Heats of Vaporization of Hydrogen-bonded Substances

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A new method is proposed for the calculation of the heat of vaporization of hydroxylated compounds to an accuracy of about ±0.5 kcal./mole from no more data than the molecular structure and a boiling point. The older methods, by comparison, achieved an accuracy of about ±1 kcal./mole with a far greater computational effort, since they required the (usually hypothetical) critical temperature and critical pressure in addition to a boiling point.

The method is here applied to aliphatic and aromatic alcohols, to ether-alcohols (e.g., the cellosolves), and to alcohols containing keto or aldehyde groups (e.g., salicylaldehyde) and supersedes previous correlations covering the heats of vaporization of these compounds. The method can also be used to assess the quality of vapor-pressure data of the compounds covered by it.

The method is based on the assumption that the heat of vaporization consists of two terms, the dispersion energy and the hydrogen-bond increment (close but not equal to the hydrogen-bond strength). The first term is calculated from a knowledge of the heat of vaporization of the equistructural hydrocarbon, now easily available from the Tables of A.P.I. Research Project 44. The hydrogen-bond term is calculated from a set of rules given in the report.

The application of the increment method of this report to other properties and other functional groups is the subject of a continuing investigation.

PURPOSE AND SCOPE

The recurrent need for heat-of-vaporization data of increasingly complex synthetic oxygenated compounds and the discovery of some inconsistencies in previous correlations prompted a short inquiry into regularities which could be used as basis for improved calculation. The choice between the direct calculation of the heat of vaporization and the older path of calculating the entropy of vaporization has been resolved in favor of the first route, since it could be shown from basic principles that more information is required to estimate the entropy of vaporization from liquids with strongly oriented molecules than to assess the extra force of cohesion caused by hydrogen bonds.

Exploratory calculations (*10, 48, 49, 51, 57*) had shown that the difference between the heat of vaporization of a hydroxylic compound and that of its hydrocarbon (or otherwise nonpolar) homomorph* constitutes a good measure of hydrogen-bond strength (*12*). This path could now be pursued in detail because of the availability of extensive and reliable heat-of-vaporization data in the A.P.I.-44 tabulation (*3*) on a wide variety of hydrocarbons that could serve as homomorphs of oxygenated compounds.

BASIC PRINCIPLES

The Hydrogen Bond

The interaction (in a condensed phase) between a hydrogen atom which is chemically bound to an atom of electronegativity $\geq$ 3 e.v. (Pauling's scale) and an atom of high electronegativity bound to another (or the same) molecule has in many respects more the character of a chemical bond than of nonspecific van der Waals attraction. The *hydrogen bond,* as this interaction is called, can therefore be characterized by a bond strength which is essentially independent of its environment and should depend primarily on the nature of the atoms to which the hydrogen atom is bound.

Contribution of Hydrogen Bond to Heat of Vaporization

In comparison with other chemical bonds the hydrogen bond is rather weak

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*A homomorph is a compound of similar molecular geometry; e.g., ethane is a homomorph of methanol, toluene of phenol, etc.

and only rarely survives the transition from condensed to vapor phase. The contribution which the hydrogen bond makes to the strength of cohesion of condensed phases is therefore a good measure of its strength (*51*).

The separation of the hydrogen-bond term from all other factors which determine the magnitude of the cohesive forces in liquids requires, in principle, a detailed calculation of the dispersion and dipole forces between the molecules of the liquid. In order to avoid this laborious and, of necessity, inexact calculation, it is here proposed to substitute for the dispersion forces between the molecules of a hydroxylic compound the (readily available) heat of vaporization ΔH_v^* of its hydrocarbon homomorph at the same reduced temperature; the dipole interaction is absorbed into the hydrogen-bond–strength increment δ(OH) of the total heat of vaporization ΔH_v of a liquid, and specific intramolecular interactions are represented as Δ, or formally as

$$\Delta H_v|_T = \Delta H_v^*|_{T_R} + \Sigma\delta(OH)|_T + \Sigma\Delta \qquad (1)$$

In this procedure it is implicit that the dispersion-energy contribution of the functional groups of a molecule is equal to that of a methyl or methylene group. The correctness of this assumption has been previously proved (*9*).

Since the increment δ(OH) is a measure of (but not identical with) the heat of formation of the hydrogen bond, and decreases with increasing temperature, comparison at the boiling point means that δ(OH) is not a constant but depends upon the absolute temperature level at which the hydroxyl compound is being considered. Such a reference curve for δ(OH) has been constructed from the heat-of-vaporization data of water (by subtraction of the dispersion-force contribution) and is shown, together with the data from other alcohols, in Figure 1. The upper curve for the hydrogen-bond increment of water may be considered as representing the upper limit of hydrogen-bond increments in liquids. The proximity of the curve for the hydrogen-bond increment of the monohydric alcohols to that of water is a bit surprising, since the proton is attached far more strongly (by about 13 kcal.) to the water oxygen than to that of the alcohols. It will be seen that vicinal effects on the hydrogen-bond strength cannot be ignored in the case of phenols, where the electron attraction of the benzene ring reduces the charge separation which is largely responsible for hydrogen bonding. It is noteworthy that the average value of $d\delta(\mathrm{OH})/dT$ along the water and alcohol curve (10 cal./°K.) is similar to that found spectroscopically for the hydrogen bond of isopropyl alcohol (6.6 cal./°K.) (*42*).

