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

Authors: Roderick ML & Shakespeare CJ

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. Thank you.

We can make the text larger on the axes of both Figures 1 and 2 as suggested in a revised submission.

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 intend to follow the suggestion of the reviewer by modifying Eqn 5 to include the additional advective flux (accounting for the "the bulk flow") that is implicitly requested by the reviewer. This will account for roughly 2% of the total flux and we note that it is actually slightly larger than the Soret effect. We will follow the standard mechanical engineering (Kreith et al 1999) and chemical engineering (Cussler 2009) texts when implementing this "bulk flow" based effect. The net effect of this change is that the original conclusions of the manuscript will be unaltered.

The reviewer has also asserted that diffusion can only be described using a mass-based framework. In our case the molar-based framework is useful because it fits in with recent existing work that also used a molar-based framework (Griffani et al 2024). Through the additional work we have found that it has long been established that one can use either mass- or molar-based frameworks interchangeably. There is a vast scientific literature on this topic (e.g. Cullinan 1965; Brady 1975; Miller 1986) that establishes the complete equivalence of mass- and molar-based frameworks for describing diffusion. On our reading we have found the key thing is not actually the units used (i.e., mass or molar) but instead it is the definition of the reference velocity. This key point is explained in detail in the above cited references (e.g. Cullinan 1965; Brady 1975; Miller 1986). 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. R1. 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.

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

Choice	Total flux (diffusion + convection)	Diffusion equation	Reference velocity	Where best used
Mass	$n_1 = j_1^m + \rho_1 v$	$j_1^m = \rho_1(v_1 - v)$ $\quad = -D\rho\nabla\omega_1$	$v = \omega_1 v_1 + \omega_2 v_2$ $\rho v = n_1 + n_2$	Constant-density liquids; coupled mass and momentum transport
Molar	$n_1 = j_1^* + c_1 v^*$	$j_1^* = c_1(v_1 - v^*)$ $\quad = -Dc\nabla y_1$	$v^* = y_1 v_1 + y_2 v_2$ $cv^* = n_1 + n_2$	Ideal gases where the total molar concentration c is constant
Volume	$n_1 = j_1 + c_1 v^0$	$j_1 = c_1(v_1 - v^0)$ $\quad = -D\nabla c_1$	$v^0 = c_1\bar{V}_1 v_1 + c_2\bar{V}_2 v_2$ $\quad = \bar{V}_1 n_1 + \bar{V}_2 n_2$	Best overall; good for constant-density liquids and for ideal gases; may use either mass or mole concentration
Solvent	$n_1 = j_1^{(2)} + c_1 v_2$	$j_1^{(2)} = c_1(v_1 - v_2)$ $\quad = -D_1\nabla c_1$	v_2	Rare except for membranes; note that $D_1 \neq D_2 \neq D$
Maxwell–Stefan		$\nabla y_1 = \dfrac{y_1 y_2}{D'}(v_2 - v_1)$	None	Written for ideal gases; difficult to use in practice

Figure R1   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 'Issac' 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, UK2009.

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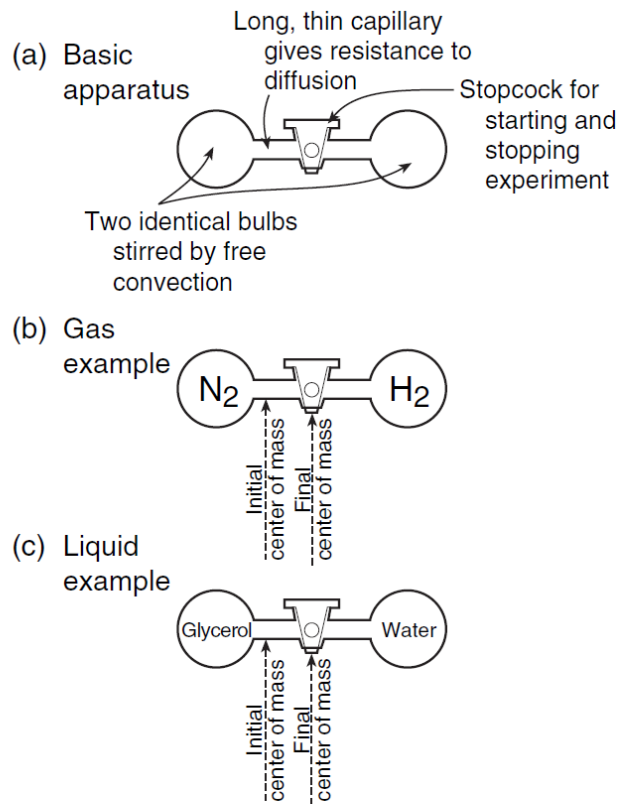
Fig. 3.1-2. An example of reference velocities. Descriptions of diffusion imply reference to a velocity relative to the system's mass or volume. Whereas the mass usually has a nonzero velocity, the volume often shows no velocity. Hence diffusion is best referred to the volume's average velocity.

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,