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Heats of Vaporization for a Number of Organic Compounds at 25°C

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Heats of vaporization have been determined calorimetrically at 25°C for a number of alcohols, bromides, esters, thiolesters, and ketones. Structure relationships and correlations between boiling points and ΔH_v (25°C) are briefly discussed.

In the present paper results are reported from calorimetric measurements of heats of vaporization at 25°C for a number of alcohols, bromides, esters, thiolesters, and ketones. Parallel to the measurements a careful study was undertaken which resulted in a gradual improvement of the calorimeter. The stated accuracies of the given results are therefore at some variance, and it is believed that the measurements made at the earlier stages could be made considerably more accurate if repeated with the equipment now available. However, at a time where satisfactory heats of vaporization data at the standard temperature of 25°C are very rare it still seems appropriate to include the results of earlier measurements.

EXPERIMENTAL

Apparatus. Two main types of calorimeters, designated A and C in the tables, have been used. Type A was described a few years ago [1] and type C is the construction described in the preceding paper.[2] The calorimeter construction was gradually developed from A to C; a number of measurements were also made with intermediate constructions which, however, essentially resembled type C. The intermediate types are denoted in the tables by B.

The performance of the calorimeters was frequently checked by measurements on test substances. Usually one or two measurements on a test substance were made between each series of measurements on the actual compounds.

Materials. The work has been performed over several years, partly in connection with other calorimetric investigations. For this reason methods of purification and degrees of purity of the compounds are not as uniform as might be desirable.

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If not otherwise stated, the compounds have been purified by repeated fractional distillation, using columns having 10—25 theoretical plates. Purities were usually checked by gas chromatography.

Test substances were those described in Ref. 2 (hydrocarbons, carbon tetrachloride and water).

Alcohols. 1-Butanol was supplied by Dr. J. Cox at National Chemical Laboratory, Teddington, England, and was a sample from the same batch as described in Ref. 3, cyclopentanol and cyclohexanol were from Ref. 4, and the other alcohols were of commercial origin. 1-Propanol and 2-propanol were purified by preparative gas chromatography as impurities present could not be removed by fractional distillation. The other alcohols were purified by repeated fractional distillation except 2-methyl-2-propanol for which repeated fractional crystallization was used. Methanol and ethanol were dried by magnesium treatment [5] whereas the others were dried with calcium hydride before the last distillation. All alcohols were stored in sealed ampoules. Water content was determined for all the alcohols except for cyclopentanol and cyclohexanol by a method recently developed at this laboratory.[6]

Results of the water determinations for the alcohols are given in Table 1. The handling of the alcohol samples in water determination experiments and in calorimetric experiments were closely similar. As judged by gas chromatography the purities for all the alcohols were better than 99.9 %.

Bromides. The bromides, except for 2-bromopropane, were supplied by Dr. L. Bjellerup, formerly at this laboratory. The samples were identical with those described in Ref. 7, and the high purity of these samples has since been confirmed by gas chromatography. 2-Bromopropane of commercial origin was purified by preparative gas chromatography. Purity was judged to be better than 99.9 %.

O-Esters. Ethyl acetate, butyl acetate and isopropyl acetate* were from Ref. 8. Ethyl propionate (99.8 %), ethyl-isobutyrate (98.7 %) and ethyl pivalate (99.8 %) were supplied by Dr G. Olofsson at this laboratory (*cf.* Ref. 9). Propyl acetate and *t*-butyl acetate were commercial products further purified to give purities $\geq$ 99.9 % (equivalent weight determination).

Thiol esters. Samples described in Ref. 10 were freshly distilled before use. Gas chromatography indicated unchanged purities (99.5—99.9 %).

Ketones. This group of compounds has been measured in connection with studies of their heats of combustion being made at this laboratory.[11] The samples were identical with those used in the combustion experiments, and water contents were in all cases less than 0.02 %.

Table 1. Heats of vaporization of some alcohols at 25°C (saturation pressure).

