430. *An Additive Function of Entropy of Boiling, and the Prediction of Latent Heat of Vaporisation and Vapour Pressure of Liquids.*

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An additive function of entropy of vaporisation is presented by means of which latent heat and vapour-pressure data of a given substance can be evaluated from a knowledge of its b. p. only. The treatment also leads to a plausible correlation of molecular structure and internal order in the liquid state.

The molar entropy of boiling, ΔS, of non-associated liquids at a given vapour pressure is approximately constant. The generalisation breaks down, however, for substances of high b. p., which have high values of ΔS, and for those of low b. p. and molecular weight, for which ΔS is very low. Attempts have been made to make ΔS more nearly constant by expressing it as a function of b. p.,[1] and Hildebrand [2] compared substances at temperatures corresponding to the same molecular concentration of vapour. The latter is generally assumed to be the more successful modification, but it is shown below that the two approaches are really equivalent, and therefore subject to the same limitations.

A theoretical examination of Hildebrand's and Trouton's rules requires the former to lead to more constant ΔS values.[3] There is no doubt that substances whose molecules permit of a degree of internal order in the liquid state tend to exhibit high ΔS values,[2] and a quantitative comparison of substances in terms of different degrees of internal order becomes possible if we choose a valid reference state characteristic of liquids of low internal order The difficulty lies in the fact that, owing to our inadequate knowledge of the liquid state, such a choice must be semi-empirical and arbitrary.

According to Pitzer,[4] the entropy of " perfect liquids " (heavier inert gases and methane; H_2, He, and to a lesser extent Ar, being excluded from quantum considerations) should be the same at corresponding states. This is indeed the case, and Pitzer and Guggenheim,[5] have shown that N_2, O_2, and CO conform fairly closely. For imperfect liquids, however, ΔS values differ greatly when compared at, say, the same reduced temperature, and increase rapidly with increasing liquid complexity.[6]

Imperfect liquids have been compared under the following conditions: (1) Staveley and Tupman [7] proceeded on the basis of Hildebrand's rule, and constructed a " reference entropy of vaporisation curve " from monatomic and " very symmetrical " molecules

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[1] Partington, " An Advanced Treatise on Physical Chemistry," Vol. 2, Longmans, Green and Co., London, 1951.

[2] Hildebrand, *J. Amer. Chem. Soc.*, 1915, **37**, 970; *J. Chem. Phys.*, 1939, **7**, 233.

[3] Hirschfelder, Curtiss, and Bird, " Molecular Theory of Gases and Liquids," Wiley, New York, 1954.

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

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

[6] See, *e.g.*, Pitzer, Lippmann, Curl, Huggins, and Petersen, *J. Amer. Chem. Soc.*, 1955, **77**, 3433 (Table 1).

[7] Staveley and Tupman, *J.*, 1950, 3597.

(Hg, Ar, Kr, Xe, CH_4, GeH_4, CMe_4, $SiMe_4$, and CCl_4), and ΔS values lying above the curve were interpreted in terms of different degrees of internal order or of restriction of molecular rotation. (2) Pitzer[4] concluded from theoretical considerations that comparison should be made at a constant ratio of vapour volume to liquid volume (a condition obeyed, of course, by the inert gases at corresponding states), and if this is correct, Hildebrand's rule is applicable only to substances of identical molar volumes in the liquid state.

Values of ΔS under these two different conditions for a number of substances are presented in Table 1, along with the values under "Trouton conditions." I calculated them by either of two methods, *viz.*, (1) first ascertaining, after the manner used by Pitzer and Hildebrand, the vapour pressure when V_g/V_l or $\log T/p$ has the required value, but then utilising my F and ΔS^r values (below) in order to arrive at more accurate corresponding values of ΔS than some previously reported; (2) from F and the b. p. as described on p. 2135. Such values have the advantage of being calculated under conditions such that (*a*) departure from ideal-gas behaviour on the part of the vapour can be ignored (corresponding vapour pressures for the Hildebrand procedure varying from 17 mm. Hg for N_2 to 125 mm. for I_2, and for the Pitzer procedure from 39 to 128 mm.), and (*b*) the three procedures can the more readily be compared. The following points are relevant:

TABLE 1.

	ΔS (cal. mole^{-1} deg.$^{-1}$)		
Substance	V_g/V_l = 3125	$\log_{10} T/p$ (mm.) = 0·5	At v. p. = 100 mm.
CH_4		26·0	22·9
SiH_4		26·0	23·7
GeH_4		25·7	23·8
GeD_4		26·7 *	24·5
CMe_4		26·5	25·7
$SiMe_4$		26·5	25·9
$SnMe_4$		26·9	26·7
CCl_4	27·9	26·8	26·6
CF_4	27·3	28·2	25·6
$SiCl_4$		26·8	26·4
$GeCl_4$		26·2	26·0
$SnCl_4$		27·3	27·4
F_2	26·5	28·1	24·2
Cl_2	26·4	27·6	26·3
Br_2	27·1	27·9 *	27·4
I_2	27·1	27·2	27·8
C_6H_5F	28·6	27·6 *	27·4
C_6H_5Cl	28·7	27·2 *	27·4
C_6H_5Br	28·7	27·0 *	27·4
C_6H_5I	28·8	27·0 *	27·6
HCl	26·3	28·3	26·3
HBr	26·1	28·5 *	26·6
HI	27·2	28·4 *	27·1
CH_3F	27·0	28·6 *	26·7
CH_3Cl	26·9	27·7	26·5
CH_3Br	27·0	27·6	26·7
CH_3I	26·7	26·9 *	26·3
O_2 †		27·1	23·5
N_2 †		26·7	22·8
CO ‡		27·1	23·3
$CFCl{:}CF_2$		27·8 *	26·4
$CCl_2{:}CCl_2$		26·9 *	27·0
$CF_3{\cdot}CH_3$		28·4 *	26·9
$CF_2Cl{\cdot}CH_3$		27·9 *	26·9
$CCl_3{\cdot}CH_3$		26·9 *	26·6
$CHClF_2$		28·5 *	27·1
$CHCl_2F$		28·3 *	27·3
$CHCl_3$		27·7 *	27·3
$CH_3{\cdot}CHF_2$		28·7 *	27·4
$CH_3{\cdot}CHCl_2$		27·5 *	27·1
$CH_2{:}CF_2$		27·8 *	25·8
$CH_2{:}CCl_2$		27·1 *	26·5
$CF_2{:}CHCl$		27·8 *	26·7
$CCl_2{:}CHCl$		27·1 *	26·9
CF_3Cl		27·9 *	26·0
CF_2Cl_2		27·2 *	25·9
$CFCl_3$		27·1 *	26·4

* Values calculated from equation (4).

†‡ Vapour pressures from refs. 128 and 129 of Tables, respectively.

(i) The tendency of ΔS to increase with b. p. is still apparent under Pitzer's conditions (highest values shown by halogeno-benzenes). (ii) Under Hildebrand's conditions, the ΔS values for the tabulated 15 fluoro-compounds are significantly higher (including the case of CF_4 of zero dipole moment) than the values for the corresponding chlorides by ~2% for each replacement of Cl by F. ΔS values for 9 bromine compounds (data for the additional compounds tabulated in Tables 5 and 6 but not reproduced in Table 1 being used) on the other hand show no significant difference from the corresponding 9 chloro-compounds. Six iodo-compounds appear to give values ~1% lower per unit replacement than the ΔS for chlorine compounds, giving an order F : Cl : Br : I = 1·02 : 1·00 : 1·00 : 0·99. Under Trouton's conditions, the above order is reversed, giving F : Cl : Br : I = 0·99 : 1·00 : 1·01 : 1·02. Choice of Pitzer's basis of comparison leads to values of ΔS showing no significant difference from one halogen type to another. Any conclusions reached as to the extent of order in any of the above substances in the liquid state are likely, therefore, to be unreliable and may arise solely from an arbitrary basis for comparison. Hence it is conceivable that the high ΔS values of fluorine compounds when compared under Hildebrand's conditions could arise from their markedly higher volatility (by an " over-correction " for the dependence of ΔS on b. p.).

(iii) The fact that the tetrahydrides have lower ΔS values than those of the " globular " tetramethyl compounds is to be expected on the basis of their closer approximation to " perfect liquids." It is difficult, however, to account on this same basis for the fact that the tetrahalides (under Hildebrand's conditions) have still higher ΔS values—higher in fact than for such flexible and non-spherically-symmetrical substances as, *e.g.*: $CMe_3·CH_2Me$, $\Delta S = 26·3$; $CHMe_2·CHMe_2$, $\Delta S = 26·4$; $CMe_3·CHMe_2$, $\Delta S = 26·4$; $CHMe_2·CMe_2·CH_2Me$, $\Delta S = 26·3$; $CH_2Me·CMe_2·CH_2·CH_2Me$, $\Delta S = 26·6$. It is difficult to believe that restriction of rotation in the spherically symmetrical molecules of the tetrahalides is greater than for such flexible hydrocarbons. Indeed, it appears [8] that rotation of the molecules of CCl_4 occurs, not only in the liquid state, but even in the solid state. Again, in the same way, the average of the ΔS values for O_2, N_2, and CO (27·0), believed by Pitzer and Guggenheim to approximate closely to perfect-liquid behaviour, should be compared with the values for, say, *n*-pentane (26·9) and *n*-hexane (27·1)—all figures calculated on the basis of Hildebrand's rule.

(iv) Comparison (again under Hildebrand's conditions) of data for carbonyl compounds with paraffins of the same chain length and degree of branching shows the latter to be uniformly lower, *e.g.*: $CH_2Me·CH_2·CHO$, $\Delta S = 27·9$; $CHMe_2·CH_2·CO·CH_2·CHMe_2$, $\Delta S = 28·1$; $CH_2Me·CH_2Me$, $\Delta S = 26·7$; $CHMe_2·CH_2·CH_2·CH_2·CHMe_2$, $\Delta S = 27·3$.

(v) As pointed out by Staveley and Tupman,[7] comparison under Pitzer's conditions likewise leads to surprising conclusions; *e.g.*, it was pointed out that ethyl acetate has a higher value of ΔS than water and ammonia in spite of the undoubtedly high degree of order arising from hydrogen-bond formation in the latter substances.

It is seen therefore that conclusions regarding relative order in liquids depend on the choice of comparison conditions and are not self-consistent, neither procedure used at present for imperfect liquids giving similar values of ΔS for substances having similar shape and therefore expected to exhibit similar degrees of molecular ordering.