An examination of the temperature coefficient of ΔH_v of the homomorph provides some information regarding the error which could be made by incorrect choice of the appropriate reduced temperature in Equation (1). This is an actual problem with many hydroxylic compounds of interest, the critical temperature of which cannot be measured but only established by means of various empirical correlations (*59*). If one then assumes that the maximum error in estimating the critical temperature is about $0.1T_R$ ($\sim$ 50°C.), the error in ΔH_v of the homomorph can be estimated by means of the equation of Watson (*32*)

$$\Delta H_v^*(T_R) = \Delta H_v(b)\left(\frac{1 - T_R}{1 - T_R(b)}\right)^{0.38} \qquad (2)$$

as of the order of $0.1\Delta H_v$ of the homomorph. Since the heat of vaporization of the homomorph is usually about 4 to 10 kcal./mole, the maximum error in δ(OH) due to very poor choice of T_c for the hydroxyl compound is about 0.4 to 1 kcal./mole. Actual errors are likely to be less than this amount since mistakes of more than ±50°C. are not very probable, nor will the discrepancy between the "true" corresponding temperatures and the temperature chosen for equal vapor pressure approach that amount.

Effect of Molecular Structure on the Hydrogen-bond Increment

The hydrogen-bond increment δ(OH) is approximately the same for a wide range of hydroxylated compounds. However, in certain types of molecule systematic variations can be observed, many of which can fortunately be assigned to rational causes and some even calculated from independent measurements. The following paragraphs will treat, in order, the monofunctional primary alcohols and phenols, then the strong intra- and intermolecular interactions due to other functional groups in the molecule, and finally the shielding effect of hydrocarbon chains adjacent to the hydroxyl group.

Primary Aliphatic Alcohols. The properties of the members of this series form the backbone of this report not only because of the simplicity of their structure and the proximity of their hydrogen-bond increments to those of the "standard hydroxyl group," namely water, but also because their data have been determined more accurately than those of any other group of hydroxyl compounds. The data, which form the basis of Figure 1, are assembled in Table 1. Combined with the curve for water, they suggest that the increment δ(OH) is essentially independent of the size of the hydrocarbon radical at temperatures above 25°C. and that the trend with absolute temperature is a measure of the temperature coefficient of δ(OH).* The data for n-amyl alcohol were not included because their accuracy was suspected.

TABLE 1. HYDROGEN-BOND INCREMENTS FOR LOWER PRIMARY n-ALIPHATIC ALCOHOLS

Alcohol \ Temp., °C.	−10	0	20	60	100
Methyl	5.7	5.6	5.6	5.4	*5.2*
Ethyl	5.7	5.7	5.6	5.2	*5.0*
n-Propyl	6.0	5.9	5.7	5.4	*4.8*

Phenols. The hydroxyl group attached to a benzene ring is subject to very strong electron withdrawal forces, as is evident by the far more acidic character of the phenol than of the aliphatic alcohols. More important is perhaps the strong attraction of the benzene ring (due to its high polarizability) for the proton of the phenolic OH group, as is shown by comparison of the infrared spectra in the series methanol, phenol, o-phenyl phenol (*46, 50, 51, 66*). The strength of the interaction between hydroxyl groups and benzene rings is also evident from the fact that for both methanol and phenol at infinite dilution the heat of solution in benzene is about 0.8 to 1 kcal./mole lower than in aliphatic hydrocarbons (*46*). This is about the amount by which δ(OH) is lower for the three unhindered phenols of Table 2 than for aliphatic alcohols at the same temperature. The attraction of the proton by the benzene ring may therefore be the dominating effect. Independent evidence regarding the possible effect of electron withdrawal from the OH group on δ(OH) can be obtained by heat-of-vaporization measurements on perfluoro and perchloro alcohols.

TABLE 2. HEATS OF VAPORIZATION OF PHENOLS AND THEIR HOMOMORPHS AT T_b

Compound	ΔH_v, kcal.	Homomorph	ΔH_v, kcal.	$\delta(\Delta H_v)$	Data sources
Phenol	10.95	Toluene	8.00	2.95	*21*
p-Cresol	11.34	p-Xylene	8.62	2.72	*21*
3,4-Xylenol	12.33	Pseudocumene	9.38	2.95	*21*

Multifunctional Alcohols, General Principles. The comparison between normal aliphatic alcohols and the phenols (and benzylalcohol) has shown the effect of competitive intramolecular interactions on the hydrogen-bond increment $\delta\Delta H_v$. One would expect, therefore, that additional functional groups in an alcohol molecule which are capable of strong intramolecular interaction with hydroxyl groups also would reduce $\delta\Delta H_v$. The conditions for effective intramolecular

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*Close inspection of Figure 1 reveals a trend toward increasing steepness of the δ(OH)-vs.-temperature curves with increasing molecular size. More accurate vapor-pressure data are required to ascertain the reality of this trend.

bonding of the hydroxyl group can be anticipated intuitively:

1. The interaction energy between the functional group and the hydroxyl group has to be of the same order as that of the OH–OH interaction. A feel for the magnitude of such competitive interaction can be obtained by inspection from the excess free energy of mixing F^E of alcohols with hydrocarbons and with solvents containing the functional groups in question (Table 3). The magnitude of the interaction between hydroxyl, ether, and carbonyl groups has also been measured spectroscopically (*41, 44, 46, 51, 63, 66*).

