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Vaporization, fusion and sublimation enthalpies of the dicarboxylic acids from C₄ to C₁₄ and C₁₆

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8 Abstract

9 The fusion enthalpies of the series butanedioic acid through to tetradecanedioic acid and hexadecanedioic acids have been measured by DSC. In addition to fusion, a number of solid–solid phase transitions have also been detected in these diacids. The vaporization enthalpies of these compounds have been measured by correlation gas chromatography using the vaporization enthalpies of butanedioic, hexanedioic and decanedioic acids as standards. The vaporization enthalpies of the diacids from C₄ to C₁₀ correlated linearly with the number of methylene groups present. Above C₁₀, the vaporization enthalpies of C₁₁–C₁₄ and C₁₆ begin to deviate from linearity. The vaporization enthalpies for these compounds are dependent on the temperature of the GC column used. Similar departure from linearity has also been observed previously in the sublimation enthalpies of these compounds. The results are discussed in terms of formation of a cyclic intramolecular hydrogen bonded network in the gas phase similar to the bimolecular association observed in smaller mono-carboxylic acids at ambient temperatures.

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20 1. Introduction

21 Recently, the vapor pressures and sublimation enthalpies of five odd numbered carbon dicarboxylic acids from malonic to undecanedioic acid have been measured by Knudsen mass loss effusion [1]. These results were combined with earlier literature values [2] reported for the even numbered carbon dicarboxylic acids C₄, C₆, C₈, C₁₀, C₁₂, C₁₆, and C₂₀ to provide reliable data for a homologous series of diacids. Both studies observed that unlike other homologous series studied thus far, the sublimation enthalpies of the longer chain diacids, C₁₁, C₁₂, C₁₆ and C₂₀, did not increase linearly with size as observed with the smaller dicarboxylic acids. The

sublimation enthalpies actually began to decrease at about C₁₁, reaching a minimum at approximately C₁₆ and followed by a gradual increase. This anomalous behavior has previously been interpreted as resulting from cyclization in the gas phase to form the intramolecular hydrogen bonded species shown in figure 1 once the size of the ring is sufficiently large enough to accommodate the hydrogen bond network of the two carboxyl groups.

We have been interested in the thermochemistry of cubane, most notably the strain energy [3,4]. The enthalpy of formation of 1,4-cubanedicarboxylic acid in the condensed phase has been reported [5]. Combined with the sublimation enthalpy of 1,4-cubanedicarboxylic acid, this would provide us with the enthalpy of formation of this compound in the gas phase, an important quantity in the evaluation of the strain energy by means of isodesmic reactions. The availability of sublimation enthalpies of the straight chain diacids and their fusion enthalpies [6] suggested a means of evaluating their

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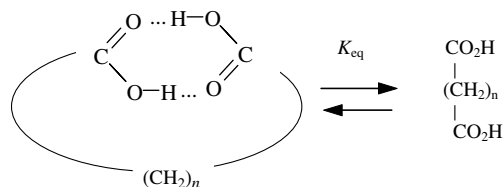


FIGURE 1. Proposed equilibrium of the larger diacids in the gas phase.

vaporization enthalpies. The use of these vaporization enthalpies as standards could provide the vaporization enthalpy of 1,4-cubanedicarboxylic acid measured by correlation-gas chromatography. Combined with an experimental fusion enthalpy, the sublimation enthalpy of 1,4-cubanedicarboxylic acid could thus be evaluated. This paper reports the vaporization and fusion enthalpies of succinic acid to tetradecanedioic acid and of hexadecanedioic acid. The evaluation of the vaporization enthalpy of these diacids was more complex than originally anticipated. As a result of the nature of various phase transitions observed in the solid state, the vaporization enthalpies of only three of the straight chain diacids were considered sufficiently reliable to be used as standards. Vaporization enthalpies were obtained by difference using sublimation enthalpies from the literature and fusion enthalpies measured in this study. These three diacids were then used to obtain the vaporization enthalpies of the remaining linear ones using correlation-gas chromatography. As an additional consequence of this study, evidence for the gas phase cyclization of the larger diacids was also obtained. This prompted some additional experiments directed at confirming these results.

2. Experimental

The compounds studied were all obtained from commercial vendors in high purity (98+%). Pentanedioic, heptanedioic, nonanedioic and undecanedioic acids were purified as previously described; recrystallized from water and dried at $T \approx 360$ K [1]. Details describing the purification of the even acids are not available [2]. All even diacids were recrystallized from water and dried except dodecanedioic and tetradecanedioic acids; these diacids were recrystallized from ethanol and dried; tridecanedioic and hexadecanedioic acids were used as obtained. All diacids were better than 99% pure as analyzed by gas chromatography. Each was analyzed by thermal gravimetric analysis on a Shimadzu TGA-50 apparatus to determine the presence of any residual solvent. None was found. The phase transitions were analyzed on a Perkin Elmer DSC-7 at 5 K min^{-1} ; nonanedioic acid was also studied at 2 K min^{-1} ; the results were identical. All analyses were performed in triplicate.

The calibration of the instrument was checked periodically using an indium standard. The gas chromatograph used was an HP 5980 Series II instrument equipped with a split-splitless capillary injection port and a FID detector. A split ratio of approximately 50:1 was used. The retention times were recorded to three significant figures following the decimal point on an HP 3356 Series II integrator. The instrument was run isothermally using a 12 m HP-1 capillary column at the lower temperatures and a 30 m SPB-5 column at the higher temperatures. Although retention times and enthalpies of transfer obtained from plots of the natural logarithm of reciprocal adjusted retention time *versus* reciprocal temperature are column dependent (*vide infra*), the vaporization enthalpies obtained in the final correlation have been shown to be independent of the column used. At the temperatures of the experiments, the solvent was not retained; the retention time of the solvent was used to determine the dead volume of the column. Column temperatures were controlled by the instrument and monitored using a Fluke 51 K/J thermometer. All correlation gas chromatography experiments were performed in duplicate except the results reported in table 3G.

Anhydride formation in the injection port was tested using succinic anhydride. The anhydride had a significantly shorter retention time than the corresponding diacid and was not formed in any detectable amounts in the injection port upon injection of the diacid. The retention times of the remaining diacids increased in a regular fashion relative to butanedioic acid, characteristic of other homologous series investigated, suggesting that anhydride formation in the injection port was also not a problem at these temperatures for the remaining diacids. Should some anhydride form during passage through the column, this would be lost in background noise and would not affect the retention time of the remaining diacid reaching the detector. Peaks remained sharp with increasing temperature. This was not the case at the highest temperatures investigated. Significant decomposition of the larger diacids was observed at the highest temperature studied (>523 K) and the decomposition products appeared to catalyze further decomposition in the injection port of the GC. Those results are not reported here.

Sublimation enthalpies from the literature [1,2] were adjusted from the mean temperature of measurement, T_m , to $T = 298.15$ K using equation (1). Similarly, fusion enthalpies were adjusted from the melting temperature to $T = 298.15$ K using equation (2). The terms $C_{p,m}(\text{cr})$ and $C_{p,m}(\text{l})$ refer to the heat capacity of the crystalline and liquid phases, respectively. Both quantities were estimated by group additivity [7]. Both these equations have been tested and found to give reasonably good temperature adjustment as judged from results using thermochemical cycles for which experimental

152 data for the sum of all solid phase transitions are avail-
 153 able over the temperature interval of interest ($\Delta_{\text{tpce}}^1 H_m$)
 154 [8]. Vaporization enthalpies at $T = 298.15$ K were calcu-
 155 lated using the thermochemical cycle defined by equa-
 156 tion (3)

$$\begin{aligned} 157 \Delta_{\text{sub}} H_m(T = 298.15 \text{ K}) = \\ \Delta_{\text{sub}} H_m(T_m) + [0.75 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + \\ 159 0.15 * C_{p,m}(\text{cr})](T_m - 298.15 \text{ K}), \end{aligned} \quad (1)$$

$$\begin{aligned} 160 \Delta_{\text{tpce}}^1 H_m(T = 298.15 \text{ K}) = \\ \Delta_{\text{tpce}}^1 H_m(T_{\text{fus}}) + [0.15 * C_{p,m}(\text{cr}) - \\ 162 0.26 * C_{p,m}(\text{l}) - 9.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \times \\ (T_{\text{fus}} - 298.15 \text{ K}), \end{aligned} \quad (2)$$

$$\begin{aligned} 163 \Delta_{\text{vap}} H_m(T = 298.15 \text{ K}) = \Delta_{\text{sub}} H_m(T = \\ 165 298.15 \text{ K}) - \Delta_{\text{tpce}}^1 H_m(T = 298.15 \text{ K}). \end{aligned} \quad (3)$$

