evaporation). However, as soon as wind and turbulence is involved, I have issues understanding to what extent the evaporation rate remains controlled by the molecular diffusion in the air. I'm no boundary-layer scientist, but from what I understand, the diffusion flux of Eq. 4 applies within the micro layer (following the wording of Roland B. Stull's "An introduction to Boundary Layer Meteorology"), i.e. the zone just above the surface where molecular diffusion dominates. Thus, if it is to be translated into Eq. 5 I would say that the gradients of concentration and temperature are to be taken across this micro-layer. And I'm not sure that the concentration and temperature at the top of this micro-layer can be taken as xa and Ta (as they are influenced by the surface). Otherwise, if xa and Ta are taken to define the gradients, I think the diffusivity should rather be some "effective" diffusivity (including turbulent effects) and thus does not match the molecular diffusivity anymore. And in this case, it is not clear to me that one can upscale the Sorret effect to the whole boundary layer in a similar fashion (i.e. that there is an effective Sorret flux, including turbulence, that has the same form and the same thermal diffusivity ratio as in the purely molecular case). In other words, I think the problem boils down to the difficulty of reconstructing the surface concentration and temperature gradients based on the "air" values, which I assume can be significantly different from what happen in the micro-layer. I would thus like the authors to clarify this point. Especially, references to pre-existing literature treating this problem and relating molecular diffusion in the micro-layer to the air temperature/concentration would be appreciated.*

We thank the reviewer for this comment. Please see the response to RC3, comment 3.

3. *2 – From what I understand the motivation behind this close look at the Sorret effect stems from the recent study of Griffani et al. (2024), that states that thermo-diffusion can be an effective mechanism of water vapor transport and should not always be neglected. However, this motivation only appears in the discussion. I think it could be quite beneficial to include this in the introduction, as it relates to the state-of-the-art on the subject.*

We accept the point and we have now added a reference to Griffani et al (2024) as well as the necessary text in the introduction as requested.

Specific and technical comments

4. *Abstract – I would systematically say "evaporation from open water" rather than simply "evaporation".*

Done.

5. *L15 – As mentioned in the General Comment 1, references to pre-existing literature would be beneficial here.*

We have added a reference to the classical Monteith and Unsworth 2008 textbook at the end of the first sentence as requested.

6. *L21 – The mention of the Duffour effect is a bit off to me, especially as it is no longer mentioned in the text. It could potentially be discussed a bit more in the Discussion and Conclusions section, notably mentioning that the Onsager reciprocal relations allows one to estimate the Duffour effect from Sorret.*

We agree that the Dufour effect is left hanging on it's own. We just wanted to make the point that the Onsager-based coupling leads to other effects. We have rewritten the text (in paragraph 1) to highlight the symmetrical nature of the Onsager-based flux-coupling to give the necessary context that we believe was missing from the original manuscript.

7. *L76 and L84 - I would say "limiting conditions" rather than "boundary conditions".*

Done.

8. *L82 – If I'm not wrong the quadratic form was proposed in the work of Chapman (and certainly others). You could refer to them to justify this specific functional form*

We have cited the first standard text on the topic (Grew and Ibbs 1952).

9. *Eq 5 - It might be just me, but I'm not fond of mixing alphabetical and digits in Equations, as it obscure physical variables from actual math constant (and I find it harder to read and interpret). I would keep alpha_T rather than 0.05.*

We accept the point that this is a matter of "taste". We also prefer using symbols but in this case we have supplied the actual numeric value that is assumed unchanging.

10. *L136 – It relates to General comment 1. Could you elaborate on the physical significance of Delta z? Is it the thickness of the micro-layer (where diffusion dominates)?*

Yes, it is the thickness you mentioned. We have modified the text after Eqn 5 to explain this more fully (also see RC2, comment 3: RC5, comment 2).

11. *Eqs 6a and 6b – Same as Eq. 5. I would go straight to the point and say that Eq 5 using some standards values yields a 99.6%/0.4% partition for the Fickian and Sorret fluxes.*

Again a matter of taste. We think that having the numbers written out makes it very clear that the Soret effect will be small regardless of the boundary layer model chosen.

