212. *Heats of Sublimation of Straight-chain Monocarboxylic Acids.*

By Mansel Davies and V. E. Malpass.

The sublimation pressures of the even-carbon monocarboxylic acids from C_{10} to C_{22} have been measured by the effusion method down to 10^{-5} mm. so as to give reliable values of the sublimation heats. Both the heats and entropies of sublimation increase linearly with chain length. The significance of the additive increments and the constant terms in these relations is discussed with reference to other similar data. Infrared absorption spectra were used as a check on the polymorphic forms of the acids, and small features peculiar to the C_{12} and the C_{20} acid are taken to be correlated with the deviations of these acids from the linear sequences formed by the others.

The lattice energy of a compound can be equated to its heat of sublimation provided (i) that there is no significant change in the configuration of the molecules on change of state; (ii) that the energies associated with molecular vibrations remain unchanged;

(iii) that the vapour in equilibrium with the solid behaves ideally. The sublimation heat can be determined from the temperature variation of the sublimation pressure. The latter has been measured for the even carbon-number monocarboxylic acids from C_{10} to C_{22} inclusive.

EXPERIMENTAL

The acids used were those described by Stenhagen and von Sydow: the m. p.s agreed satisfactorily with those in ref. (1). To obtain immediately comparable values of the heats and entropies of sublimation the same polymorphic form of the homologues should be measured.

TABLE 1. *Observed sublimation pressures.*

(*a*) n-Decanoic acid (C_{10}): $\log_{10} p$ (mm.) = 17·130 − 6119/T									
t (°c)	27·83	27·60	27·55	25·55	22·80	22·00	20·00	16·80	
10^4p (mm.), obs....	6·56	6·25	5·74	4·49	2·89	2·47	1·84	$1{\cdot}07_5$	
Devn. (%)	+3·2	+1·2	−4·3	+0·4	+0·0	−1·6	+1·3	+0·0	
(*b*) n-Dodecanoic (C_{12}): $\log_{10} p$ (mm.) = 19·897 − 7322/T									
t (°c)	41·44	41·44	41·44	41·35	39·54	35·20	30·20	29·70	22·70
10^4p (mm.), obs....	4·07	4·29	4·01	4·31	3·04	1·53	0·570	0·548	0·139
Devn. (%)	−2·5	+2·6	−4·1	+4·9	+0·1	+7·8	−1·7	+2·6	−1·4
(*c*) n-Tetradecanoic acid (C_{14}): $\log_{10} p$ (mm.) = 18·740 − 7291/T									
t (°c)	52·17	52·14	49·39	46·85	44·90	42·65	38·85		
10^5p (mm.), obs....	$21{\cdot}3_5$	$21{\cdot}2_1$	14·5	8·3	$6{\cdot}5_2$	$4{\cdot}3_5$	$2{\cdot}4_5$		
Devn. (%)	−0·9	−0·5	+5·8	−7·9	−0·6	−2·4	+3·8		
(*d*) n-Hexadecanoic acid (C_{16}): $\log_{10} p$ (mm.) = 20·217 − 8069/T									
t (°c)	60·14	59·19	57·89	56·94	55·29	51·19	46·64		
10^5p (mm.), obs.	$10{\cdot}0_4$	8·80	7·05	6·14	4·75	2·16	0·98		
Devn. (%)	−1·8	−0·1	±0·0	+1·1	+5·2	−3·3	+1·4		
(*e*) n-Octadecanoic acid (C_{18}): $\log_{10} p$ (mm.) = 21·180 − 8696/T									
t (°c)	67·19	66·89	66·09	64·89	62·79	61·99	57·89		
10^5p (mm.), obs....	4·28	4·17	3·46	3·06	1·94	1·69	$0{\cdot}82_7$		
Devn. (%)	+0·1	+1·5	−1·1	+7·0	−2·6	−0·5	+1·5		
(*f*) n-Eicosanoic acid (C_{20}): $\log_{10} p$ (mm.) = 25·453 − 10424/T									
t (°c)	72·90	72·60	69·99	68·50	68·50	66·25	63·80	63·80	
10^6p (mm.), obs....	21·0	20·9	12·2	$8{\cdot}2_4$	$8{\cdot}7_9$	$5{\cdot}3_6$	$2{\cdot}9_2$	$3{\cdot}8_6$	
Devn. (%)	−3·6	+3·1	−0·4	−5·8	+0·5	−3·2	−12·8	+15·2	
(*g*) n-Docosanoic acid (C_{22}): $\log_{10} p$ (mm.) = 23·604 − 10102/T									
t (°c)	78·56	77·93	76·67	75·86	74·75	72·67	71·60		
10^6p (mm.), obs....	7·9	$6{\cdot}6_1$	$5{\cdot}6_3$	$4{\cdot}5_8$	$3{\cdot}8_5$	$2{\cdot}4_2$	$2{\cdot}0_8$		
Devn. (%)	+3·4	−3·0	+1·9	−0·1	+3·5	−3·2	+2·4		