166 3. Results

167 Examination of the fusion enthalpies reported in the
 168 literature for the diacids [6], reveals a number of transi-
 169 tions occurring in the solid phase. Since the method of
 170 purification of these materials differed from those used
 171 in the sublimation experiments, the possibility of poly-
 172 morphism could not be ruled out. In addition, some of
 173 the vapor pressure measurements were performed near
 174 the reported solid–solid transitions. As a result of these
 175 uncertainties, the fusion enthalpies of butanedioic to
 176 dodecanedioic acid were re-determined. In addition,
 177 the fusion enthalpies of tridecanedioic, tetradecanedioic
 178 and hexadecanedioic acids were also measured. The re-
 179 sults of these measurements along with the literature
 180 values are provided in table 1. Columns 2–6 report the
 181 results of this study; columns 7–10 summarize the liter-
 182 ature values. The term $\Delta_{\text{tpce}}^1 H_m$ represents the total
 183 phase change enthalpy calculated as the sum of all the
 184 phase transitions from $T = 298.15$ K to $T = T_{\text{fus}}$. As
 185 noted in the table, a number of the diacids exhibit so-
 186 lid–solid phase transitions. Columns 2 and 3 list the
 187 enthalpies of transition; the temperatures of transition
 188 are provided below these values in parentheses. Col-
 189 umns 4 and 8 compare the fusion temperatures of this
 190 study with those in the literature. Discrepancies in the
 191 two numbers probably reflect differences in methods of
 192 measurement. The values in column 4 are DSC onset
 193 temperatures. The onset temperatures may also be af-
 194 fected by other solid–solid phase transitions occurring
 195 just prior to melting but not resolved by the calorimeter.
 196 It is not clear how the literature values were measured
 197 [6]. The last column in the table describes whether these
 198 transitions were observed after heating to $T \approx 360$ K for
 199 several hours, conditions used prior to measurement of

the sublimation enthalpies of the odd alkanedioic acids 200
 [1]. It should also be emphasized that based on TGA 201
 experiments, these endothermic transitions were not 202
 the result of loss of solvent. The results of these phase 203
 change studies did pose some problems that become 204
 apparent upon examination of the DSC curves of the 205
 C_5 , C_7 – C_9 and C_{11} diacids shown in figures 2–6. The 206
 temperature range over which vapor pressures of penta- 207
 nedioic, heptanedioic, nonanedioic and undecanedioic 208
 acids appear very close to the region where, according 209
 to DSC analysis, substantial phase transitions are occur- 210
 ring. Even at slower scan rates, the scans indicate sub- 211
 stantial energy absorption. The temperature range over 212
 which vapor pressures of octanedioic acid were mea- 213
 sured also appears to include at least a portion of a 214
 phase transition. It is not obvious how much of an effect 215
 these transitions would have on the vapor pressure mea- 216
 surements; nor is it clear whether or not to include the 217
 phase transitions in calculating $\Delta_{\text{tpce}}^1 H_m$, or how to cor- 218
 rect the sublimation enthalpies for these factors. The 219
 DSC curves of the remaining diacids of table 1 were 220
 not problematic. As a result of this ambiguity, it was 221
 decided to determine the vaporization enthalpies of the 222
 C_5 , C_7 – C_9 and C_{11} diacids, indirectly by correlation- 223
 gas chromatography. The vaporization enthalpies of 224
 the C_4 , C_6 , and C_{10} diacids in table 1 were used as 225
 standards. 226

A second value for the sublimation enthalpy of but- 227
 anedioic is available in the literature. A mean value of 228
 $(120.5 \pm 0.2) \text{ kJ mol}^{-1}$ (at $T = 368$ K) has been reported 229
 [9]. Adjusted to $T = 298.15$ K using equation (1) results 230
 in a value of $(122.2 \pm 0.6) \text{ kJ mol}^{-1}$, in good agreement 231
 with the value reported by Davies and Thomas [2]. 232
 The average of these two values, listed as the last entry 233
 for butanedioic acid in table 2 was used in evaluating 234
 the vaporization enthalpy of this diacid. Vaporization 235
 enthalpies for some of the other diacids are available 236
 in the compilation by Stull [10]. These values were not 237
 used because of the possibility of anhydride formation 238
 and/or decomposition at high temperatures needed to 239
 obtain the vapor pressures reported as described in the 240
 experimental section. 241

The vaporization enthalpies of all the diacids that 242
 could be calculated using equation (3) are given in 243
 the last column of table 2. Literature sublimation 244
 enthalpies, column 6, measured at some mean temper- 245
 ature (column 7) were adjusted to $T = 298.15$ K using 246
 equation (1). The adjusted values are reported in col- 247
 umn 8. In the first series of correlations, the three 248
 acids, C_4 , C_6 , and C_{10} , were used to evaluate the vapor- 249
 ization enthalpies of the C_5 , C_7 , C_8 , and C_{11} diacids. 250
 Once evaluated, the C_6 – C_{10} diacids were then used in 251
 additional correlations to evaluate the vaporization 252
 enthalpies of undecanedioic, dodecanedioic and tetra- 253
 decanedioic acids. A total of four correlations were ini- 254
 tially performed. Retention time data measured at 255

TABLE 1

Phase transition (T_t) and fusion temperatures (T_{fus}) and the corresponding phase change and total phase change enthalpies of the dicarboxylic acids from $T = 298.15$ K to $T = T_{fus}$ ^a

Acid	$\Delta_t H_m(T_t)$ (III \rightarrow II)	$\Delta_t H_m(T_t)$ (II \rightarrow I)	T_{fus}/K ^b	$\Delta_{fus} H_m(T_{fus})$	$\Delta_{tpce}^1 H_m(T_{fus})$	$\Delta_t H_m(T_t)$	T_{fus}/K ^c	$\Delta_{fus} H_m(T_{fus})$ [6]	$\Delta_{tpce}^1 H_m(T_{fus})$	Transitions after heating ^d
	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$		$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$		$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$	
	$(T_t \text{ III-II}/K)$ ^b	$(T_t \text{ II-I}/K)$ ^b				$(T_t \text{ II-I}/K)$ ^c				
Butanedioic			455.2 \pm 1.2	34.0 \pm 0.3	34.0		457	32.9	32.9	
Pentanedioic		2.3 \pm 0.3 (340.5 \pm 1.8)	363.9 \pm 6.4	18.8 \pm 0.2	21.1	2.5 (348.5)	371.0	20.9	23.4	Yes
Hexanedioic			419.0 \pm 1.4	33.7 \pm 0.4	33.7		425.5	34.9	34.9	
Heptanedioic	1.5 \pm 0.3 (337.7 \pm 1.6)	na ^e (366.3 \pm 1.4)	368.2 \pm 1.6	23.7 \pm 1.2	25.2	1.3 (369)	377.5	27.6	28.9	Only II \rightarrow I
Octanedioic	2.0 \pm 0.8 (355.9 \pm 0.8)	9.1 \pm 0.1 (403.6 \pm 0.2)	413.2 \pm 0.2	30.7 \pm 0.4	41.8	9.0 (407)	415.5	29.2	38.2	Yes
Nonanedioic	0.01 (330.6)	0.7 \pm 0.3 (339.8 \pm 4.2)	372.4 \pm 1.2	29.7 \pm 0.9	30.4		380	32.7	32.7	No
Decanedioic		0.4 \pm 0.06 (370.3 \pm 0.2)	403.9 \pm 0.4	46.6 \pm 5.0	47.0		404	40.8	40.8	Yes
Undecanedioic		1.6 \pm 0.5 (355.3 \pm 0.4)	380.1 \pm 0.8	41.2 \pm 1.6	42.8		385	39.7	39.7	No
Dodecanedioic	0.06 \pm 0.04 (359.5 \pm 4.8)	-0.1 \pm 0.2 (387.0 \pm 0.4)	400.3 \pm 0.6	49.8 \pm 1.1	49.7		402	50.6	50.6	No
Tridecanedioic			386.3 \pm 1.4	49.4 \pm 0.2	49.4					
Tetradecanedioic			397.3 \pm 0.2	56.5 \pm 1.6	56.5					
Hexadecanedioic			395.4 \pm 0.6	52.2 \pm 0.2	52.2					

^a Uncertainities are reported as 2 standard deviations ($\pm 2\sigma$).