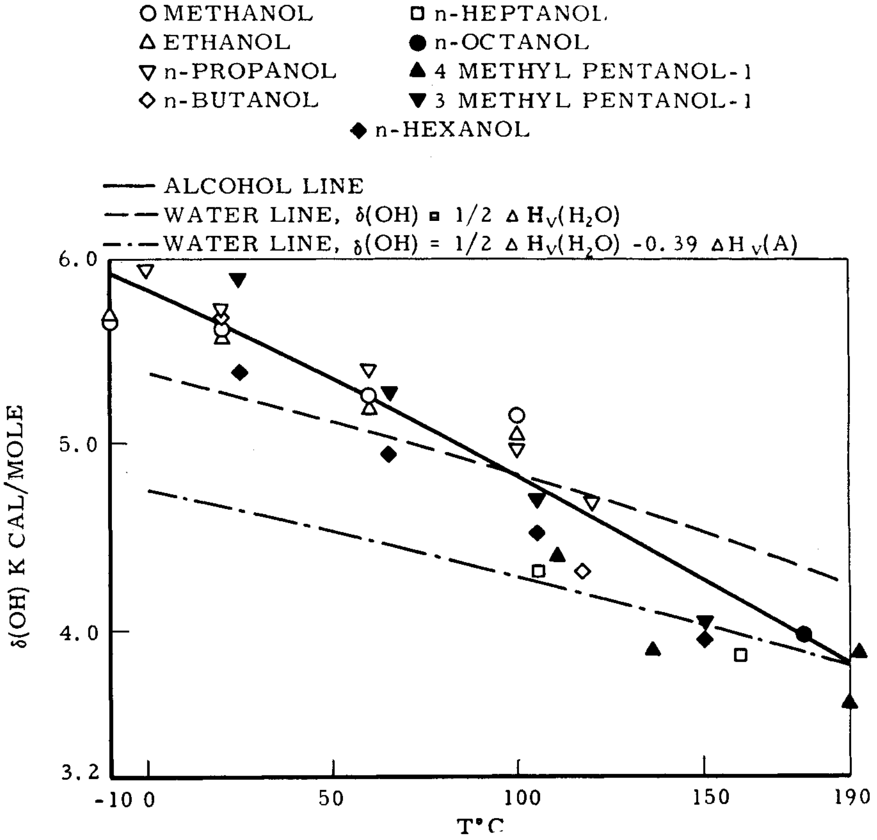
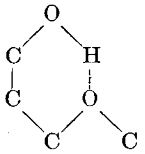


Fig. 1. Hydrogen-bond increments δ(OH) of primary aliphatic alcohols and water.

TABLE 3. SOLUTIONS OF ALCOHOL IN HYDROCARBONS AND IN OXYGENATED SOLVENTS (760 mm.)

(1)	(2)	Log γ_{12}^{∞}	F^E cal./mole	Data sources
Ethanol	*n*-hexane	1.12	1,800	*35*
Ethanol	ethyl ether	0.42	670	*52*
Ethanol	ethyl acetate	0.38	610	*24*
Methanol	*n*-heptane	1.313	2,200	*7*
Methanol	acetone	0.25	420	*52*

2. Since the bonding interaction decreases very rapidly with distance, unhindered mutual approach of the interacting groups is a prerequisite of intramolecular interaction. Ideally, a six-or-more–membered ring has, therefore, to be obtainable in the manner



if any effect of the group (here –O–) on $\delta\Delta H_v$ is to be expected. A weak effect is sometimes noted (as will be seen below) even when only a five-membered ring can be formed.

3. When the intramolecular bond formed is stable, no effect on ΔH_v could be expected. The factors determining this stability are still somewhat elusive, but some features can be discerned. The entropy decrease ΔS_c that accompanies ring formation has to be compensated for by the heat of formation of the hydrogen bond ΔH_c so that the free energy of formation of the hydrogen bond is zero or smaller. An estimate of ΔS_c, obtained by a comparison of S^0 for alkene-1 and cycloalkane gives $\Delta S_c = -13$ e.u. for the five-membered ring and $\Delta S_c = -20$ to -22 e.u. for six- to eight-membered rings. Hence at 300°K. ΔH_c must be ≥ 6 kcal./mole to give a significant fraction of intramolecularly bonded molecules.

