519. *Some Correlations between Thermodynamic Properties and the Structure of Liquids.*

By D. H. Everett.

A set of *standard molecular liquids* is selected whose thermodynamic properties conform to certain simple equations and with which the properties of other liquids can be compared. The group is found to consist of molecules all of which are effectively spherical, and deviation of a liquid from standard behaviour is closely related to lack of spherical symmetry of its molecules. The method involves a modification of Trouton's rule, similar to Hildebrand's well-known variant but much easier to apply. The criterion adopted is related thermodynamically to the Barclay–Butler equation between heats and entropies of vaporisation, and leads to a more general heat–entropy relation. Equations for other thermodynamic properties of these liquids (heat of vaporisation, vapour pressure, and heat-capacity change on vaporisation) are also derived. The liquids selected do not follow the principle of corresponding states accurately and it is concluded that their intermolecular forces are not conformal.

Many attempts have been made to define the properties of " normal," " ideal," or " perfect " liquids with which the behaviour of real liquids can be compared. Most have been based on a study of the entropy of vaporisation of liquids considered either empirically, as in the classical work of Trouton,[1] of Hildebrand,[2] and, more recently, of Barclay and Butler,[3] or theoretically by using the principle of corresponding states (*e.g.*, Pitzer,[4] Guggenheim,[5] Longuet-Higgins [6]). However, as far as the author is aware, the simple modification of Trouton's rule described below [7] has not previously been employed as a basis for the comparison of liquids. Its ease of application, the precision with which it applies to a group of quasi-spherical hydrocarbon molecules, and the close relation between deviations from the rule and the asymmetry of the molecules concerned, are all factors contributing to its usefulness. It should have considerable value, not only for the qualitative discussion of the freedom of rotational motion in liquids, but also as a basis with which the predictions of theories of liquids may be compared.

Entropies of Vaporisation.—The standard entropy of vaporisation of a liquid can be defined in various ways depending on the choice of " standard state " of the vapour phase. Three alternative definitions are summarised in Fig. 1. Previous " rules " relating to the entropy of vaporisation have been concerned mainly with Δs^b, *i.e.*, with the entropy difference between a liquid and vapour in equilibrium with it under specified conditions. We accept Hildebrand's well-known criticism of the original Trouton rule, but correct for its shortcomings in a different way. We retain, provisionally, the normal boiling point as the appropriate temperature at which to make the comparison, but instead of considering the process of evaporation to the saturated vapour, we consider evaporation to vapour (not now in equilibrium with the liquid) having a definite chosen molar volume $v^{\ddagger}$. The entropy change in this process, which (see Fig. 1) we denote by $\Delta s^{\ddagger}$, is given by

$$\Delta s^{\ddagger} = \Delta s^b + \boldsymbol{R} \ln v^{\ddagger}/v^{\text{sat}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where v^{sat} is the molar volume of saturated vapour at 1 atm. pressure. If we assume that

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[1] Trouton, *Phil. Mag.*, 1884, **18**, 54.

[2] Hildebrand, *J. Amer. Chem. Soc.*, 1915, **37**, 970; 1918, **40**, 45.

[3] Barclay and Butler, *Trans. Faraday Soc.*, 1938, **34**, 1445.

[4] Pitzer, *J. Chem. Phys.*, 1939, **7**, 583.

[5] Guggenheim, *ibid.*, 1945, **13**, 253.

[6] Longuet-Higgins, *Proc. Roy. Soc.*, 1951, *A*, **205**, 247.