^b Onset temperatures determined by DSC.

^c Melting temperatures determined by an unknown method [6].

^d This column indicates which phase transitions persisted after heating to $T = 360$ K, condition used prior to the sublimation enthalpy measurements.

^e Not available; this transition appears as a shoulder in the fusion peak and is included in the fusion enthalpy.

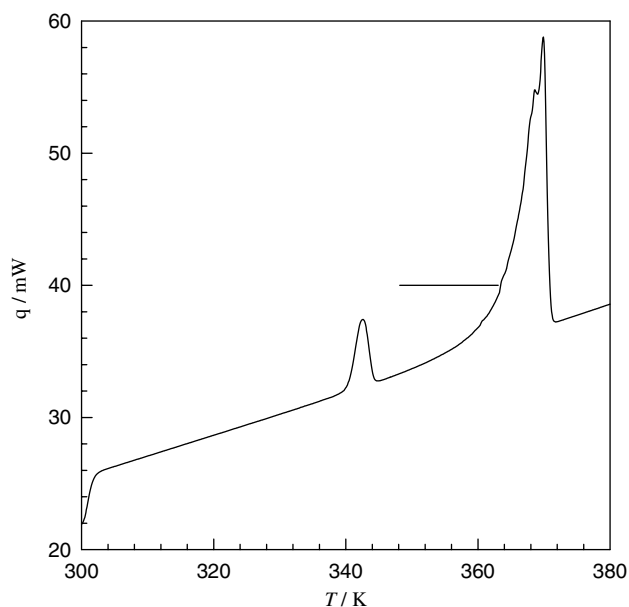


FIGURE 2. Heat flow (q) as a function of temperature for pentanedioic acid (endotherms up). The horizontal line indicates the approximate temperature range over which the sublimation enthalpy was measured.

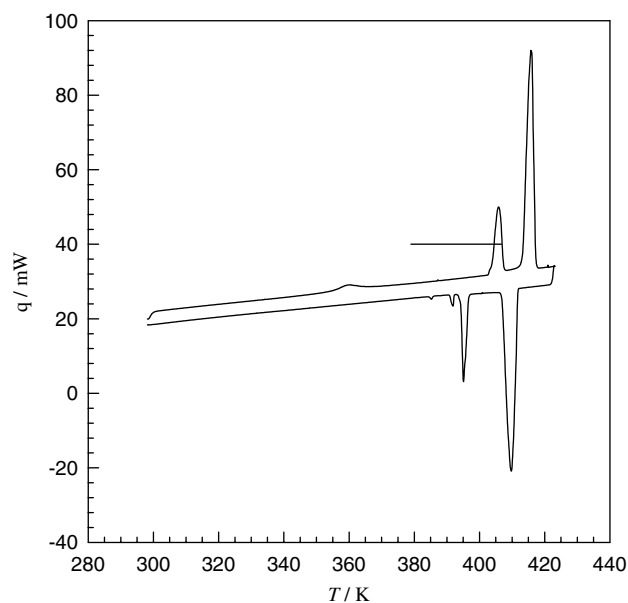


FIGURE 4. Heat flow (q) as a function of temperature for octanedioic acid (endotherms up). The horizontal line indicates the approximate temperature range over which the sublimation enthalpy was measured.

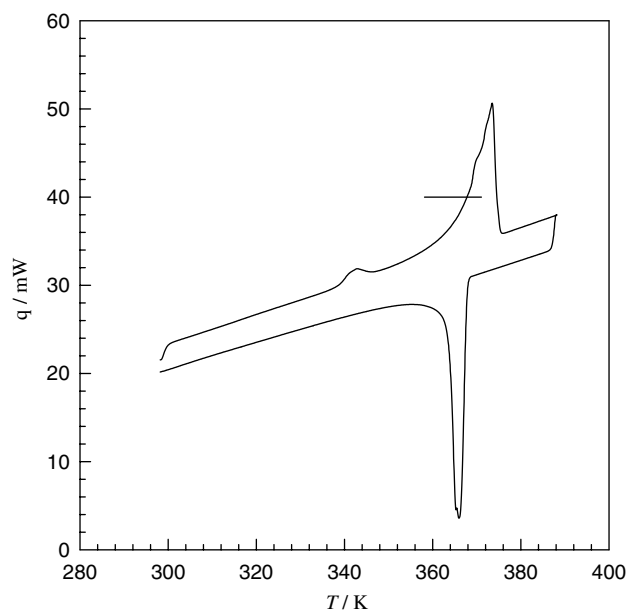


FIGURE 3. Heat flow (q) as a function of temperature for heptanedioic acid (endotherms up). The horizontal line indicates the approximate temperature range over which the sublimation enthalpy was measured.

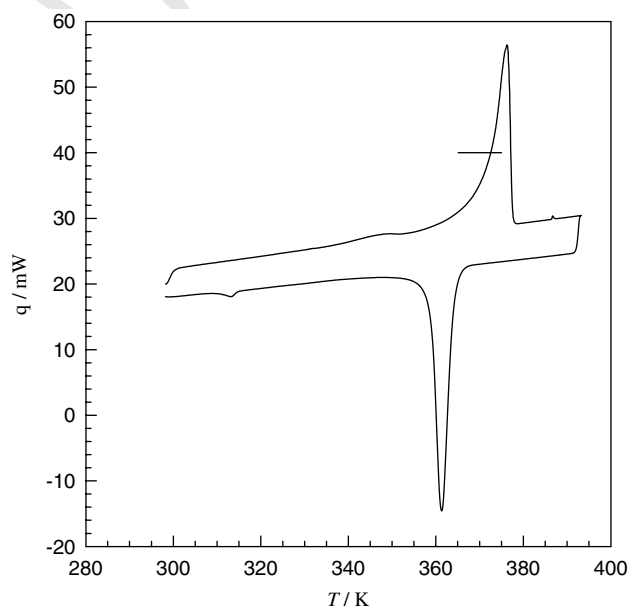


FIGURE 5. Heat flow (q) as a function of temperature for nonanedioic acid (endotherms up). The horizontal line indicates the approximate temperature range over which the sublimation enthalpy was measured.

256 different temperatures and compositions and summaries of these initial results are given in tables 3A–D, 257 and in tables 4 and 5, respectively. Undecanedioic acid 258 was treated as an unknown in all these correlations for 259 reasons discussed below. On the basis of the vaporization 260 enthalpies obtained as discussed below, additional 261

correlations were performed with the larger homologues at higher temperatures to confirm the temperature dependence observed for these vaporization enthalpies. The retention times at the higher temperatures are given in tables 3E–G and a summary of the temperature dependence of their retention times are reported in table 7. 262 263 264 265 266 267 268

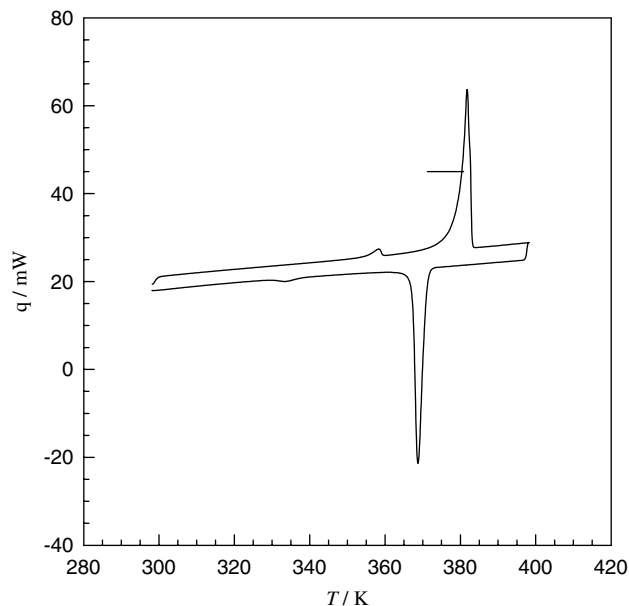


FIGURE 6. Heat flow (q) as a function of temperature for undecanedioic acid (endotherms up). The horizontal line indicates the approximate temperature range over which the sublimation enthalpy was measured.

