710. *Entropies of Vaporization, and Internal Order in Liquids.*

By L. A. K. Staveley and W. I. Tupman.

For each of 53 liquids, the entropy of vaporization is estimated over as wide a range of temperature as possible up to the normal boiling point. These entropy changes are compared according to Hildebrand's rule, and the alternative method of comparison suggested by Pitzer is briefly discussed. The liquids are classified according to the geometrical or chemical character of their molecules. A plot of entropy of vaporization against a convenient measure of the molar volume of the vapour for the class of liquids having monatomic or highly symmetrical molecules is used to establish empirically a reference curve, representing the lowest possible values of the vaporization entropy. The vaporization entropies of the other liquids are considered in relation to this reference curve. An attempt is made to interpret the excess entropy over the values furnished by the reference curve in terms of the degree of order in the liquids and the extent to which molecular rotation therein is inhibited, making qualitative use of Pitzer's analysis of the thermodynamic properties of restricted rotators. Among the molecular properties whose effect on the order and restriction of rotation are considered are the moment of inertia, polarity, length of the carbon chain in paraffins, and the presence in such a chain of double bonds. It is stressed that the influence of polarity must be considered in conjunction with molecular size.

In connection with an investigation recently carried out in this laboratory into some thermodynamic properties of binary liquid mixtures, it was desirable to obtain as much information as possible about order in pure liquids and about the variation of this order with temperature. This we have attempted to do from a consideration of entropies of vaporization. In 1915, Hildebrand (*J. Amer. Chem. Soc.*, **37**, 970) enunciated his well-known modification of Trouton's rule, that the entropies of vaporization, ΔS, of different liquids are more nearly constant when compared at such temperatures that the molar volume of the saturated vapour is the same, than when the comparison is made at their b. p.s. Later (*J. Chem. Physics*, **1939**, **7**, 233), he pointed out that the values of ΔS for different liquids when compared on this basis still do not agree exactly, and he suggested that the differences between them can be related to the internal order which these liquids might reasonably be expected to possess in virtue of the shape, polarity, and other characteristics of their molecules. More recently, Halford (*ibid*, 1940, **8**, 496) has suggested that differences in vaporization entropies, compared according to Hildebrand's rule, can be correlated with the extent to which molecular rotation is restricted. Pitzer (*ibid.*, 1939, **7**, 583) has considered the problem of the comparison of vaporization entropies from a more fundamental standpoint, and has concluded that the comparison should be made at a constant ratio of vapour volume to liquid volume. If this is correct, Hildebrand's rule is only strictly applicable to a group of substances with identical molar volumes in the *liquid* state.

There now exist numerous data, mostly determined for the purpose of evaluating calorimetric entropies, from which the vaporization entropies of a wide variety of liquids can be calculated accurately over a range of temperature. This we have done for 53 liquids over as wide a temperature range as possible up to the normal b. p.s, using for each liquid one or more of the following methods :

(*a*) From a value of L, the molar heat of evaporation, directly determined at any one temperature (usually at or near the normal b. p.), and the formula

$$\frac{\mathrm{d}L}{\mathrm{d}T} = C_{pg} - C_{pl} + \frac{L}{T}\left[1 - \frac{T}{\Delta V}\left(\frac{\partial(\Delta V)}{\partial T}\right)_p\right]$$

To evaluate the term in square brackets the Berthelot equation was used, and ΔV was assumed to be equal to the molar volume of the vapour since this is very much larger than that of the liquid. Experimental values of C_{pl} were used. C°_{pg}, the molar heat capacity of the vapour at vanishingly small pressures, was usually calculated from the intramolecular vibration frequencies. C_{pg} is the molar heat capacity of the vapour at the saturation vapour pressure p, and the difference $C_{pg} - C^{\circ}_{pg}$ was estimated by using the Berthelot equation, according to which it is $81\boldsymbol{R}pT_c^{\,3}/32p_cT^3$, p_c and T_c being respectively the critical pressure and temperature. When accurate compressibility data for a gas at low pressures are available, it can be shown that use of the Berthelot equation tends to overestimate the quantity $C_{pg} - C^{\circ}_{pg}$, which makes the values of L at temperatures well below that of the direct determination rather too high. For a few substances, there exist directly determined values of the gaseous heat capacity at temperatures below the normal b. p.

(*b*) From accurate vapour-pressure data and the Clapeyron–Clausius equation, from which

$$\Delta S = 2{\cdot}3026\,\frac{\mathrm{d}\log_{10}p}{\mathrm{d}T}\,(pV_g - pV_l)$$

pV_g was evaluated by using the Berthelot equation. As is well known, the effect of the imperfection of the vapour is rather large near the b. p., and as estimated by the Berthelot equation may give rise to errors in L and ΔS of 1 or 2%. The lower the temperature, however, the smaller the correction, so that with sufficiently accurate vapour-pressure data the error in the values of ΔS estimated in this way diminishes as the temperature drops. Wherever possible, we have derived values of ΔS by both methods (*a*) and (*b*), in the belief that the first method gives more accurate values near the b. p., while the second is superior at lower temperatures. Usually the values obtained by the two methods differed by less than 1%. Sometimes, *e.g.*, for the higher paraffins, lack of a direct value of L or of the data necessary for the evaluation of C°_{pg} made (*b*) the only possible method.