12. *L149 – For me, "vanishingly small" implies that the Sorret contribution strictly goes to zero when xs equals xa. However, I do not think it's the case as small Sorret contribution remains non zero (if xs is different from 0 or 1, and Ts different from Ta).*

We have modified the text accordingly.

13. *L155 – If it's the air temperature, please use Ta rather than T.*

Done.

14. *Figure 2 – I find it hard to determine the relative contribution of the Sorret flux in panel c near the origin of the graph. Perhaps add a second y-scale the relative contribution of the Sorret flux as a scatter of the total evaporation flux.*

We agree that the Soret flux is hard to precisely determine near the origin but the main point here is not the exact numerical value, but rather that it is very small.

15. *L194 – I think the wording could be improved. From what I understand, the issue is that Griffani et al.'s work is based on Landau's derivation which assumes that (ii) the water vapor molecule are much lighter than the dry air and (ii) the collisions are elastic; both assumption not applying to the actual mixture of water and dry air. The current wording rather suggests that the issues are (i) Griffani et al. is based on Landau (M=1 and elastic collisions) and (ii) the collisions are assumed elastic; in which the same issue actual appears twice.*

We have completely rewritten this paragraph (lines 295-306) and we believe the new wording satisfies this suggestion.

16. *L209 – Taking alpha_t as 0.05 rather than 0.5 effectively reduces the Sorret flux by an order of magnitude, and the 30% contribution of Sorret in Griffani et al. now becomes a 3% contribution, which is deemed negligible. That being said, I would still leave the door open that in almost all natural conditions, the Sorret effect appears negligible, but that pathological cases (i.e. very high temperature gradients with little concentration gradients) can still exist (and it links with the paragraph below).*

Reviewer 3 raised a similar sentiment (see point 3 in the response to Reviewer 3).

We have now modified the text (lines 237-265) to include a more extensive analysis, and we have added an example (Persian Gulf Heatwave, Appendix D). This point is further pursued in the discussion with a new paragraph (lines 308-327) describing this important point.

Response to RC1 (Dr Andrew Kowalski, 3 Sep 2024)

Review comments in italics.

Author Response in bold.

Given the nature of the review we have chosen to reverse the order of the questions to be addressed.

2. Independent of this, I point out that the authors' Eq. (1) is dimensionally inhomogeneous unless the diffusive flux density (J) is specified in molar terms, with units as in Table 1 rather than the mass-based units that they indicate at line 62. Also, the axis labels should be larger in order to be legible, particularly for Figure 2.

Yes, there was a 'typo' on line 62 where the units should have been molar.

We have made the text larger on the axes of both Figures 1 and 2 as suggested.

Thank you.

1. *The manuscript by Roderick and Shakespeare purports to characterise the influence of the Soret effect, whereby temperature gradients influence mass diffusion, versus the classical concentration-dependent mass ('Fickian') diffusion. But in order to do this requires first correctly characterising Fickian diffusion, and this I believe the authors have not yet done. In brief, the authors have specified Fick's law based on gradients in the molar fraction, whereas Newtonian analyses demonstrate that it must be specified in terms of the mass fraction, and the difference between the two is hardly trivial for fluids of varying molecular mass. Respectfully, I therefore believe that the manuscript should be*

> *rejected. My arguments for why their specification of Fick's 1st Law is incorrect are laid out in an open-access paper (Kowalski et al., 2021) that can be accessed here (https://link.springer.com/article/10.1007/s10546-021-00605-5; see sections 3.2 and 4 in particular), but are reinforced in the attached PDF file.*