269 Table 3 lists the experimental gas chromatographic
270 retention times measured for all the correlations. A
271 plot of $\ln(t_a^o/t_a)$ versus $1/T$, where t_a represents the ad-
272 justed retention time, calculated as the difference in
273 retention time between each solute and the solvent at
274 each respective temperature, and t_a^o represents a refer-
275 ence time of 1 min, resulted in linear plots character-
276 ized by correlation coefficients >0.99 . At the

temperatures of these experiments, the solvent was
not retained and the retention time of the solvent
was used to measure the dead volume of the column.
Table 4A and B summarizes the results of these calcu-
lations using the data in table 3A and B, respectively.
Columns 2 and 3 of this table report the slopes,
 $-\Delta_{\text{sln}}^{\text{g}}H_m(T_m)/R$, and intercepts, b , of the resulting
lines. Correlating the enthalpies of transfer from solu-
tion to the vapor as measured by gc, $\Delta_{\text{sln}}^{\text{g}}H_m(T_m)$, to
the enthalpies of vaporization at $T = 298.15$ K of the
standards in table 4A and B, resulted in equations
(4) and (5), respectively. Using these equations, the
vaporization enthalpies of

$$\Delta_1^{\text{g}}H_m(T = 298.15 \text{ K}) = (1.518 \pm 0.004)\Delta_{\text{sln}}^{\text{g}}H_m \times$$

$$(T = 39 \text{ K}) + (23.54 \pm 0.05) \text{ kJ mol}^{-1}, \quad (4)$$

$$\Delta_1^{\text{g}}H_m(T = 298.15 \text{ K}) = (1.532 \pm 0.03)\Delta_{\text{sln}}^{\text{g}}H_m \times$$

$$(T = 441 \text{ K}) + (27.01 \pm 0.42) \text{ kJ mol}^{-1}. \quad (5)$$

C_5 , C_7 – C_9 , and C_{11} could be derived. These values are
given in the last column of the table. The uncertainties
represent two standard deviations associated with the
potential error in the intercept. The average of the two
experiments for C_5 , and C_7 – C_9 along with the original
vaporization enthalpies for hexanedioic and decanedioic
acids were then used in conjunction with the results of a
second set of correlations derived from the data in table
3C and D; the results are summarized in table 5A and B,
respectively. These correlations resulted in equations (6)
and (7) which were then used to evaluate the vaporiza-
tion enthalpies of undecanedioic, dodecanedioic and tet-
radecanedioic acids.

TABLE 2
Calculation of the vaporization enthalpies of the diacids at $T = 298.15$ K

	$\Delta_{\text{tpcc}}^{\text{l}}H_m$ (T_{fus})	$C_p(\text{l})$	$C_p(\text{cr})$	$\Delta_{\text{tpcc}}^{\text{l}}H_m$ ($T = 298.15 \text{ K}$) ^{a,b}	$\Delta_{\text{cr}}^{\text{g}}H_m(T_m)$	T_m/K	$\Delta_{\text{cr}}^{\text{g}}H_m$ ($T = 298.15 \text{ K}$) ^a	$\Delta_1^{\text{g}}H_m$ ($T = 298.15 \text{ K}$)
	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$		$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$
Butanedioic acid					117.4 ² 120.5 ± 0.2 ⁹	386.7 368	119.6 ± 1.7 122.2 ± 0.6	
Pentanedioic acid	34.0	238.6	169	26.5 ± 2.3	117.0 ¹	355.7	120.9 ± 2.6 ^c	94.4 ± 3.6
Hexanedioic acid	21.1	270.5	186.9	17.6 ± 1.1	129.4 ²	382.7	121.0 ± 1.7 ^d	103.3
Heptanedioic acid	33.7	302.4	213.8	26.9 ± 2.1	136.6 ¹	364.9	132.1 ± 0.9	105.2 ± 2.2
Octanedioic acid	25.2	334.3	240.7	20.9 ± 1.8	143.1 ²	393.2	139.1 ± 1.2	118.1
Nonanedioic acid	41.8	366.2	267.6	34.4 ± 2.3	148.9 ± 1.9 ^c	372.1	148.9 ± 1.9 ^c	116.6
Decanedioic acid	30.4	398.1	294.5	24.5 ± 1.8	156.2 ¹	389.2	159.5 ± 1.9	135.0
Undecanedioic acid	47.0	430	321.4	40.4 ± 5.5	160.7 ²	376.1	165.2 ± 1.5	124.8 ± 3.0
Dodecanedioic acid	42.8	461.9	348.3	36.4 ± 2.5	158.6 ¹	385.7	162.7 ± 2.3	126.3
Tridecanedioic acid	49.7	493.8	375.2	41.4 ± 2.7	153.3 ²		158.3 ± 1.7	116.9
Tetradecanedioic acid	49.4	525.7	402.1	41.8 ± 2.3				
Hexadecanedioic acid	56.5	557.6	429	47.5 ± 3.0				
Hexadecanedioic acid	52.2	621.4	482.8	42.6 ± 2.9	151.0 ²	387.7	166.4 ± 5.7	

^a Uncertainties represent two standard deviations.

^b Calculated using equation (2); the uncertainty represents the total uncertainty associated with the measurements and with the uncertainty accompanying the use of equation (2).

^c Average of two values; the uncertainty represents two standard deviations of the mean.

^d This value includes the transition enthalpy of 2.3 $\text{kJ} \cdot \text{mol}^{-1}$ that occurs at $T = 340.5$ K.