Compound	Water content %	Calorimeter	ΔH_v, kcal/mole
Methanol	0.028	C	8.91 ± 0.02
Ethanol	0.012	C	10.11 ± 0.02
1-Propanol	0.015	C	11.31 ± 0.02
2-Propanol	0.017	C	10.81 ± 0.03
1-Butanol	0.008	C	12.50 ± 0.02
2-Methyl-1-propanol	0.012	C	12.15 ± 0.02
2-Butanol	0.017	C	11.87 ± 0.02
2-Methyl-2-propanol	0.020	C	11.14 ± 0.02
1-Pentanol	0.015	C	13.61 ± 0.04
Cyclopentanol	—	A	13.74 ± 0.07
1-Hexanol	0.020	B	14.73 ± 0.04
Cyclohexanol	—	A	14.82 ± 0.07

* d_4^{25} for i-PrOAc = 0.8668. Earlier [8] an erroneous value was reported for this sample.

RESULTS AND DISCUSSION

Results from the calorimetric measurements are summarized in Tables 1 and 3. Each value reported is the mean from 5 or more determinations. Un-

Table 2. Comparison between recent heats of vaporization data for some alcohols. Values are given in kcal/mole and refer to 25°C and to the real gas at saturation pressure.

Compound	Green's compilation[a]	McCurdy and Laidler[b]	Other recent results	This work
Methanol	8.94 ± 0.01	9.01		8.91 ± 0.02
Ethanol	10.12 ± 0.02	10.09		10.11 ± 0.02
1-Propanol	11.35 ± 0.10	11.13	11.36[c]	11.31 ± 0.02
2-Propanol		10.52	10.88[d]	10.81 ± 0.03
			10.89[e]	
1-Butanol	12.62 ± 0.20	12.19	12.59[f]	12.50 ± 0.02
2-Methyl-1-propanol		11.91		12.15 ± 0.02
2-Butanol		11.59	12.03[g]	11.87 ± 0.02
2-Methyl-2-propanol		10.72	11.12[h]	11.14 ± 0.02
1-Pentanol	13.80 ± 0.25			13.61 ± 0.04
1-Hexanol	15.00 ± 0.30			14.73 ± 0.04

[a] Ref. 12.
[b] Ref. 13. The overall uncertainty was estimated to 0.5 %.
[c] Mathews and McKetta.[14]
[d] Hales, Cox and Lees.[15]
[e] Berman, Larkam and McKetta.[16]
[f] Counsell, Hales and Martin.[17]
[g] Berman and McKetta.[18]
[h] Beynon, Jr. and McKetta.[19]

certainties given in the tables include estimates of possible systematic errors. (Standard deviations are usually of the order of 10—20 cal.

Alcohols. Despite the general importance of reliable heats of vaporization data and the special interest for these data in connection with highly associated compounds the reported values for the simple alcohols have been surprisingly uncertain. Recently, Green made a compilation[12] (see Table 2) of ΔH_v data for the straight chain alcohols from C_1 to C_{12}. The poor status of data for this very important group of compounds was clearly indicated by the large uncertainty range assigned to the values except for the three lowest members. McCurdy and Laidler have since reported[13] calorimetric measurements at 25°C on 14 of the lowest straight chain and branched alcohols.

A few very careful calorimetric vaporization studies at different temperatures higher than 25°C have recently been made.[14–19] These values, extrapolated* to 25°C, are shown in Table 2 where values from Green's compilation,

* It should be noted that equations made up for the purpose of interpolation at higher temperatures have been used for these extrapolations.

Table 3. Heats of vaporization of some bromides, esters, thiol esters and ketones at 25°C (saturation pressure).

Compound	Calorimeter	ΔH_v, kcal/mole
1-Bromopropane	C	7.62 ± 0.02
2-Bromopropane	C	7.21 ± 0.02
1-Bromobutane	C	8.76 ± 0.03
2-Bromobutane	C	8.21 ± 0.02
1-Bromopentane	B	9.83 ± 0.03
1-Bromohexane	B	10.91 ± 0.03
1-Bromoheptane	C	12.05 ± 0.04
Ethyl acetate	A	8.40 ± 0.05
Propyl acetate	A	9.34 ± 0.05
Isopropyl acetate	A	8.89 ± 0.05
Butyl acetate	A	10.42 ± 0.05
t-Butyl acetate	A	9.09 ± 0.05
Ethyl butyrate	B	10.04 ± 0.03
Ethyl isobutyrate	B	9.52 ± 0.03
Ethyl pivalate	B	9.86 ± 0.03
Ethyl thiolacetate	A	9.56 ± 0.05
Propyl thiolacetate	A	10.54 ± 0.05
Isopropyl thiolacetate	A	10.10 ± 0.05
Butyl thiolacetate	A	11.49 ± 0.05
t-Butyl thiolacetate	A	10.26 ± 0.05
Di-isopropyl ketone	C	9.92 ± 0.02
Ethyl-*t*-butyl ketone	C	10.12 ± 0.02
Isopropyl-*t*-butyl ketone	C	10.35 ± 0.03
Di-*t*-butyl ketone	C	10.85 ± 0.02