[7] Originally communicated at a meeting of the Chemical Society, 18th February 1954; see *Chem. and Ind.*, 1954, 429.

the vapour can be treated as a perfect gas, and choose $v^{\ddagger} = 22{,}414$ cm.^{3} mole^{-1}, it follows immediately that

$$\Delta s^{\ddagger} = \frac{\Delta h^b}{T_b} + \boldsymbol{R}\ln\frac{273{\cdot}15}{T_b} \qquad . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

Examination of the data for all saturated hydrocarbons up to C_{14} listed in the American Petroleum Institute tables of properties of hydrocarbons,[8] shows that for these ninety substances

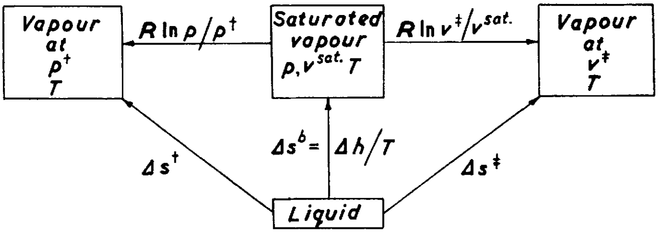
$$\Delta s^{\ddagger} = 19{\cdot}7 \pm 0{\cdot}7 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \qquad . \ . \ . \ . \ . \ . \quad (3)$$

whereas the conventional Trouton constant

$$\Delta s^{b} = 19{\cdot}5 \pm 2{\cdot}1 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \qquad . \ . \ . \ . \ . \ . \quad (4)$$

and shows a steady drift with the boiling point of the compound. Furthermore, when the

FIG. 1. *Definition and notation of entropies of vaporisation (vapour assumed to be a perfect gas).* [Δs^b is the difference in entropy between vapour and liquid in equilibrium with one another at a temperature T; $\Delta s^{\dagger}$ is the difference between the entropy of vapour at a standard pressure $p^{\dagger}$ (not necessarily 1 atm.) and liquid at the same T; $\Delta s^{\ddagger}$ is that between vapour occupying a standard volume $v^{\ddagger}$ and liquid.]



Entropy rules

Trouton (1884), Δs^b = const., p = const. (usually 1 atm., *i.e.*, at the normal b. p.).
Hildebrand (1915), Δs^b = constant, $\boldsymbol{R}T/p$ = const., *i.e.*, $v^{\text{sat.}}$ = const.
Pitzer (1939), Δs^b = const., $v^{\text{sat.}}/v^l$ = const.
Guggenheim (1945), Δs^b = const., p/p_c = const.
Barclay and Butler (1938), $\Delta s^{\dagger} = A + B\Delta h^{\dagger}$, T = const.
This paper, $\Delta s^{\ddagger}$ = const., p = const.

TABLE 1(*a*). *Entropies of vaporisation of standard hydrocarbons* (in calories).

Compound	T_b (p = 1 atm.)	Δs^b (p = 1 atm.)	$\Delta s^{\ddagger}$ ($v^{\ddagger}$ = 22·4 l.)
Methane	111·67°	17·51	19·29
Isopentane	301·01	19·41	19·22
Neopentane	282·66	19·24	19·18
2,3-Dimethylbutane	331·15	19·68	19·30
2,2-Dimethylbutane	322·90	19·47	19·14
2,2-Dimethylpentane	352·37	19·78	19·28
3,3-Dimethylpentane	359·23	19·72	19·18
2,2,3-Trimethylbutane	354·03	19·54	19·03
2,2,4-Trimethylpentane	372·40	19·90	19·29
2,2,3,3-Tetramethylbutane	379·46	19·92	19·27
2,3,3,4-Tetramethylpentane	414·70	20·13	19·31
2,2,4,4-Tetramethylpentane	395·44	19·86	19·13

TABLE 1(*b*). *Entropies of vaporisation of heptanes.*

(Similar behaviour is found with all sets of isomers of alkanes up to C_9.)

