An Explanation of the Paradox Underlying the Trouton-Hildebrand-Everett Rule

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The Trouton-Hildebrand-Everett rule, which is a refinement of Trouton's rule, requires that the so-called molar liquid free volume, V_1^0, in the expression $\Delta S_b^0 = R\ln(V_g^0/V_1^0)$ for the entropy of vapourization of molecular liquids is a constant with a volume of 1.5 cm, whereas V_g^0, the corresponding vapour free volume, is directly dependent on the value of the boiling point, T_b. This paradox is resolved using a statistical mechanical rationale for ideal systems which shows that V_1^0 is in reality N times a molecular volume derived from a characteristic distance in the liquid-vapour transition state. This distance is the same for all ideal molecular liquids.

Key words: Trouton-Hildebrand-Everett rule, Paradox, Statistical mechanical rationale, Characteristic transition state distance.

The best analytical form [1, 2] of Trouton's rule is given by the expression $\Delta S_b^0 = R(4 + \ln T_b)$, where ΔS_b^0 is the molar entropy involved, and T_b is the boiling point. This equation is very readily derived [3] using the following molar partition functions for ideal systems:

Q_1: Solid (Einstein)
$(kT/h\nu)^{3N}$,

Q_2: Liquid (cell theory)
$(kT/h\nu)^{3N} \cdot e^N$,

Q_3: Gas
$(2\pi m kT/h^2)^{3N/2} \cdot V^N/N!$,

Q_4: Liquid/gas transition state
$(2\pi m kT/h^2)^{3N/2} \cdot (N\delta^3)^N/N!$.

Here m is the molecular mass, N Avogadro's number, V the molar gas volume and δ a characteristic transition state distance.

The equivalence of functions Q_2 and Q_4 is realized, following Eyring's transition state theory in kinetics, by putting $\delta = 1/\nu(kT/2\pi m)^{1/2}$, where ν is the liquid/gas transition-state frequency.

ΔS_b^0 is then simply evaluated as $k\ln Q_3/Q_2$, or $k\ln Q_3/Q_4 = R\ln(V/N\delta^3)$, which can be expressed as $R\ln(22{,}410 \cdot T_b/1.5 \cdot 273)$, assuming that $N\delta^3$ is a characteristic molar volume independent of T with a value of 1.5 cm^3. Such expressions have been derived previously [1] giving ΔS_b^0 as $R\ln V_g^0/V_1^0$, where V_g^0 is the molar free volume of the vapour at the boiling point and V_1^0 is the corresponding value for the liquid.

However, the real theoretical enigma is that, while V_g^0 is a simple function of T at one bar ($PV = RT$), the corresponding quantity V_1^0 would have to be independent of T if $R\ln V_g^0/V_1^0$ is to be expressed as $R(4 + \ln T_b)$. The answer lies in the paradox that $R\ln(V/N\delta^3)$ is expressed better as $R\ln V_g^0/v_1^0 - R\ln N$, where v_1^0 is the transition state standard free molecular volume in the liquid. Thus V_g^0 is both a molecular and a molar free volume, subject to the ideal gas law, and thus a linear function of T, whereas v_1^0 is strictly a molecular property which is a constant for a series of similar liquids, and is independent of T_b [3].

The significance of the expression $R\ln V_g^0/v_1 - R\ln N$ can only be fully appreciated by using the detailed partition functions. Each molecule escapes from a molecular-size box in the liquid into a molar-size box for the vapour phase, but the statistics show that there is an additional entropy term, $R\ln N$, arising from the interchange of N identical cells in the liquid. V_1^0 therefore has no reality as a molar quantity, and its usage as an equality for $v_1^0 N$ merely disguises the fact that v_1^0 is the true physical quantity.

A recent extensive and thorough analysis [4] of all of the theory and much of the data pertaining to Trouton's rule has confirmed that V_1^0 has a value of 1.5 cm^3 and is indeed a constant for all the substances investigated. This accords completely with the idea of a characteristic liquid/vapour transition state distance for all ideal molecular liquids [3].

The treatment therefore illustrates the continuity of ideal states of matter from characteristic frequency and Einstein theory of heat capacity of solids, through the cell theory of liquids, to the idea of a characteristic distance at the liquid/vapour equilibrium. In this respect it also represents the change from a frequency to a distance in Eyring's treatment of transition states in kinetics, i.e. a continuity from reactants to products in which bonds (oscillators) are broken and the separate parts become translators.

Reprint requests to Prof. J. J. Rooney.

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