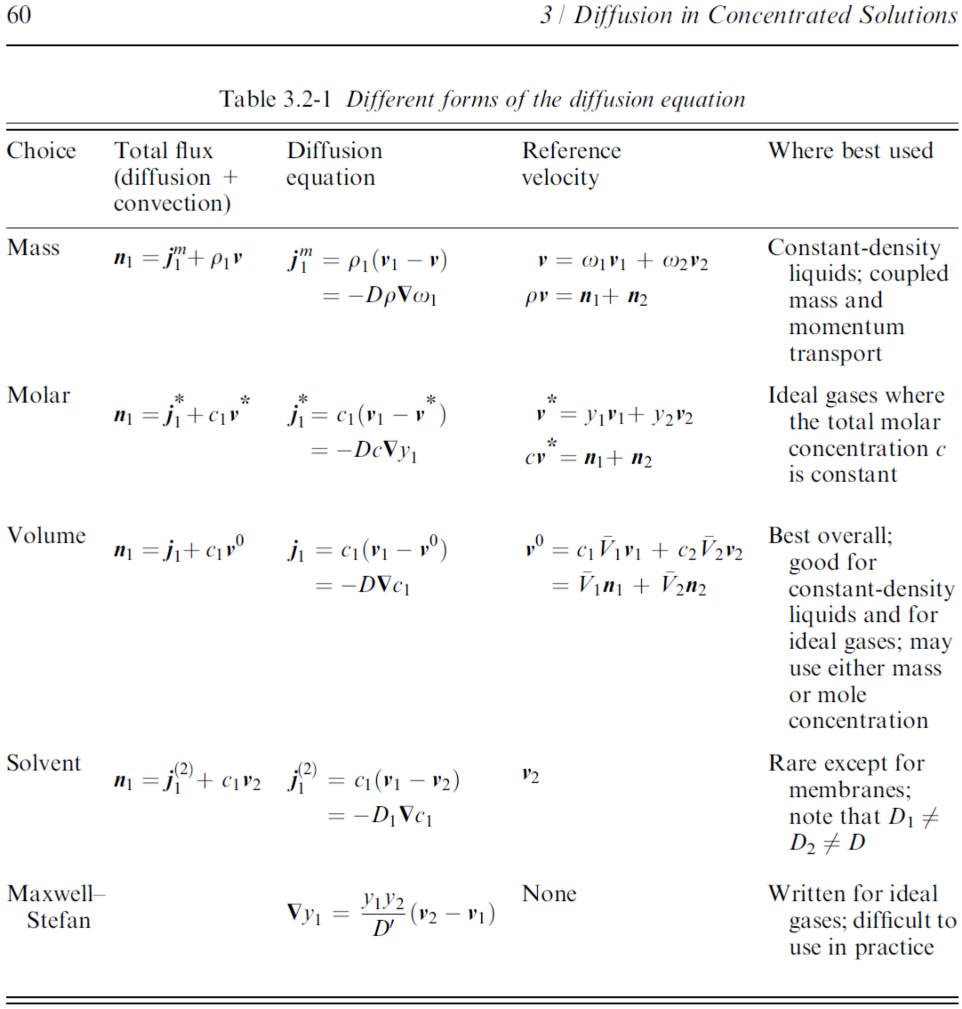
We thank the reviewer for their considered response and for the additional document (i.e., the uploaded PDF) based on "Isaac" which we enjoyed reading. We have also carefully read the cited 2021 Boundary Layer Meteorology article as well as the earlier 2017 article in AtmChemPhys.

We were somewhat surprised by the ferocity (i.e., recommend complete rejection) given the highly favourable comments by the other six reviewers of the manuscript. With that background we have taken the comment seriously. In fact this was the first comment posted on our manuscript (on 3 Sep 2024) and one of us (MLR) has spent nearly all of the available time since then undertaking additional reading/research to seriously address the comment. Our combined knowledge of "diffusion" has increased substantially and for that we thank the reviewer. The extra work was worth it in this case.

The underlying basis of the assertion that we MUST use a mass-based framework has two separate points. The first is simply that one has to use a mass-based framework and the second is that we have ignored a small advective flux (i.e., the so-called Stefan flow). For the latter we accept the criticism and we have now included the advective flux (see new Eq. 9, line 211) and a justification for this new flux (lines 194-211) has now been added. In addition we have included the mathematical derivation of the new Eq. 9 in Appendix B and modified the discussion (lines 329-333).