Monohydric Ether and Keto Alcohols. Only a limited amount of vapor-pressure data among the members of this class of compounds was good enough to permit valid conclusions to be drawn from the resulting heats of vaporization, shown in Table 4. All of these could have formed six-membered rings in intramolecular hydrogen-bond formation, and although infrared spectroscopic evidence points to relatively high concentrations of bonded hydroxyl groups in the dilute solution of 3-ethoxypropanol-1 (*63*) and of diacetone alcohol (*51*), the observed heats of vaporization are in rather good agreement with those calculated on the assumption of an unbonded hydroxyl group in the vapor phase.* The absence of extensive internal ring formation in the vapor phase suggested by the data of Table 4 is in agreement with the probable magnitude of ΔH_f for the O–H····O bond as compared with the ≥ 6 kcal./mole required to compensate for the large entropy of ring formation mentioned in the introduction to this section. No acceptable reconciliation between the vapor pressure and the infrared spectral observation has yet been found.

A large number of monohydric ether alcohols derived from ethylene oxide are made commercially. The remarkable discordance among the many published vapor-pressure measurements on these compounds suggests that most of the available samples may have been impure. Since most of the probable impurities, especially water, are likely to decrease the heat of vaporization below its true value, one may consider the data leading to the highest value of ΔH_v (shown in Table 5) as perhaps more reliable than the others. There is a suggestion of a systematic lowering of about 1 kcal. of the hydrogen-bond contribution to ΔH_v below the typical value of δ(OH) especially as the size of the group tied to the far end of the ether oxygen increases beyond that of the ethyl group. The likelihood of impurities being responsible for the lowering of ΔH_v of these products is very high because of notorious difficulty involved in their purification. Lowering of ΔH_v as a result of a finite width of boiling range may be a general phenomenon worthy of further investigation. Until more reliable data have been obtained, one can only record this information but can hardly use it for generalizations.

Aliphatic Polyhydric Alcohols. Intramolecular bonding of hydroxyl groups might be expected to lower $\delta\Delta H_v$ significantly, since there is ample evidence for its occurrence from infrared-absorption-spectra (*46*), electron (*5*), and X-ray-diffraction data (*5*) as well as for various physical properties (*5, 6, 56*). But the

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*The assumption of dimer formation in the vapor phase would reconcile the infrared and the vapor-pressure data and would lead to values of ΔH_v(calc.) which while invariably higher than observed would almost all be within the experimental error of the observed data.

TABLE 4. HEATS OF VAPORIZATION OF MONOHYDRIC ETHER AND KETO ALCOHOLS

Compound	T_b, °C.	ΔH_v	$\Delta H_v{}^*$	δ(OH) from Fig. 1	$\Delta H_v{}^* + \delta$(OH), calc.	ΔH_D D = dimer	Data sources
3 Methoxybutanol-1	161.1	11.8	7.36	4.08	11.42	~12.2	*22, 60*
3 Ethoxypropanol-1	162–3	11.5	7.58	4.08	11.66	~12.4	*2, 63*
3 Methoxypropanol-1	~150	11.1	6.90	4.18	11.18	11.4	*2, 58*
Diacetone alcohol	~166	11.4	7.41	4.05	11.46	12.7	*57*
Acetyl acetone	~135	10.3	7.41	4.2	11.6	~12.5	*18, 22, 40*
4-Hydroxypentanone-2	~176	11.4	7.05	3.98	11.03	~12.5	*45, 47*
4 Me 4 hydroxy-pentanone-2	~187	12.4	7.82	3.94	11.76	12.7	*45*

TABLE 5. HEATS OF VAPORIZATION OF MONOHYDRIC ETHER ALCOHOLS

Compound	T_b, °C.	ΔH_v, kcal. (exptl.)	δ(OH)*	Homomorph $\Delta H_v{}^*$, kcal.	$\Delta H_v{}^* + \delta$(OH)	Data sources
Glycol ethers (cellosolve)						
Methyl	124.6	9.13	4.4	6.16	10.6	*15*
		9.39				*26*
		9.60				*15*
		10.16				*14*
		10.3				*26, 27*
Ethyl	135.6	9.41	4.3	6.90	11.2	
		9.46				*14*
		9.85				*15*
		10.93				*20*
		11.13				*15*
n-Hexyl	208.1	9.59	3.6	9.39	13.0	*15*
		11.34				*14*
		11.94				*15*
Diglycol ethers (carbitols)						
Methyl	193.6	11.5	3.8	8.22	12.0	*14*
		11.30				*15*
		10.88				*15*
		12.08				*14*
Ethyl	201.9	12.90	3.7	8.82	12.5	*19*
n-Butyl	230.4	10.00	3.4	9.92	13.3	*15*
		11.99				*15*
		12.62				*14*
n-Hexyl	259.1	13.75	3.1	10.91	14.0	*15*
		12.84				*15*
		13.51				*14*
		12.8				*14*

*From Figure 1.