In the absence then of an acceptable reference state, I attempted a new approach *via* structural contributions, in the hope that any departure from additivity could be interpreted in terms of degree and type of internal molecular order. As an empirical observation it immediately became apparent that, for substances incapable of rotational isomerism, the function $F = ZT/E$, where Z is the molecular number (sum of atomic numbers of constituent atoms) and $E/T = \boldsymbol{R}T\mathrm{d}\log_e p/\mathrm{d}T$ at a given vapour pressure p, is additive for the various atoms and bonds in the molecule. At sufficiently low vapour pressure (say at 100 mm. Hg or lower), F becomes ZT/L, where L is the molar heat of vaporisation. Such a treatment removes the difficulty of a choice of comparison conditions, and automatically allows, *e.g.*, of CF_4 possessing a different value of ΔS than CCl_4 without thereby carrying the assumption that the degree of order is different in the two substances. It is obvious therefore that the method, whilst possibly of limited applicability to the problem of order in liquids, seeks to interpret degree of ordering in a given substance over and above that which may appertain in the simplest molecules. The conclusions reached,

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[8] Smyth, *J. Amer. Chem. Soc.*, 1939, **61**, 1695, 2798.

however, should be more acceptable than those arrived at on the basis of Hildebrand's or Pitzer's comparison conditions.

I have already shown [9] that the ratio of the values of E/T for any two non-associated liquids at temperatures corresponding to the same saturated vapour pressure is constant. The additive relationship is therefore generally valid no matter at what vapour pressure we choose to evaluate the additive constants. In this paper, all values are quoted for a vapour pressure of 100 mm. Hg.

It is readily seen that the treatment is equivalent to assuming that LZ_e/ZT is constant where Z_e ($\sim Z$) is the "effective molecular number," *i.e.*, $n_1k_1z_1 + n_2k_2z_2 + \ldots$, evaluated by summation of the contribution of n_1 atoms of an element of atomic number z_1, and so on. The numerical coefficients k_1, k_2, . . . are then characteristic of each element, and approximate to unity. It was hoped that these coefficients could be related to electron configuration and/or atomic polarisabilities, but all such attempts have failed, and it must be admitted that the additivity of F remains a purely empirical observation. It will be shown, however, that the function does lead to conclusions regarding order in the liquid state in keeping with the requirements of certain theoretical considerations.

Relationship between the Hildebrand and Trouton Entropies of Vaporisation and Boiling Point.—As pointed out by Hildebrand and Scott,[10] when $\log T/p$ is plotted against $\log p$ in order to ascertain the value of p at a given vapour concentration (*i.e.*, when $\log T/p$ has a chosen set value, c), a virtually linear plot is obtained. Furthermore, it becomes apparent that the plots are parallel, and differ only in the values of the intercepts they make with the $\log p$ axis. The value of $\log p$ corresponding to a given constant vapour concentration is therefore uniquely determined by the vapour pressure at any one temperature, *e.g.*, by the normal b. p. Hence we may write $(\log p_B - x)/(c + \log p_B - \log T_B) = K$, where x is the value of $\log p$ when $\log T/p = c$, and K is a universal constant. (The suffix B refers to normal boiling conditions.) With vapour pressure in mm. of Hg, and decadic logarithms, x becomes $(2{\cdot}881 - 3{\cdot}381K + K \log T_B)$ when conditions are chosen such that $\log T/p = \frac{1}{2}$. The " best " value of K was determined from the vapour pressures of 13 compounds of very diverse chemical nature and with b. p.s ranging from $-190°$ (N_2) to $+271°$ (*n*-pentadecane). The individual values did not show any dependence on b. p., and the average deviation from the mean, $K = 1{\cdot}094$, was 0·3%. We may therefore write

$$x = 1{\cdot}094 \log T_B - 0{\cdot}817 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now it was shown previously [9] that the ratio of the value of ΔS for any given substance to the corresponding value ΔS^r for an "ideal reference substance" is constant independently of vapour pressure. Hence

$$(\Delta S)_{\text{Hildebrand}}/(\Delta S^r)_{\text{Hildebrand}} = (\Delta S)_{\text{Trouton}}/(\Delta S^r)_{\text{Trouton}}$$

The " Trouton conditions " being taken as a vapour pressure of 100 mm., which give $(\Delta S^r)_{\text{Trouton}} = 97{\cdot}4$, then

$$(\Delta S)_{\text{Hildebrand}} = 0{\cdot}01027(\Delta S^r)_{\text{Hildebrand}}(\Delta S)_{\text{Trouton}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

but, certainly [9] between the limits $p = 10$—1000 mm., ΔS^r is strictly a linear function of $\log p$; *i.e.*,

$$\Delta S^r = 141{\cdot}6 - 22{\cdot}1 \log p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Combining equations (1), (2), and (3) we then get

$$\begin{aligned}(\Delta S)_{\text{Hildebrand}} &= (1{\cdot}640 - 0{\cdot}248 \log T_B)(\Delta S)_{\text{Trouton}} \\ &= Z(1{\cdot}640 - 0{\cdot}248 \log T_B)/F \quad . \quad . \quad . \quad . \quad . \quad (4)\end{aligned}$$

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[9] Thomas, *J.*, 1953, 1233.

[10] Hildebrand and Scott, " Solubility of Non-electrolytes," 3rd edtn., Reinhold Publ. Corp., New York, 1950.

which gives the relationship between (*a*) ΔS under the condition that $\log T/p = \frac{1}{2}$ and (*b*) ΔS at a vapour pressure of 100 mm.

Methods of Evaluation of F.—(1) The method generally preferred is by use of the equation

$$\log_{10}(T/100) = A + B\log_{10}(T/100)_{\text{benzene}}$$

benzene being used as reference substance in the manner indicated,[9] where $B = (T/E)(E/T)_{\text{benzene}}$, and solved by application of Campbell's "zero-sum" method[11] wherever possible. In some cases the vapour-pressure data are not sufficiently well spaced to allow of mathematical solution, and a graphical solution with a plot of log T against log T_{benzene} is more reliable. The value of $(E/T)_{\text{benzene}}$ at 100 mm. has been determined by numerical differentiation of the "best" vapour-pressure data[9] as 27·2 cal. mole^{-1} deg.$^{-1}$, so that $F = ZB/27{\cdot}2$. In this paper for convenience all such F values have been multiplied by 100.

(2) By differentiation of the three-constant Antoine equation $\log p_{\text{mm}} = \beta - [\alpha/(T - C)]$ in such cases where the constants have been accurately calculated, and from which F in the chosen units is given by $100/F = 4{\cdot}571\{\alpha(\beta - 2) + C(\beta - 2)^2\}/\alpha Z$. Values so calculated from the highly accurate data of the National Bureau of Standards are slightly but significantly higher than the corresponding values calculated by the first method by ~0·1% averaged over 70 compounds. It is not profitable to enquire whether such a small difference is due to a slightly inaccurate evaluation of $(E/T)_{\text{benzene}}$ by method (1), or due to failure of the Antoine equation to lead to correct values of $\mathrm{d}\log p/\mathrm{d}T$. Indeed, it is surprising that any vapour-pressure equation containing only three constants should be so accurate. In order, however, to make values strictly comparable, all values calculated directly from the Antoine equation have been "corrected" by dividing by the factor 1·001. Differentiation of other three-constant equations such as, *e.g.*, the well-known Dupré–Kirchoff equation gives unreliable values of F.

(3) In certain cases, data are readily available only in the form of $\mathrm{d}T/\mathrm{d}p$ (°c per 10 mm.) at the normal b. p. (in particular, Timmermans[12]) and from these the value of E/T at the b. p. can be readily calculated. The values corresponding to a vapour pressure of 100 mm. then follow by multiplying by a factor independent of the nature of the compound.[9] Hence $F = 3{,}040Z(\mathrm{d}T/\mathrm{d}p)/T_{\text{B}}$ where T_{B} is the b. p. (°K) at 760 mm. The method leads to values somewhat lower than those calculated by the first two methods for low-boiling liquids, and to values somewhat higher for high-boiling liquids. The difference varies approximately linearly with F from +0·5% for the lower paraffins to −1·5% for the C_{17}—C_{20} hydrocarbons. Again, for strict comparison, all values calculated by method (3) have been "corrected" by application of the equation

$$F_{\text{corr.}} = 1{\cdot}007F - 0{\cdot}000042F^2$$

(4) Data for many compounds have been published only in the form of the two-constant equation $\log p = \gamma - \delta/T$. Fairly reliable values of F can then be calculated from the equation $F/100 = Z(\log T_2 - \log T_1)/27{\cdot}2(\log T_2 - \log T_1)_{\text{benzene}}$, where T_2 and T_1 are the limits for which the equation is stated to hold, and $(T_2)_{\text{benzene}}$ and $(T_1)_{\text{benzene}}$ are the corresponding temperatures for benzene. Data published in the form of three- or more-constant equations, other than the Antoine equation, have been similarly used.

Comparison of the Methods.—Methods 2 and 3 ("corrected" as above) when applied to the same vapour-pressure data agree very closely. Thus for 70 hydrocarbons studied by the National Bureau of Standards, covering a normal boiling range of −161° to 343°, the average difference between the values calculated by the first two methods is 0·15%. Similarly the average difference for methods 2 and 3 is 0·2% for 64 hydrocarbons and over the same boiling range. The fourth method, tested on data published in the form of the

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[11] Campbell, *Phil. Mag.*, 1920, **39**, 177; 1924, **47**, 816.

[12] Timmermans, "Physicochemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

two-constant equation, gave results which did not differ systematically from those calculated by the other methods, the mean difference over 20 compounds of diverse types being 1·1%.

Reliability of F Values.—The absolute accuracy in the accurate measurements of the National Bureau of Standards is believed to be, on the average, about 0·2%, although reliability in individual cases might be a little less. Thus, method 2, applied to the data of Forziati, Norris, and Rossini,[13] and to the earlier data of Willingham, Taylor, Pignocco, and Rossini [14] for 15 hydrocarbons to which slightly different values for the Antoine constants were assigned at the two dates, leads to F values which agree to within 0·1%.

It is difficult to assess experimental error in the majority of other measurements. A rough idea may be gained by consideration of temperatures corresponding to vapour pressures of, say, 760 and 100 mm.; *e.g.*, for *n*-heptane, taking $T_{760} = 371·5°$ and $T_{100} = 314·9°$, we get $F = 212·9$. An error in T_{100} of only 0·2° gives $F = 212·0$, 0·4% lower than the previous figure (see also Table 7). It is believed that F values reliable to 1% necessitate very accurate determination of vapour pressure and elaborate purification of the materials. In the Tables, only mean F values are given in cases where more than one source of data has been employed, or when more than one method of evaluation has been applied to a given set of vapour-pressure values.

