The Rationale of Trouton's Rule and of the Trouton-Hildebrand-Everett Rule

S. R. Logan

School of ABCS, University of Ulster, Coleraine, BT52 1SA, N-Ireland, UK

Z. Naturforsch. **51a,** 1247–1248 (1996);
received October 9, 1996

In seeking a rational basis for the general rules regarding the enthalpy of vaporisation of a liquid, it is shown that whereas Trouton's Rule is consistent with the assumption that the effective molar volume, *v*, for translational motion in the liquid is a constant fraction (2×10^{-5}) of the molar volume of *vapour* at 1 atm, the rather better approximation of Trouton, Hildebrand and Everett (THE), which corrects for the effects of varying molecular density in the vapour, requires that *v* be 1.5 $\text{cm}^3\,\text{mol}^{-1}$ for all substances. The introduction of the apparently more reasonable assumption that *v* is a constant fraction of the molar volume of the *liquid*, is shown to lead to an expression exhibiting much poorer correlation. It thus offers no improvement to Trouton's rule nor to the THE rule.

Key words: Trouton's rule, The THE rule, Entropy of vaporisation, Translational entropy, Sackur-Tetrode equation.

In 1884, Trouton [1] drew attention to the fact that, for a wide range of liquids, the ratio of the molar enthalpy of vaporisation ΔH_b to the boiling point T_b on the Kelvin scale is approximately constant. With the calorie serving as the unit of energy, the relevant number was 21 to 22 $\text{cal K}^{-1}\,\text{mol}^{-1}$; now, that the joule is the recommended international unit, it is appropriate to say *ca* 90 $\text{J K}^{-1}\,\text{mol}^{-1}$, but allowing rather greater numerical latitude.

The quotient $\Delta H_b/T_b$ to which Trouton drew attention is, of course, the molar entropy of vaporisation of the liquid at the boiling point, ΔS_{vap}. So Trouton's rule, which may be found in the indexes of most textbooks of physical chemistry, is, in effect, an assertion that ΔS_{vap} can be expected to be the same for all substances.

However, as applied to liquids with a wide range of boiling points, this "rule" is less than satisfactory. Methane (boiling at 112 K) and argon (87.5 K) give ΔS_{vap} values of 77.7 and 86.5 $\text{J K}^{-1}\,\text{mol}^{-1}$, whereas zinc (1180 K) and copper (2868 K) give the high values of 98.8 and 108.5 $\text{J K}^{-1}\,\text{mol}^{-1}$. Hildebrand [2] pointed out that a comparison of ΔS_{vap} for different substances at their respective boiling points, while it implied a constancy of the vapour pressure at one atmosphere, also meant that the entropy change was being measured under conditions where the vapour phase occupied a whole range of different molar volumes. He suggested, instead, that "the entropy of vaporisation for normal liquids is the same when evaporated to the same concentration", meaning that the entropy change should be measured with all substances evaporating to the same molar volume in the vapour phase.

This proposal of Hildebrand was subsequently recast by Everett [3], and is normally written:

$$\Delta S_{\text{vap}} = \frac{\Delta H_b}{T_b} = R\,\{4.0 + \ln(T_b/\text{K})\}\,. \qquad (1)$$

This revised equation implies that the boiling point, T_b, is a relevant parameter in this connection and that it is $(\Delta S_{\text{vap}} - R\ln T_b)$ which is to be expected to be constant. Alternatively, it asserts that, for a range of substances, ΔS_{vap} should vary with $R\ln(T_b/\text{K})$ and Shinoda [4] has demonstrated that this is so, with a slope of +1.0.

The main thrust of (1) is that it appreciably modifies the picture in regard to liquids with either very high or extremely low boiling points. It may reasonably be claimed that (1), otherwise known as [5] the Trouton-Hildebrand-Everett (THE) rule, is a superior approximation to that of Trouton. However, it is scarcely to be found in physical chemistry texts.

In the paper in which (1) was derived, Everett [3] discussed the entropy change in terms of the behaviour of a set of non-polar quasi-spherical molecules. What is significant, of course, is the difference in the molecular behaviour of the liquid and the vapour states. Such molecules may be expected to vibrate and to rotate in the liquid phase, just as they do in the vapour. In the liquid, molecules are not fixed in one position, so they will undergo translational movements. However, the scope for this translational motion must be severely restricted in the liquid phase.

On this basis, an estimate of the entropy of vaporisation, ΔS_{vap}, can be obtained from the difference in the Sackur-Tetrode equations which are pertinent to the respective translational entropies. In the case of

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Reprint requests to Dr. S. R. Logan.