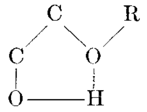
TABLE 6. HYDROGEN-BOND INCREMENT IN ALIPHATIC POLYOLS

Compound	T_b, °C.	ΔH_v, kcal.	Homomorph	$\Delta H_v{}^*$, kcal.	$\delta\Delta H_v$, kcal.	Decrease in ΔH_v, kcal. Total	Per OH group	Data sources
Ethylene glycol	197.2	12.58	Butane	5.35	7.23	0.4	0.2	*1, 17, 19, 25*
Propylene glycol	187.4	12.90	2-Methyl butane	5.90	7.00	0.6	0.3	*17, 19*
1,3-Butanediol	207.5	13.97	2-Methyl pentane	6.64	7.33	~0	~0	*19*
Pentaerythritol	256*	24*	3,3-Diethyl pentane	10.8	13.2	~0	~0	*11, 31*
Glycerol	290.5	~16	3-Methyl pentane	6.7	9.3	~0	~0	*19*

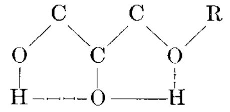
*At the melting point.

data assembled in Table 6 indicate that the vapor concentration of internally bonded molecules is not large. One would probably predict the heat of vaporization of aliphatic polyols to within the experimental error if one assigned the full value of δ(OH) per OH group present.

Aliphatic Polyhydric Ether Alcohols. The polyhydric ether alcohols can be divided into two groups: (1) those with single hydroxyl groups on either side of an ether linkage, as in diethyleneglycol, and (2) those with more than one adjacent hydroxyl group on one or both sides of an ether linkage as in glycerol-α-ethyl ether or in diglycerol, respectively. Inspection of the possible structures in Figure 2 clearly shows the difference between the two types of compounds. The diethylene or triethyleneglycol type would hardly be expected to behave very differently from the monohydric ether alcohols of the same class. The data of Table 7 indicate that this is indeed the case in every respect. The range of reported ΔH_v value is large, within the probable range of error, and one again finds only small deviations from the behavior of monohydric alcohols, equivalent to but small concentrations of internally bonded molecules in the vapor phase.



Di- or triethylene glycol structure



Glycerol-α-ether structure

Fig. 2. Types of polyhydric ether alcohol structures.

The structure of the glyceryl ether type, on the other hand, suggests mutual reinforcement of the interacting groups OH---OH---O. It is not surprising to find, therefore, that in all the α-glyceryl ethers only one out of two hydroxyl groups contributes its full share, δ(OH), to the heat of vaporization, or, in other words, that here the vapor concentration of internally bonded molecules is quite high.

Multifunctional Phenols

In spite of the much older technology, far fewer physical-property data are available on phenol derivatives than on the relatively recent aliphatic alcohols. This paucity of information coupled with the early dates of the reported measurements should be kept in mind whenever the data of this section are used as a basis for further extrapolation.

Phenols with Orthocarbonyl Groups. The classical example of intramolecular hydrogen bonding is salicyl aldehyde, by spectral evidence (*51*) as well as in terms of its heat of vaporization, as shown by the data of Table 8. Methyl salicylate likewise exhibits just the ΔH_v of its hydrocarbon homomorph, indicating essentially complete internal binding of the hydroxyl group.

The reason for the exceptionally strong interaction between the phenolic OH group and the adjacent carbonyl oxygen may be the planarity of the ring system and the consequent lack of hindering barriers in the path of the interacting groups. Stabilization of hydrogen bond by resonance among various possible electronic configurations may also play a role here.

Dihydroxy Benzenes. The data of Table 9 show the expected pattern. The interaction between adjacent (ortho) hydroxyl groups reduces ΔH_v by about the same amount found for the glycols (about 0.5 kcal./OH group). The meta- and para-oriented OH groups do not interact.

SHIELDING EFFECTS

Methyl or other shielding groups located adjacent to or near the hydroxyl group of a molecule reduce the intermolecular hydrogen bonding (*51*) in the liquid and thereby the heat of vaporization of an alcohol. Even a cursory inspection of the extensive data on isomeric butanols, hexanols (*34*), and octanols (*54*) in the literature reveals that essentially two different types of shielding can be discerned: one group (*A*) for which the difference Δ between the observed hydrogen-bond increment and that of Figure 1 is about 0.5 to 1.5 kcal. and essentially temperature independent and another group (*B*) for which the observed hydrogen-bond increment is about 1 to 2 kcal./mole nearly independently of temperature; hence the decrement Δ is about 4 kcal./mole of room temperature, decreasing to about 2 kcal./mole at 160°C.

All the alcohols of group *B* have a methyl group at three carbon atoms' distance from the hydroxyl group. Typical examples are listed in group *B* of Table 10. The weak hydroxyl bonding among the members of this group must be due to the hindrance which the attached propyl group presents to the formation of OH-association chains. The maximum observed value of Δ is—in accordance with this view—of the order of the barrier to internal rotation of a methyl-methylene couple.