As, owing to the low sublimation pressures, all the measurements were necessarily made at temperatures adjacent to the m. p., the acids were carefully melted and resolidified near their m. p. This should have ensured that they were each in the *C*-form.[1]

The sublimation pressures were determined by Knudsen's effusion method, details of which have been given.[2] The weights effused were determined on an Oertling air-damped micro-balance with an uncertainty of ±10 µg. Effective hole diameters were determined by measurements at temperatures of 29—39° by using benzophenone [3] or at 50—70° by using benzoic acid,[4] the ranges and mean values of the observed areas (cm.^{2}) being $23{\cdot}7 \pm 0{\cdot}3 \times 10^{-3}$, $7{\cdot}23 \pm 0{\cdot}06 \times 10^{-3}$, $1{\cdot}24 \pm 0{\cdot}03 \times 10^{-3}$. For the C_{22} acid the effusion of 250 µg. in 10 hr. corresponded to a sublimation pressure of 5×10^{-6} mm. In addition to the checks already described,[2] it is noteworthy that the residual pressure is unlikely to influence significantly the determination of such low values. From Binks and Bradley's study,[5] a residual air pressure as high as 10^{-3} mm. would change the rate of effusion by only about 1%.

---

[1] Stenhagen and von Sydow, *Arkiv Kemi*, 1953, **6**, 310.
[2] Davies, A. H. Jones, and Thomas, *Trans. Faraday Soc.*, 1959, **55**. 1100.
[3] Neumann and Volker, *Z. phys. Chem.*, 1932, **161**, 33.
[4] Davies and J. I. Jones, *Trans. Faraday Soc.*, 1954, **50**, 1042.
[5] Binks and Bradley, *Proc. Roy. Soc.*, 1949, *A*, **198**, 231.

Thermometers calibrated in the N.P.L. were used, and any necessary corrections applied after thermostat temperatures had been read.

Infrared spectra were run in a heated cell having a similarly heated compensator, whose temperature was controllable to ±1°. The Grubb–Parsons G.S.3 double-beam grating instrument was used, and the region 670—2000 cm.$^{-1}$ (15—5 μ) systematically recorded under standardized conditions.

Results.—The data for each compound were plotted as $\log p$(sub.) against $1/T$. It was frequently found that some of the determinations first made near the m. p. with a new compound were abnormally high. They were repeated until satisfactory reproducibility showed that the volatile impurities (very probably moisture) were no longer noticeable. After rejection of any such early points, the " least-squares " line from the remaining observations was calculated, the origin of co-ordinates being first brought to the " centre of gravity " of the points. The data are summarized in the Tables, where " Devn. (%) " is 100 $[p(\text{obs.}) - p(\text{calc.})]/p(\text{calc.})$ and p(calc.) is the value given by the equation quoted.