(*c*) For a few substances, directly determined values of L at more than one temperature are available, leading to an empirical relation between L and T.

For most substances, the facts required for the estimation of the vaporization entropies have been taken from papers published within the last 20 years giving the experimental data necessary for the evaluation of calorimetric entropies. In particular, considerable use has been made of the work of W. F. Giauque and of J. G. Aston and their collaborators (published in the *J. Amer. Chem. Soc.*), and of K. Clusius and his co-workers (published in the *Z. physikal. Chem.*).

Finally, all values of ΔS have, for uniformity, been corrected by means of the Berthelot equation so as to become the entropy increase if the vapour of the liquid were a perfect gas; *i.e.*, to the values of L/T have been added the quantity $\frac{27}{32}\boldsymbol{R}\frac{p}{p_c}\left(\frac{T_c}{T}\right)^3$. In comparing the entropies of vaporization of different liquids at a fixed vapour molar volume, we have assumed the vapours to be perfect gases and have taken the ratio p/T as the measure of their molar volumes, where p

is the vapour pressure in mm. (The actual molar volume in c.c. is then $6{\cdot}24 \times 10^4 T/p$.) In no case has a liquid been considered above its normal b. p.

We shall now present and discuss the vaporization entropies of 53 liquids, which for convenience have been grouped into the following classes :

(1) Substances with monatomic or very symmetrical molecules : mercury, argon, krypton, xenon, methane, germane, *neo*pentane, tetramethylsilane, carbon tetrachloride.

(2) Substances with diatomic or linear molecules : (i) Diatomic molecules : chlorine, oxygen, nitrogen, carbon monoxide, hydrogen chloride, bromide, and iodide, nitric oxide. We shall also include in this group methyl chloride and bromide as quasi-diatomic molecules. (ii) Polyatomic linear molecules : carbon disulphide, carbon oxysulphide, cyanogen, dimethylacetylene.

(3) Substances with triangular or quasi-triangular molecules (excluding water) : hydrogen sulphide, sulphur dioxide, dimethyl ether, dimethyl sulphide.

(4) Substances with pyramidal or quasi-pyramidal molecules : ammonia, phosphine, mono-, di-, and tri-methylamine.

(5) Aliphatic hydrocarbons : (i) Normal paraffins up to octane, and also *n*-decane. (ii) Branched-chain paraffins : *iso*butane, *iso*pentane, 2 : 2-dimethylbutane. (iii) Unsaturated hydrocarbons : ethylene, propylene, but-1-ene.

(6) Substances with cyclic molecules : *cyclo*propane, *cyclo*pentane, *cyclo*hexane, benzene.

(7) Hydroxylic substances : water, methanol, ethanol.

Class (1) (*Monatomic or Highly Symmetrical Molecules*).—In a consideration of the ΔS values of a group of liquids at one fixed p/T value, Hildebrand pointed out that the substances with the lowest values were mercury and *neo*pentane, *i.e.*, the liquids with the most symmetrical molecules, in which the order should be a minimum. The substances for class (1) were selected with the object of examining the possibility of constructing empirically a basic or reference entropy of vaporization curve. On Hildebrand's rule, this would be a curve of ΔS against some measure of the vapour molar volume : on the basis of Pitzer's considerations, a plot of ΔS against the ratio of vapour to liquid volume. Values of ΔS for liquids of this class are plotted against $\log_{10} (10^3 p/T)$ in Fig. 1. The choice of the logarithm of our measure of the molar vapour volume is simply a matter of convenience. The ΔS values for any one substance then fall on a gentle curve, whereas if they are plotted against p/T itself the curve rises very steeply at low p/T values. Except for the points for tetramethylsilane and carbon tetrachloride at low temperatures (*i.e.*, at low p/T values), which we shall shortly consider separately, a curve can be drawn in Fig. 1 such that no point lies more than $\sim$1 e.u. from the curve, and most are much closer to it.