Compound	T_b (p = 1 atm.)	Δs^b p = 1 atm.)	$\Delta s^{\ddagger}$ ($v^{\ddagger}$ = 22·4 l.)	Compound	T_b (p = 1 atm.)	Δs^b (p = 1 atm.)	$\Delta s^{\ddagger}$ ($v^{\ddagger}$ = 22·4 l.)
n-Heptane	371·59°	20·38	19·77	2,4-Dimethylpentane	353·67°	19·93	19·42
2-Methylhexane	363·21	20·18	19·62	2,2-Dimethylpentane	352·37	19·78	19·28
3-Ethylpentane	366·63	20·18	19·60	3,3-Dimethylpentane	359·23	19·72	19·18
3-Methylhexane	365·11	20·15	19·58	2,2,3-Trimethylbutane	354·03	19·54	19·03
2,3-Dimethylpentane	362·95	20·01	19·45				

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[8] American Petroleum Institute Project 44, " Selected properties of hydrocarbons " (Washington 1944—1951; Pittsburg, 1951—).

drift of Trouton constant with boiling point has been eliminated, a striking relation between $\Delta s^‡$ and molecular structure is revealed: the more symmetrical the molecule the lower the value of $\Delta s^‡$. We select the twelve " spherical hydrocarbons " in Table 1(*a*) to represent a class of *standard molecular liquids* for which $\Delta s^‡$ lies between very close limits:

$$\Delta s^‡ = 19{\cdot}16 \pm 0{\cdot}15 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

All other hydrocarbons have values of $\Delta s^‡$ greater than this standard value. This figure refers to evaporation to the real gas state: by taking 0·20 as a mean value for the correction to the vapour entropy for gas imperfection at the normal boiling point, we obtain a value for $\Delta s^‡$ for evaporation to the perfect gas state of 19·36 cal. deg.$^{-1}$ mole^{-1}.

The constancy of $\Delta s^‡$ implies that the conventional Trouton constant should vary with normal boiling point according to the equation

$$\Delta s^b = 8{\cdot}00 + \boldsymbol{R} \ln T_b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

An equation of this form, but with 8·75 as the constant term, was suggested on quite different (and in the author's view erroneous) grounds by Kistiakowsky[9] and used by Watson[10] and Schumacher;[11] its connection with the constancy of $\Delta s^‡$ seems not to have been recognised previously.

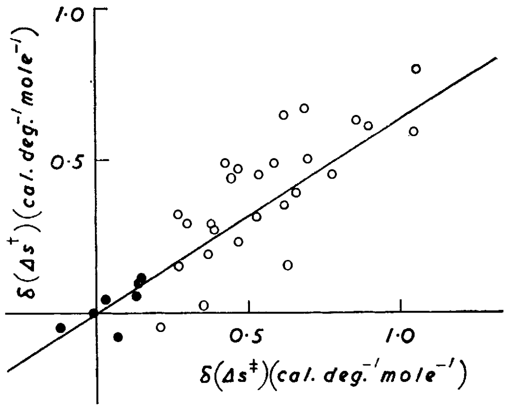

FIG. 2. *Correlation between deviations of entropy of vaporisation from Barclay–Butler equation, $\delta(\Delta s^†)$, and from the new entropy rule, $\delta(\Delta s^‡)$.*

Full line: $\delta(\Delta s^†) = 0{\cdot}64\delta(\Delta s^‡)$.
● Standard liquids.
○ Other hydrocarbons.

A different approach to the problem of deviations from Trouton's rule led Barclay and Butler[3] to suggest that heats and entropies of vaporisation were related, for " normal " liquids, by an equation of the form

$$\Delta s^† = A + B\Delta h^† \text{ (constant } T) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $\Delta s^†$ and $\Delta h^†$ refer to evaporation to a chosen standard pressure $p^†$, not necessarily equal to 1 atm. Frank[12] used an equation of this type as a basis for a discussion of the deviations of real liquids from the properties he ascribes to an " ideal " liquid. Data given in the A.P.I. Tables for the twelve hydrocarbons selected as " standard liquids," show that at 25° and $p^† = 1$ atm. eqn. (7) is followed to within $\pm 0{\cdot}10$ cal. deg.$^{-1}$ mole^{-1} when $A = 12{\cdot}40$ cal. deg.$^{-1}$ mole^{-1} and $B = 0{\cdot}001225$ deg.$^{-1}$. In this case the data given in the A.P.I. Tables are corrected to the ideal-gas state. Points for all other hydrocarbons fall above this line (*i.e.*, have larger values of $\Delta s^†$). Moreover, the deviations from eqn.