Additivity of F for Compounds Incapable of Rotational Isomerism. That F is additive for such compounds is evident from data in Table 5 using the series: (*a*) H_2 through HCl to Cl_2, (*b*) CH_4 by successive chlorination to CCl_4, (*c*) C_2H_4 through C_2H_3Cl, three isomers $C_2H_2Cl_2$, and C_2HCl_3 to C_2Cl_4, and (*d*) C_6H_6 through C_6H_5Cl to the three isomeric dichlorobenzenes. Graphical solution gives $F_{(Cl-H)} = 57·3$.

Similar treatment for the series H_2 to Br_2, CH_4 to CBr_4, C_2H_4 to $CH_2{:}CHBr$, and C_6H_6 to $C_6H_4Br_2$ gives $F_{Br-H} = 120·0$. Four intervals only are available for the corresponding cyanide series, *viz.*, H_2 to C_2N_2, CH_4 to $CH_3{\cdot}CN$, C_2H_4 to $CH_2{:}CHCN$, and C_6H_6 to $C_6H_5{\cdot}CN$, giving $F_{(CN-H)} = 38·7$.

Calculation of the atomic and structural contributions (hereafter expressed as [H] etc.) now gives [2H] = 13, [CH_2] = 30, [Cl] = 64, [Br] = 127, [CN] = 45, [benzene] = 154, and [double bond] = 6. These values agree very closely with those ultimately evaluated (p. 2151) from more extensive data.

A stringent test for any additive function is to ascertain whether the value of [H] so determined agrees with the value for the element. (It is relevant that the value of the Trouton constant for hydrogen is less than half of the " normal " value.) Thus $F_{HCl} = 68·4$ leads to [H] = 11; Cl_2 similarly to [15], HBr to [15], Br_2 to [15], HCN to [12], and C_2N_2 to [13], the mean value to the nearest significant figure being [13]. The figure derived from hydrogen itself is [13·3].

The Additivity Function for Paraffins.—Values of F for paraffins as well as for alkyl-*cyclo*pentanes and -*cyclo*hexanes, alkylbenzenes, and, except where otherwise indicated, for olefins, have been calculated by methods (2) and (3) from the data in " Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," [15] supplemented and checked wherever possible by use of method (1) applied to the measured vapour pressures if published as such.[12,13,14,16] The values (by method 1) for the *n*-paraffins from methane to octane are those based on vapour pressures selected by Thodos.[17] As previously mentioned, the three methods agree so closely that the results are not tabulated since they may be so easily calculated from Antoine's equation.

From theoretical considerations it has been concluded [6] that " the decrease in entropy from the ideal gas state to some comparable state in the liquid region " would be greater

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[13] Forziati, Norris, and Rossini, *J. Res. Nat. Bur. Stand.*, 1949, **43**, 555.

[14] Willingham, Taylor, Pignocco, and Rossini, *ibid.*, 1945, **35**, 219.

[15] American Petroleum Institute Research Project 44, Carnegie Press, 1953.

[16] Rossini *et al.*, *J. Res. Nat. Bur. Stand.*, 1950, **45**, 406; *J. Phys. Chem.*, 1956, **60**, 1446.

[17] Thodos, *Ind. Eng. Chem.*, 1950, **42**, 1514.

for " globular " molecules than for molecules of simple fluids. Further, the behaviour of a non-polar substance of non-spherical shape is expected to conform closely to that of globular molecules.

I found, however, that under " Trouton conditions " the observed values of F for paraffins of chain length $\ngtr 3$ carbon atoms are in good agreement with the values calculated on the basis of [C] = 17 and [H] = 6·5 derived as above; *i.e.*, the entropy of vaporisation of ethane, propane, *iso*butane, and *neo*pentane are all accountable on the basis of the same F increments. It seems likely therefore that any increase in ΔS expected for these compounds on the basis of departure from spherical shape as such is automatically allowed for by the choice of comparison conditions, or by the method of derivation of the structural parameters. It may be also that the effect is relatively small, undetectable within the limits of experimental accuracy in the determination of F. (Even in the case of *polar* non-flexible molecules, when the increase in ΔS over and above that of a simple fluid would be expected to be substantially higher, it is shown below that the effect is still qute small.) The extent of mutual alignment or of restricted " external " rotation of these substances is therefore held to be small or nil (but see allenes, p. 2144).

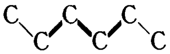
For normal paraffins C_nH_{2n+2}, where $n \geqslant 4$, and for their branched-chain derivatives, the values (F') calculated from the atomic constants are unquestionably higher than the experimental values by an amount (ΔF) clearly increasing with n. The physical interpretation of this appears to be that, in the liquid state, the longer molecules are arranged in an orderly manner with respect to neighbouring molecules, probably, from consideration of close-packing and their known configuration in the crystalline state, with the chain axes parallel.

Moore, Gibbs, and Eyring,[18] using Pauling's values for atomic dimensions and bond angles, compared the calculated molar volumes of *n*-paraffins with the experimental values on the basis of a regular zig-zag carbon chain (with the carbon atoms in one plane), and concluded that there are three liquid regions: at the lowest temperatures, the chains are interlocked, with the molecular spacings only slightly greater than their values in the crystalline solid; at higher temperatures, this condition gives way to a " libration " region where rocking of the molecules occurs, to be succeeded at still higher temperatures by a region of essentially free rotation of the molecules on their long axes, so that the liquid may now be visualised as a hexagonal close-packing of rotating cylindrical molecules. (Irrespective of which of these conditions may appertain at a given temperature for a given paraffin, the mere existence of parallel-packed zig-zag chains will add to the entropy of boiling, and the same remark would apply if the carbon atoms assumed a helical configuration as postulated by Mumford.[19]) In particular, it was concluded that at temperatures approaching (in the case of butane) or somewhat below the b. p. (with higher members), the *n*-paraffins higher than propane have attained such free rotation. Such a conclusion fits in well with the assignment of finite values to n commencing at unity for *n*-butane.

Methane as a sphere, and ethane as a cylinder of diameter 4·0 Å and length 5·5 Å, were held to be rotating even at their m.p.s. Propane, on the other hand, of corresponding dimensions 4·9 and 6·5 Å, was concluded to have incomplete rotation even at its b. p. With the possible exception of propane, therefore, the assignment of zero n value corresponds to the freely rotating cylinders of Moore *et al.*[18] However, my method leads to the further conclusion that in ethane and propane (and *iso*butane), the molecule as a whole has essentially free *external* rotation, and is not to be regarded as packing with its longer axis parallel to a neighbouring molecule. This conclusion seems likely from consideration of the above molecular dimensions, which show close approach to a spherical molecule with a ratio of longer to shorter dimensions of 1·37 for ethane and with a *lower* value 1·32 for propane. It seems, therefore, that the favoured configuration of, say, *n*-hexane can

[18] Moore, Gibbs, and Eyring, *J. Phys. Chem.*, 1953, **57**, 173.

[19] Mumford, *J.*, 1952, 4897.

be written  with restricted rotation about the bonds printed in heavy type. Vaporisation then implies absorption of energy consumed in the " uncoiling " of the molecules. Rotation about the two end C–C bonds is free, since the terminal hydrogen atoms lie within the confines of the cylinder.

My treatment leads to the requirement that free rotation of methyl groups also occurs in (methyl) branched-chain derivatives, and indeed in methyl*cyclo*alkanes considered below; thus, *e.g.*, $CH_3{\cdot}CHMe{\cdot}CHMe{\cdot}CH_3$ and $CH_3{\cdot}CHMe{\cdot}CHMe{\cdot}CHMe{\cdot}CH_3$ have to be assigned values of n of 1 and 2 respectively. How this arises in a close-packed assembly is difficult to see. (The above observations describe the average behaviour of the molecules, and it is not, of course, implied that no molecule ever suffers internal rotation about its C–C bonds. Rotation of a methyl group would presumably be statistically more probable on account of the smallness of the hydrogen atoms. Its moment of inertia is also low, and both factors may combine to give apparently free rotation.)

The above principles regarding the value of n apply in general to any chain of type A–B–C–D, where A, B, C, D are atoms other than hydrogen (but see special circumstances, below).

Values of ΔF plotted against n fall on a smooth curve passing through the origin, and up to $n \sim 8$, the plot is linear in agreement with the equation

$$\Delta S - (\Delta S)^1 = an; \text{ or } \Delta F = KnFF^1/Z \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which implies that the difference in molar entropy between the experimental value and that value the substance would possess in the absence of the above-described molecular alignment is approximately proportional to the number of bonds about which rotation is thus restricted.

For values of $n > \sim 8$, eqn. (5) is only a first approximation, a more accurate fit being $\Delta S - (\Delta S)^1 = an - bn^2$. This implies that, under Trouton conditions, the longer chains are increasingly less ordered. It should be remembered that the corresponding temperatures are also increasing, which will operate against the tendency to mutual chain-alignment. The last equation is cumbrous; a closely related but more convenient one is

$$\Delta F = Z(k_1n - k_2n^2) = (\text{say})\ Z\Sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where k_1 and k_2 are constants.

It is clear then that the " entropy of uncoiling " is

$$(L/T) - (L/T)^1 = (Z^2/FF^1)(k_1n - k_2n^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Equation (6) was solved for the n-paraffin series from C_4H_{10} to $C_{20}H_{42}$, by use of $[H] = 6{\cdot}5$ and $[CH_2] = 30$, to give $k_1 = 0{\cdot}0480$ and $k_2 = 0{\cdot}000622$.

A paraffin containing a *neo*-group is found to have a value of F significantly higher than the corresponding value for an isomer containing only *iso*-groups and of the same chain length. Examples will be found in Table 2. The percentage effect is small, and is considered to arise through interference with chain packing (closer approach to globular molecule behaviour). The behaviour of 30 such compounds in the paraffin and *cyclo*alkane series is in fact satisfactorily accounted for by assuming a reduction in n of 1/2 for each *neo*-group.

For two paraffins of the same chain length,

$$\Delta F_1 - \Delta F_2 = (Z_2 - Z_1)\Sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

a quantity which is quite small and of value not materially affected by any final adjustment in the values of k_1 and k_2. A series (Table 2) derived from a given n-paraffin by successive replacement of hydrogen by methyl (other than at the terminal CH_3 groups) may then be visualised, and the values " corrected " by the use of (8) so as to be comparable with the

F value for the *n*-paraffin. The *neo*-paraffins can be included by adjustment in the *n*-value.