In implementing the new flux we have followed the standard engineering literature and cited two main references who show that one can use a molar or mass-based analysis (Kreith, Cussler).

We note that there is a vast scientific literature (e.g. Cullinan 1965; Brady 1975; Miller 1986) that establishes the complete equivalence of mass- and molar-based frameworks for describing diffusion. We also identified a very succinct and elegant tabular summary of this very point in the famous Cussler textbook on diffusion (Cussler 2009: Table 3.2-1) that is reproduced below in Fig. R2. Interestingly, in Hydrology (and other climate related fields) we usually specify the diffusion coefficient of water in air based on laboratory experiments. It turns out that those experimental results are actually based on a volume-based reference velocity as is most gas-based analysis and that most closely maps to a molar average velocity.



60 3 / *Diffusion in Concentrated Solutions*

Table 3.2-1 *Different forms of the diffusion equation*

Choice	Total flux (diffusion + convection)	Diffusion equation	Reference velocity	Where best used
Mass	$\boldsymbol{n}_1 = \boldsymbol{j}_1^m + \rho_1 \boldsymbol{v}$	$\boldsymbol{j}_1^m = \rho_1(\boldsymbol{v}_1 - \boldsymbol{v})$ $= -D\rho\boldsymbol{\nabla}\omega_1$	$\boldsymbol{v} = \omega_1 \boldsymbol{v}_1 + \omega_2 \boldsymbol{v}_2$ $\rho \boldsymbol{v} = \boldsymbol{n}_1 + \boldsymbol{n}_2$	Constant-density liquids; coupled mass and momentum transport
Molar	$\boldsymbol{n}_1 = \boldsymbol{j}_1^* + c_1 \boldsymbol{v}^*$	$\boldsymbol{j}_1^* = c_1(\boldsymbol{v}_1 - \boldsymbol{v}^*)$ $= -Dc\boldsymbol{\nabla}y_1$	$\boldsymbol{v}^* = y_1 \boldsymbol{v}_1 + y_2 \boldsymbol{v}_2$ $c\boldsymbol{v}^* = \boldsymbol{n}_1 + \boldsymbol{n}_2$	Ideal gases where the total molar concentration c is constant
Volume	$\boldsymbol{n}_1 = \boldsymbol{j}_1 + c_1 \boldsymbol{v}^0$	$\boldsymbol{j}_1 = c_1(\boldsymbol{v}_1 - \boldsymbol{v}^0)$ $= -D\boldsymbol{\nabla}c_1$	$\boldsymbol{v}^0 = c_1 \bar{V}_1 \boldsymbol{v}_1 + c_2 \bar{V}_2 \boldsymbol{v}_2$ $= \bar{V}_1 \boldsymbol{n}_1 + \bar{V}_2 \boldsymbol{n}_2$	Best overall; good for constant-density liquids and for ideal gases; may use either mass or mole concentration
Solvent	$\boldsymbol{n}_1 = \boldsymbol{j}_1^{(2)} + c_1 \boldsymbol{v}_2$	$\boldsymbol{j}_1^{(2)} = c_1(\boldsymbol{v}_1 - \boldsymbol{v}_2)$ $= -D_1\boldsymbol{\nabla}c_1$	$\boldsymbol{v}_2$	Rare except for membranes; note that $D_1 \neq D_2 \neq D$
Maxwell–Stefan		$\boldsymbol{\nabla}y_1 = \frac{y_1 y_2}{D'}(\boldsymbol{v}_2 - \boldsymbol{v}_1)$	None	Written for ideal gases; difficult to use in practice

Figure R2 Reproduction of Table 3.2-1 from Cussler (2009: p. 60) showing the equivalence of different forms of the diffusion equation.

Finally, we refer back to the 'Isaac' examples provided by the reviewer. These involve two different gases (of different molecular mass) and what happens when they mix. This problem has been explicitly dealt with by Cussler (2009: p. 58-59) and Cussler agrees with the reviewer that that centre of mass will change. But Cussler also points out that the volume (and mole) average velocity is zero and so this is the easiest diffusion equation to use and is recommended for that reason which refutes the assertion by the reviewer. We have included "snapshots" from p. 58-59 of Cussler in an appendix to this response.