TABLE 3
Retention times of the diacids as a function of temperature

T/K:	423.8	428.8	433.8	438.7	443.6	448.4	453.4
	t/min						
(A) $T_m = 439$ K							
Methanol	0.625	0.62	0.603	0.637	0.642	0.646	0.643
Butanedioic acid	1.245	1.097	1.012	0.985	0.944	0.91	0.88
Pentanedioic acid	1.637	1.375	1.245	1.174	1.097	1.042	0.989
Hexanedioic acid	2.246	1.829	1.62	1.485	1.36	1.265	1.18
Heptanedioic acid	3.345	2.609	2.255	1.993	1.77	1.61	1.463
Octanedioic acid	4.96	3.785	3.21	2.757	2.391	2.127	1.889
Nonanedioic acid	7.205	5.497	4.584	3.867	3.309	2.881	2.519
Decanedioic acid	11.044	8.291	6.805	5.618	4.701	4.019	3.437
Undecanedioic acid	16.261	12.089	9.83	8.004	6.629	5.588	4.719
T/K:	428.9	433.8	438.5	443.5	448.4	453.4	
(B) $T_m = 441$ K							
Methanol	0.619	0.617	0.623	0.632	0.626	0.655	
Butanedioic acid	1.079	1.019	0.968	0.937	0.894	0.891	
Pentanedioic acid	1.34	1.244	1.154	1.099	1.02	1.007	
Hexanedioic acid	1.78	1.614	1.464	1.363	1.242	1.198	
Heptanedioic acid	2.52	2.234	1.969	1.79	1.578	1.493	
Octanedioic acid	3.649	3.17	2.73	2.427	2.086	1.93	
Nonanedioic acid	5.332	4.53	3.834	3.33	2.844	2.549	
Decanedioic acid	8.015	6.702	5.565	4.75	3.965	3.493	
Undecanedioic acid	11.619	9.64	7.913	6.685	5.525	4.786	
T/K:	443.7	448.6	453.6	458.4	463.4	468.4	473.3
(C) $T_m = 458$ K							
Methanol	0.622	0.637	0.639	0.65	0.661	0.657	0.665
Hexanedioic acid	1.332	1.253	1.186	1.135	1.077	1.029	0.995
Heptanedioic acid	1.74	1.594	1.491	1.402	1.287	1.207	1.15
Octanedioic acid	2.34	2.094	1.912	1.758	1.591	1.47	1.374
Nonanedioic acid	3.263	2.855	2.539	2.285	2.036	1.847	1.695
Decanedioic acid	4.77	4.087	3.673	3.273	2.743	2.391	2.17
Undecanedioic acid	6.638	5.615	4.947	4.333	3.61	3.124	2.78
Dodecanedioic acid	9.294	7.838	6.955	6.066	4.906	4.13	3.662
Tetradecanedioic acid	16.077	13.643	12.16	10.582	8.489	7.074	6.201
T/K:	443.7	448.6	453.6	458.5	468.3	473.3	
(D) $T_m = 458$ K							
Methanol	0.635	0.648	0.64	0.665	0.667	0.67	
Hexanedioic acid	1.368	1.264	1.191	1.142	1.031	0.992	
Heptanedioic acid	1.806	1.604	1.501	1.400	1.214	1.148	
Octanedioic acid	2.413	2.107	1.925	1.757	1.47	1.368	
Nonanedioic acid	3.335	2.874	2.555	2.284	1.843	1.683	
Decanedioic acid	5.034	4.077	3.696	3.203	2.443	2.177	
Undecanedioic acid	6.962	5.622	4.978	4.256	3.162	2.779	
Dodecanedioic acid	9.922	7.797	6.988	5.900	4.253	3.68	
Tetradecanedioic acid	17.269	13.645	12.213	10.315	7.295	6.232	
T/K:	443.9	448.7	453.7	458.6	463.5	468.5	473.5
(E) $T_m = 458$ K							
Methanol	0.375	0.381	0.376	0.365	0.382	0.384	0.394
Octanedioic acid	1.346	1.21	1.08	0.977	0.907	0.825	0.785
Nonanedioic acid	1.859	1.634	1.427	1.274	1.154	1.029	0.961
Decanedioic acid	2.63	2.266	1.941	1.709	1.514	1.323	1.212
Undecanedioic acid	3.71	3.155	2.667	2.32	2.02	1.731	1.559
Dodecanedioic acid	5.105	4.313	3.625	3.13	2.699	2.277	2.025
Tridecanedioic acid	6.987	5.887	4.947	4.249	3.643	3.029	2.654
Tetradecanedioic acid	9.007	7.648	6.494	5.583	4.816	3.958	3.474

(continued on next page)

Table 3 (continued)

T/K:	473.5	478.4	483.4	488.4	493.3	498.4	503.4
(F) $T_m = 488$ K							
Methanol	0.406	0.398	0.399	0.394	0.41	0.409	0.408
Octanedioic acid	0.813	0.749	0.707	0.672	0.66	0.631	0.61
Nonanedioic acid	0.998	0.903	0.838	0.785	0.76	0.717	0.684
Decanedioic acid	1.262	1.121	1.024	0.945	0.898	0.836	0.785
Undecanedioic acid	1.62	1.422	1.28	1.156	1.082	0.993	0.919
Dodecanedioic acid	2.095	1.825	1.628	1.434	1.325	1.196	1.092
Tridecanedioic acid	2.744	2.379	2.114	1.805	1.647	1.467	1.322
Tetradecanedioic acid	3.569	3.11	2.794	2.28	2.066	1.818	1.62
Hexadecanedioic acid	6.485	5.551	4.975	3.915	3.46	2.97	2.582
T/K:	503.3	508.3	513.2	518.3	523.4		
(G) $T_m = 513$ K							
Methanol	0.48	0.482	0.482	0.48	0.48		
Octanedioic acid	1.101	1.037	0.979	0.924	0.883		
Nonanedioic acid	1.348	1.252	1.166	1.088	1.027		
Decanedioic acid	1.682	1.54	1.415	1.305	1.216		
Undecanedioic acid	2.129	1.925	1.746	1.59	1.465		
Dodecanedioic acid	2.722	2.432	2.182	1.965	1.79		
Tridecanedioic acid	3.51	3.103	2.755	2.454	2.212		
Tetradecanedioic acid	4.527	3.969	3.5	3.082	2.755		
Hexadecanedioic acid	7.894	6.802	5.889	5.085	4.468		

TABLE 4

A summary of calculated $\Delta_{\text{sln}}^{\text{g}}H_m(T_m)$ and $\Delta_{\text{f}}^{\text{g}}H_m(T = 298.15 \text{ K})$ values for C_4 - C_{11} obtained by correlation

	$\Delta_{\text{sln}}^{\text{g}}H_m(T_m)/R$	b	$\frac{\Delta_{\text{sln}}^{\text{g}}H_m(T = 439 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_{\text{f}}^{\text{g}}H_m(T = 298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1} (\text{lit.})}$	$\frac{\Delta_{\text{f}}^{\text{g}}H_m(T = 298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1} (\text{calcd.})^a}$
(A) $T = 493$ K					
Butanedioic acid	-5611.1	13.84	46.65	94.4	94.4 ± 0.1
Pentanedioic acid	-6249.1	14.86	51.95		102.4 ± 0.1
Hexanedioic acid	-6472.2	14.91	53.81	105.2	105.2 ± 0.1
Heptanedioic acid	-7057.0	15.78	58.67		112.6 ± 0.1
Octanedioic acid	-7418.4	16.15	61.67		117.2 ± 0.1
Nonanedioic acid	-7588.7	16.12	63.09		119.3 ± 0.1
Decanedioic acid	-8020.2	16.67	66.68	124.8	124.8 ± 0.1
Undecanedioic acid	-8223.6	16.74	68.37		127.4 ± 0.1
	$\Delta_{\text{sln}}^{\text{g}}H_m(T_m)/R$	b	$\frac{\Delta_{\text{sln}}^{\text{g}}H_m(T = 441 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_{\text{f}}^{\text{g}}H_m(T = 298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1} (\text{lit.})}$	$\frac{\Delta_{\text{f}}^{\text{g}}H_m(T = 298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1} (\text{calcd.})}^b$
(B) $T = 441$ K					
Butanedioic acid	-5308.7	13.16	44.13	94.4	94.6 ± 0.8
Pentanedioic acid	-5796.4	13.84	48.19		100.8 ± 0.8
Hexanedioic acid	-6111.2	14.10	50.81	105.2	104.9 ± 0.8
Heptanedioic acid	-6622.6	14.80	55.06		111.4 ± 0.8
Octanedioic acid	-6996.5	15.20	58.17		116.1 ± 0.8
Nonanedioic acid	-7304.4	15.48	60.73		120.0 ± 0.8
Decanedioic acid	-7686.5	15.92	63.90	124.8	124.9 ± 0.8
Undecanedioic acid	-7859.3	15.93	65.34		127.1 ± 0.8

^a Calculated using equation (4).^b Calculated using equation (5).

$$\Delta_{\text{f}}^{\text{g}}H_m(T = 298.15 \text{ K}) = (1.275 \pm 0.1)\Delta_{\text{sln}}^{\text{g}}H_m \times (T = 458 \text{ K}) + (48.61 \pm 1.20) \text{ kJ mol}^{-1}, \quad (6)$$

$$\Delta_{\text{f}}^{\text{g}}H_m(T = 298.15 \text{ K}) = (1.404 \pm 0.1)\Delta_{\text{sln}}^{\text{g}}H_m \times (T = 458 \text{ K}) + (38.67 \pm 1.09) \text{ kJ mol}^{-1}. \quad (7)$$

TABLE 5

A summary of calculated $\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$ and $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})$ values for C_6 – C_{12} and C_{14} obtained by correlation at $T = 458 \text{ K}$

	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(T_{\text{m}})/R$	b	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(T = 458 \text{ K})$ kJ · mol ⁻¹	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})$ kJ · mol ⁻¹	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})$ kJ · mol ⁻¹ (calcd.) ^a
A					
Hexanedioic acid	-5439.4	12.60	45.22	105.2	106.3 ± 2.4
Heptanedioic acid	-5955.1	13.31	49.51	112.0	111.7 ± 2.4
Octanedioic acid	-6282.1	13.62	52.23	116.7	115.2 ± 2.4
Nonanedioic acid	-6674.4	14.08	55.49	119.7	119.4 ± 2.4
Decanedioic acid	-7277.7	14.96	60.50	124.8	125.8 ± 2.4
Undecanedioic acid	-7469.1	15.03	62.10		127.9 ± 2.4
Dodecanedioic acid	-7654.8	15.07	63.64		129.8 ± 2.4
Tetradecanedioic acid	-7404.4	13.92	61.56		127.1 ± 2.4
B					
Hexanedioic acid	-5781.5	13.35	48.07	105.2	106.2 ± 2.2
Heptanedioic acid	-6257.3	13.96	52.02	112.0	111.7 ± 2.2
Octanedioic acid	-6568.2	14.24	54.61	116.7	115.4 ± 2.2
Nonanedioic acid	-6916.6	14.61	57.50	119.7	119.4 ± 2.2
Decanedioic acid	-7453.4	15.34	61.96	124.8	125.7 ± 2.2
Undecanedioic acid	-7684.4	15.49	63.89		128.4 ± 2.2
Dodecanedioic acid	-7833.4	15.45	65.12		130.1 ± 2.2
Tetradecanedioic acid	-7626.0	14.39	63.40		127.7 ± 2.2

^a Calculated using equation (6).