TABLE 2. *Heat and entropies of sublimation.*

No. of C atoms	Temp. range studied (°c)	No. of dtmns.	ΔH (obs.)	ΔH (calc.)	ΔS (obs.)	ΔS (calc.)
			(kcal. mole^{-1})		(cal. mole^{-1} deg.$^{-1}$)	
10	16·80—27·83	8	28·0 ± 0·4	27·7	65·2 ± 1·5	64·6
12	22·70—41·44	9	33·5 ± 0·8	30·7	77·9 ± 3·0	69·4
14	38·85—52·17	7	33·4 ± 0·9	33·7	72·6 ± 3·5	74·2
16	46·64—60·14	7	36·9 ± 1·0	36·7	79·3 ± 4·0	79·0
18	57·89—67·19	7	39·8 ± 1·0	39·7	83·7 ± 3·0	83·8
20	63·80—72·90	8	47·7 ± 1·8	42·7	103·3 ± 4·5	88·5
22	71·60—78·56	7	46·2 ± 1·9	45·7	94·8 ± 5·0	93·4

DISCUSSION

Addivity of Enthalpy and Entropy Factors.—The results for the individual acids conform in each case fairly well to linearity between $\log_{10} p$ (sub.) and $1/T$. For the C_{20} and the C_{22} acid the weights effusing in 8 hr. were usually less than 500 μg.; an uncertainty of ±2% was then expected in individual determinations of these sublimation pressure. We have, in terms of the equation $\log_{10} p\ (\text{mm.}) = A + B/T$:

$$\Delta H\ (\text{sub.}) = -\ 2\cdot303\boldsymbol{R}B$$

$$\Delta S\ (\text{sub.}) = 2\cdot303\boldsymbol{R}(A - 2\cdot8808)$$

After representing the probable uncertainties of individual points in the $\log p$–$1/T$ plot, generous estimates of the likely limits for the resultant ΔH and ΔS values are given in Table 2. At pressures of *ca.* 30 mm. and temperatures similar to ours, the lower carboxylic acids show only some 10—20% of the molecules to be dimeric in the vapour.[6] As all the sublimation pressures were less than 10^{-3} mm., it seems safe to conclude that the vapours were then essentially ideal. The experimental ΔH values thus provide, to almost within their significance, a measure of the lattice energies.

The simple expectation that the lattice energy may be proportional to the chain-length is well substantiated. In Table 2, ΔH (calc.) are the values, in kcal. mole^{-1}, derived from

$$\Delta H\ (\text{sub.}) = 14\cdot2 + 1\cdot50(n - 1) \quad . \ . \ . \ . \ . \ . \quad (1)$$

where the acid is $C_{n-1}H_{(2n-1)}\cdot CO_2H$. For all but C_{12} and C_{20} the deviation from the " best " observed values is within 1%. The two exceptions will be discussed later. Not surprisingly, a similar relation is found for the molar entropy of sublimation, in cal. mole^{-1} deg.$^{-1}$:

$$\Delta S\ (\text{sub.}) = 43\cdot0 + 2\cdot4(n - 1) \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

---

[6] Taylor, *J. Amer. Chem. Soc.*, 1951, **73**, 315; 1952, **74**, 4151.

This is the relation which gives the ΔS (calc.) of Table 2, and, by using the units of cal. mole^{-1} deg.$^{-1}$ for ΔS and kcal. mole^{-1} for ΔH, the sublimation parameters are related by

$$\Delta S = 20{\cdot}3 + 1{\cdot}60\Delta H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The values of ΔS given by the linear equation (3) are, with the exceptions of those for C_{12} and C_{20}, all within 2% of ΔS (obs.), the average deviation being only 0·7%. This simple interdependence emphasizes that, for the five compounds concerned, the sublimation process follows a strictly uniform pattern, the energy involved depending simply on the enhancement of the configurational freedom which is attained. It is for such phase changes, and homologous series of compounds, that these additivities and linear relations of the thermodynamic parameters [7] are most likely to arise.

Equation (1) is of particular interest as it shows the constant contribution of 1·50 kcal. mole^{-1} by each CH_2 group to the lattice energy. In some long-chain primary amides the value of 1·72 kcal. mole^{-1} has been found for this factor,[2] 1·66 kcal. mole^{-1} in some *N*-methylamides,[8] and 1·62 kcal. mole^{-1} in straight-chain dicarboxylic acids.[9] The " constant " term of 14·2 kcal. mole^{-1} represents the residuum in the lattice energy when the contribution of the $(n - 1)$ CH_2 groups has been removed, *i.e.*, it includes the difference between the CH_3 and CH_2 groups and the totality of the contribution by the CO_2 group. In the normal paraffins,[10] the CH_3 and CH_2 groups contribute 2·25 and 1·7 kcal. mole^{-1} to the heats of vaporization: their contributions might differ by 1 kcal. mole^{-1} in the sublimation heat. Accordingly, 13·2 kcal. mole^{-1} is a reasonable estimate for the CO_2H group contribution.