If, however, the same ΔS values are plotted against the ratio of the molar volume of the vapour to that of the liquid (or against the logarithm of this ratio), the curves for the several substances are now much more widely dispersed, or in other words, the considerable measure of uniformity shown in Fig. 1 is largely destroyed simply by the introduction of the molar volume of the liquid. One of the five assumptions on which Pitzer's reasoning was based was that the potential energy of a pair of molecules in the liquid is given by the expression $A\phi(R/R_0)$, where A and R_0 are constants for any one substance, R is the intermolecular separation, and ϕ a universal function. As Halford (*loc. cit.*) has pointed out, in an elaboration of a suggestion made by Pitzer himself, this postulate cannot hold for polyatomic molecules for which the intermolecular potential energy largely depends on the interaction between the peripheral atoms, and if this factor were taken into account, Pitzer's reasoning would, for such substances, lead to something very much like Hildebrand's rule. It cannot be denied that when ΔS values for polyatomic liquids are compared on the basis suggested by Pitzer, they often stand in a relationship which is surprising when the chemical nature of the substances concerned is borne in mind. Thus, ethyl and butyl acetates have to be ascribed higher ΔS values (*i.e.*, are to be regarded as considerably more ordered in the liquid state) than water and ammonia. For the hydrogen halides, the order of decreasing ΔS would be $\Delta S_{\mathrm{HBr}} > \Delta S_{\mathrm{HCl}} > \Delta S_{\mathrm{HI}}$, whereas the order which we should expect from the dipole moments, and which in fact is given by Hildebrand's rule, is $\Delta S_{\mathrm{HCl}} > \Delta S_{\mathrm{HBr}} > \Delta S_{\mathrm{HI}}$. Again, according to Pitzer, hydrogen chloride has considerably lower ΔS values than *neo*pentane, in spite of the fact that the molecule of the latter substance is a compact, non-polar molecule of high symmetry, whereas hydrogen chloride is strongly polar and from spectroscopic evidence (Lee, Sutherland, and Wu, *Proc. Roy. Soc.*, 1940, *A*, **176**, 493) appears to be associated in the liquid state. We shall therefore, without further justification, carry out our comparison of vaporization entropies according to Hildebrand's rule, and see to what extent differences in ΔS values can be plausibly interpreted in terms of different degrees of internal order or of restriction of molecular rotation. We may add that we shall not, as a rule, attempt to distinguish clearly between order and restriction of molecular rotation, since the two may be closely related. Hindrance to molecular rotation implies a potential barrier, which can arise from the tendency of the molecules to adopt certain preferred orientations with respect to each other under the influence of the intermolecular forces, which in turn means that there is some molecular ordering.

The curve in Fig. 1 has been drawn so that none of the points lies appreciably below it, and this curve, which we shall refer to as the reference curve, will be taken as giving empirically the lowest possible values of the entropy of vaporization at different p/T values. At low p/T values this curve admittedly depends entirely on the points for mercury, and it may be, for the reasons which Pitzer has given, that the fact that the entropy values for this metal do join on fairly smoothly to those for germane is fortuitous (in the sense that it arises from the mutual cancellation of two opposing, unconsidered factors), and that metals should be considered apart from substances where the intermolecular forces are wholly of the van der Waals type. However, many of the conclusions we shall draw do not depend on the exact position of the reference curve at low p/T values.

FIG. 1.

Variation of the entropy of vaporization, ΔS, with the logarithm of the quantity $10^3p/T$ for substances with monatomic or highly symmetrical molecules. (ΔS is in calories per mole per degree; p is the vapour pressure in mm. at T, °K.) The curve is the so-called reference curve.

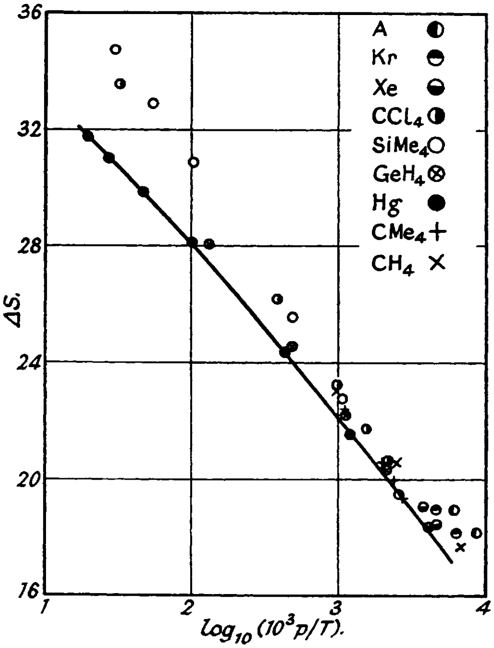
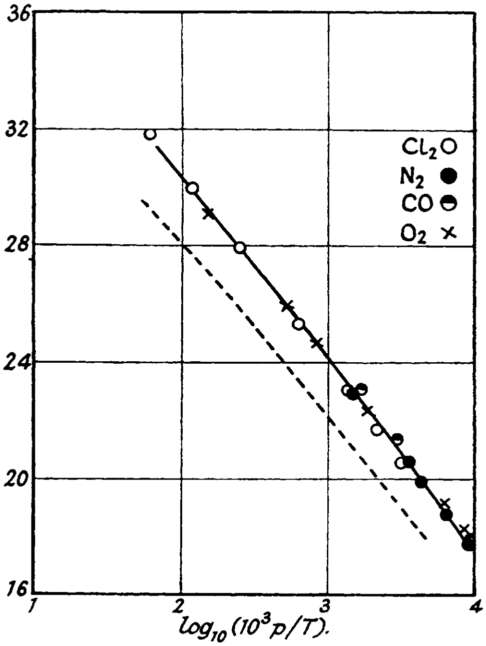


FIG. 2.

Variation of ΔS for substances with non-polar diatomic molecules. The dotted line is the reference curve of Fig. 1.