McCurdy and Laidler's work and results from the present investigation are also summarized. From Table 2 may be seen that data from Green's compilation agree within the given uncertainty range with the present work. McCurdy and Laidler's results, however, show a poor agreement except for methanol and ethanol. It seems as if their technique, although precise, is impaired by large systematic errors.

Mathews and McKetta's measurements on 1-propanol are in good agreement with the present result and so are the measurements by Beynon and McKetta for 2-methyl-2-propanol.

For 2-propanol there is excellent agreement between the two values extrapolated from measurements at higher temperatures. These values are slightly higher than the present result, but all values are probably within the limits of combined uncertainties. In earlier calorimetric measurements at this laboratory (calorimeter A was used) 10.89 ± 0.03 kcal/mole was obtained (*cf.* Ref. 15). In still another series of measurements (calorimeter of type B) a value of 10.85 kcal/mole was obtained. The agreement between the different series is not as good as expected from experiments on test substances. Possibly the water content was high in the sample which was run on calorimeter A. In separate experiments it was shown that if the sample ampoule was left open for a few hours significantly higher values were obtained. (ΔH_v = 10.95, calorimeter A.)

The value for 1-butanol by Counsell, Hales and Martin [17] is slightly higher than the present value. Also for 2-butanol the value, which is extrapolated from measurements made at higher temperatures, is higher than the present result, the difference being 0.16 kcal/mole.

Bromides. In a compilation by Dreisbach [20] ΔH_v data for a large number of bromides are given. The values seem to be mainly calculated by empirical methods. Green and Holden [21] recently calculated heats of vaporization from vapor pressure data for a number of straight chain bromides. In Table 4 these

Table 4. Comparison between heats of vaporization data (kcal/mole, 25°C and saturation pressure) for some bromides.

Compound	Dreisbach's compilation[20]	Green and Holden's compilation[21]	This work
1-Bromopropane	7.64	7.75	7.62 ± 0.02
2-Bromopropane	6.66	—	7.21 ± 0.02
1-Bromobutane	8.80	8.82	8.76 ± 0.03
2-Bromobutane	8.02	—	8.21 ± 0.02
1-Bromopentane	9.98	9.85	9.83 ± 0.03
1-Bromohexane	11.18	10.91	10.91 ± 0.04
1-Bromoheptane	12.38	11.93	12.05 ± 0.04

non-calorimetric values are compared with the present results. It may be seen that for the lower straight chain compounds the three sets of data agree reasonably well, but that for the higher homologs Dreisbach's data are considerably higher. For the branched compounds there is a large deviation between Dreisbach's data and the present work. Green and Holden's set of values seem to agree with the present results within estimates of reasonable uncertainty limits.

No fruitful comparison between earlier data and the present results can be made for the esters, thiol esters or the ketones. It should be noted, however, that several of the measurements reported for these compounds were made at an early stage of this work (calorimeter A) and are therefore not considered quite as reliable as the more recent determinations.

Correlations between structure and heat of vaporization

An extensive comparison between heats (and entropy) of vaporization for different groups of compounds should be able to give information concerning structural features of the liquid state. As pointed out earlier, few accurate data are available at the standard reference temperature of 25°C and therefore this topic must wait until more experimental work has been done in this field.

From the present results together with well verified data for hydrocarbons and thiols a few correlations can be made.