This large term includes the energy of one of the hydrogen bonds formed by the dimerization of the carboxyl groups. As has already been pointed out,[2,4] it necessarily includes items other than those localized in the $(O\text{–}H \cdots O)$ interaction. A more significant estimate of this hydrogen-bond energy in the solid will become available when we can subtract from 13·2 kcal. mole^{-1} the lattice energy term for a non-associated carboxyl group. It should be possible to estimate this from the data for a series of increasingly " hindered " carboxylic acids. The possibility remains that the hydrogen-bond energy in these instances may be at least as large as in the vapour state (*ca.* 7 kcal. mole^{-1}), despite the fact that the medium (*via* its dielectric constant and other factors) usually greatly reduces the energy.[11] Maximum interaction can be expected in the solid state from the fixed orientations imposed in the crystal: there the sequence in interaction energy values characteristic of free gas molecules, *viz.*, dispersion > induction $\geqslant$ dipole, can be reversed, *e.g.*, as the dipole term becomes proportional to (distance)$^{-3}$.

There are some other values which can be compared with the constant term of 14·2 kcal. mole^{-1} for these aliphatic acids. In the straight-chain dicarboxylic acids [9] the same factor is 12·2 kcal. mole^{-1}: in some benzoic acids [4] it is 11·5 kcal. mole^{-1}. These variations are probably expressions of the non-localized factors and of the influence of the environment upon the net interaction energies of the carboxyl groups. There is no clear evidence that the geometry of the carboxyl group interactions differs in these instances: thus the $(O\text{–}H \cdots O)$ distance is the same [12] in crystalline benzoic as in succinic acid (2·64 Å). Other total head-group interactions to be compared with 14·2 kcal. mole^{-1} for the crystalline aliphatic acids are (in kcal. mole^{-1}): 17·6 for primary amides (two hydrogen bonds per molecule), 8·0 for some *N*-methylamides, 5·7 for the hydroxyl group in phenols,[11] and *ca.* 9 for the same group in supercooled liquid alcohol structures.[10] As could be expected

---

[7] Cf. Janz, " Estimation of Thermodynamic Properties of Organic Compounds," Academic Press, New York, 1958.

[8] Davies and A. H. Jones, *Trans. Faraday Soc.*, 1959, **55**, 1329.

[9] Thomas, M.Sc. Thesis, University of Wales, 1959.

[10] (*a*) Moelwyn-Hughes, " Physical Chemistry," Pergamon Press, London, 1957; (*b*) Davies, *J. Polymer Sci.*, 1959, **40**, 247.

[11] Davies, in " Hydrogen Bonding," ed. D. Hadži, Pergamon Press, London, 1959.

[12] " Interatomic Distances," ed. Sutton, *Chem. Soc. Special Publ.* No. 11, 1958.

from other data, the hydrogen bond in the carboxylic acids is the strongest of these examples.

Anomaly of C_{12} *and* C_{20} *Factors.*—Clearly, the data for the C_{12} and the C_{20} acid do not fit into the foregoing pattern: the deviations from the linear relations are far larger than the uncertainties in the individual ΔH and ΔS values. For the C_{12} acid two specimens were studied with essentially identical results. The only likely explanation of these findings is that they relate to some slight difference in the crystalline *C*-form pertaining to these acids. The established transition points [1] indicate that the *C*-forms are stable for a range of 12° below the m. p. for C_{12} and for 23° below the m. p. for C_{20}, thus including all but the lowest determinations for the C_{12} acid. Again, the *C*-forms are usually produced from the melt or by rapid cooling of a solution. They can be described as metastable below the transition temperatures and it has been found [13] that the C_{12} and the C_{14} acid revert to the *A*-form when kept for two years at room temperatures. Even then, heating to within a few degrees of the m. p. produced the *C*-form. It was these observations that gave us preliminary confidence that the acids would all be isomorphous in the sublimation-pressure measurements.[14]