TABLE 2.

Compounds	*F*	*F* adjusted for *neo*-group	Mean values	$Z - Z_{n\text{-}C_5H_1}$	$\Delta F - \Delta F_{n\text{-}C_5H_1}$	" Corrected " mean values	$[CH_3] - [CH_2] + [CH]$
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	159·1	159·1	159·1			159·1	
$CH_3{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	189·0	189·0	188·8	8	0·8	189·6	30·5
$CH_3{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_3$	188·6	188·6					
$CH_3{\cdot}CHMe{\cdot}CHMe{\cdot}CH_2{\cdot}CH_3$	217·4	217·4	217·7	16	1·5	219·2	29·6
$CH_3{\cdot}CHMe{\cdot}CH_2{\cdot}CHMe{\cdot}CH_3$	217·0	217·0					
$CH_3{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	218·9	217·6					
$CH_3{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_3$	220·3	219·0					
$CH_3{\cdot}CHMe{\cdot}CHMe{\cdot}CHMe{\cdot}CH_3$	246·3	246·3	247·1	24	2·3	249·4	30·2
$CH_3{\cdot}CMe_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_3$	247·4	245·9					
$CH_3{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_3$	249·5	248·0					
$CH_3{\cdot}CHMe{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_3$	249·6	248·1					
$CH_3{\cdot}CMe_2{\cdot}CHMe{\cdot}CHMe{\cdot}CH_3$	276·8	275·1	275·0	32	3·0	278·0	28·6
$CH_3{\cdot}CHMe{\cdot}CMe_2{\cdot}CHMe{\cdot}CH_3$	277·0	275·3					
$CH_3{\cdot}CMe_2{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_3$	279·3	275·8					
$CH_3{\cdot}CMe_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_3$	277·3	273·8					31·8
$CH_3{\cdot}CMe_2{\cdot}CMe_2{\cdot}CHMe{\cdot}CH_3$	311·4	307·5	306·0	40	3·8	309·8	
$CH_3{\cdot}CMe_2{\cdot}CHMe{\cdot}CMe_2{\cdot}CH_3$	308·3	304·4					

We can in this way compile the following series from which the fundamental interval $[CH_3] - [CH_2] + [CH]$ may be evaluated by application of Campbell's method.[11]

Series	No. of CH_2 intervals	No. of compounds in series	Value of increment
C_3H_8 to CMe_4	2	3	30·5
n-C_4H_{10} to C_8H_{18}	4	6	29·6
n-C_5H_{12} to $C_{10}H_{22}$	5	17	29·9
n-C_6H_{14} to $C_{10}H_{22}$	4	20	30·0
n-C_7H_{16} to C_9H_{20}	2	13	29·8
n-C_8H_{18} to C_9H_{20}	1	4	30·2

In conjunction with 16 additional values similarly derived from alkyl-*cyclo*pentanes and -*cyclo*hexanes, and also from sulphides, thiols, and aliphatic nitro-compounds, the most probable value of the increment appears to be 29·9 ± 0·2.

For two isomeric paraffins differing by unity in chain length, we may write $\Delta F_2 - \Delta F_1 = Z(\Sigma_2 - \Sigma_1)$—a quantity again small and of value little affected by slight adjustment in the values of k_1 and k_2. A series of type

$$CH_3{\cdot}CHMe{\cdot}CH_2{\cdot}CH_3 \longrightarrow n\text{-pentane}$$

$$CH_3{\cdot}CHMe{\cdot}CHMe{\cdot}CH_3 \longrightarrow CH_3{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3, \text{ etc.}$$

can thus be built up, " correcting " for the difference in chain length as indicated.

A large number of such transitions occur in the paraffin series alone, and it was found that $[CH_3] + [CH] - 2[CH_2]$ is zero within the limits of experimental uncertainty. Hence $[CH_2] = 29{\cdot}9 \pm 0{\cdot}2$. The value of $[CH_3]$ derived from ethane and propane is 36·2, making $[CH] = 23{\cdot}6$ and $[C] = 17{\cdot}7$ (from CMe_4 and C_2Me_6). We thus have the values

	[C]		[CH]		$[CH_2]$		$[CH_3]$		F_{CH_4}
	17·7		23·6		29·9		36·2		43·6
Difference (= [H])		5·9		6·3		6·3		7·4	

leading to [2H] = 13·0, a figure very close to the value 13·3 for hydrogen itself. Within the limits of accuracy, therefore, we may assume F^1 to be truly additive in the paraffin series, and write (" smoothing " the values for convenience): [C] = 17·0, [H] = 6·5, and $[CH_2] = 30{\cdot}0$, the same values as previously derived.

Final adjustment of the values of k_1 and k_2 was made by taking into account (*a*) the *n*-paraffin " equivalent " values derived as in Table 2 and subtracting 30·0 or a multiple of this figure from each *F* value, (*b*) the data for olefins, taking [double bond] = 5·5, derived as below, and (*c*) the reliable data on sulphur compounds up to $n = 6$. The values finally selected were $k_1 = 0{\cdot}0480$ and $k_2 = 0{\cdot}000618$, which lie so close to those previously derived from the *n*-paraffin series alone that reassessment of the structural parameters was not necessary.

Those paraffins containing ethyl or higher-alkyl branches are given *n* values in accordance with a principle which is obvious from the examples

$CH_3{\cdot}CH_2{\cdot}CHEt{\cdot}CH_2{\cdot}CH_3$, $n = 3$. $F = 215{\cdot}2$; $F_{\text{calc.}} = 215{\cdot}0$
$CH_3{\cdot}CH_2{\cdot}CMeEt{\cdot}CH_2{\cdot}CH_3$, $n = 2{\cdot}5$. $F = 248{\cdot}2$; $F_{\text{calc.}} = 245{\cdot}3$.
$CHMe_2{\cdot}CH_2{\cdot}CHEt{\cdot}CH_2{\cdot}CH_3$, $n = 3$. $F = 270{\cdot}8$; $F_{\text{calc.}} = 269{\cdot}5$

The average deviation between experimental and calculated *F* values for 13 such compounds is 0·7%. Such an assignment of *n* values is further justified in connection with alkyl borates (p. 2150).

The average deviation for the 20 *n*-paraffins from methane to eicosane is 0·2%, for 27 *iso*-paraffins 0·3%, and for 24 paraffins containing *neo*- or *neo*- plus *iso*-groups 0·5%. In no case does the deviation exceed 1·0%. It is noteworthy that, for the higher *n*-paraffins, the fraction of the total entropy of boiling to be attributed to molecular uncoiling is substantial [*e.g.*, 16% for *n*-eicosane calculated from equation (7)].

TABLE 3. *Alkyl*cyclo*pentanes and alkyl*cyclo*hexanes.*

Compound	*F* (exptl.)	Methods used	*n*	Δ*F* (calc.)	$\frac{(F_{\text{exptl.}} - F_{\text{calc.}}) \times 100}{F_{\text{calc.}}}$	Ref.
*cyclo*Pentane	151·7	1, 2	0	0·0	+0·7	6, 8
cis-1 : 2-Dimethyl*cyclo*pentane	210·0	1	0	0·0	−0·3	16
trans-1 : 2-Dimethyl*cyclo*pentane	210·4	1	0	0·0	−0·1	16
1 : 1-Dimethyl*cyclo*pentane	211·3	1	0	0·0	+0·3	16
n-Propyl*cyclo*pentane	234·8	1, 2	2	6·0	±0·0	6, 16
n-Decyl*cyclo*pentane	402·5	2	9	45·9	−0·6	17
Perdeutero*cyclo*hexane	179·9	2	0	0·0	+1·3	18
1 : 1 : 3-Trimethyl*cyclo*hexane	272·8	1, 2	0	0·0	+0·8	6, 16
*iso*Propyl*cyclo*hexane	265·0	1	1	3·0	−1·0	16
n-Butyl*cyclo*hexane	289·0	1, 2	3	11·1	−0·2	6, 16
n-Decyl*cyclo*hexane	429·8	2	9	49·0	−0·4	17

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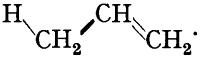
*Alkyl*cyclo*pentanes and Alkyl*cyclo*hexanes* (see Table 3).—Methyl groups are again to be considered as free to rotate in the liquid state, and *n* is finite starting from an ethyl side chain as unity. The mean deviation is 0·35% over 36 compounds, taking [5 and 6 membered ring] = 0·7.

Alkylbenzenes.—The *n* values for *iso*propyl, *iso*butyl, *sec.*-butyl, and *tert.*-butyl, as well as for *n*-propyl- and higher *n*-alkyl-benzenes, are normal (Table 4). However, it is apparent that methyl groups are no longer " free " when attached to the benzene nucleus (see also pyridine homologues, Table 6). Thus each methyl group must be assigned a value of $n = 1$, the inference being that in the packing of such compounds in the liquid state, a time average fraction of the molecules possess rigid methyl groups. Whether this is due to hyperconjugation's stiffening the bond between the nucleus and the methyl group, or, which seems more likely, because the planarity of the molecule results in a particularly close or stable packing, flat on flat, must remain undecided. It is relevant that a similar (but less pronounced) lowering of F is also apparent in the ethyl derivatives where hyperconjugation must be less important. Until additional data are available, each ethyl (or methoxy-group) is assigned an n value of 1·5. The alternative treatment of allotting an F increment as such to each CH_3 or ethyl group does not agree with the facts.

TABLE 4.