Table 5. CH_2-increments in heats of vaporization for some group of compounds, $CH_3(CH_2)_nR$ (kcal/mole, 25°C, ideal gas).

n	R					
	CH_3[a]	OH[b]	SH[c]	Br[d]	$OCOCH_3$[d]	$SCOCH_3$[d]
0 → 1	1.70	1.11				
1 → 2	1.22	1.15	1.07		0.94	0.98
2 → 3	1.21	1.18	1.09	1.14	1.08	0.95
3 → 4	1.16	1.11	1.10	1.07		
4 → 5	1.18	1.12		1.08		
5 → 6	1.18			1.14		

[a] API-values.[22]

[b] Corrections to the ideal gaseous state for methanol, ethanol, and propanol were taken as +0.13, 0.06 and 0.01 kcal/mole, respectively.[12b] For 2-propanol it was estimated as 0.03 kcal/mole.[23]

[c] ΔH_v data for a number of thiols have been determined at Bureau of Mines, Bartlesville, Okla. For references see, *e.g.*, Ref. 24.

[d] Corrections to the ideal gaseous state assumed to be negligible.

CH_2-increments. In Table 5, CH_2-increments for straight chain hydrocarbons, alcohols, thiols, O- and S-acetates, and bromides are listed. It is seen that within each group there is a fair constancy although the first step for the hydrocarbons falls completely outside the rest of the series of increments. For the hydrocarbons these will be constant and equal to 1.18 kcal/mole after C_5. For alcohols the first step is "normal" and it is seen that the CH_2-increments are similar but slightly lower than for the hydrocarbons. The values for the thiols and bromides also tend to be slightly lower than the hydrocarbon values. Finally, the short series of O- and S-acetates seem to indicate still lower increment values for these groups of compounds.

In Table 6 are compiled some $\Delta(\Delta H_v)$ data for the effect of branching in the carbon chain adjacent to the functional groups. Values listed are the differences in ΔH_v values for propyl and iso-propyl compounds and between butyl

Table 6. Change in heat of vaporization value with branching of hydrocarbon chain (kcal/mole, 25°C, ideal gas)[a]

Isomerization process	R					
	CH_3[b]	OH	SH	Br	$OCOCH_3$	$SCOCH_3$
$CH_3(CH_2)_2$-R → $(CH_3)_2CH$-R	−0.39	−0.48	−0.57	−0.41	−0.45	−0.44
$CH_3(CH_2)_3$-R → $(CH_3)_3C$-R	−1.05	−1.36	−1.35	–	−1.33	−1.23

[a] For references see Table 5.

[b] Similar values are obtained for higher homologs. Mean values (for C_1 → C_5) are −0.40 and −0.99 kcal/mole, respectively.

and *t*-butyl compounds. It is seen that branching, propyl → isopropyl, causes a decrease in the ΔH_v value which is similar for all the groups of compounds, being about 0.5 kcal/mole.

In the other isomerization reaction, butyl → *t*-butyl, the $\Delta(\Delta H_v)$ value is considerably greater for all R, but here a marked difference is noted between R = hydrocarbon group and the other groups listed in Table 6. This seems rather surprising. With results from CH_2-increments and the above isomerization process in mind one would expect a reasonable constancy for all R — with the possible exception of R = OH, where a structure perturbating effect (change in the H-bond energy term contributing to the ΔH_v values) should be reflected in the $\Delta(\Delta H_v)$ value.

Estimation of heats of vaporization data

It is often essential to know or to be able to estimate heats of vaporization values in connection with thermochemical calculations. At present, and presumably for a long time to come, few accurate heats of vaporization data are available. It is therefore important to have reasonably reliable and, as far as possible, generally applicable empirical or semi-empirical rules available. The above discussion, although very limited, seems to indicate the difficulties involved in constructing such additivity rules (group or bond energies) for the estimation of heats of vaporization.

