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

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Combined Response to:

RC6 (Demetris Koutsoyiannis, 26 Sep 2024)

RC7 (Andrew Kowalski, 27 Sep 2024)

RC8 (Demetris Koutsoyiannis, 27 Sep 2024)

Author Response in bold.

The review (RC6) did not raise any issues (other than the units typo also identified by Dr Kowalski). We thank Dr Koutsoyiannis for his careful analysis of the mass vs molar based expressions for diffusion (RC6).

In a further response, Dr Kowalski (RC7) has argued that the mass vs molar-based derivation by Dr Koutsoyiannis (RC6) made an error and that the density cannot be taken inside the derivative which has subsequently been noted (RC8).

In summary, if the density were to be placed outside the derivative then one can still convert between mass and molar based expressions.

To pursue this topic further we consulted a standard engineering reference on the topic, i.e., the CRC Mechanical Engineering Handbook (Kreith et al 1999) and the relevant “snapshot” from that text is shown below (Fig. R1). This handbook firstly asserted that Fick’s Law can be specified on either a mass or molar basis and that both expressions are equivalent. Second, the text agreed with the point of view of Dr Kowalski that the density must be outside the integral (as we had done in our submitted manuscript).

We also read widely on the topic and agree with Dr Kowalski that diffusion has been described in many ways over the years. In practice the expression using density inside the derivative (as used in RC7) is commonly used in liquids and solids without much error. However, in a gas the kinetic theory predicts that the density should be outside the derivative.

We thank the reviewers (Kowalski, Koutsoyiannis) for forcing us to look more into this issue than we had done previously.

Mechanisms of Diffusion

Ordinary Diffusion

Fick's law of ordinary diffusion is a linear relation between the rate of diffusion of a chemical species and the local concentration gradient of that species. It is exact for a binary gas mixture, for which the kinetic theory of gases gives

$$j_1 = -\rho D_{12} \nabla m_1 \text{ kg/m}^2 \text{ sec} \quad (4.7.24a)$$

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Section 4

on a mass basis, and

$$J_1^* = -c D_{12} \nabla x_1 \text{ kg/m}^2 \text{ sec} \quad (4.7.24b)$$

on a molar basis; \mathcal{D}_{12} (m²/sec) is the binary diffusion coefficient (or mass diffusivity), and $\mathcal{D}_{21} = \mathcal{D}_{12}$. Equations (4.7.24a) and (4.7.24b) are mathematically equivalent; however, notice that it is incorrect to write

$$j_i = -\mathcal{D}_{12} \nabla \rho_1 \quad (4.7.25)$$

since $\nabla \rho_1 \neq \rho \nabla m_1$ in general. Fick's law in the form of Equations (4.7.24a) and (4.7.24b) is also valid for dilute liquid and solid solutions, for which it is often possible to assume ρ (or c) constant, and then Equation (4.7.25) or its molar equivalent are good approximations.

Fig. R1 "Snapshot" of part of pages 4-211 and 4-212 from Kreith et al (1999).

References

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.