Group *A* contains a wide variety of isomers. Several of its members would have been classed intuitively in group *B* because they possess methyl groups three carbon atoms removed from the hydroxyl group; however, one finds in each case that either the interacting methyl group or the hydroxyl group has been locked into some fixed position in space, thus apparently permitting more ready access to intermolecular hydrogen bonding. Typical examples have been enumerated under group *A*-2 in Table 10. Other members of group *A* are the alcohols with OH groups attached to tertiary and secondary carbon atoms.

Shielding effects are difficult to separate from interaction effects in aliphatic polyols. Using the shielding decrements given in Table 10, one can estimate $\delta(\Delta H_v)$ for 2-methyl-2, 4 pentanediol [$\delta(\Delta H_v)$ calc. = 5.8 kcal./mole] and 2-ethyl-1, 3 hexanediol [$\delta(\Delta H_v)$ calc. = 6.2 kcal./mole] without appeal to hydroxyl interaction, as shown by comparison with the data of Table 11.

TABLE 7. HEAT OF VAPORIZATION OF POLYHYDRIC ETHER ALCOHOLS

Compound	T_b, °C.	ΔH_b, kcal./mole	$\sum \delta$(OH) (Fig.1)	Homomorph, ΔH_v^*, kcal./mole	$\Delta H_v^* + \sum \delta$(OH)	Data sources
Diethylene glycol	245.0	15.92	6.6	7.58	14.4	*19*
		12.49				*25*
		11.36				*19*
Triethylene glycol	289.8	14.93	5.6	9.39	15.0	*19*
		17.07				*25*
Glycerol ethyl ether	224	12.40	7.0	8.10	15.1	*57*
Glycerol α-isopropyl ether	226	12.3	7.0	8.50	15.5	*57*
Glycerol α-allyl ether	245	12.9	6.6	8.79	15.4	*57*

TABLE 8. HEATS OF VAPORIZATION OF PHENOLS WITH ORTHO CARBONYL GROUPS

Compound	T_b, °C.	ΔH_v, kcal./mole	ΔH_v^*, kcal./mole	Data sources
Salicylaldehyde	196	9.14	9.29	*40, 21*
Methyl Salicylate	223.3	9.58	9.94	*62, 21*

TABLE 9. HYDROGEN BOND INCREMENTS FOR DIHYDROXY BENZENES

Compound	T_b, °C.	ΔH_v	Homomorph	ΔH_v^*	$\delta \Delta H_v$	Decrease in $\delta \Delta H_v$	Data sources
o-Dihydroxybenzene	245.5	13.95	*o*-Xylene	8.80	5.13	0.9	*4, 21*
m-Dihydroxybenzene	276.5	16.29	*m*-Xylene	8.71	7.58	—	*4, 21*
p-Dihydroxybenzene	268.2	16.38	*p*-Xylene	8.62	7.76	—	*61, 21*

TABLE 10. SHIELDING EFFECTS IN ALIPHATIC ALCOHOLS

Group	Compound	*t*, °C.	$\delta(\Delta H_v)$, kcal./mole	Δ, kcal./mole
A-1	*n*-butanol-2			
Secondary	*n*-hexanol-2	110	3.1–4.0	1.0 ± 0.5
alcohols	*n*-octanol-2	140	3.3–3.9	0.5 ± 0.3
	n-octanol-4			
A-2	*t*-butanol	25	4.3	1.4
Tertiary	2-methyl pentanol-2	70	3.4–4.0	1.4 ± 0.3
alcohols	2-methyl heptanol-2	150	2.1–3.2	1.3 ± 0.5
A-3	3-methyl heptanol-3			
"Locked"	2,2 dimethyl butanol-3	25	4.3–4.7	1.2 ± 0.2
propyl	2-methyl heptanol-3	60	3.7–4.2	1.3 ± 0.3
interaction	3-methyl pentanol-2	150	2.2–3.0	1.4 ± 0.4
	2-methyl pentanol-3			
B	*n*-hexanol-3			
Propyl	*n*-octanol-3			
interaction	2-methyl heptanol-5			
	2-methyl heptanol-1	25	1.2–2.2	4.0 ± 0.5
	3-methyl heptanol-2	60	1.1–2.1	3.6 ± 0.5
	3-methyl heptanol-4	150	1.2–1.9	2.4 ± 0.3
	3-methyl heptanol-5			
	4-methyl heptanol-3			

TABLE 11. SHIELDING EFFECTS IN ALIPHATIC COMPOUNDS

Compound	T_b, °C.	ΔH_v, kcal.	Homomorph	ΔH_v^*, kcal.	$\delta \Delta H_v$, kcal.	Data sources
2-Methyl-2,4-pentanediol	197.1	13.66	2,2,4-Trimethylpentane	7.44	6.25	*19*
2-Ethyl-1,3-hexanediol	244.2	14.95	9-Ethyl-4-methylheptane	9.00	5.95	*19*

A somewhat larger effect of shielding groups is noted with phenols (Table 12), where the orthomethyl group reduces δ(OH) by about 1 kcal./mole. The larger effect here may be due to the rigidity of the molecule which precludes close approach of a colliding molecule to the OH group by bending of the carbon skeleton. With the aliphatic compounds, on the other hand, rotation around the C–C axis is relatively free, thus reducing the shielding effect of the alkyl group adjacent to the hydroxyl.