Table 2 shows the observed ΔH (sub.) for C_{12} and C_{20} to be 2·8 and 5·0 kcal. mole^{-1} above the figures expected for the *C*-forms. Per chain-carbon CH_2 in these acids, the deviation is sensibly constant (0·25 and 0·26 kcal. mole^{-1}). That this is a reasonable difference for a polymorphic change is perhaps indicated by the varying lattice-energy increments per CH_2 in various established sequences: in kcal. mole^{-1} the even-carbon dicarboxylic acids give 1·71; the lower odd-carbon primary amides 1·20; the lower even-carbon primary amides 1·02; and (above) the acids, 1·50. For a series of long-chain (odd-carbon) carboxylic acids, Garner *et al.*[15] found heats of transition between polymorphic forms of 1—2 kcal. mole^{-1}. The fact that these heats of transition showed little dependence on chain length suggests that they were principally concerned with different head-group interactions, as is confirmed by the constant angle of tilt for their hydrocarbon chains (59° 12′). More significantly, when the ethyl esters of the even monocarboxylic acids change the tilt of their chains from 90° to about 66°, then the heat of transition is 4·87 kcal. mole^{-1} for the C_{18} compound and it increases for each successive $(CH_2)_2$ added by 0·59, 0·65, 0·54, 0·69 kcal. mole^{-1}, or a mean value of 0·31 kcal. mole^{-1} per CH_2 group.[15] This is similar to the deviation shown in our data by C_{12} and C_{20}. It will be of some interest to confirm the ΔH values now suggested for possible polymorphic transformations in the C_{12} and C_{20} acid.

Infrared Study of the Crystalline Acids.—A direct examination for any obvious phase changes can be made from the infrared absorption spectra of the solid acids.[16] A systematic check for all the acids was made. A difficulty here is that of ensuring the same form in the infrared examination as was present at each stage of the sublimation measurements. In practice the acids were each melted between rock-salt plates and the films (both liquid and solid) examined after being kept for various times at temperatures between the m. p. and 25° in an appropriately heated infrared absorption cell. In this way it was hoped to simulate the conditions in the sublimation work.

In these circumstances none of the solid acids showed marked changes in the infrared absorptions between their m. p. and 25°, even when kept for periods up to a week: considerable changes in detail occurred on melting but the same solid form reappeared on cooling. For the solids, such changes as occurred with temperature or time were smaller than would betoken a phase change in the compounds. One consistent feature was the

---

[13] Lomer, *Nature*, 1955, **176**, 653.

[14] See also Malkin, " Progress in Chemistry of Fats and other Lipids," Vol. I, Pergamon Press, London, 1952, p. 10.

[15] See Ralston, " Fatty Acids and their Derivatives," John Wiley and Sons, New York, 1948, pp. 344, 355, 362.

[16] R. N. Jones *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 2570; von Sydow, *Acta Chem. Scand.*, 1955, **9**, 1119.

progressive reduction in the resolution of the doublet absorption at 720—728 cm.$^{-1}$ found in all these acids: as the temperature approached the m. p. the higher-frequency component was sometimes reduced in relative intensity and the trough between them invariably became less pronounced. The broad absorption centre near 940 cm.$^{-1}$ in all the acids also showed minor changes, in the form of somewhat sharper shoulders as the temperature decreased.

The spectra of the different acids have also been compared with a view to assess the similarity of the crystalline forms. The spectra are all nearly identical, apart from the well-established increase in the number of sharp absorptions between 1180 and 1340 cm.$^{-1}$ as the number of CH_2 groups in the chain increases. There are, however, features between 670 and 1000 cm.$^{-1}$ which distinguish the C_{12} and C_{20} from the other acids. This is illustrated in Figs. 1 and 2, where the records (on a linear wavelength scale) for C_{12} and C_{20} are compared with those for the immediately lower and higher even acids: C_{12} shows a sharp absorption at 871 cm.$^{-1}$ (11·48 μ) not present in C_{10} or C_{14} and it lacks all but a trace of the peak near 816 cm.$^{-1}$ (12·25 μ) present in its neighbours; the 779 cm.$^{-1}$ (12·84 μ) feature in C_{12} is much stronger than in C_{10} or C_{14}, and C_{12} fails to show the equivalent of the well-defined absorptions near 746 cm.$^{-1}$ (13·4 μ) in C_{10} and C_{14}. These changes are in minor features of the solid-state spectra but they are significant in the present circumstances in that C_{12} appears to depart slightly from the very closely similar infrared fingerprints of C_{10} and C_{14}. As Fig. 2 illustrates, C_{20} shows similar small deviations from its nearest neighbours in the even-acid series: the C_{20} solid shows distinct absorptions at 835 cm.$^{-1}$ (11·97 μ) and 746 cm.$^{-1}$ (13·4 μ) not present in C_{18} or C_{22}, whilst the 781 cm.$^{-1}$ (12·8 μ) feature in C_{20} is much more pronounced than in C_{18} or C_{22}; conversely, the latter both show absorptions near 870 cm.$^{-1}$ (11·5 μ) and 763 cm.$^{-1}$ (13·1 μ) which are much reduced or absent in C_{20}.