In the literature several other methods are described.[25] Presumably the oldest as well as the simplest is "Troutons rule" (eqn. 1) which states that the entropy of vaporization at the normal boiling point is for all "non-associated" compounds equal to 21 cal/mole.deg.

$$\Delta S_{bp} = (\Delta H_v/T)_{bp} = 21 \quad (1)$$

Klages [26] took advantage of the observation that the temperature derivative of the heat of vaporization is roughly the same for all non-associated liquids and modified eqn. (1) to give heats of vaporization (kcal/mole) at 25°C:

$$\Delta H_v = A + B \cdot t_{bp} \quad (2)$$

where $A = 5.4$, $B = 0.036$ and t_{bp} is the boiling point at atmospheric pressure in °C. (For solid compounds an estimate of the heat of melting should be added.) Eqn. (2) was claimed to give fair estimates (mean deviation about ± 0.3 kcal/mole) for compounds like hydrocarbons, halogen compounds ethers, esters, nitriles, and amines. Klages found eqn. (2) to hold also for mono- and polyalcohols if the constants were changed to $A = 6.8$ and $B = 0.045$. For other highly associated compounds like carboxylic acid, phenols and amides no simple relationships of the type eqn. (2) could be established.

It is doubtful, however, if eqn. (2) will give reasonable results for compounds with boiling points much above 170°C. (Klages claimed the equation to be applicable to compounds with b.p. up to 300°C.) Eqn. (2) holds well for the low boiling hydrocarbons whereas already for decane (b.p. 174°C) the predicted value is 0.6 kcal/mole too low, For heptadecane (b.p. 302°C) the predicted value is 4.3 kcal/mole lower than the API-value [22] (a presumably accurate extrapolation from the lower members of the alkane series). It is

obvious that equations of type (2) call for an additional term containing, *e.g.*, a higher power of t_{bp}, if expected to hold over large ranges of t_{bp}. (*Cf.* the fact that for a series of compounds the CH_2-increments usually are reasonably constant in ΔH_v whereas the increments in t_{bp} are decreasing.) However, Klages' eqn. (2) is extremely simple to use and seems to give estimates (in the b.p. range up to 170°) which are as reliable as considerably more cumbersome methods. It should be noted, that for the high boiling compounds any estimate of ΔH_v (25°C) is always very uncertain. This has proved to be true also for values calculated from vapor pressures (Clausius-Clapeyron's equation) if these are not measured with ultimate accuracy.

In Fig. 1 are plotted heats of vaporization values reported in this work *versus* normal boiling points. Constants given by Klages give reasonable estimates for all the compounds although a better agreement is obtained by eqns. 3a and 3b.

Slightly associated compounds $\Delta H_v = 5.0 + 0.041 \cdot t_{bp}$ (3a)

Alcohols: $\Delta H_v = 6.0 + 0.055 \cdot t_{bp}$ (3b)

It may be seen from Fig. 1 that a significant linear ordering occurs within each group of compounds.* Thus, it should be possible to make quite accurate

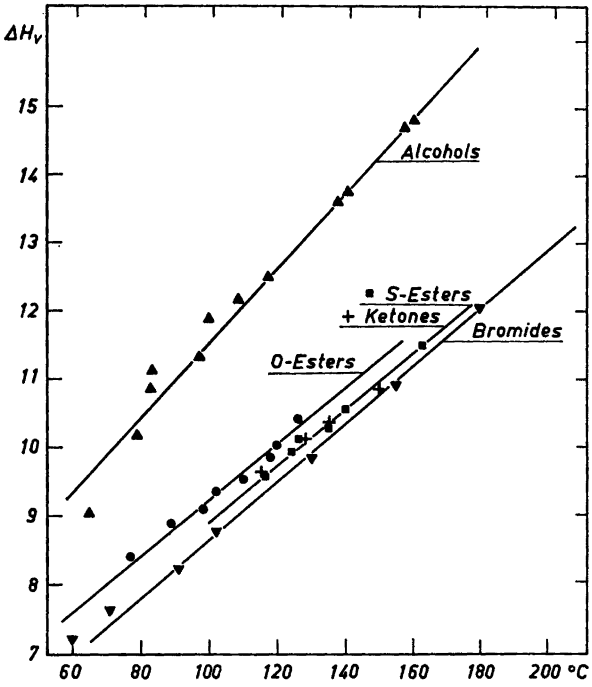

Fig. 1. Heats of vaporization *versus* normal boiling points for some alcohols, O- and S-esters, ketones and bromides.

* This is true also for other groups not represented in Fig. 1. [27].

estimates of ΔH_v, if data are known for one or preferably several compounds belonging to the same group.

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