TABLE 12. SHIELDING EFFECTS IN PHENOLS

Compound	T_b, °C.	ΔH_v, kcal./mole	Homomorph	ΔH_v^*, kcal./mole	$\delta\Delta H_v$	Decrease in δ(OH)	Data sources
Phenol	181.7	10.95	Toluene	8.00	2.95	0	*21*
o-Cresol	191.0	10.72	*o*-Xylene	8.80	1.92	1	*21*
m-Cresol	202.2	11.32	*m*-Xylene	8.71	2.61	~0.3	*21*
p-Cresol	201.9	11.34	*p*-Xylene	8.62	2.72	~0.2	*21*
2,3-Xylenol	218.0	11.33	Hemimellitene	9.57	1.76	~1.2	*21*
3,4-Xylenol	225.0	12.33	Pseudocumene	9.38	2.95	0	*21*

TABLE 13. HYDROGEN BOND AND STRONG DIPOLE INCREMENTS

Functional group	Increment, δ at 100°C. kcal./mole	$-\frac{d\delta}{dT}$, $\frac{\text{cal.}}{\text{mole}(°\text{K.})}$	Number of compounds investigated
–OH (aliphatic)	4.6 ± 0.2	10	>10
$-NH_2$ (aliphatic)	1.6 ± 0.2	4.5	5
–NH (aliphatic)	~0	—	3
–C≡N (aliphatic)	2.1 ± 0.4	7.0	10
$-NH_2$ (aromatic)	2.6 ± 0.2	—	3
$-\underset{H}{\underset{\vert}{C}}=O$ (aliphatic)	1.4 ± 0.2	2.9	9

SUMMARY OF HEAT-OF-VAPORIZATION INCREMENTS

In surveying the results of this investigation, one is struck by the simplicity of the relationships obtained. Much of this simplicity is hardly real but must be ascribed to the crudeness of most of the published data. Many trends in deviations may have to be accepted as real, once better data are available, which now fall within the bounds of experimental uncertainty.

In the meantime the hydroxyl-bond increments of Figure 1 may be considered as directly applicable to normal aliphatic alcohols, monohydric ether alcohols (Tables 4 and 5), monohydric keto alcohols (Table 4), polyhydric ether alcohols (Table 7), and with very small increments to aliphatic polyols (Table 6). Fairly large deviations for intramolecular hydrogen bonding, namely −0.8 δ(OH)/glyceryl group, are found with α-glycerol ethers (Table 7). Steric shielding effects are most prominent with the larger aliphatic alcohols, all of which are assembled in Table 10. Similar but less well established rules are found to hold for aromatic hydroxyl compounds and can easily be deduced from the data of Tables 2 (basic increments), 8 (intramolecular bonding), 9 (dihydroxy interaction), and 11 (shielding effects).

EVALUATION OF EXPERIMENTAL DATA

The correlations for predicting ΔH_v also provide a means for critically analyzing existing data. This analysis may be desirable for assessing the accuracy of vapor-pressure data or of a calorimetric technique. Even though the values predicted by the correlations of this report may be in error by 0.5 kcal., the differences between reported ΔH_v are so great that one can sharply delineate between the reasonable values and the impossible ones by the methods outlined here. An example of this technique is shown for the case of diethylene glycol. Literature values of ΔH_v have been given in kilocalories as 12.49 (*25*), 13.6 (*19*), and 15.92 (*1*). The difference between the highest and lowest value is great, being 3.43 kcal. The present method predicts a ΔH_v of 14.4 to 15.5 kcal. The evidence seems clear here that the 12.49 value is quite unreasonable.

When miscellaneous vapor-pressure data are used to estimate the heat of vaporization, a wide divergence of values can often be obtained. A case in point is diglycerol. The vapor-pressure data of eleven investigations were collected and plotted as log P vs. $1/T$. Using different sets of points, the extremes of which were widely separated in $1/T$ value, one can estimate ΔH_v at the boiling point to be between 18.4 and 51.4 kcal. The "best" line through the points gave a value of 22.5 kcal.; the group increment method predicts a value of 17.3 to 23.2 kcal.

FURTHER APPLICATIONS OF THE METHOD

An exploratory investigation has shown that the contribution of other hydrogen-bonding and strong dipole groups to the heat of vaporization can also be treated as addition to the heat of vaporization of the hydrocarbon homomorph. The resulting increments, collected in Table 13, are supported by much less experimental evidence than has been available for the hydroxylic compounds and should therefore be used with caution.

Description of the application of the principles outlined above to the calculation of vapor pressure, viscosity, etc., of hydroxylic compounds would obviously exceed the scope of this paper and must therefore be deferred.

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APPENDIX

A. Calculation of Boiling Point and of Critical Temperature

The method of calculation described in the paper requires knowledge of either the atmospheric boiling point or the critical temperature of the alcohol. If the boiling point is known, the critical temperature can be calculated by any one of the many variants of Guldberg's rule [Ref. 32, pp. 71–72; L. Riedel, *Chem. Ing. Tech.*, **24**, 353 (1952); or R. Herzog, *Ind. Eng. Chem.*, **36**, 997 (1944)].