References

Brady, J. B.: Reference frames and diffusion coefficients, American Journal of Science, 275, 954-983, doi.org/10.2475/ajs.275.8.954, 1975.

Cullinan, H. T., Jr.: Analysis of Flux Equations of Multicomponent Diffusion, Industrial & Engineering Chemistry Fundamentals, 4, 133-139, 10.1021/i160014a005, 1965.

Cussler, E. L.: Diffusion: Mass Transfer in Fluid Systems, 3rd ed., Cambridge University Press, Cambridge, UK, 2009.

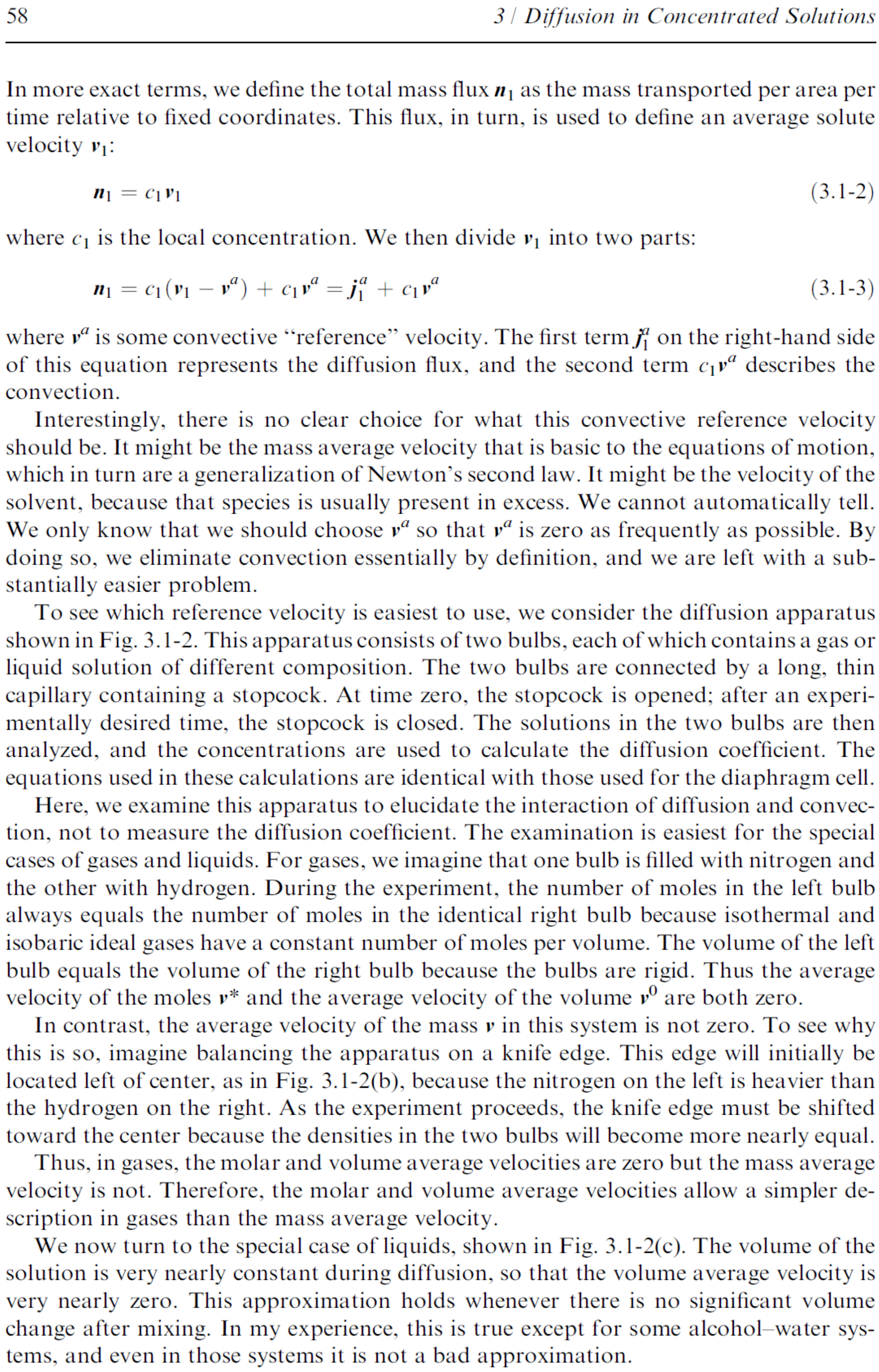
Kowalski, A. S., Serrano-Ortiz, P., Miranda-García, G., and Fratini, G., 2021. "Disentangling turbulent gas diffusion from non-diffusive transport in the boundary layer." Boundary-Layer Meteorology, ***179*** *(3), 347-367.*