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[9] Kistiakowsky, *Z. phys. Chem.*, 1923, **107**, 65.
[10] Watson, *Ind. Eng. Chem.*, 1931, **23**, 360.
[11] Schumacher, *Oel und Kohle*, 1943, **39**, 634.
[12] Frank, *J. Chem. Phys.*, 1945, **13**, 493.

(5) correlate very closely with those from eqn. (7). This is shown in Fig. 2 where the full line represents

$$\delta(\Delta s^{\dagger}) = 0{\cdot}64\delta(\Delta s^{\ddagger}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $\delta(\Delta s^{\dagger})$ and $\delta(\Delta s^{\ddagger})$ are the deviations from eqns. (7) and (5), respectively.

Relation between the New Entropy Rule and the Barclay–Butler Rule.—The fact that two empirical equations, (5) and (7), one of which refers to isothermal conditions and the other to isopiestic, lead to the selection of the same set of compounds to represent " standard " behaviour, and that the deviation of a given liquid from one equation is so closely correlated with its deviation from the other, suggests that these equations are two aspects of a more general relation.

First, we observe that Trouton's rule and the Barclay–Butler equation can be thermodynamically self-consistent if, in eqn. (7),

$$A = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9a)$$

$$B = B'/T; \;\; B' = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9b)$$

A preliminary study by F. W. Smith[13] of the validity of eqn. (7) at −80° and −120° suggests that eqn. (9*b*) is valid, while eqn. (9*a*) is only approximately true. From the value of B at 25° we obtain $B' = 0{\cdot}365$, and this value, together with A at 25°, leads to the Trouton ratio at the normal boiling point

$$\Delta s^{b} = 19{\cdot}5 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

in agreement with 19·5 ± 2·1 for the standard hydrocarbons.

Similarly, the new entropy rule and the Barclay–Butler equation are mutually consistent if

$$\Delta s^{\ddagger} = \Delta s^{b} - \boldsymbol{R} \ln (T_b/273{\cdot}15) = A/(1 - TB) - \boldsymbol{R} \ln (T_b/273{\cdot}15) = \text{constant} \quad (11)$$

This is most simply satisfied by accepting eqn. (9*b*), when

$$A = A' + \boldsymbol{R}(1 - B') \ln T; \;\; A' = \text{constant} \quad . \quad . \quad . \quad . \quad (12a)$$

$$B = B'/T; \;\; B' = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12b)$$

Equation (12*a*) implies a slow increase of A with temperature and is consistent with Smith's findings. Taking $A = 12{\cdot}40$ cal. deg.$^{-1}$ mole^{-1} at 25°, we have $A' = 5{\cdot}22$ cal. deg.$^{-1}$ mole^{-1} and on insertion in eqn. (11),

$$\Delta s^{\ddagger} = 19{\cdot}37 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

at the normal boiling point. This is in exact agreement with the value found experimentally. Furthermore, if deviations from standard behaviour can be attributed to changes in A', then it is easily shown that

$$\delta(\Delta s^{\dagger}) = 0{\cdot}635 \; \delta(\Delta s^{\ddagger}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

again in agreement with the observed relation (8).

We conclude therefore that the equation

$$\Delta s^{\dagger} = A' + \boldsymbol{R}(1 - B') \ln T + (B'/T)\Delta h^{\dagger} \quad . \quad . \quad . \quad . \quad (15)$$

or numerical values being inserted

$$\Delta s^{\dagger}/\boldsymbol{R} = 2{\cdot}63 + 0{\cdot}635 \ln T + 0{\cdot}365 \; \Delta h^{\dagger}/\boldsymbol{R}T \quad . \quad . \quad . \quad . \quad (16)$$

represents the behaviour of all standard liquids and embraces both the Barclay–Butler equation and the new entropy rule. The approximate equation, in which the first two

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[13] Smith, F. W., Ph.D. Thesis, St. Andrews, 1951.

terms on the right-hand side are given the constant value 6·25, embraces the Barclay–Butler equation and Trouton's rule.