TABLE 6

A summary of the $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})$ and $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})$ values

	$\Delta_{\text{l}}^{\text{g}}(H_{\text{m}}T = 298.15 \text{ K})$ kJ · mol ⁻¹ (calcd.)	$\Delta_{\text{tpcc}}^{\text{l}}(H_{\text{m}}T = 298.15 \text{ K})$ kJ · mol ⁻¹	$\Delta_{\text{ct}}^{\text{g}}(H_{\text{m}}T = 298.15 \text{ K})$ kJ · mol ⁻¹ this work	$\Delta_{\text{ct}}^{\text{g}}(H_{\text{m}}T = 298.15 \text{ K})$ kJ · mol ⁻¹ (lit.) [1,2,9]
Butanedioic acid	94.4 ^a	26.5 ± 2.3		120.9 ± 2.6
Pentanedioic acid	101.60.8	17.6 ± 1.1	119.2 ± 1.4	121.0 ± 1.7
Hexanedioic acid	105.2 ^a	26.9 ± 2.1		132.1 ± 0.9
Heptanedioic acid	112.0 ± 0.8	20.9 ± 1.8	132.9 ± 2.0	139.1 ± 1.2
Octanedioic acid	116.7 ± 0.8	34.4 ± 2.3	151.1 ± 3.2	148.9 ^d ± 1.9
Nonanedioic acid	119.70.8	24.5 ± 1.8	144.2 ± 2.4	159.5 ± 1.9
Decanedioic acid	124.8 ^a	40.4 ± 5.5		165.2 ± 1.5
Undecanedioic acid	127.3 ± 0.8 ^b 128.2 ± 2.3 ^c	36.4 ± 2.5	163.7 ± 2.6 164.6 ± 3.4	162.7 ± 2.3
Dodecanedioic acid	130.0 ± 2.3	41.42.7	171.4 ± 3.5	158.3 ± 1.7
Tetradecanedioic acid	127.4 ± 2.3	47.5 ± 3.0	174.9 ± 3.8	

^a Calculated from literature values and used as standards; see table 2.

^b The average of values obtained at $T = (441 \text{ and } 339) \text{ K}$ (table 4).

^c The average of values obtained at $T = 458 \text{ K}$ (table 5).

^d Does not include the enthalpy of transition of $9.06 \text{ kJ} \cdot \text{mol}^{-1}$ observed at $T = 403.6 \text{ K}$.

315 4. Discussion

316 A summary of the vaporization enthalpies of the
 317 diacids at $T = 298.15 \text{ K}$ obtained in this work is re-
 318 ported in the second column of table 6. The third col-
 319 umn in this table contains the enthalpy associated with
 320 all the solid–solid and solid–liquid phase transitions
 321 occurring from $T = 298.15 \text{ K}$ to T_{fus} , adjusted to
 322 $T = 298.15 \text{ K}$ using equation (2). Addition of these two
 323 terms according to equation (3) results in
 324 $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})$. The last two columns in this ta-
 325 ble compare the results for $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})$ ob-
 326 tained in this study (column 4) with those measured
 327 directly (column 5). Excluding the three compounds

used as standards and C_{11} and C_{12} , the results of which
 are discussed below, agreement within experimental er-
 ror is obtained for the C_5 diacid. Agreement for the
 C_8 diacid is satisfactory only if the phase transition
 occurring at $T = 355.9 \text{ K}$ is included in evaluation of
 the sublimation enthalpy at $T = 298.15 \text{ K}$. Including
 the phase transition at $T = 403.6 \text{ K}$ for this diacid results
 in a value for $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})$ of
 $(158.0 \pm 1.9) \text{ kJ} \cdot \text{mol}^{-1}$, in much poorer agreement with
 the results of the current work. The sublimation enthal-
 pies measured directly for the C_7 and C_9 dicarboxylic
 acids are somewhat larger than the values obtained in
 this work. A possible explanation of this is that some
 of the phase transitions leading to broadness in the fu-

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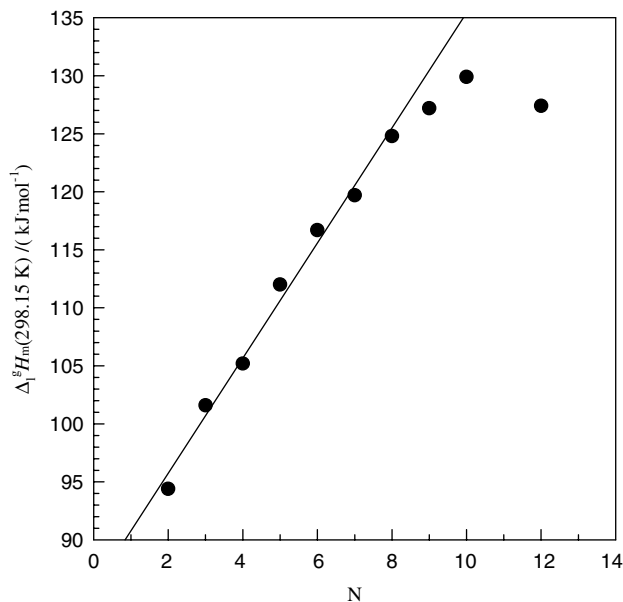


FIGURE 7. A graph of $\Delta_1^g H_m(T = 298.15 \text{ K})$ obtained by correlation-gas chromatography as a function of the number of methylene groups, N . The line was drawn using the values of butanedioic acid ($N = 2$) to decanedioic acid ($N = 8$) according to equation (8).

342 sion peaks of heptanedioic and nonanedioic acids have
343 had an influence on the measured sublimation
344 enthalpies.

345 The vaporization enthalpies listed in column 2 of
346 table 6 are plotted as a function of the number of
347 methylene groups in figure 7. As found for other
348 homologous series [11,12], a good linear correlation
349 is observed for the smaller members of the series.
350 However, once the number of methylene groups ex-
351 ceeds 8, a definite departure from linearity is observed.
352 Similar behavior has been reported for the behavior of
353 $\Delta_{cr}^g H_m(T = 298.15 \text{ K})$ as a function of the number of
354 methylene groups. This departure from linearity has
355 been interpreted as a result of an equilibrium estab-
356 lished between a linear and cyclic form of the diacid
357 in the gas phase as depicted in figure 1. It has been
358 suggested that as the number of methylene groups in
359 the diacid increases, the ring becomes large enough
360 to accommodate the type of hydrogen bonding ob-
361 served in the gas phase dimerization of smaller
362 mono-carboxylic acids at ambient temperatures. A lin-
363 ear regression of the vaporization enthalpies of the
364 C_4 - C_{10} dicarboxylic acids as a function of the number
365 of CH_2 groups, N , results in equation (8). The vapor-
366 ization enthalpies of the acyclic forms of undecanoic,
367 dodecanedioic and tetradecanedioic acids are predicted
368 by equation (8) to be: (130.5, 135.4 and
369 145.4) $\text{kJ} \cdot \text{mol}^{-1}$, respectively,

$$370 \Delta_1^g H_m(T = 298.15 \text{ K}) =$$

$$372 (4.96 \pm 0.226)N + (85.8 \pm 1.2) \text{ kJ mol}^{-1}. \quad (8)$$

This results in differences between calculated and ob-
373 served values of (2.8, 5.4 and 18.0) $\text{kJ} \cdot \text{mol}^{-1}$, respec-
374 tively. The trend in these differences suggests that the
375 optimal ring size for maximum hydrogen bonding
376 may not have yet been reached in tetradecanedioic
377 acid.