As regards the individual substances in class (1), the points for the inert gases lie above the reference curve, argon showing the greatest divergency and xenon the least. For these substances (liquid at normal pressure over a range of only a few degrees) the agreement between the entropies when compared according to Pitzer's scheme is undoubtedly better. For the other substances it will be seen that if $\delta(\Delta S)$ is the amount by which the actual entropy of vaporization exceeds the value on the reference curve for the same p/T value, then $\delta(\Delta S)$ tends to become greater the lower the temperature (*i.e.*, the smaller the p/T value). We shall see that this tendency is a general one, and we regard it as demonstrating that the internal order in a liquid becomes more pronounced, or the molecular rotation more restricted, the lower the temperature. For tetramethylsilane and carbon tetrachloride at low temperatures the quantity $\delta(\Delta S)$ appears to be quite large (cf. the points for these substances with those for germane at lower p/T values). In tetramethylsilane, there is little doubt that there is considerable molecular interlocking, which will impede free rotation, but to a lesser degree as the temperature rises and the liquid expands. Such interlocking would be expected to be less for methane and germane, which are more compact molecules than tetramethylsilane, and indeed for methane it seems that the molecules have considerable rotational freedom even in the solid state (Eucken and Veith, *Z. physikal. Chem.*, 1936, *B*, **34**, 275; 1937, *B*, **38**, 393; Bitter, Alpert, Poss, Lehr, and Lin, *Physical Rev.*, 1947, **71**, 738). This is presumably why the values of $\delta(\Delta S)$ for methane and germane near their m. p.s are smaller than for tetramethylsilane and carbon tetrachloride.

Class (2) (*Diatomic and Linear Molecules*).—In Fig. 2, ΔS is plotted against $\log_{10}(10^3p/T)$ for the non-polar diatomic molecules chlorine, oxygen, and nitrogen, and for carbon monoxide (which has an almost zero moment). The points conform closely to a single curve, which lies about 2 e.u. above the reference curve. (This is to be contrasted with the points for substances like germane, methane, and tetramethylsilane, where the individual curves tend to run into the reference curve at higher temperatures.) This suggests that molecular rotation in these liquids is considerably restricted, and that the hindrance to rotation is about equally effective in all four of them. There is no evidence of any abnormality in the vaporization entropy of oxygen which might be attributed to the formation of O_4 molecules.

We may conveniently use the curve in Fig. 2 as an arbitrary basis for the comparison of the vaporization entropies of the remaining substances of this class. ΔS values for these at selected values of $\log_{10}(10^3p/T)$ are given in Table I, together with the corresponding values from the curve of Fig. 2 and from the reference curve. The very large ΔS values for nitric oxide are, of course, attributable primarily to its association, probably to N_2O_2, in the liquid state. Of the hydrogen halides, the chloride has the largest values of ΔS. This is to be expected, since this molecule has not only the highest dipole moment of the three, but also the smallest halogen atom, permitting closest intermolecular approach. Since the interaction energy between two fixed dipoles of equal moment depends on the square of this moment and inversely on the cube of their distance apart, the extent to which polarity causes molecular orientation and hence inhibits rotation will rapidly diminish as we pass from the chloride to the bromide and then to the iodide. For hydrogen chloride the ΔS values are in fact appreciably higher than for the non-polar substances with diatomic molecules, whereas for hydrogen iodide they are less. The dipole moment of hydrogen iodide is small, and the moment of inertia of the molecule is less than those of the homopolar diatomic molecules we have considered. Pitzer's theoretical treatment of restricted rotators (*J. Chem. Physics*, 1937, **5**, 469) has shown that the amount by which the entropy for the free rotators exceeds that for the restricted rotators becomes less as both V/kT and IV decrease (where V is the height of the potential barrier restricting rotation and I is the moment of inertia). For hydrogen iodide the small values of I combined with the low polarity (and hence small V) may account for the low ΔS values, which suggest that molecules in this liquid enjoy a greater measure of rotational freedom than do those of, say, liquid chlorine.

TABLE I.

ΔS *for certain substances of Class* (2).

[In this and all other tables, ΔS is the entropy of vaporization in calories per mole per degree, and p is the vapour pressure in mm. at the absolute temperature T.]

	Values of ΔS for various values of $\log_{10}(10^3p/T)$:				
	2.	2·5.	3.	3·2.	3·5.
NO	—	—	—	30·85	29·05
HCl	—	—	24·55	23·29	21·30
HBr	—	—	—	22·99	20·96
HI	—	—	—	22·15	20·03
CH_3Cl	30·75	27·52	24·17	—	20·69
CH_3Br	30·51	27·23	23·85	—	20·37
CS_2	29·01	25·86	22·64	—	—
COS	30·21	26·98	23·65	—	20·21
$CH_3\cdot C\equiv C\cdot CH_3$	—	27·84	24·23	—	—
$(CN)_2$	—	—	—	—	22·08
Mean ΔS for non-polar diatomic substances	30·4	27·3	24·05	22·75	20·7
Reference curve	28·1	25·2	22·1	20·85	19·0

The ΔS values for methyl chloride and methyl bromide lie very near the curve for the non-polar diatomic molecules at all p/T values. This is to be expected, since there would be relatively little restriction of rotation about the carbon–halogen axes compared with that of rotation about the remaining two axes. Again, the more polar molecule (methyl chloride) has the higher ΔS values, but since there is comparatively little difference between the dipole moments of the two, the differences in ΔS may be partly due to the increased size of the halogen atom in the bromide, with its corresponding reduction in the closeness of approach of neighbouring molecules and hence in their orientating influence on one another.