Some Consequences of the New Entropy Equation.—Other thermodynamic properties of standard liquids can be deduced from eqn. (7) when the temperature dependence of the parameters A and B is known. Eqns. (9) and (12) provide this at two levels of accuracy. Using eqn. (9), we obtain the following equations which have a validity consistent with that of Trouton's rule:

$$\Delta h^{\dagger}/\boldsymbol{R}T = 9{\cdot}74(T_b/T)^{1{\cdot}575} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (17)$$

$$\Delta c_p{}^{\dagger}/\boldsymbol{R} = -5{\cdot}64(T_b/T)^{1{\cdot}575} \quad . \; . \; . \; . \; . \; . \; . \quad (18)$$

$$-\log_{10} p \text{ (atm.)} = 2{\cdot}70\,[(T_b/T)^{1{\cdot}575} - 1] \quad . \; . \; . \; . \; . \quad (19)$$

To obtain eqn. (19) it is necessary to integrate the Clausius–Clapeyron equation, the assumptions being made that the volume of the liquid phase can be neglected, and that the vapour is perfect. The error thus introduced can be allowed for approximately by replacing 2·70 by 2·76. The resulting one-parameter equation

$$-\log_{10} p \text{ (atm.)} = 2{\cdot}76\,[(T_b/T)^{1{\cdot}575} - 1] \quad . \; . \; . \; . \; . \quad (20)$$

is found to represent the vapour pressures of the standard liquids to within ±2% in the temperature range $T_b/T = 0{\cdot}9$—$1{\cdot}4$, which in most cases extends down to the f. p. It is much more precise than the equation

$$-\log_{10} p \text{ (atm.)} = 4{\cdot}60\,[(T_b/T) - 1] \quad . \; . \; . \; . \; . \; . \quad (21)$$

derived by using Trouton's rule, together with the assumption that $\Delta h^{\dagger}$ is independent of temperature. An abridged table of values of $[(T_b/T)^{1{\cdot}575} - 1]$ and of $\log_{10} p$ corresponding to eqn. (20) is given in Table 2.

TABLE 2. *Vapour pressure of standard liquids according to* (20).

T_b/T	$[(T_b/T)^{1{\cdot}575} - 1]$	$\log p$ (mm. Hg)	p (mm. Hg)	T_b/T	$[(T_b/T)^{1{\cdot}575} - 1]$	$\log p$ (mm. Hg)	p (mm. Hg)
0·90	−0·1529	3·303	2010	1·20	0·3326	1·963	91·8
0·95	−0·0776	3·095	1250	1·25	0·4211	1·719	52·4
1·00	0·000	2·881	760	1·30	0·5117	1·469	29·4
1·05	+0·0799	2·660	457	1·35	0·604	1·214	16·4
1·10	0·1619	2·434	272	1·40	0·698	0·955	9·02
1·15	0·2462	2·201	159				

The more precise approximation leads to the following equations:

$$\Delta h^{\dagger}/\boldsymbol{R}T = (3{\cdot}51 + \ln T_b)(T_b/T)^{1{\cdot}575} + 0{\cdot}635 \quad . \; . \; . \; . \quad (22)$$

$$\Delta c_v/\boldsymbol{R} = \Delta c_p/\boldsymbol{R} - 1 = -0{\cdot}575\,(3{\cdot}51 + \ln T_b)(T_b/T)^{1{\cdot}575} - 0{\cdot}365 \; . \; . \quad (23)$$

$$\log_{10} p \text{ (atm.)} = [0{\cdot}969 + 0{\cdot}635 \log_{10} T_b][(T_b/T)^{1{\cdot}575} - 1] + 0{\cdot}635 \log_{10} (T_b/T) \quad (24)$$

This more precise vapour-pressure equation is also limited in accuracy by approximations involved in integrating the Clausius–Clapeyron equation. If the coefficient of $[(T_b/T)^{1{\cdot}575} - 1]$ is replaced by a value which fits the experimental data at one other temperature, this equation is a slight improvement on eqn. (20), although its more complex mathematical form makes it less attractive as an empirical equation.