Compound	F exptl.	Methods used	n	$\Delta F_{calc.}$	Deviation (%)	Refs.
Hexadeuterobenzene	154·0	1, 2	0	0·0	+0·4	18, 19
1 : 2 : 3-Trimethylbenzene	236·2	1, 2	3	9·1	+0·1	6, 8, 16
1 : 2 : 4 : 5-Tetramethylbenzene	260·9	2	4	13·5	−0·2	6
Ethylbenzene	211·5	1, 2	1·5	4·1	+0·3	6, 20
2-Ethyl-*p*-xylene	264·4	2	3·5	11·8	+0·5	6
4-Ethyl-*o*-xylene	261·9	2	3·5	11·8	−0·5	6
1 : 2-Diethylbenzene	263·1	1, 2	3	10·2	−0·6	6, 16
*iso*Propylbenzene	239·2	1, 2	1	3·1	−1·1	6, 21
3-*iso*Propyltoluene	267·4	2	2	7·0	−0·2	6
2-*n*-Propyltoluene	264·0	2	3	10·2	−0·3	6
sec.-Butylbenzene	268·0	1, 2	2	7·0	±0·0	6, 16
n-Butylbenzene	264·4	1, 2	3	10·2	−0·2	6, 16
n-Decylbenzene	407·4	2	9	46·6	−0·2	17
Buta-1 : 2-diene	114·0	2, 3	1	1·4	+1·1	6
3-Methylbuta-1 : 2-diene	141·4	2	2	3·6	+0·6	6
Penta-2 : 3-diene	138·9	1, 2	2	3·6	−1·2	6, 22
Penta-1 : 2-diene	141·4	1, 2	1·5	2·7	−0·1	6, 22
Acetylene	52·6	2	0	0·0	+2·1	23
Methylacetylene	81	1, 3	0	0·0	−0·6	6, 8
Ethylacetylene	109·7	1	0	0·0	−1·6	24
Dimethylacetylene	111	1, 3	0	0·0	−0·4	6, 8
Vinylacetylene	104·5	1	0	0·0	+0·5	25
Propene	93·8	1, 2	1	1·1	−0·6	6, 26
But-1-ene	123·7	1, 2	1·5	2·2	+0·2	6, 8
Dodec-1-ene	329·3	1, 2	9	36·7	+0·2	6, 22
Eicos-1-ene	504·9	2, 3	17	102·0	+0·3	6
trans-But-2-ene	122·6	1, 2	2	3·0	+0·1	6, 27
2 : 3-Dimethylbut-2-ene	177·2	2, 3	4	8·7	+0·2	6, 28
cis-3-Hexene	178·5	2	3	6·6	−0·2	28
2-Methylpent-2-ene	177·5	2	3·5	7·7	−0·2	28
3 : 3-Dimethylbut-1-ene	183·1	2	0·5	1·1	−0·7	28
2 : 3-Dimethylbut-1-ene	181·5	3	2	4·5	+0·3	28
Buta-1 : 3-diene	114·8	2, 3	1	1·4	−1·6	6
2 : 3-Dimethylbuta-1 : 3-diene	172·9	2	3	6·1	+0·6	29
trans-Penta-1 : 3-diene	142·5	1, 2	2	3·6	−1·3	6, 22
Hexa-1 : 5-diene	174·1	2	3	6·1	+1·3	29
*cyclo*Pentene	143·2	1, 3	0	0·0	+0·1	6, 22
3-Methyl*cyclo*pentene	172·5	3	0	0·0	−0·3	6
1-Ethyl*cyclo*pentene	201·6	3	1·5	3·8	+1·1	6
1-Methyl*cyclo*hexene	201·0	3	1	2·5	+0·2	6

The F value assigned to benzene is 155·0. Now 6[CH] + [six membered ring] = 141·7. Hence the value of each " aromatic " double bond is 4·4, significantly lower than the value for a normal double bond. This lower value is considered to arise from the circumstance that the very flat (coplanarity of the carbon and hydrogen atoms) molecules of benzene are, at least partially, restricted to rotation in the plane of its own ring. Such a restriction is presumed absent from *cyclo*hexane and larger, saturated, ring compounds, and in the case of smaller rings, the molecules would not depart greatly from spherical shape. The normal double-bond value appears to appertain in the case of acyclic dienes.

Olefins and Dienes.—These are given expected n values; methyl groups attached to a carbon atom carrying a double bond must again be regarded as " rigid " (Table 4), *e.g.*, propene is to be regarded as packing  $H\diagdown CH_2\diagup CH\diagdown CH_2$. Ethyl groups so attached also appear to be more restricted than when attached to a saturated carbon atom, and are allotted an

n value of 1·5. It is accepted for the remainder of the paper that n must increase by 1 or by 1·5 in all compounds having (*a*) a methyl or (*b*) an ethyl (or methoxy-) group, respectively, attached to any atom carrying a multiple bond, provided that rotational isomerism is possible about these groups (see ketones, esters, etc., below).

The mean deviation over 43 straight- and branched-chain olefins is 0·4%, over 11 alkyl*cyclo*pentenes and alkyl*cyclo*hexenes 0·7, and over 7 diolefins (conjugated and non-conjugated) 1·1.

Allenes.—Although data are to hand for only five compounds, it seems necessary to assign the value 3·6 to each double bond, the mean deviation being 0·7%. Two values of F for allene itself, calculated by methods (2) and (3) of ref. 6 to Tables, do not agree. The higher values of ΔS probably arise from the circumstance that allenes possess relatively long linear molecules giving rise to restricted (external) rotation.

Acetylenes.—Accurate data are available for only five compounds (Table 4). Owing to the linearity of the C–C≡CH group, n is taken as zero in ethylacetylene and also in methylacetylenes (compare cyanides, below). The mean deviation is 1·0%.

Deuterium Compounds.—The value of [D] appears to be slightly but significantly lower than that of [H]. By weighting the experimental values in proportion to the % of D in the compound, the most probable value is in accordance with [H] — [D] = 0·3, or, on the basis of [H] = 6·5, [D] = 6·2. F values for 7 deuterium compounds are included in the tables.

Halogen Compounds.—The substances so far considered have zero or small permanent dipole moments (μ), and the interaction potential arises essentially from London forces. The majority of compounds considered below, however, are polar, and it is of interest to ascertain whether it may be possible to correlate polarity with an increase in ΔS. Even in the favourable case of HCl (excluding compounds which are definitely associated, and where the hydrogen bonds result in a high degree of order), it has been calculated [20] that, in the gaseous state, dipole association forces make only a relatively small contribution (14%) to the van der Waals forces, and that the main contribution still arises from dispersion forces. Induced dipole association accounts for a still smaller contribution (2%).

In the gaseous state, when the distance apart of the molecules (r) is considerably greater than the length of the dipole, the energy of dipole interaction is given by $E_\mu = -\frac{2}{3}\mu^4/kTr^6$. Another limiting form, $E_\mu = -2\mu^2/r^3$, applies at very low temperatures.

In the liquid state, at close distance, the interaction not only depends on μ and r, but is also highly sensitive to the mutual orientation of the dipoles, being actually repulsive for a half of the possible solid angle. It is clear, then, that the magnitude of the contribution of dipole interaction to the energy and hence to ΔS in the liquid state is problematical, but is likely to be low compared with that arising from dispersion forces. It might also be that induced dipole interaction is now of greater relative importance, and this will depend on bond polarisabilities. In other words, knowledge of the mode and extent of molecular alignment is a pre-requisite to solution of the problem of total interaction in the liquid state. I believe that order due to dipole–dipole or dipole–induced dipole interaction will be superimposed on that arising from the considerations above, so that a chain including a polar group will be likely to be " stiffer," and mutual alignment statistically more probable, than in a non-polar hydrocarbon of the same length.

On such assumptions, F data for 9 chlorine compounds of zero μ give a weighted (according to estimated accuracy of the experimental data and the % chlorine in the compound) mean of [Cl] = 64·5 (see Table 5; Table 6 for $SiCl_4$, $SnCl_4$, and $GeCl_4$). On the other hand, a mean value of 63 (to nearest half unit) is derived from compounds with finite dipole moment (63·1 from 15 compounds of zero n, and 63·4 from 11 substances with flexible molecules). The increase in ΔS for polar chlorides is thus small, but believed to be significant.

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[20] London, *Trans. Faraday Soc.*, 1937, **33**, **8**.

TABLE 5.

Compound	*F* (exptl.)	Method of calcn.	Refs.	*n*	μ (D)	Deviation (%)
Hydrogen	13·3	1	1, 2, 126	0	—	+2·3
Deuterium	11·9	1	126	0	—	−3·4
Hydrogen deuteride	12·0	1	126	0	—	−5·8
Methane	43·6	1, 2, 3	6, 7	0	—	+1·4
Ethylene	64·4	2, 2, 3	6, 13, 14	0	—	−1·6
Benzene	154·5	—	—	0	—	−0·3
Chlorine	129·2	1	4, 5	0	Zero	+0·2
Carbon tetrachloride	278·6	1, 2	10, 11, 4, 12	0	,,	+1·3
p-Dichlorobenzene	266·8	1	10	0	,,	−1·6
trans-1 : 2-Dichloroethylene	179·7	1	8	0	,,	−1·0
Tetrachloroethylene	296·3	1	10	0	,,	−0·4
Hexachloroethane	427	1	8	1	,,	+2·7
Hydrogen chloride	68·4	1	3	0	1·0	−1·9
Methyl chloride	98·1	1	8	0	1·9	−0·4
Methylene chloride	155·9	1	8	0	1·6	−0·3
Chloroform	212·4	1, 3	4, 9	0	1·0	−1·5
Vinyl chloride	122·9	1	10	0	1·4	+1·0
1 : 1-Dichloroethylene	181·0	1	8	0	1·2	+0·6
cis-1 : 2- ,, ,,	177·1	1	8	0	1·9	−0·8
Trichloroethylene	237·9	1	4	0	0·9	−0·1
Chlorobenzene	211·7	1, 3	8, 15	0	1·7	+0·4
m-Dichlorobenzene	268·5	1	10	0	1·7	−0·1
o- ,, ,,	265·7	1	10	0	2·5	−0·8
1 : 1-Dichloroethane	184·5	2	46	0	2·1	−1·0
1 : 1 : 1-Trichloroethane	248	1	8	0	1·8	+1·3
Ethyl chloride	130·0	1	42	0	2·1	+1·3
*iso*Propyl chloride	158·7	1	8	0	2·2	+0·4
n-Propyl chloride	156	1, 4	4, 8, 49	1	2·0	−0·3
sec.-Butyl chloride	190·7	1	8	1	2·0	+2·5
Allyl chloride	149·4	1	45	1	2·0	+0·3
1 : 2-Dichloropropane	216·1	1	8	1	1·8	+1·0
1 : 2-Dichloroethane	182·7	1	49	1	1·2	−1·3
1 : 1 : 2-Trichloroethane	234·5	1	10	1	1·4	−3·2
1 : 1 : 2 : 2-Tetrachloroethane	302	1, 4	10, 4	1	1·4	+1·0
1 : 1 : 1 : 2-Tetrachloroethane	297·2	1	10	1	*2·0	−0·4
n-Butyl chloride	184·4	1	10	2	2·0	+0·4
n-Pentyl chloride	214·6	1	43, 44	3	2·0	+1·9
n-Hexyl chloride	234·3	1	44	4	2·1	−0·9
Fluorine	74·3	1	50	0	Zero	+0·4
Carbon tetrafluoride	164·0	1	8	0	,,	−0·6
Perfluoro*cyclo*butane	362·8	1	55	0	,,	−0·9
Perfluoroethane	252·4	4	124	1	,,	−0·2
Perfluoro-*n*-butane	431·6	1	56	3	,,	+2·2
,, *n*-pentane	497·0	4	130	4	,,	−1·4
,, *n*-heptane	667·6	1	56	6	,,	+0·9
Chlorotrifluoroethylene	211·7	2	54	0	0·4	−1·0
Chlorotrifluoromethane	192·3	1	49	0	0·4	+0·5
Chlorodifluoromethane	154·8	1	125	0	1·4	−1·9
Dichlorofluoromethane	182·8	1	125	0	1·3	−1·5
Fluorobenzene	182·7	2, 1	57, 15	0	1·6	+1·1
1 : 1 : 1-Trifluoroethane	156	1	8, 51	0	2·3	−1·0
Trichlorofluoromethane	250·2	1	8	0	0·4	+1·6
1 : 1-Difluoroethane	124	1, 4	51	0	*2·3	−2·5
1 : 1-Difluoroethylene	124	4, 1	51	0	1·4	+1·4
1-Chloro-1 : 1-difluoroethane	186	1, 4	51	0	2·2	+0·3
Methyl fluoride	67·5	1	8, 49	0	1·8	−0·9
Dichlorodifluoromethane	223·7	1	125	0	0·5	+2·3
1-Chloro-2 : 2-difluoroethylene	180·0	1	51	0	*1·0	−0·8
1 : 1-Dichlorotetrafluoroethane	304	4, 1	51	1	*1·0	−0·0
1 : 2- ,, ,, ,,	305·4	1	49	1	0·8	+0·2
Chloropentafluoroethane	281·0	1	52	1	0·8	+1·2
1 : 2 : 2-Trichlorotrifluoroethane	328·9	1	49	1	*1·5	−0·3
Perfluoromethyl*cyclo*hexane	622·0	1	56	1	*2·0	−0·3
3-Fluorotoluene	210·9	2	45	1	*1·6	+1·4
4- ,, ,,	211·1	2	45	1	1·8	+1·7
2 : 2 : 3-Trichloroheptafluorobutane	492·5	2	53	3	0·9	−1·3