Of the compounds with polyatomic linear molecules, carbon disulphide has low values of ΔS, which lie nearer to the reference curve than to the curve for the non-polar diatomic substances. This is perhaps surprising: there is, for example, evidence from the Kerr effect that the rotation of the molecules in the liquid is hindered (Debye, *Chem. Reviews*, **1936**, **19**, 171). For carbon oxysulphide, which is polar, ΔS values are about one unit higher than for carbon disulphide, and approach fairly closely to the figures for the non-polar diatomic molecules, while these are slightly exceeded by the values of ΔS for dimethylacetylene. For cyanogen, $\delta(\Delta S)$ is greater. The reason for this may be that, although non-polar as a whole, the cyanogen molecule contains two polar bonds [cf. the larger ΔS of tetranitromethane than of carbon tetrachloride, as pointed out by Hildebrand (*loc. cit.*, 1939)].

Class (3) (*Triangular or Quasi-triangular Molecules*).—Of these four substances, sulphur dioxide shows the largest ΔS values (Table II). The quantity $\delta(\Delta S)$ increases as the temperature falls, and is perhaps larger than would be expected for a molecule of the size and polarity of sulphur dioxide (cf. the figures for dimethyl sulphide). It may be that some more specific form of association is involved here. ΔS values for hydrogen sulphide, though smaller than those of sulphur dioxide, are greater than those for non-polar diatomic molecules and also for dimethyl sulphide. Since the mean moment of inertia of the hydrogen sulphide molecules is small, this appears to indicate a considerable restraint on their rotational movement (*i.e.*, a high V), and the comparison with dimethyl sulphide emphasizes once more that, in its bearing on association in polar liquids, the size of the molecule and the relation of this to the intermolecular separation is quite as important as the magnitude of the dipole moment. The replacement of the oxygen atom in dimethyl ether by the larger sulphur atom likewise reduces ΔS, even though the dipole moment and the moment of inertia are thereby slightly increased.

TABLE II.

ΔS *for substances of class* (3) *and class* (4).

	Values of ΔS for various values of $\log_{10}(10^3p/T)$:					Values of ΔS for various values of $\log_{10}(10^3p/T)$:			
	2.	2·5.	3.	3·5.		2.	2·5.	3.	3·5.
SO_2	32·99	29·60	26·12	22·47	NH_3 ...	—	30·15	26·85	23·35
H_2S	—	—	24·85	21·44	PH_3 ...	—	26·17	23·05	19·82
SMe_2 ...	—	26·96	23·72	—	NH_2Me	33·95	30·55	26·9	—
OMe_2 ...	—	27·76	24·33	20·73	$NHMe_2$	—	30·35	26·47	—
Reference curve	28·1	25·2	22·1	19·0	NMe_3 ...	30·32	26·95	23·3	—

Class (4) (*Pyramidal or Quasi-pyramidal Molecules*).—ΔS values for these substances (Table II) demonstrate the well-known fact that ammonia and primary and secondary amines show considerable association in the liquid state, in contrast to tertiary amines and phosphine. The values for phosphine lie close to the reference curve, and are much the same as those for hydrogen iodide. The reason for this may also be that the low polarity of the molecule coupled with its small moment of inertia combine to give the molecules considerable rotational freedom in the liquid. With trimethylamine the dipole moment is small, and moreover the dipole is screened by the methyl groups. The values of ΔS for this substance suggest that there is little if any molecular ordering or restriction on rotation arising from permanent dipole–dipole interaction. Rather does the trend of ΔS in relation to the reference curve recall the behaviour of tetramethylsilane, suggesting that the excess entropy of vaporization at low temperatures is derived mainly from the inhibition of molecular rotation due to steric interaction between the methyl groups (*i.e.*, to dispersion forces of attraction and short-range repulsive forces). It is noteworthy that whereas the interaction energy between fixed permanent dipoles is proportional to R^{-3}, that due to dispersion forces varies as R^{-6}. Consequently, a given proportional increase in R, due to the expansion of the liquid on heating, will cause a more rapid drop in potential barrier height when this is controlled by dispersion forces than when it depends mainly on dipole–dipole interaction. Halford (*loc. cit.*) has attempted to relate ΔS with the degree of restriction of molecular rotation as given by the ratio of the calculated molar volume of the " free covalent rotator " to the actual molar volume of the liquid. From the curve in his paper which represents this relationship, it would be possible for a 10% change in the molar volume to alter ΔS by as much as ~1 e.u. (For the average organic liquid, a temperature change of ~80—100° causes such an alteration in volume.) It is of interest that the *rates* at which ΔS drops with increasing p/T values are in the order $NHMe_2 > NH_2Me > NH_3$. For ammonia, the molecular ordering and consequent restriction on rotation must depend largely on the permanent dipole–dipole interaction. For mono-and di-methylamine it will also arise from the steric effects associated with the methyl groups, but in the light of what has just been said the contribution from the latter source should decrease relatively more rapidly with rising temperature.