0932-0784 / 96 / 1200-1247 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen

the vapour, this is well documented as

$$S_v = R\left[\frac{3}{2}\ln(T/\mathrm{K}) + \ln(V/\mathrm{m}^3) + \frac{3}{2}\ln(M/\mathrm{kg\,mol}^{-1}) + 18.61\right], \tag{2}$$

where V denotes the molar volume of the vapour at 1 atmosphere pressure, and M is the molar mass. For the liquid, a similar equation applies but the relevant volume in the second term is now very much smaller and will be denoted by v:

$$S_1 = R\left[\frac{3}{2}\ln(T/\mathrm{K}) + \ln(v/\mathrm{m}^3) + \frac{3}{2}\ln(M/\mathrm{kg\,mol}^{-1}) + 18.61\right]. \tag{3}$$

Subtracting (3) from (2), we obtain, for the entropy of vaporisation at the boiling point

$$\Delta S_{\mathrm{vap}} = R\ln(V/v). \tag{4}$$

If V/v were a constant equal to 5×10^4 then Trouton's rule would be the consequence. However, V is heavily dependent on the boiling point of the liquid, to which (to a good approximation) it is proportional. There would seem no valid reason why v, the effective volume for translational motion in the liquid, should show a comparable dependence on the boiling point.

Starting from (2), if for V, the molar volume of the vapour, we were to substitute RT/P, we obtain

$$S_v = R\left[\frac{3}{2}\ln(T/\mathrm{K}) + \ln\left(\frac{R}{P}\middle/\mathrm{m}^3\,\mathrm{K}^{-1}\,\mathrm{mol}^{-1}\right) + \frac{3}{2}\ln(M/\mathrm{kg\,mol}^{-1}) + \ln(T/\mathrm{K}) + 18.61\right]. \tag{5}$$

When (3) is subtracted, we now have

$$\Delta S_{\mathrm{vap}} = R\left[\ln\left(\frac{R}{P}\middle/\mathrm{m}^3\,\mathrm{K}^{-1}\,\mathrm{mol}^{-1}\right) + \ln(T/\mathrm{K}) - \ln(v/\mathrm{m}^3\,\mathrm{mol}^{-1})\right]. \tag{6}$$

On the right-hand side of this equation, the first term is a constant at the boiling point, since the pressure is then one atmosphere. If v is also constant, then the expression is of the same form as (1). In fact, the THE rule results if v for all substances has a constant value of 1.5 $\mathrm{cm}^3\,\mathrm{mol}^{-1}$.

An alternative viewpoint might be that the value of v, the effective volume regarding the translational motion of the molecules in the liquid, is unlikely to be the same for all substances, but might reasonably be a constant fraction of the total molar volume of the liquid, $\boldsymbol{v}$. Let this fraction be f, so we have

$$v = f\boldsymbol{v} = f\,M/\varrho\,, \tag{7}$$

where ϱ denotes the density of the liquid. If we substitute this into (6), we obtain

$$\Delta S_{\mathrm{vap}} = R\left[\ln\left(\frac{R}{Pf}\middle/\mathrm{m}^3\,\mathrm{K}^{-1}\,\mathrm{mol}^{-1}\right) + \ln(T/\mathrm{K}) - \ln\left(\frac{M}{\varrho}\middle/\mathrm{m}^3\,\mathrm{mol}^{-1}\right)\right], \tag{8}$$

where the first term is presumed to be a constant. By this equation, in order to obtain an invariant quantity from the entropy of vaporisation at the boiling point, one needs to correct both for variations in the boiling point and in the molar volume.

As a token test of the usefulness of (8), calculations were made of the fluctuations exhibited by ΔS_{vap}, by $(\Delta S_{\mathrm{vap}} - R\ln(T_b/\mathrm{K})$ and by $[\Delta S_{\mathrm{vap}} - R\ln(T_b/\mathrm{K}) + R\ln(M\varrho^{-1}/\mathrm{m}^3\,\mathrm{mol}^{-1})]$ for the linear alkanes, C_1 to C_{10}. It was found that, whereas the standard deviation of the second was less than that of the first, the standard deviation of the third was greater. Similar calculations were made with a more extensive list of more than 40 inorganic and organic substances, from which all that associate by hydrogen bonding were excluded. This produced the same result, with manifestly greater scatter from $[\Delta S_{\mathrm{vap}} - R\ln(T_b/\mathrm{K}) + \ln(M\varrho^{-1}/\mathrm{m}^3\,\mathrm{mol}^{-1})]$ than from ΔS_{vap}. Clearly (7), reasonable as its origins may seem, receives no endorsement from the data.

The best available correlation of the entropies of vaporisation of different substances would thus seem to be the THE rule, which can be rationalised on the basis of a constant value, for all substances, of the effective volume in relation to translational motion in the liquid state. The exclusion of hydrogen bonding substances from consideration in this regard, on the grounds that they are strongly associated in the liquid state, is merited because association will inhibit both translational and rotational motion. In consequence, the entropies of vaporisation of such substances would be expected to be anomalously large, and it is well known that this is indeed the case.

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