The equilibrium constant for cyclization of the larger
379 dicarboxylic acids, K_{eq} in figure 1, should be charac-
380 terized by negative enthalpy and entropy contributions.
381 Higher temperatures should favor the acyclic form and
382 the vaporization enthalpies measured at higher temper-
383 atures, once adjusted to $T = 298.15 \text{ K}$ would be expected
384 to increase to values predicted by the linear correlation
385 observed for the smaller diacids, equation (8). 386

The mean temperatures of measurement of
387 $\Delta_{cr}^g H_m(T_m)$ for undecanedioic and dodecanedioic acids
388 are $T_m = (376.1 \text{ and } 385.7) \text{ K}$, respectively; the mean
389 temperatures of measurement of $\Delta_{sln}^g H_m(T_m)$ for these
390 two diacids from table 5 is $T_m = 458 \text{ K}$. Accordingly,
391 the equilibrium constant for cyclization should be smal-
392 ler at the higher temperature resulting in a larger value
393 for $\Delta_1^g H_m(T_m)$ and subsequently a larger value for
394 $\Delta_{cr}^g H_m(T = 298.15 \text{ K})$ calculated indirectly. A compar-
395 ison of the two entries listed for $\Delta_{cr}^g H_m(T = 298.15 \text{ K})$ in
396 table 6 for undecanedioic acid (columns 4 and 5) shows
397 that the value measured indirectly at the higher temper-
398 ature is larger but still within experimental error of the
399 direct measurement. However the two values of
400 $\Delta_{cr}^g H_m(T = 298.15 \text{ K})$ for dodecanedioic acid are quite
401 different, reflecting substantial differences in
402 $\Delta_1^g H_m(T = 298.15 \text{ K})$ as expected. 9

As a test of the cyclization hypothesis, we decided to
404 investigate the vaporization enthalpies of the larger
405 diacids as a function of temperature and included trid-
406 ecanedioic and hexadecanedioic acids in this study.
407 Retention times were measured for octanedioic to tetra-
408 decanedioic over the temperature ranges $T = (444 \text{ to } 409$
409 $473, 473 \text{ to } 503 \text{ and } 503 \text{ to } 523) \text{ K}$, and from $T = (473$
410 $\text{ to } 503 \text{ and } 503 \text{ to } 523) \text{ K}$ for octanedioic to hexadec-
411 anedioic acid (exclusive of C_{15}), table 3E-G, respec-
412 tively. Octanedioic, nonanedioic and decanedioic acids
413 were used as vaporization standards for all these corre-
414 lations. The correlations obtained are summarized in ta-
415 ble 7A-C and resulted in equations (9)-(11),
416 respectively, 417
418

$$419 \Delta_1^g H_m(T = 298.15 \text{ K}) =$$

$$420 (1.347 \pm 0.205)\Delta_{sln}^g H_m(T = 459 \text{ K}) +$$

$$421 (43.39 \pm 0.87) \text{ kJ mol}^{-1} \quad (9)$$

$$422 \Delta_1^g H_m(T = 298.15 \text{ K}) =$$

$$423 (1.064 \pm 0.186)\Delta_{sln}^g H_m(T = 488 \text{ K}) +$$

$$(67.54 \pm 1.0) \text{ kJ mol}^{-1}, \quad (10)$$

TABLE 7

A summary of calculated $\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$ and $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})$ values for using C₈–C₁₀ as standards at various temperatures using the retention times of table 3E–G

	$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(T_{\text{m}})/R$	b	$\frac{\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(T = 459 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1a}}$	$\frac{\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1} \text{ (calcd.)}^b}$
(A) $T = 459 \text{ K}$					
Octanedioic acid	−6515.5	14.71	54.2	116.7	116.3
Nonanedioic acid	−6878.5	15.11	57.2	119.7	120.4
Decanedioic acid	−7238.6	15.50	60.2	124.8	124.4
Undecanedioic acid	−7505.6	15.71	62.4		127.4
Dodecanedioic acid	−7594.2	15.56	63.1		128.4
Tridecanedioic acid	−7639.1	15.32	63.5		128.9
Tetradecanedioic acid	−7346.4	14.39	61.1		125.6
	$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(T_{\text{m}})/R$	b	$\frac{\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(T = 488 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1a}}$	$\frac{\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1} \text{ (calcd.)}^b}$
(B) $T = 488 \text{ K}$					
Octanedioic acid	−5512.0	12.56	45.8	116.7	116.3
Nonanedioic acid	−5987.0	13.19	49.8	119.7	120.5
Decanedioic acid	−6423.5	13.74	53.4	124.8	124.4
Undecanedioic acid	−6814.2	14.22	56.7		127.8
Dodecanedioic acid	−7167.0	14.62	59.6		131.0
Tridecanedioic acid	−7510.5	15.02	62.4		134.0
Tetradecanedioic acid	−7777.4	15.26	64.7		136.4
Hexadecanedioic acid	−8343.8	15.8	69.4		141.4
	$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(T_{\text{m}})/R$	b	$\frac{\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(T = 513 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1a}}$	$\frac{\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1} \text{ (calcd.)}^b}$
(C) $T = 513 \text{ K}$					
Octanedioic acid	−5708.4	11.82	47.5	116.7	116.3
Nonanedioic acid	−6084.9	12.24	50.6	119.7	120.4
Decanedioic acid	−6452.5	12.64	53.6	124.8	124.4
Undecanedioic acid	−6783.8	12.98	56.4		128.0
Dodecanedioic acid	−7068.1	13.24	58.8		131.1
Tridecanedioic acid	−7356.4	13.51	61.2		134.3
Tetradecanedioic acid	−7580.4	13.67	63.0		136.7
Hexadecanedioic acid	−8167.9	14.23	67.9		143.1

^a Literature values or values obtained in this study.

^b Calculated using equation (9).

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$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T = 298.15 \text{ K}) = (1.308 \pm 0.205)\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(T = 513 \text{ K}) + (54.27 \pm 0.89) \text{ kJ mol}^{-1} \quad (11)$$

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427 Table 8 summarizes the results of these experi-
 428 ments. Column 2 of the table lists the vaporization
 429 enthalpies of the standards at $T = 298.15 \text{ K}$ used in
 430 the correlations at all three mean temperatures. Col-
 431 umn 4 contains the resulting vaporization enthalpies
 432 calculated from the measured enthalpies of transfer
 433 (column 3) according to equations (9)–(11) for each
 434 respective temperature range. The last column in the
 435 table lists the sublimation enthalpies calculated using
 436 equation (3) at each mean temperature. Values in
 437 brackets in the fourth column are the limiting vapor-
 438 ization enthalpies calculated using the linear correla-
 439 tion observed for the smaller diacids, equation (8),

and the bracketed values in the last column are the
 limiting sublimation enthalpies calculated by means
 of equation (3). A comparison of the bracketed num-
 bers to the number directly above indicates that the
 limiting temperature was not reached in these experi-
 ments. Decomposition became a problem at higher
 gc column temperatures. However, the results are con-
 sistent with the hypothesis that the larger diacids exist
 in equilibrium with a cyclic and acyclic form. An
 examination of figure 8 graphically illustrates the
 trend in vaporization enthalpy observed with increas-
 ing temperature. As predicted, the vaporization
 enthalpies increase with increasing temperature. The
 results are entirely consistent with the hypothesis illus-
 trated by figure 1.