Class (5) (*Aliphatic Hydrocarbons*).—(i) *Normal paraffins.* In evaluating ΔS, use has been made of the very accurate measurements of the vapour pressures of hydrocarbons recently carried out by Willingham, Taylor, Pignocco, and Rossini (*J. Res. Nat. Bur. Stand.*, **1945**, **35**, 219). Entropies of vaporization at two p/T values are recorded in Table III, together with the corresponding temperatures. The b. p.s are also given for comparison.

The ΔS values show an interesting trend. As the number of carbon atoms in the molecule increases, they first fall, but then increase. This rise in ΔS with increasing chain length is to be expected. It reflects the growing internal order in the liquid and the greater restriction on molecular rotation which arises from the increasing tendency of the chains to align themselves parallel to one another. The lower the temperature, the less will thermal agitation interfere with the tendency. The rise in ΔS with increasing molecular weight is therefore more pronounced at the lower p/T value than the upper (cf., *e.g.*, the two sets of values for pentane and dodecane). Even at the higher p/T value, however, the effect is still apparent, that is at temperatures which, for the higher hydrocarbons, are near their normal b. p.s.

The drop in ΔS for the early members of the series may perhaps arise as follows. Whereas the molecule of ethane is like a dumb-bell, with propane rotation about C–C bonds makes the existence of different molecular configurations possible. With the hydrocarbons from butane onwards, the possibility of different configurations rapidly multiplies, and the distance between carbon atoms separated by two or more atoms can now vary over a considerable range. Table III shows that at the higher p/T value ΔS falls until pentane is reached. It is suggested that this is due to increased disorder in the liquids as the chain becomes longer, owing to the increasing possibility of the existence of the molecules in a variety of configurations, which will militate against ordered packing. This will operate against the tendency of the chains to align themselves parallel to one another, but if this latter effect increases relatively more rapidly with increasing chain length, it will eventually gain the upper hand and so give rise to increasing values of ΔS. It then follows naturally that the minimum in the ΔS values should be reached at a hydrocarbon with a smaller number of carbon atoms, the weaker the thermal agitation and hence the lower the temperature. It will be seen from Table III that, at the lower p/T value, propane in fact has the lowest value of ΔS. Admittedly, the differences between the entropies of vaporization of the first four hydrocarbons in the table are small, but we shall see later that a similar state of affairs appears to prevail for a series of unsaturated hydrocarbons.

TABLE III.

ΔS *for normal paraffins.*

	$p/T = 0.3$.		$p/T = 1.5$.		
	ΔS.	T, °K.	ΔS.	T, °K.	B. p., °K.
Ethane	26·96	143·3	22·30	165·0	184·1
Propane	26·73	185·0	22·04	213·2	231·0
Butane	26·80	222·1	21·82	265·1	272·7
Pentane	26·80	254·2	21·79	294·2	309·2
Hexane	27·05	285·7	21·82	328·75	341·9
Heptane	27·30	313·55	21·88	360·4	371·6
Octane	27·42	339·3	21·92	389·6	398·8
Nonane	27·59	363·3	21·98	416·6	423·9
Decane	27·79	385·65	22·04	442·0	447·3
Dodecane	28·14	426·5	22·16	487·85	489·4
Reference curve	25·4	—	21·0	—	—

(ii) *Branched-chain hydrocarbons.* In Table IV the ΔS values of some straight- and branched-chain paraffins are compared. These illustrate a fact to which Hildebrand has already drawn attention, namely, that a branched-chain hydrocarbon has a smaller ΔS for a given vapour molar volume than the straight-chain isomer. The data in Table IV suggest, moreover, that

ΔS for a branched-chain paraffin is less than that for the *normal* paraffin with as many carbon atoms as there are in the straight-chain part of the branched-chain hydrocarbon, since ΔS for *iso*butane is less than that for propane, and ΔS for *iso*pentane and 2 : 2-dimethylbutane is less than that for butane. The lowest ΔS values for the substances considered are shown by that with the most symmetrical molecule, namely, 2 : 2-dimethylbutane.

TABLE IV.

ΔS *for hydrocarbons of class* (5), (ii) *and* (iii).

