

## ABSTRACT

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### **Effect of Cross Phenomenological Constants of Onsager Formalism (Vacancy Wind Effect) on Estimated Diffusion Coefficients in Binary, Ternary/Multicomponent Systems Considering Molar Volumes of Diffusing Elements**

Aloke Paul

Department of Materials Engineering, Indian Institute of Science, Bangalore, India 560012

Manning (1967-70) established the intrinsic and tracer diffusion coefficient correlation by considering both main and cross-phenomenological constants of Onsager formalism, albeit assuming constant molar volume, simplifying the analysis. He mentioned the need for correction when molar volume variation is not constant, although it has never been practiced until now. The variation in molar volume with composition in real systems is never exactly constant. This may vary (almost) ideally following the rule of mixture (Vegard's law) or deviate positively and negatively. Therefore, the correct correlation considering the actual molar volume in a real system is first derived in this study. The differences in the contribution of the vacancy wind effect (role of cross phenomenological constants of Onsager) considering actual and constant molar volume variation (which was practiced previously) are calculated and explained first in the binary systems. This shows that the contribution was underestimated or overestimated by considering a constant molar volume variation and depending on whether the element with higher or lower partial molar volume has higher or lower relative mobility. The tracer diffusion coefficients calculated in different systems from intrinsic diffusion coefficients estimated following the Kirkendall marker experiment explains the importance of considering the ideal or non-ideal molar volume instead of the constant molar volume variation. Moreover, the values considering ideal or non-ideal molar volume variation do not show much difference. Therefore, this analysis is then extended to ternary and multicomponent systems considering the molar volume of diffusing elements (ideal variation) instead of assuming constant molar volume, which is invariably done until now. Analysis conducted until now indicates a significant error in calculation for neglecting the molar volume variation depending on the difference in actual molar volumes of the elements and diffusivities.