* Estimated values.

TABLE 6.

Compound	*F* (exptl.)	Method of calc.	Refs.	*n*	Deviation (%)
Bromine	255·5	1	4	0	−0·2
Hydrogen bromide	135·3	1	47	0	+0·6
Methyl bromide	164·6	1	8	0	±0·0
Ethyl bromide	192·5	1, 3	48, 9	0	−0·8
n-Propyl bromide	225·3	4	4	1	+1·6
*iso*Propyl bromide	226·7	1	8	0	+1·0
Methylene bromide	281·5	1	49	0	−1·6
Tribromomethane	413·0	1	49	0	+1·2
Carbon tetrabromide	519·6	1	49	0	−2·1
Vinyl bromide	186·7	1	8	0	−0·2
1 : 2-Dibromoethane	311·1	1	10	1	−0·3
1 : 2-Dibromopropane	340·9	1	8	1	−0·2
Bromobenzene	277·1	3	9	0	+0·2
o-Dibromobenzene	395·7	1	10	0	−0·6
Iodine	381·7	1	15	0	−2·2
Methyl iodide	234·7	1	8	0	+1·4
Ethyl iodide	261·5	1	58	0	±0·0
*iso*Propyl iodide	296·0	1	8	0	+1·5
Iodobenzene	341·0	1	15	0	−0·7
Hydrogen iodide	199·3	1	49	0	−1·1
Cyanogen	89·4	1	47, 59	0	+1·6
Hydrogen cyanide	50·9	1	60, 61	0	+0·8
Methyl cyanide	80·6	1	10	0	+0·1
Ethyl cyanide	109·3	1	10, 62	0	−1·1
n-Propyl cyanide	137·2	1	8	1	−1·1
n-Butyl cyanide	165·2	1	10, 62	2	−0·6
n-Pentyl cyanide	192·0	1	10	3	−0·5
n-Hexyl cyanide	222·2	1	8	4	+1·3
n-Heptyl cyanide	244·2	1	8	5	−0·2
Cyanogen chloride	107·8	1	63, 64	0	+0·7
Cyanobenzene	192·8	1	8	0	+0·2
Vinyl cyanide	102·9	1	65	0	−0·1
Allyl cyanide	128·2	1	8	1	−2·4
cis-β-Methylvinyl cyanide	131·3	1	8	1	±0·0
trans-β-Methylvinyl cyanide	130·7	1	8	1	−0·3
cis-1-Cyanobuta-1 : 3-diene	149·5	2	66	1	−2·7
Chloropicrin	254·5	2	67	0	+1·2
Nitromethane	112·6	1, 2	10, 68	1	−0·4
Nitroethane	141·3	1	69	1·5	−0·3
1-Nitropropane	171·4	1	69	2	+0·8
2-Nitropropane	171·4	1	69	1	−0·5
1-Nitrobutane	196·5	1	69	3	−0·2
2-Nitrobutane	198·8	1	69	2	−0·2
2-Methyl-3-nitropropane	199·3	2	70	2	±0·0
Trimethylnitromethane	201·7	2	70	0·5	+0·7
2 : 2-Dinitropropane	240·6	1	69	1·5	−0·1
Ethyl nitrate	171·1	2	71	2	+2·4
n-Propyl nitrate	195·9	2	71	3	+1·1
*iso*Propyl nitrate	197·8	2	71	2	+0·8
n-Butyl nitrate	222·3	2	71	4	+1·1
*iso*Butyl nitrate	223·9	2	71	3	+0·5
Hydrogen sulphide	65·5	1	4	0	−3·8
Hydrogen disulphide	119·4	1	72	0	−3·0
Methanethiol	96·5	1	8	0	−1·5
Ethanethiol	126·6	1	8	0	−1·1
Propane-1-thiol	155·6	1	73	1	−0·3
Propane-2-thiol	156·2	2, 3	6, 74	0	−1·2
Butane-1-thiol	182·8	2, 3	6, 75	2	−0·3
Butane-2-thiol	185·7	3	6	1	±0·0
1 : 1-Dimethylethane-1-thiol	188·2	3	6	0	+1·4
Pentane-1-thiol	209·9	3	6	3	±0·0
Thiophenol	206·4	2	76	1	−0·4
Dimethyl ether	97·2	1	77	0	−2·9
Diethyl ether	153·7	3	8	2	−1·5
Methyl *n*-propyl ether	155·4	1	8	2	−0·4
Ethyl *n*-propyl ether	184·5	1	4	3	+0·8
Di-*n*-propyl ether	212·5	1	8	4	+1·4
Di*iso*propyl ether	213·1	2	78	2	−0·7

TABLE 6. (*Continued.*)

Compound	*F* (exptl.)	Method of calc.	Refs.	*n*	Deviation (%)
Di-*n*-butyl ether	262·0	1	10	6	+0·7
Di-*n*-pentyl ether	310·8	1	10	8	+0·5
Dimethyl formal	150·4	2	78	2	−1·7
Dimethyl acetal	181·8	2	78	2	−0·3
Diethyl formal	211·4	2	78	4	+2·3
Diethyl acetal	236·3	2	78	4	+0·5
Di-*n*-butyl acetal	333·3	1	79	8	±0·0
Chlorine monoxide	151·3	1	80	0	−1·2
Tetrahydrofuran	148·6	1	81	0	+0·7
Dioxan	170·4	1	82	0	−2·4
Formaldehyde	58·0	1	83	0	+0·9
Acetaldehyde	86·0	1	84	1	−0·5
Propionaldehyde	115·3	1	85	1·5	±0·0
n-Butyraldehyde	144·5	1	84	2	+0·5
Acetone	114·3	1, 3	8, 4	2	−0·2
Ethyl methyl ketone	142·7	1	10	2·5	−0·2
Diethyl ketone	170·7	1	10	3	−0·1
Di*iso*propyl ketone	230·9	1	10	2	−0·3
*iso*Butyl methyl ketone	200·0	1	43	3	−0·1
Di*iso*butyl ketone	280·0	2	85	4	−1·0
Methyl formate	112·2	1	8	1·5	+0·4
Methyl acetate	137·7	3	8	2·5	−1·2
Ethyl acetate	166·3	1, 3	8, 4	3	−0·7
Ethyl propionate	193·6	3	8	3·5	−0·7
Methyl *n*-butyrate	194·4	1	4	3·5	−0·3
*iso*Butyl formate	197·7	1	86	3	+0·7
*iso*Butyl acetate	223·3	1	86	4	+0·4
n-Butyl acetate	221·3	3	8	5	+0·8
Ethyl *n*-butyrate	222·2	1	86	4	±0·0
n-Propyl propionate	224·0	1	15	4·5	+1·3
n-Propyl *n*-butyrate	250·3	1	86	5	+1·0
Ethyl trimethylacetate	255·2	1	8	2·5	−0·2
*iso*Butyl propionate	249·2	1	86	4·5	−0·1
*iso*Propyl *iso*butyrate	253·8	1	8	3	−0·1
Methyl *n*-hexanoate	247·3	2	87	5·5	+0·4
*iso*Butyl *iso*butyrate	277·6	1	8	4	−0·6
Methyl *n*-octanoate	298·3	2	87	7·5	+1·0
Methyl borate	196·3	1	88	3	−0·8
Ethyl borate	275·4	1	88	6	+0·4
n-Propyl borate	345·3	1	43	9	−0·1
n-Butyl borate	416·9	1	43	12	+0·9
n-Pentyl borate	474·4	1	43	15	−0·6
Trimethylborine	123·5	1	89	0	−0·8
Triethylborine	207·1	1	4	3	−0·1
Dimethylmethoxyborine	148·7	1	32	1	−0·6
Dimethylfluoroborine	119·7	1	8	0	−3·8
Methoxydichloroborine	202·5	1	88	1	+0·3
Dimethoxychloroborine	202·3	1	89	2	+1·3
Ethoxydichloroborine	228·3	1	88	2	−0·1
Diethoxychloroborine	251·3	1	88	4	−0·2
Trimethylamine	128·8	1	8	0	−0·5
Diethylmethylamine	186·7	2	90	2	+1·0
Triethylamine	213·5	1	91	3	+0·9
NN-Dimethyl*cyclo*hexylamine	260·0	1	44	1	−1·4
Dimethylformamide	138·2	1	44	1	−2·8
Methyldimethylaminoborine	150·4	1	92	1	+0·9
Tetramethylhydrazine	184·7	1	93	1	−0·5
Phosphorus trichloride	246·0	1	15	0	±0·0
Phosphine	73·8	1	4	0	−3·6
Ethyldichlorophosphine	246·7	1	94	1	+0·1
n-Propyldichlorophosphine	270·6	1	94	2	−0·7
n-Butyl ,, ,,	295·0	1	94	3	−1·1
n-Pentyl ,, ,,	322·0	1	94	4	−0·3
n-Hexyl ,, ,,	353·3	1	94	5	+1·7
n-Heptyl ,, ,,	379·5	1	94	6	+2·1
Silane	76	1	4	0	−0·7
Disilane	139	1	4	0	−0·7
Methylsilane	107·3	1	4	0	+0·7