	Values of ΔS for various values of $\log_{10}(10^3p/T)$.				
	2.	2·5.	3.	3·3.	3·5.
Ethylene	—	27·03	23·74	—	20·37
Ethane	—	26·82	23·62	—	20·12
Propylene	30·19	26·86	23·43	—	19·89
Propane	29·83	26·57	23·21	21·13	19·71
*iso*Butane	29·69	26·42	22·95	20·75	—
Butane	30·19	26·66	23·10	20·87	19·35
1-Butene	30·27	26·90	23·29	—	19·49
Dimethylacetylene	—	27·84	24·23	—	—
*iso*Pentane	—	26·32	22·95	20·68	—
Pentane	—	26·66	23·11	20·78	—
2 : 2-Dimethylbutane	—	26·39	22·54	20·35	—
Hexane	—	26·88	23·13	—	—

(iii) *Unsaturated hydrocarbons.* Since the introduction of a double bond into a carbon chain increases its rigidity, an unsaturated molecule is capable of less variety in its configurations than the paraffin with the same number of carbon atoms. The decrease in molecular flexibility which accompanies the introduction of a double bond should favour a more ordered packing in the liquid. It will be seen from Table IV that the unsaturated hydrocarbons have, in fact, consistently higher ΔS values than the corresponding paraffins. The highest vaporization entropies are shown by dimethylacetylene, which, of those substances whose molecules contain three or four carbon atoms, is the only one with a linear molecule. The data in Table IV also give some indication that in a series of unsaturated hydrocarbons the variation of ΔS with chain length has a similar dependence on p/T, and hence on temperature, to that which, as already pointed out, obtains for the normal paraffins; for, while at the highest p/T value, the order is

$$\Delta S_{C_2H_4} > \Delta S_{C_3H_6} > \Delta S_{C_4H_8}$$

yet propylene has the lowest value of ΔS when $\log_{10}(10^3p/T)$ is 2·5.

Class (6) (*Cyclic Molecules*).—All of these substances are non-polar, but while the molecules of *cyclo*propane and benzene are planar and that of *cyclo*pentane almost so, the *cyclo*hexane molecule is not. It is interesting to observe that this has a noticeable effect on the trend of the b. p.s of the *cyclo*paraffins. The increment in the b. p., ΔT_b, per CH_2 group has the following values for the ascent of the series: $C_3 \rightarrow C_4$, 44·3; $C_4 \rightarrow C_5$, 37·8; $C_5 \rightarrow C_6$, 31·5; $C_6 \rightarrow C_7$, 38; $C_7 \rightarrow C_8$, 30. This is in contrast to the normal paraffins, where the values of ΔT_b decrease smoothly as the series is ascended, and it seems as if the b. p. of *cyclo*hexane, by comparison with that of its predecessors, is somewhat low. As regards vaporization entropies, we should expect that the molecules of benzene, *cyclo*propane, and *cyclo*pentane, being flat, would experience little hindrance to rotation in the plane of the ring, but considerable restriction to rotation about the remaining two axes, and that these liquids would therefore have ΔS values roughly the same as for substances with non-polar diatomic molecules. In *cyclo*hexane, with its buckled molecule, there should be less hindrance to three-dimensional rotation, so that we might expect that the ΔS values for this substance would be rather lower. These predictions are, in fact, supported by the experimental ΔS values (Table V). There is, unfortunately, some uncertainty about the figures for *cyclo*pentane. Those given in Table V depend on the application of method (*a*) to the data of Aston, Fink, and Schumann (*J. Amer. Chem. Soc.*, 1943, **65**, 341), who determined L at ~25° [very near to the temperature corresponding to $\log_{10}(10^3p/T) = 3$]. The value of ΔS calculated in this way for the normal b. p. is, however, ~0·4 e.u. higher than that obtained from a later direct determination of L at the b. p. (Spitzer and Pitzer, *ibid.*, 1946, **68**, 2537). The figures given for *cyclo*pentane may therefore be somewhat too high. Fortunately, for *cyclo*hexane there is excellent agreement between different observers' data. Thus, at the b. p., direct determinations of L give for ΔS, 20·51 (Mathews, *ibid.*, 1926, **48**, 562) and 20·46 (Spitzer and Pitzer, *loc. cit.*), while the application of method (*b*) to the vapour-pressure data of Willingham *et al.* (*loc. cit.*) gives 20·42. The figures for benzene should also be very reliable, as they depend on direct determinations of L at different temperatures (Fiock, Ginnings, and Holton, *J. Res. Nat. Bur. Stand.*, 1931, **6**, 881). Thus, in spite of the uncertainty in the figures for *cyclo*pentane, it does seem that of the three *cyclo*paraffins, *cyclo*hexane has the lowest ΔS values, and that these are moreover definitely less than those for benzene, even though the f. p.s, b. p.s, and critical temperatures of these two liquids are almost the same.

TABLE V.

ΔS *for substances of classes* (6) *and* (7).