The entropy change $\Delta s^{\ddagger}$ at the normal b. p. is discussed above. However, it is easily shown that $\Delta s^{\ddagger}$ at any other chosen pressure is constant for standard liquids, and that its value at a pressure p (atm.) is given by

$$\Delta s^{\ddagger}/\boldsymbol{R} = -1{\cdot}32 \log_{10} p \text{ (atm.)} + 9{\cdot}74 \quad . \; . \; . \; . \; . \; . \quad (25)$$

Deviations from the New Entropy Rule, and Molecular Structure.—Empirically, it is found that deviations of $\Delta s^{\ddagger}$ at the normal b. p. from the standard value are closely related to the lack of spherical symmetry of the molecule: in each group of isomers the normal hydrocarbon has the highest, and the most symmetrical isomer the lowest, value of $\Delta s^\ddagger$ [Table 1(*b*)]. This is the behaviour to be expected if the freedom of rotation of molecules in the liquid state is restricted when the molecule is unsymmetrical in shape or has an unsymmetrical force field.[14] A quantitative measure of the lack of symmetry of hydrocarbons is difficult to define, but an approximate assessment can be made by constructing molecular models, measuring the ratio of the maximum and minimum dimensions in various configurations, and taking an appropriate average. This asymmetry factor (α) is fairly easy to calculate for the smaller hydrocarbons (to about C_6), but for larger molecules the number of configurations to be considered becomes very large and it is difficult to lay down the proper method of averaging. For each molecular weight (M), deviations from the entropy rule are linearly related to (α — 1), but for a given (α — 1) the deviation decreases with increase in molecular weight. Fig. 3 shows that the entropy deviation is roughly proportional to $(\alpha - 1)/M$. Qualitatively, this is not unexpected since the effect of a given energy barrier on the entropy of a restricted rotator decreases as the moment of inertia of the rotating group increases.[15]

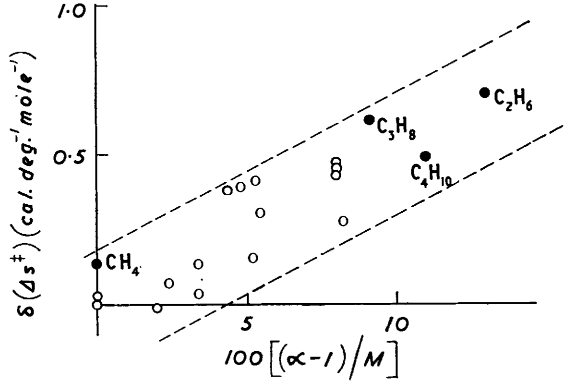

FIG. 3. *Correlation between deviations from the new entropy rule and the lack of spherical symmetry of hydrocarbon molecules.* (*Full circles represent n-alkanes.*)

Applicability to Other Molecules.—These considerations apply most precisely to the entropies of vaporisation of hydrocarbons, for which the data are most extensive and reliable. It is interesting, however, to examine the more general applicability of the new rule. Table 3 summarises the available data on molecules of the form XY_4.[16] The data are of very variable accuracy, but it appears that, while the hydrides have values of $\Delta s^\ddagger$ close to the standard value, other molecules tend to have higher values, the largest being for silicon tetrafluoride which, as it happens, is the molecule for which the electronegativity of the constituent atoms differs most. This suggests that these molecules do not behave exactly as spherical molecules but have certain preferred mutual orientations which lead to a reduction in the freedom of rotation.

TABLE 3. *Tetrahedral* XY_4 *molecules.*

$\Delta s^\ddagger$ (cal. deg.$^{-1}$ mole^{-1}).