TABLE 6. (*Continued.*)

Compound	*F* (exptl.)	Method of calc.	Refs.	*n*	Deviation (%)
Tetramethylsilane	193·3	1	8	0	−1·7
Tetrachlorosilane	310	1	49, 95	0	+0·5
Trichlorosilane	253·3	2	95	0	+2·9
Trimethylchlorosilane	221·0	2	95	0	−0·9
Methyltrichlorosilane	277·9	2	95	0	+0·7
Dimethyldichlorosilane	249·2	2	95	0	−0·1
Methylchlorosilane	160·9	1	4	0	−1·3
Methyldichlorosilane	221·9	1, 2	4, 95	0	+1·1
Ethyltrichlorosilane	299·0	2	95	1	−1·0
Diethyldichlorosilane	301·2	2	95	2	−0·2
1 : 2-Bistrichlorosilylethane	517·5	2	95	3	−0·3
Trichloro-1 : 2-dichloroethylsilane	404·6	2	95	2	−1·1
Phenyltrichlorosilane	378·9	2	95	1	−1·0
Vinyltrichlorosilane	303·7	2	95	1	+2·9
Ethylvinyldichlorosilane	295·7	2	95	2	+0·4
Triethoxyvinylsilane	358·1	2	95	7	±0·0
Triethoxyethylsilane	361·9	2	95	8	+0·2
Tetraethyl silicate	401·6	1	8	8	+3·8
Tetra*iso*propyl silicate	497·6	1	96	8	+0·7
Tin tetrachloride	431·0	1	15	0	−0·5
Tetramethylstannane	321·5	1	97	0	+0·2
Ethyltrimethylstannane	347·2	1	97	1	+0·2
Trimethyl-*n*-propylstannane	373·0	1	97	2	+0·4
Antimony trichloride	337·0	1	4	0	−0·0
Antimony tribromide	535·0	1	4	0	±0·0
Antimony tri-iodide	736·5	1	4	0	+0·1
Arsenic trichloride	305	4	4	0	−1·6
Trimethyl arsenite	303·3	1	98	3	+1·1
Dimethylarsine	203·0	1	99	0	+1·2
GeD_4	147	4	100	0	−0·8
Ge_2D_6	273	4	100	0	−3·9
Ge_2H_6	278	1	101	0	−2·5
Ge_3D_8	423	4	100	0	+0·9
Ge_3H_8	428	1	101	0	+1·6
GeH_4	151·4	1	49	0	+1·0
$GeCl_4$	383·8	1	49	0	+0·7
Naphthalene	244·0	1, 2	6, 102	0	−0·7
1-Methylnaphthalene	271·1	2	6	1	−0·4
2-Methylnaphthalene	271·4	2	6	1	−0·3
1-Ethylnaphthalene	294·2	2	6	1·5	−1·9
2-Ethylnaphthalene	295·4	2	6	1·5	−1·5
Phenanthrene	335·4	1	103, 104	0	−0·3
Anthracene	337·4	1	103, 104	0	+0·3
Indene	224·0	1	102	0	−0·1
Thiophen	160·7	2, 3	105, 6	0	+1·3
2-Methylthiophen	188·4	2, 3	105, 6	1	+1·0
3-Methylthiophen	188·1	2, 3	105, 6	1	+0·7
Furan	130·3	2	106	0	−0·2
Pyridine	150·1	1	107	0	−0·3
2-Methylpyridine	178·1	2	107	1	−0·1
3-Methylpyridine	178·2	2	107	1	−0·1
4-Methylpyridine	178·4	2	107	1	+0·1
2 : 5-Dimethylpyridine	205·7	2	107	2	+0·2
2 : 6-Dimethylpyridine	204·5	2	107	2	−0·3
Quinoline	238·0	1	15	0	−1·3
Nicotine	314·2	1	8	1	+1·1
*cyclo*Propane	93·3	1	8	0	+1·4
*spiro*Pentane	141·9	2	108	0	−1·6
Ethylene sulphide	117·8	2, 3	109, 6	0	+0·7
Ethylene oxide	87·2	2, 1	4, 8	0	−2·1
*cyclo*Butane	123·2	1, 2	110, 111	0	+1·0
*cyclo*Butene	115·6	1	110	0	+0·9
*cyclo*Butanone	135·5	1	112	0	−0·7
*cyclo*Heptane	208·5	2	113	0	+0·8
*cyclo*Hepta-1 : 3 : 5-triene	184·5	2	113	0	±0·0
*cyclo*Octane	236·9	2	113	0	±0·0
*cyclo*Octatetraene	204·0	1	8	0	−1·5
4-Methylpent-4-en-2-one	189·7	2	114	4	−0·3

TABLE 6. (*Continued.*)

Compound	*F* (exptl.)	Method of calc.	Refs.	*n*	Deviation (%)
4-Methylpent-3-en-2-one	191·0	2	114	4	+0·4
α-Methylvinyl cyanide	131·0	2	45	1	−0·3
Acetyl chloride	143·1	1	115	1	+0·7
Methylbismethylthioborine	231·1	1	116	2	+1·1
Tetrahydronaphthalene	260·8	3	6	0	−0·7
cis-Decalin	291·0	1	117	0	+1·0
trans-Decalin	284·0	1	117	0	−1·5
*cyclo*Hexylbenzene	314·7	1	117	1	−1·2
Di*cyclo*hexyl	341·0	1	117	1	−0·8
*cyclo*Pentanone	166·4	1	112	0	+0·8
α-Pinene	280·2	1	118	1	−0·2
Nitrobenzene	225·0	1	8	1	−0·7
2-Nitrotoluene	250·2	1	10	2	+0·2
4-Nitrotoluene	251·2	1	10	2	+0·6
Benzaldehyde	195·4	1	8	1	−0·8
o-Chlorobenzaldehyde	257·0	1	10	1	+1·7
Benzoyl chloride	255·2	1	8	1	+1·0
Acetophenone	222·1	1	8	2	−0·6
p-Chloroacetophenone	279·1	1	10	2	+0·2
Propiophenone	244·5	1	10	2·5	−2·7
Benzophenone	323·0	1	10	2	−2·9
Dibenzyl ketone	369·5	1	15	4	−3·1
Methyl benzoate	248·8	1	10	2·5	+0·4
Phenethyl acetate	294·1	1	10	5	−0·4
Dimethylaniline	232·7	1	119, 120	1·5	−1·8
1-Chloro-4-ethylbenzene	263·6	1	10	1·5	−1·0
o-Methylstyrene	226·6	2	121	2	−2·1
m- ,,	228·8	2	121	2	−1·2
p- ,,	229·5	2	121	2	−0·9
o-Ethylstyrene	255·2	1	10	2·5	−1·5
m- ,,	250·4	1	10	2·5	−3·5
o-Chlorostyrene	264·5	1	10	1	+1·5
p- ,,	267·0	1	10	1	+2·4
o-Bromostyrene	334·7	1	10	1	+3·0
p- ,,	325·3	1	10	1	+0·1
Anisole	202·7	1	10	1·5	−2·5
Phenetole	227·8	1	10	2	−3·5
p-Chlorophenetole	280·9	1	10	2	−3·5
Phenyl *n*-propyl ether	262·7	1	10	3	+0·3
n-Butyl phenyl ether	288·0	1	10	4	+0·3

This further lowering in F due to dipole interaction being written as $(\Delta F)_\mu$, the corresponding increase in molar entropy of vaporisation, $(\Delta S)_\mu$, will be $\propto (\Delta F)_\mu/Z$. Making the simplest possible assumption (any more complicated function is clearly not justified at present) that $(\Delta S)_\mu$ varies directly with μ and inversely with the size (taken as $\propto Z$), we may write $(\Delta S)_\mu \propto \mu/Z \propto (\Delta F)_\mu/Z$, giving $(\Delta F)_\mu = c\mu$, where c is a constant. The average value of c is 1·3, and the deviation between the experimental values of F and those calculated on the basis of [Cl] = 64·5 and $c = 1{\cdot}3$ is 1·0% averaged over all 32 chlorine compounds.

The value [F] = 37 was similarly derived from CF_4, F_2, and perfluoro*cyclo*butane, and also from the perfluoroparaffins C_2F_6, C_4F_{10}, and C_7F_{16}, μ of the last two compounds being assumed to be zero. The n values assigned to these two compounds are in agreement with the general principle outlined above, each terminal CF_3 group adding one unit to the chain length, and retaining the values of k_1 and k_2 derived essentially from hydrocarbon chains. The c value chosen was 3, thereby implying (as expected) that the dipole alignment in fluorides is of greater importance than in chlorides. In mixed chlorine–fluorine compounds, the higher c value associated with fluorides is assumed to apply. The mean deviation over 28 fluorine compounds is 1·1%.

Evaluation of c for polar substances other than fluorides and chlorides cannot be undertaken at present owing to paucity of data on suitable poly-derivatives of zero μ

(*e.g.*, in the bromine series, data are available only for bromine itself, the F value for CBr_4 being very unreliable). The atomic or structural constants for all other polar groups are therefore to be regarded as values which include any polar orientating effect. It may well be, on the other hand, that, apart from fluorine and chlorine compounds, the effect is too small to be detected; *e.g.*, in the hydrogen halide series, the effect would be expected to decrease in the order $HCl > HBr > HI$, in view of (*a*) the decrease in μ, and (*b*) the fact that the increasing size of the halogen atom from Cl to I prevents closeness of approach of neighbouring molecules and hence of significant mutual orientating effect.

It is to be understood, therefore, that all the compounds included in Table 6 have been treated on the assumption that the atomic or structural constants automatically include any dipole effect—including polyfunctional molecules which contain Cl or F (CCl_3CN, Cl_2O, $CH_3{\cdot}COCl$, etc.), and for which [Cl] = 63 and [F] = 36. The percentage deviation involved in this procedure will clearly be small except in the case of small molecules of either very low or very high polarity (the high negative deviations for, say, Me_2BF and $H{\cdot}CO{\cdot}NMe_2$ may arise in this way). The F values for symmetrical compounds possessing zero μ have, however, been calculated on the basis of [Cl] = 64·5 ($SiCl_4$, $SnCl_4$, $GeCl_4$).