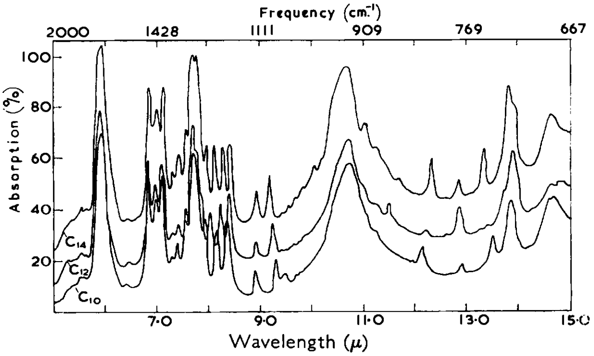

FIG. 1. *Absorptions of crystalline films of n-aliphatic acids at 25°. (For C_{14} the absorptions are displaced upwards by 20%.)*

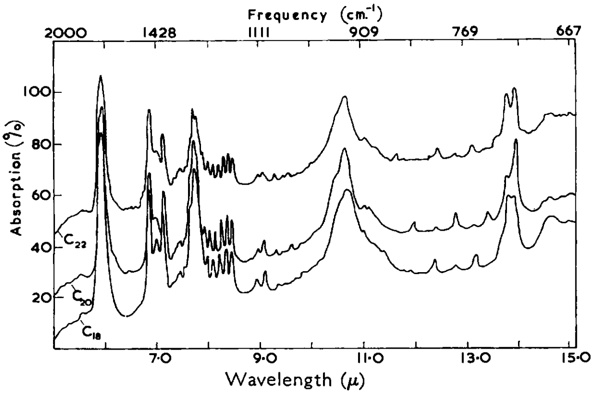

FIG. 2. *Absorptions of crystalline films of n-aliphatic acids at 25°. (For C_{20} the absorptions are displaced upwards by 20%, and for C_{22} by 40%.)*

Such changes probably mean only small differences in the force fields of the molecules in the crystal lattice but, when multiplied by the number of CH_2 groups involved, they might correspond to the anomalies observed in the lattice energies of C_{12} and C_{20}. At least there is a qualitative indication in that sense.

The identity of the forms whose spectra we have recorded is established by comparison with the published accounts of the alternative forms for palmitic (C_{16}) and stearic (C_{18}) acids.[16] Our spectra were run fairly rapidly, and both that and the natural widths of some of the solid phase absorptions do not allow us to expect an accuracy of better than ±3 cm.$^{-1}$ for our measurements. All of von Sydow's and most of Jones's spectra relate to Nujol mulls, which may itself be the source of some differences: owing to the Nujol absorptions their records show gaps on either side of 1430 cm.$^{-1}$. Using the features singled out by von Sydow as discriminating between the various spectra, the comparisons in Table 3 show our solid acids to be in the *C*-form. (Our reading of cm.$^{-1}$ from the curves of R. N. Jones *et al.* might itself be in error by ±2 cm.$^{-1}$.)