Kowalski, A. S.: The boundary condition for vertical velocity and its interdependence with surface gas exchange, Atmos. Chem. Phys., 17, 8177-8187, 10.5194/acp-17-8177-2017, 2017.

Kreith, F., Boehm, R., Raithby, G., Hollands, K., Suryanarayana, N., Modest, M., VP, V., Chen, J., Lior, N., Shah, R., Bell, K., Moffat, R., Mills, A., Bergles, A., Swanson, L., Antonetti, V., Irvine Jr, T., and Capobianchi, M.: Heat and Mass Transfer, in: Mechanical Engineering Handbook, edited by: Kreith, F., CRC Press LLC, Boca Raton, 1999.

Miller, D. G.: Some comments on multicomponent diffusion: negative main term diffusion coefficients, second law constraints, solvent choices, and reference frame transformations, The Journal of Physical Chemistry, 90, 1509-1519, 10.1021/j100399a010, 1986.

Appendix – Snapshots of pages 58 and 59 from Cussler (2009)



In more exact terms, we define the total mass flux $\boldsymbol{n}_1$ as the mass transported per area per time relative to fixed coordinates. This flux, in turn, is used to define an average solute velocity $\boldsymbol{v}_1$:

$$\boldsymbol{n}_1 = c_1 \boldsymbol{v}_1 \tag{3.1-2}$$

where c_1 is the local concentration. We then divide $\boldsymbol{v}_1$ into two parts:

$$\boldsymbol{n}_1 = c_1(\boldsymbol{v}_1 - \boldsymbol{v}^a) + c_1 \boldsymbol{v}^a = \boldsymbol{j}_1^a + c_1 \boldsymbol{v}^a \tag{3.1-3}$$

where $\boldsymbol{v}^a$ is some convective “reference” velocity. The first term $\boldsymbol{j}_1^a$ on the right-hand side of this equation represents the diffusion flux, and the second term $c_1 \boldsymbol{v}^a$ describes the convection.

Interestingly, there is no clear choice for what this convective reference velocity should be. It might be the mass average velocity that is basic to the equations of motion, which in turn are a generalization of Newton’s second law. It might be the velocity of the solvent, because that species is usually present in excess. We cannot automatically tell. We only know that we should choose $\boldsymbol{v}^a$ so that $\boldsymbol{v}^a$ is zero as frequently as possible. By doing so, we eliminate convection essentially by definition, and we are left with a substantially easier problem.

To see which reference velocity is easiest to use, we consider the diffusion apparatus shown in Fig. 3.1-2. This apparatus consists of two bulbs, each of which contains a gas or liquid solution of different composition. The two bulbs are connected by a long, thin capillary containing a stopcock. At time zero, the stopcock is opened; after an experimentally desired time, the stopcock is closed. The solutions in the two bulbs are then analyzed, and the concentrations are used to calculate the diffusion coefficient. The equations used in these calculations are identical with those used for the diaphragm cell.

Here, we examine this apparatus to elucidate the interaction of diffusion and convection, not to measure the diffusion coefficient. The examination is easiest for the special cases of gases and liquids. For gases, we imagine that one bulb is filled with nitrogen and the other with hydrogen. During the experiment, the number of moles in the left bulb always equals the number of moles in the identical right bulb because isothermal and isobaric ideal gases have a constant number of moles per volume. The volume of the left bulb equals the volume of the right bulb because the bulbs are rigid. Thus the average velocity of the moles $\boldsymbol{v}^*$ and the average velocity of the volume $\boldsymbol{v}^0$ are both zero.