	Values of ΔS for various values of $\log_{10}(10^3p/T)$.			
	2.	2·5.	3.	3·3.
*cyclo*Propane ...	—	27·08	23·68	21·51
*cyclo*Pentane ...	—	26·92	23·71	21·43
*cyclo*Hexane ...	—	26·82	22·99	20·70
Benzene	—	27·08	23·47	21·19
Reference curve	28·1	25·2	22·1	20·2

	Values of ΔS for various values of $\log_{10}(10^3p/T)$.			
	2.	2·5.	3.	3·3.
Methanol	33·86	30·78	27·50	25·38
Ethanol	35·92	32·58	29·01	27·03
Water	34·59	31·45	28·16	26·12

Class (7) (*Hydroxylic Substances*).—ΔS values for water, methanol, and ethanol are recorded in Table V. In deriving these, the correction for vaporization to the ideal gaseous state was applied, as usual, by means of the Berthelot equation. As the vapours of these substances are associated to a small extent into dimers and probably higher polymers, a further correction to the ΔS values should be made to take account of this association. This additional correction cannot be accurately assessed for all of these substances, but data for water (see, *e.g.*, Rowlinson, *Trans. Faraday Soc.*, 1949, **45**, 974) indicate that for this liquid it will not exceed ∼0·3 e.u. at the b. p. As it will be less at lower temperatures, and moreover is unlikely to be significantly greater for the alcohols, it is very improbable that the relationship between the ΔS values of these substances would be seriously affected by it.

The order of the vaporization entropies is

$$\Delta S_{CH_3\cdot OH} < \Delta S_{H_2O} < \Delta S_{C_2H_5\cdot OH}$$

The intermediate position of water is perhaps rather surprising, since one water molecule can be involved in four intermolecular hydrogen bonds, whereas an alcohol molecule can only be concerned in two. The excess entropy of vaporization (which, by comparison with the reference curve, amounts to between 5 and 8 e.u.) is a measure of the amount by which the entropy of the liquids is abnormally low, and its magnitude depends on the extent to which molecular rotation is impeded, and on the degree of quasi-crystalline ordering of the molecules. A rough measure of the hindrance to molecular rotation can be obtained from the dielectric constants by applying Debye's theory. According to this, for water at the b. p., V (the height of the potential barrier restricting rotation) is $\sim 7{\cdot}4\boldsymbol{k}T$, whereas for methanol and ethanol it is $\sim 3{\cdot}2\boldsymbol{k}T$ and $\sim 1{\cdot}7\boldsymbol{k}T$ respectively. Now Pitzer's calculations (*loc. cit.*, 1937) of the effect of restricted rotation on thermodynamic properties show that the amount $(S_f - S)$ by which the entropy of a system of molecules each with restricted rotation in one degree of freedom falls short of the value for free rotation is a function of both $V/\boldsymbol{k}T$ and n^2/IV, where n is the number of maxima in the potential-energy curve per one complete revolution. For a given value of $V/\boldsymbol{k}T$, however, variation in n^2/IV has less effect on $(S_f - S)$ than variation in $V/\boldsymbol{k}T$ at a fixed value of n^2/IV. As compared with water, the larger values of I for the alcohols are to some extent offset by the smaller V values, so that there will probably not be wide differences in the value of n^2/IV for the three compounds. Rather will the magnitude of $(S_f - S)$ be primarily determined by $V/\boldsymbol{k}T$, and we should expect from the figures given by Pitzer that restriction on molecular rotation would reduce the entropy of water more than that of the alcohols. If this is accepted, then for ethanol at least, for which ΔS is greater than for water, a greater degree of quasi-crystallinity must prevail than in water, and this in spite of the fact that, as already noted, the possibilities which an alcohol molecule has for association are more limited. There is, however, some evidence that the hydrogen bond in alcohols is stronger than that in water. Thus, the change in the vibration frequency connected with the hydroxyl group is larger for methanol than for water (Badger, *J. Chem. Physics*, 1940, **8**, 288), and the O—H---O distance in alcohols seems to be shorter than that in ice (Wells, " Structural Inorganic Chemistry," Oxford, 1945, quotes 2·69 A. for this distance in pentaerythritol and 2·76 A. in ice). Nevertheless, there is no reason to believe that there is much difference in hydrogen-bond strengths in methanol and ethanol, while there is a considerable difference in the ΔS values of these two substances. This suggests that the effect of the hydrogen bond in promoting order is somehow enhanced by the presence of the ethyl group. We have already noted that in the normal paraffins, as the chain length increases, ΔS at higher p/T values first falls and then rises. It was suggested that the fall in ΔS for the lower members was due to the variety of molecular configurations made possible by the increasing flexibility of the chain, and that this was eventually offset by the tendency of the chains to adopt a parallel alignment. In the alcohols, the chains are as it were anchored at one end by the hydrogen bond in such a way as to favour parallelism of the hydrocarbon residues in any case, so that the increase in cohesion consequent on the lengthening of the chain might now be expected to make itself evident right from the start of the series. Such an augmentation of the molecular ordering would, however, decrease with increasing thermal agitation, owing to the breaking of hydrogen bonds and the increasing violence of the movement of the alkyl groups, and it will, in fact, be seen from Table V that the difference in the ΔS values for methanol and ethanol diminishes as the temperature rises.

Finally, we may note that although hydroxylic compounds are correctly considered as highly associated, of all the substances we have discussed that with the largest ΔS values is nitric oxide.

THE INORGANIC CHEMISTRY LABORATORY, OXFORD. [*Received, August* 21*st*, 1950.]