Y: X	H	F	Cl	Br	I
C	19·3 ± 0·1	22·0 ± 0·1	20·4 ± 0·05	21·9 ± 1·0	—
Si	19·5 ± 0·4	26·5 ± 2·0	20·2 ± 1·5	20·3 ± 0·6	19·5 ± 0·9
Ge	19·0 ± ?	—	19·5 ± 2	17·5 ± 2	—
Sn	20·4 ± ?	—	20·4 ± 1	19·3 ± 2	20·4 ± 2
Ti	—	—	20·3 ± 0·1	19·7 ± 0·8	18·9 ± 1·5

Mean (excluding SiF_4) = 19·9 (range 17·5 — 22·0).

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[14] *E.g.*, Hildebrand, *Proc. Phys. Soc.*, 1944, **56**, 221.

[15] See, *e.g.*, Taylor and Glasstone, " Textbook of Physical Chemistry," Vol. 1, Appendix II.

The influence of molecular symmetry on $\Delta s^\ddagger$ is well illustrated by molecules of the type XH_aY_b where $a + b = 4$, and Y is a halogen. The data are summarised in Fig. 4: in each case $\Delta s^\ddagger$ for the unsymmetrical molecules is higher than that of either of the symmetrical molecules XH_4 or XY_4.

Finally, consideration of values of $\Delta s^\ddagger$ may be useful in picking out other groups of similar liquids. For example, among the metals the six elements Cu, Zn, Ag, Cd, Au, and Hg (whose conventional Trouton constants lie in the range 22·0—25·3) have values of $\Delta s^\ddagger$ of 20·4 ± 0·2 cal. deg.$^{-1}$ mole^{-1}. Unfortunately, the precision with which the heats of evaporation of most metals are known is so low that other possible regularities are difficult to discern.

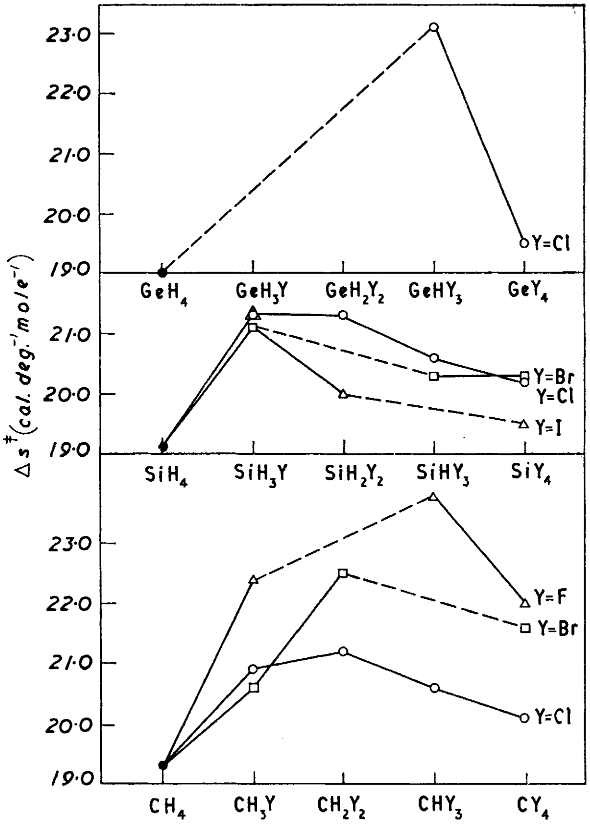

FIG. 4. *Influence of asymmetry of tetrahedral molecules* XH_aY_b *on* $\Delta s^\ddagger$.

Interpretation of the New Entropy Rule.—The present analysis provides a series of equations for the thermodynamic properties of " standard liquids," and any adequate statistical mechanical theory of such liquids must at least provide close approximations to them. The entropy change $\Delta s^\ddagger$ is given by the fundamental statistical-mechanical equation

$$\Delta s^\ddagger = \boldsymbol{R} \ln Q^g/Q^l + \boldsymbol{R} \ln v^\ddagger + \boldsymbol{R} - \{\partial\, (\boldsymbol{k}T \ln \Omega/\partial T\}_V \quad . \quad . \quad . \quad (26)$$