TABLE 3. *Comparison of discriminating absorptions (cm.$^{-1}$) in polymorphic forms.*

			Palmitic acid (C_{16})						
Present work	1695	1405	1298	1269	1248	1225	1206	1188	941
C-form (E. v. S.)	1701	1412	1294	1271	1250	1226	1205	1187	939
A-form (E. v. S.)	1698	1408	1295	1271	1252	1230	1209	1197	935
			Stearic acid (C_{18})						
Present work	1691	1408	1297		1255		1238		
C-form (E. v. S.)	1701	1414		1282	1263	1243			
B-form (E. v. S.)	1701	1403	1290	1276	1264	1248			
C-form (R. N. J. *et al.*)	1698	1409	1292		1258		1235		
B(+ *C*) form (R. N. J. *et al.*)	—	—	1298	1284	1269	1263	1237		
Present work	1218	1200	1186	951(sh)	937(centre)				
C-form (E. v. S.)				952(sh)	941(centre)				
B-form (E. v. S.)				941(sh)	887(centre)				
C-form (R. N. J. *et al.*)	1217		1182	958	937(centre)				
B(+ *C*) form (R. N. J. *et al.*)	1219				884(centre)				

The additivity of some energy factors other than heats of sublimation is already well established for the carboxylic acids. Thus Ralston[17] quotes, in the units of equations (1) and (2) for the even mono-acids:

$$\Delta H\ (\text{melting}) = -2{\cdot}58 + 1{\cdot}030(n - 1)$$
$$\Delta S\ (\text{melting}) = -1{\cdot}65 + 2{\cdot}652(n - 1)$$

From these (only rough approximations) by difference from the equations (1) and (2), the corresponding values for the vaporization process are:

$$\left.\begin{aligned}\Delta H\ (\text{vap.}) &= 16{\cdot}9 + 0{\cdot}47(n - 1)\\ \Delta S\ (\text{vap.}) &= 44{\cdot}6 - 0{\cdot}26(n - 1)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

These values will only obtain near the m. p. and only in so far as the vapour behaves ideally.

The values suggested by equation (4) may be compared with those calculated directly from the few vapour-pressure measurements (0·2—1 mm.) by Jantzen and Erdmann:[18] the uncertainty in their ΔH (obs.) values is at least ±0·5 kcal. mole^{-1}. [The most extensive data of Spizzichino[19] lead to ΔH (vap.) values varying by ±20% in a negligible temperature range.] The agreement in Table 4 is better than could have been expected.

[17] Ralston, ref. 15, p. 325.

[18] Jantzen and Erdmann, *Fette und Seifen*, 1952, **54**, 197.

[19] Spizzichino, *J. Récherches C.N.R.S.*, 1956, No. 34.

TABLE 4. *Comparison of predicted and observed heats of vaporization of the liquid acids near their m. p.s (kcal. mole*$^{-1}$*).*

Acid	C_{14}	C_{16}	C_{18}	C_{22}
ΔH (vaporization, eqn. 4)	23·0	24·0	24·9	26·8
ΔH (obs.)[18]	23·0	24·8	24·3	26·6

For a limited number of the monocarboxylic acids, the heats of solution in water at 55° in kcal. mole^{-1} are approximately[10b]

$$\Delta H \text{ (solution in } H_2O \text{ at } 55°) = -4·60 + 1·03(n - 1)$$

From this and equation (1) one finds for the heat of solvation, *i.e.*, for the process

Carboxylic acid in dilute vapour ⟶ carboxylic acid in saturated aqueous solution at 55°,

$$\begin{aligned}\Delta H \text{ (solvation in } H_2O \text{ at } 55°) &= \Delta H \text{ (solution)} - \Delta H \text{ (sublimation)} \\ &= -18·8 - 0·47(n - 1)\end{aligned}$$

If the water is replaced by glacial acetic acid as the solvent, the heat of solution is less dependent on temperature and we find[10b]

$$\Delta H \text{ (solvation in glacial acetic acid)} = -45·6 + 2·64(n - 1)$$

These relations can be of value both in estimating unknown parameters for these compounds and in revealing the extent of the contributions to the factors by the component groups in such compounds. The large energies made available by the solvation of the carboxylic group are noticeable and, for the glacial acetic acid solutions, remarkable.

We acknowledge a grant from the Chemical Society and a Maintenance Award to V. M. from the D.S.I.R. We particularly thank Professor E. Stenhagen of Göteborg University for samples of the pure acids.

EDWARD DAVIES CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

[*Received, July 26th,* 1960.]