Cyano-compounds.—The mean deviation is 1·1% over 17 compounds.

Nitro-compounds.—A mean deviation of 0·4% is shown by 9 nitro-alkanes; n must be such a value as to recognise extension of the chain by the terminal oxygen atom.

Alkyl Nitrates.—The mean deviation for 5 compounds is 1·2%, the same value of $[NO_2]$ being used as in nitro-compounds, and [O] being taken as 27 as in ethers (see below).

Additivity Function for Compounds containing Bivalent Atoms or Radicals.—Sulphur compounds. The vapour pressures of a large number of sulphur compounds have been accurately measured by White, Barnard-Smith and Fidler,[21] and the corresponding F values have been calculated by using the published Antoine constants. Such values, for reasons already mentioned in connection with hydrocarbons, are not tabulated. Data for certain additional compounds have been taken from other sources (Table 6). As expected, the insertion of S into a carbon chain adds one unit to the total chain length, and for –S–S– n is assumed to increase by 2. With [S] = 55, the deviation averaged over 15 alkyl sulphides is 0·4%, over 9 thiols 0·6%, and over 9 alkylthio*cyclo*alkanes 0·3%. The value of [S–S] (114) would appear to be higher, by 4 units, than 2[S], the mean deviation being 0·8% over 7 alkyl disulphides. The corresponding deviation, with [S–S] = 110, would be 1·8%.

Ethers. Sixteen oxygen compounds of diverse types are tabulated, the mean deviation being 1·1%.

Carbonyl compounds. The CO group, just like O or S, when inserted into a carbon chain, adds one unit to the total chain length. The mean deviation for 10 open-chain compounds is 0·4%.

Esters. The type $R{\cdot}CO{\cdot}OR$ has a chain length equal to that of $R{\cdot}CH_2{\cdot}CH_2R$. Methyl groups attached to the CO group (but not to the oxygen atom) are again to be regarded as " rigid " in the liquid state. It should be observed that the sum of the contributions [CO] + [O] = 71·5 is almost equal to the value $[\text{–}CO_2\text{–}] = 71$ assigned to esters. This small difference could obviously be due to uncertainty in the assessment of group contributions. The mean deviation is 0·6% over 17 compounds.

Additivity Function for Compounds containing Ter- and Quadri-valent Atoms.—The most extensive data are for boron compounds, the mean deviation being 0·8% over 13 compounds of quite diverse types. The value [N] = 20 should be considered provisional, being based on data for only 7 compounds. The value [P] = 57 is based in the main on the series $R{\cdot}PCl_2$. Vapour pressures were recorded in the literature only in graphical form, and the uncertainty in reading off individual values leads to some unreliability in the calculated F values. Table 6 also includes 21 silicon compounds, the mean deviation

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[21] White, Barnard-Smith, and Fidler, *Ind. Eng. Chem.*, 1952, **44**, 1430.

being 1·1%, taking [Si] = 51, as well as 4 compounds of tin, 7 of germanium, and 3 each of antimony and arsenic.

Polynuclear aromatics and heterocyclics. Values calculated on the assumption that each (Kekulé) carbon–carbon double bond has the " aromatic " value 4·4 are in excellent agreement with the observed values. The value of [pyridine] is taken as 150·6.

Compounds containing three- and four-membered rings. Seven such compounds show a mean deviation of 1·2%, [3 and 4 membered rings] being taken as = 2.

Compounds containing seven- and eight-membered rings. Four such compounds show a mean deviation of 0·6% if we take [7 and 8 membered rings] = – 3. The double bonds in *cyclo*hepta-1 : 3 : 5-triene and in *cyclo*octatetraene are assumed to be of normal, *i.e.*, non-aromatic, type.

Compounds of Hybrid Type.—The last section of Table 6 lists 41 polyfunctional substances not taken into consideration in the earlier evaluation of atomic and structural constants. It includes many data of questionable reliability, and the mean deviation of 1·3% can be regarded as satisfactory. The somewhat large deviations shown by styrene derivatives (mean 1·8% over 9 compounds) might be expected on the grounds of possible polymerisation during measurements. Large negative errors are exhibited by propiophenone (2·7%), benzophenone (2·9%), anisole (2·5%), and phenetole (3·5%). All four measurements were carefully carried out on materials estimated as of 99·6—100 mole % purity, and it would appear that such errors lie outside the limits of experimental error.

Compounds containing Elements in Higher Valency States.—The observed values of *F* for such compounds are consistently lower by appreciable amounts than the values calculated on the basis of the atomic constants previously evaluated. Structural increments in respect of possible double bonds would still further increase the discrepancy. Owing to insufficient data, the behaviour cannot yet be rationalised, and a few examples will suffice (Table 7).

TABLE 7.

Compound	*F* (exptl.)	*F* (calc.)	Diff. (%)	Refs.	Method of calcn.	Compound	*F* (exptl.)	*F* (calc.)	Diff. (%)	Refs.	Method of calcn.
B_2H_6	63·5	69·0	9	30	1	SF_6	220·0	271·0	23	37	1
B_5H_{11}	130·3	146·5	12	31	1	ClF_3	149·3	171·0	15	38	2
$Me{\cdot}PH_2,BH_3$	121·0	141·0	17	32	1	BrF_3	199·8	236·0	18	39	2
SO_3	103·0	136·0	32	33, 34, 35	1	ClO_2	109·3	117·0	7	40	1
SF_4	174·9	199·0	14	36	1	$Me{\cdot}PO(OMe)_2$	214·2	241·3*	13	41	1

* Taking *n* = 2.

Associated Compounds.—Alcohols, phenols, primary and secondary amines, and amides have *F* values considerably lower than the values calculated on the basis of monomeric formulæ, owing to the absorption of energy in the breaking up of the polymers. I hope in the immediate future to re-examine my views on molecular association [22] in the light of the more accurate estimates of entropies of boiling now presented.

List of atomic and structural constants.

H	= 6·5	Zn	= 120	C–C treble bond	= 4·5
D	= 6·2	Ge	= 123	3- & 4-membered rings	= 2
B	= 15	As	= 121	5- & 6- ,, ,,	= 0·7
C	= 17·0	Se	= 121	7- & 8- ,, ,,	= –3
N (tertiary)	= 20	Br	= 128	–C≡N	= 44
O	= 27	Sn	= 175	–CO–	= 44·5
F	= 36 (37)	Sb	= 148	–CO–O–	= 71
Si	= 50·5	I	= 195	$-NO_2$ (nitro)	= 78
P	= 57	C–C double bond	= 5·5	Pyridine	= 150·6
S	= 55	C–C double bond (aromatic)	= 4·4	Benzene	= 155·0
Cl	= 63 (64·5)	C–C double bond (allene type)	= 3·6		

Estimation of Latent Heat and Vapour Pressure of Liquids.—If vapour-pressure data are

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[22] Thomas, *J.*, 1948, 1345, 1349.

to hand, the latent heat of vaporisation of a given compound at any temperature up to the critical can readily and conveniently be calculated in the manner described earlier.[23] The present paper supplements these methods in the case of a compound whose b. p. is known at one pressure only. Thus the b. p. (T°K) under any other pressure can be evaluated from the equation

$$\log_{10} T = \log_{10} \theta + (F/Z)(Z/F)_{\text{benzene}} \log_{10} (T/\theta)_{\text{benzene}}$$

where T_{benzene} and θ_{benzene} are the b. p.s of benzene under the same two pressures, and F is the value calculated from the atomic and structural constants and equation (6). This equation can obviously be used to calculate θ_{benzene} from a known T value. The vapour pressure of benzene at θ_{benzene} then, of course, equals that of the substance at T°. Table 8 shows the b. p.s of a number of hydrocarbons under a pressure of 10 mm. so calculated from the b.p.s under 760 mm. Hg. The magnitude of the error likely to be involved in this procedure has been discussed on p. 2136. In Table 8 the average deviation involved in the calculation of T is 0·2°, whereas the mean deviation in the corresponding calculated F values is 0·4%.

TABLE 8.

$$\log_{10} (T/100) = \log_{10} (\theta/100) - 0{\cdot}03742F/Z.$$

	B. p. (°c)/10 mm.	
Substance	Exptl.	Calc.
Ethane	−142·9	−143·0
Propene	−112·1	−112·5
Penta-1 : 4-diene	−57·1	−57·5
n-Pentane	−50·1	−50·0
*cyclo*Pentane	−40·4	−40·0
3-Methylpentane	−30·1	−29·9
2 : 3-Dimethylpentane	−10·3	−10·3
Methyl*cyclo*hexane	−3·2	−3·2
cis-1-Ethyl-2-methyl*cyclo*pentane	14·5	14·3
Ethylbenzene	25·9	26·1
2 : 3 : 3 : 4-Tetramethylpentane	27·2	26·9
Non-1-ene	35·5	35·9
1 : 4-Diethylbenzene	62·8	62·6
n-Butylbenzene	62·4	62·6
n-Dodecane	91·6	91·3
Hexadec-1-ene	147·3	147·5

To find the latent heat of vaporisation (Table 9) at a temperature T°(K), it is first necessary to calculate from the known b. p. the corresponding vapour pressure as above. The value of E then follows from the relationship $E = ZTx/F$, where x is the ratio of the value of E/T at the determined vapour pressure to its value at 100 mm. pressure. The method to be used in evaluating x has been outlined in ref. 9, Table 1.

TABLE 9.

		p (mm.)		l (cal./g.)		
Substance	T (°K)	(calc.)	(exptl.)	(calc.)	(exptl.)	Refs.
n-Octane	298·1	14·2	14·0	86·3	86·8	122
3-Methylheptane	,,	19·8	19·5	82·9	83·3	,,
2 : 5-Dimethylhexane	,,	30·7	30·4	78·9	79·2	,,
2 : 2 : 5-Trimethylhexane	,,	16·7	16·6	74·3	74·9	,,
Toluene	,,	28·2	28·4	99·8	98·6	,,
Ethylbenzene	293·9	7·3	6·8	95·7	95·6	123

At temperatures sufficiently removed from the b. p. (say, below ~50 mm., when the difference between E and L will not exceed ~½%), we may equate E to L, so that the latent heat per g. $= ZTx/MF$. Its value at any temperature up to the critical may then be calculated in the manner previously outlined.[23]

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[*Received, May* 13*th*, 1958.]

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[23] Thomas, *J.*, 1949, 3415.