In the absence of experimental boiling-point data for the alcohol a method must be found to estimate them. Following the technique of the paper, one can estimate the boiling point of an alcohol T_B by reference to that of its hydrocarbon homomorph T_B^* through the relation

$$T_B/T_B^* = a + b/(T_B^*)^2$$

where a and b are constants characteristic of a (homologous) series. Furthermore, b is proportional to the ratio $(\delta(\text{OH}) - \Delta)/\Delta S_v$, where ΔS_v $(= \Delta H_v/T_B)$ is the entropy of vaporization of the alcohol. Since the constants a and b are readily determined empirically for the more important series of alcohols, the need to use the awkward relation of b to the physical constants to be determined arises only for the adjustment of b for isomer and other structure effects. In that case

$$b(\text{isomer})/b(\text{normal}) = [\delta(\text{OH})_i - \Delta_i] \cdot \Delta S_v(n)/\delta(\text{OH})_n \cdot \Delta S_v(_i)$$

where one obviously must make some guesses, which need not be very accurate, regarding the anticipated magnitude of T_B for the "isomer." Empirical, and still tentative, values for a and b are

	a	b × 10⁴ (°K.²)
Normal aliphatic monohydric alcohols	0.925	3.2
Aliphatic glycols	0.98	5.5
Phenols	0.96	3.4

Combination of the calculated boiling point with the heat of vaporization calculated by the method outlined in the body of the paper makes it possible now to estimate the vapor-pressure curve of a new polar compound from no more information than its molecular structure. The basic tools are the A.P.I.-44 tables and the hydrogen-bond (or dipole interaction) correlation presented in the paper.

B. Calculation of Heat of Vaporization

1. Calculate the heat of vaporization at the atmospheric boiling point.

a. The atmospheric boiling point of the alcohol is known:

Step 1: Write down the molecular structure and select the appropriate hydrocarbon homomorph.

Step 2: Find the heat of vaporization (at boiling point of the homomorph (ΔH_v^*) in the A.P.I.-44 tables (*3*).

Step 3: Take $\delta(\mathrm{OH})$ from *Figure* 1 at the boiling point of the alcohol or extrapolate, if necessary, with $d\delta(\mathrm{OH})/dT \doteq -10$ cal./°C.

Step 4: Find the appropriate value of Δ from the requisite table of the paper. (See Summary of Heat-of-vaporization Increments for guidance.)

Step 5: Calculate $\Delta H_v = \Delta H_v{}^* + n\delta(\mathrm{OH}) - n\Delta$ where n = number of OH groups in molecule.

(*b*) The atmospheric boiling point of alcohol is not known:

Step 1: Same as in (a).

Step 2: Same as in (a).

Step 3: Calculate the atmospheric boiling point of the alcohol T_B by means of the procedure given in Appendix A.

For the balance of the calculation, follow the procedure from step 3 under (a) onward.

2. Calculate the heat of vaporization at a fixed temperature T:

(a) The critical temperature of the alcohol is known:

Step 1: Same as in 1(a).

Step 2: Find critical temperature $T_c{}^*$ and heat of vaporization $\Delta H_v{}^*$ of homomorph in the A.P.I.-44 tables.

Step 3: Calculate the reduced temperature T/T_c for the alcohol.

Step 4: Calculate $\Delta H_v{}^*$ for the reduced temperature $T^*/T_c{}^* = T/T_c$, by means of Equation (2) in the paper.

Step 5: Take $\delta(\mathrm{OH})$ from *Figure* 1 for the temperature T, or extrapolate if necessary.

Steps 6
and 7: Same as steps 4 and 5 under 1(*a*).

(b) The critical temperature of the alcohol is not known:

Step 1: Same as under 1(a).

Step 2: Calculate the critical temperature T_c of the alcohol. If the atmospheric boiling point of the alcohol is known, use the methods referred to in the first paragraph of Appendix A. If no physical property of the alcohol is known, the boiling point calculated according to the method of Appendix A may be substituted for the experimental datum point in the calculation of T_c by the usual methods.

All subsequent steps are the same as under 2(a).

NOTATION

F^E = excess free energy of mixing, cal./mole
ΔH_v = heat of vaporization
ΔS_c = entropy due to ring formation, e.u.
ΔS_V = entropy of vaporization, e.u.
T = temperature, °C. or °K.
T_B = boiling point, °C. or °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T
V = molal volume, cc./mole

Greek Letters

$\gamma_{12}{}^{\infty}$ = activity coefficient of alcohol at infinite dilution
$\delta(\mathrm{OH})$ = hydrogen-bond increment as defined by Equation (1)
Δ = structural contribution to the heat of vaporization
$\delta(\Delta H_v)$ = change in heat of vaporization due to polar or structural effects

Superscripts

$*$ = physical property of hydrocarbon homomorph

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