where Q^g and Q^l are the partition functions for the internal degrees of freedom (including rotations of the molecules as a whole) in the gas and the liquid respectively, and $\Omega = \frac{1}{N!}\int . . . \int \exp\,(-W/\boldsymbol{k}T)\mathrm{d}\omega$ is the configurational part of the partition function of liquid containing N molecules confined to a volume V; W is the potential energy of a given configuration, and integration is over all configurations in the given volume. In the cell-theory of liquids it is usual to define a so-called free volume (v_f) of the liquid by $\Omega = (v_f)^N/N!$ whence

$$\Delta s^\ddagger = \boldsymbol{R} \ln Q^g/Q^l + \boldsymbol{R} \ln v^\ddagger/v_f - \boldsymbol{R}T(\partial \ln v_f/\partial T)_V \quad . \quad . \quad . \quad (27)$$

The last term is often assumed to be zero. If it is retained the equation may be simplified by defining another free volume, w_f, by

$$\ln w_f = \ln v_f + T(\partial \ln v_f/\partial T)_V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

If Q^g and Q^l are equal, then

$$\Delta s^\ddagger = \boldsymbol{R} \ln v^\ddagger/w_f \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

The constancy of $\Delta s^\ddagger$ for a series of liquids thus implies that, at their normal boiling points (*i.e.*, when the free energy of the liquid relative to vapour at unit pressure is zero) these liquids are characterised by the same value of w_f, independent of the size of the molecules themselves. It also follows, from eqns. (29) and (25), that the vapour pressure is directly determined by w_f through the equation

$$\ln p \text{ (atm.)} = 1{\cdot}74 \ln w_f \text{ (cm.}^3\text{ mole}^{-1}) + 0{\cdot}414 \quad . \quad . \quad . \quad . \quad (30)$$

when $p = 1$ atm., $w_f = 1{\cdot}31$ cm.^{3} mole^{-1}. A relation between p and w_f will always follow from the existence of a heat–entropy correlation, but the significant feature of eqn. (30) is that, contrary to the principle of corresponding states, neither the pressure nor the volume scales are related to the critical constants.

A statistical-mechanical basis for the Barclay–Butler relation is provided by the theory of conformal fluids,[6] according to which the entropies and heats of evaporation of pure liquids should be linearly related, the slope of the line having the value $B = (\Delta c_p{}^\dagger - \boldsymbol{R})/(T\Delta c_p{}^\dagger + \Delta h^\dagger)$ where $\Delta c_p{}^\dagger$ and $\Delta h^\dagger$ refer to the vaporisation of any one substance. The theory does not, however, predict the temperature-dependence of B. The present analysis gives B either as $\Delta c_p{}^\dagger/(T\Delta c_p - \Delta h^\dagger)$ or as $(\Delta c_p - \boldsymbol{R})/(T\Delta c_p{}^\dagger - \Delta h^\dagger - \boldsymbol{R}T)$ depending on the approximation used, and indicates also that B is inversely proportional to T. The standard reference behaviour here defined thus approaches closely to conformal behaviour, but the spherical hydrocarbons do not fall exactly into this class.

In this connection it may be noted that the rare gases (which do follow the principle of corresponding states) do not conform to the new rule with any accuracy, as shown by the following figures, although the standard value of $\Delta s^\ddagger$ is approached as the size of the atom increases:

Element	Ne	Ar	Kr	Xe	Rn
$\Delta s^\ddagger$ (cal. deg.$^{-1}$ mole^{-1}) ...	20·0	20·0	19·3	19·3	19·1

Conformal liquids satisfy the theorem of corresponding states and are characterised by intermolecular potentials which are of the same mathematical form when expressed as a function of the distance between *molecular centres*. The emphasis, in the present case, on the absolute magnitude of w_f, rather than on its ratio to molar volume, supports the view [17,18,19] that, for polyatomic molecules, it may be more appropriate to consider the shape of the intermolecular potential as a function of the *distance between the nuclei of surface atoms*. Theoretical studies of this model have, however, not been taken far enough to establish whether it provides an explanation of the behaviour of the quasi-spherical polyatomic molecules described in the present paper.

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