In contrast, the average velocity of the mass $\boldsymbol{v}$ in this system is not zero. To see why this is so, imagine balancing the apparatus on a knife edge. This edge will initially be located left of center, as in Fig. 3.1-2(b), because the nitrogen on the left is heavier than the hydrogen on the right. As the experiment proceeds, the knife edge must be shifted toward the center because the densities in the two bulbs will become more nearly equal.

Thus, in gases, the molar and volume average velocities are zero but the mass average velocity is not. Therefore, the molar and volume average velocities allow a simpler description in gases than the mass average velocity.

We now turn to the special case of liquids, shown in Fig. 3.1-2(c). The volume of the solution is very nearly constant during diffusion, so that the volume average velocity is very nearly zero. This approximation holds whenever there is no significant volume change after mixing. In my experience, this is true except for some alcohol–water systems, and even in those systems it is not a bad approximation.

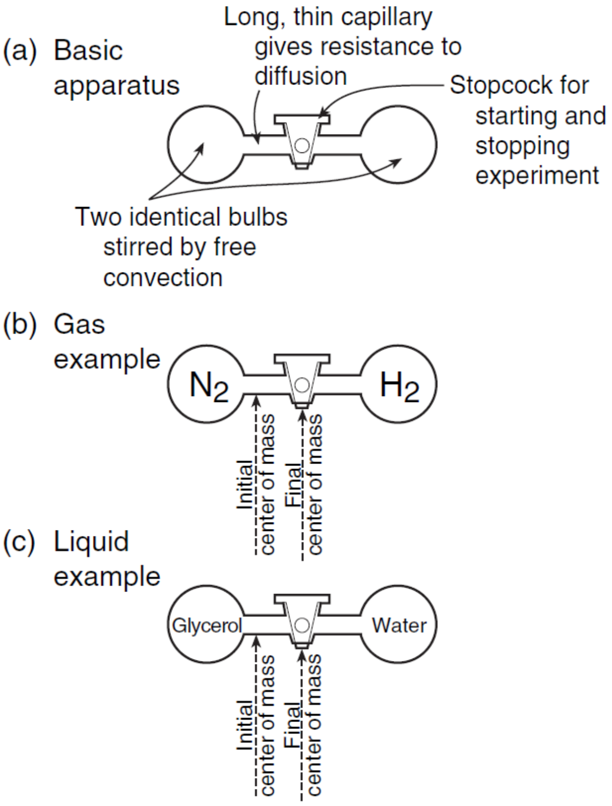


Fig. 3.1-2. An example of reference velocities. Descriptions of diffusion imply reference to a velocity relative to the system's mass or volume. Whereas the mass usually has a nonzero velocity, the volume often shows no velocity. Hence diffusion is best referred to the volume's average velocity.

The other two velocities are more difficult to estimate. To estimate these velocities for one case, imagine allowing 50-weight percent glycerol to diffuse into water. The volume changes less than 0.1 percent during this mixing, so that the volume average velocity is very nearly zero. The glycerol solution has a density of about 1.1 g/cm^3, as compared with water at 1 g/cm^3, so that the mass density changes about 10 percent. In contrast, the glycerol solution has a molar density of about 33 mol/l, as compared with water at 55 mol/l; so the molar concentration changes about fifty percent. Thus the mass average velocity will be nearer to zero than the molar average velocity.

Thus in this set of experiments, the molar and volume average velocities are zero for ideal gases and the volume and mass average velocities are close to zero for liquids. The mass average velocity is often inappropriate for gases, and the molar average velocity is rarely used for liquids. The volume average velocity is appropriate most frequently, and so it will be emphasized in this book.

3.2 Different Forms of the Diffusion Equation

The five most common forms of diffusion equations are given in Table 3.2-1. Each of these forms uses a different way to separate diffusion and convection. Of course,