The Trouton-Hildebrand-Everett Rule

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Fundamental scientific reasons are advanced for preferring the formulation of the THE Rule offered in a Note of 1996 to that employed by Rooney in a Note of 1997. These illustrate that, whereas Transition State theory has been of considerable service to the development of chemical kinetics, it has not been of any utility in regard to issues of thermodynamics

Key words: Trouton-Hildebrand-Everett Rule, Entropy of Vaporisation, Transition State Theory.

The author's previous comments [1] on the Trouton-Hildebrand-Everett (THE) rule have been followed by a note from Professor Rooney [2] which tends to put them in a context which this author did not intend. The purpose of this note is to explain the reasons for the consequent unease.

The THE rule [3], which was shown [1, 4, 5] to be a better correlation for the molar entropy of vaporisation of a range of substances than is the original and more widely known one of Trouton [6], may be written as

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} = R\ (4.0 + \ln\ T_{\text{b}}). \qquad (1)$$

Within the conventions of thermodynamics, this entropy change reflects only the difference between the initial and the final states in this operation. For that reason, reference was made [1] only to the respective nature of the vapour and the bulk liquid phases, and the necessary assumption in regard to the latter phase such that the entropy difference between the two could be expressed as in (1), was then deduced.

While Rooney's recent comments [2] are along the same lines as his earlier paper [7], they do not appear fully consistent with that well-known maxim of thermodynamics, regarding the independence of the change in any state function of the path from the initial to the final state. In the context of an evaluation of either the enthalpy of vaporisation, ΔH_{vap}, or the entropy of vaporisation, ΔS_{vap}, the concept of a transition state at the liquid-vapour interface can only be seen as an irrelevance. After all, the removal of a whole layer of molecules from the surface of a liquid would serve only to leave an equal number of other molecules exposed. Clearly, the passage of a molecule from the interface to the vapour phase does not actually represent the process to which the entropy of vaporisation refers.

Another unusual aspect of Rooney's formulation of this question, given that he invokes Transition State theory, is his use of the cube of δ, the characteristic distance within which the transition state is deemed to exist. While this has the appreciable merit of yielding a quantity with the dimensions of a volume, which is obviously convenient in the context in which [2, 7] it is used, it cannot realistically be claimed, whether in regard to this issue of thermodynamics or any other, that δ^3 can have any physical significance.

For these reasons, I would prefer to continue to describe the figure of 1.5 cm^3 mol^{-1}, which emerged from my previous deliberations [1] in regard to the rationale of (1), as the effective molar volume for translational motion in a liquid.

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