In conclusion, it should be noted that although the
 larger diacids $>C_{11}$ exist in equilibrium with a cyclic
 and acyclic form, the degree of association in the

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TABLE 8

A summary of the $\Delta_f^{\text{g}}H_m(T=298.15\text{ K})$ and $\Delta_{\text{cr}}^{\text{g}}H_m(T=298.15\text{ K})$ values obtained for C_{11} – C_{14} and C_{16} as a function of temperature using $\Delta_f^{\text{g}}H_m(T=298.15\text{ K})$ of C_8 – C_{10} as standards

	$\Delta_f^{\text{g}}H_m$ (298.15 K)	$\Delta_{\text{sln}}^{\text{g}}$ $H_m(T_m)$	$\Delta_f^{\text{g}}H_m$ ($T=298.15\text{ K}$)	$\Delta_{\text{cr}}^{\text{g}}H_m$ (298.15 K)
	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1a}$	$\text{kJ}\cdot\text{mol}^{-1b}$
Octanedioic acid				
$T_m = 459\text{ K}$		54.2	116.3	
$T_m = 488\text{ K}$	116.7	45.8	116.3	150.7
$T_m = 513\text{ K}$		47.5	116.3	
$T_m = T_{\text{limiting}}$			[115.6]	[150.0]
Nonanedioic acid				
$T_m = 459\text{ K}$		57.2	120.4	
$T_m = 488\text{ K}$	119.7	49.8	120.5	144.9
$T_m = 513\text{ K}$		50.6	120.4	
$T_m = T_{\text{limiting}}$			[120.5]	[145.1]
Decanedioic acid				
$T_m = 459\text{ K}$		60.2	124.4	
$T_m = 488\text{ K}$	124.8	53.4	124.4	164.8
$T_m = 513\text{ K}$		53.6	124.4	
$T_m = T_{\text{limiting}}$			[125.5]	[165.9]
Undecanedioic acid				
$T_m = 459\text{ K}$		62.4	127.7	164.1
$T_m = 488\text{ K}$		56.7	127.8	164.2
$T_m = 513\text{ K}$		56.4	128.0	164.4
$T_m = T_{\text{limiting}}$			[130.5]	[166.9]
Dodecanedioic acid				
$T_m = 459\text{ K}$		63.1	128.4	169.8
$T_m = 488\text{ K}$		59.6	131.0	172.4
$T_m = 513\text{ K}$		58.8	131.1	172.5
$T_m = T_{\text{limiting}}$			[135.4]	[176.9]
Tridecanedioic acid				
$T_m = 459\text{ K}$		63.5	128.9	170.7
$T_m = 488\text{ K}$		62.4	134.0	175.8
$T_m = 513\text{ K}$		61.2	134.3	176.1
$T_m = T_{\text{limiting}}$			[140.4]	[182.2]
Tetradecanedioic acid				
$T_m = 459\text{ K}$		61.1	125.6	173.1
$T_m = 488\text{ K}$		64.7	136.4	183.9
$T_m = 513\text{ K}$		63.0	136.7	184.2
$T_m = T_{\text{limiting}}$			[145.4]	[192.9]
Hexadecanedioic acid				
$T_m = 488\text{ K}$		69.4	141.4	184.0 ^c
$T_m = 513\text{ K}$		67.9	143.1	185.7 ^c
$T_m = T_{\text{limiting}}$			[155.3]	[197.8]

^a Vaporization enthalpies calculated from the equations (9)–(11) as appropriate; values in brackets calculated from equation (8).

^b Values in brackets calculated using equation (3) and appropriate values from column 5 of table 2.

^c This value can be compared to the value reported by Davies and Thomas

458 gas phase has not been firmly established. Therefore
459 the experimental vaporization and sublimation enthal-
460 pies for these materials reported in this and previous
461 publications [1] are not state properties and should
462 not be used in adjusting heats of formation data or
463 in any other thermochemical cycle without appropri-
464 ate adjustments for the equilibrium observed in the
465 gas phase as reported previously for the mono-car-
466 boxylic acids [13]. The vaporization enthalpies of
467 the smaller homologues are for the most part consis-
468 tent with previous literature results on sublimation

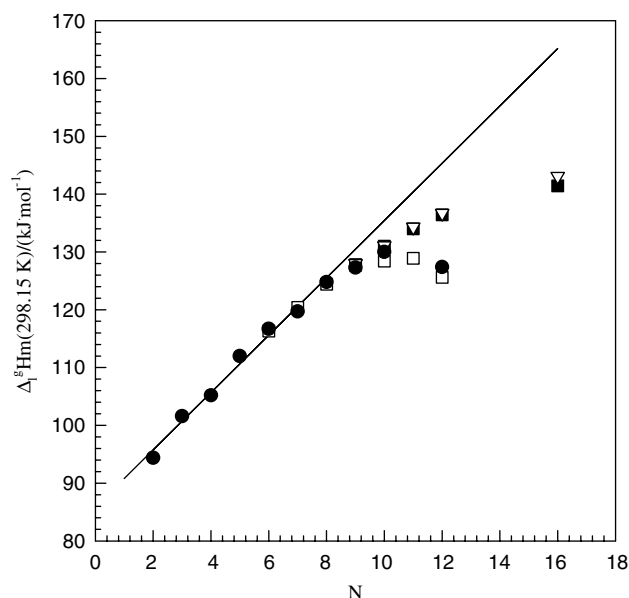


FIGURE 8. A graph of $\Delta_f^{\text{g}}H_m(T=298.15\text{ K})$ obtained by correlation–gas chromatography versus N , the number of methylene groups, as a function of the following gc column temperatures: solid circles, $T=458\text{ K}$; empty squares, $T=459\text{ K}$; solid squares, $T=488\text{ K}$; triangles, $T=513\text{ K}$. The line was drawn using the values of butanedioic acid ($N=2$) to decanedioic acid ($N=8$) according to equation (8).

enthalpies. The linearity observed in the vaporization 469
and sublimation enthalpy [1] between the liquid and 470
gas phase for the homologous series coupled the fact 471
that the larger homologues do cyclize suggest that the 472
smaller diacids are not associated in the gas phase 473
and that both $\Delta_f^{\text{g}}H_m(T=298.15\text{ K})$ and 474
 $\Delta_{\text{cr}}^{\text{g}}H_m(T=298.15\text{ K})$ for C_4 – C_{11} are valid state 475
properties. 476

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References 483

- [1] M.A.V. Ribeiro da Silva, M.J.S. Monte, J.R. Ribeiro, J. Chem. 484
Thermodyn. 31 (1999) 1093–1107. 485
- [2] M. Davies, G.H. Thomas, Trans. Faraday Soc. 56 (1960) 185–192. 486
- [3] M.V. Roux, J.Z. Dávalos, P. Jiménez, R. Notario, O. Castaño, 487
J.S. Chickos, W. Hanshaw, H. Zhao, N. Rath, J.F. Liebman, B.S. 488
Farivar, R. Gilardi, A. Bashir-Hashemi, unpublished results. 489
- [4] A. Bashir-Hashemi, J.S. Chickos, W. Hanshaw, H. Zhao, B.S. 490
Farivar, J.F. Liebman, Thermochim. Acta 424 (2004) 91–97. 491
- [5] V.V. Avdonin, E.I. Kirpichev, Y.I. Rubtsov, L.E. Romanova, 492
M.E. Ivanova, L.T. Eremenko, Russ. Chem. Bull. 45 (1996) 2342. 493
- [6] A. Cingolani, G. Berchiesi, J. Therm. Anal. 6 (1974) 87–90. 494

495	[7] J.S. Chickos, D.G. Hesse, J.F. Liebman, <i>Struct. Chem.</i> 4 (1993)	[11] J.S. Chickos, W. Hanshaw, <i>J. Chem. Eng. Data</i> 49 (2004) 620–640.	501
496	261–269.	[12] J.S. Chickos, Z. Hui, G. Nichols, <i>Thermochim. Acta</i> 424 (2004)	502
497	[8] J.S. Chickos, <i>Thermochim. Acta</i> 313 (1998) 19–26.	111–121.	503
498	[9] H.G.M. DeWit, J.C. Van Miltenburg, C.G. DeKruif, <i>J. Chem.</i>	[13] J. Konicek, I. Wadsö, <i>Acta Chem. Scand.</i> 24 (1970) 2612–2616.	504
499	<i>Thermodyn.</i> 15 (1983) 651–663.		505
500	[10] D.R. Stull, <i>Ind. Eng. Chem.</i> 39 (1947) 517–540.	JCT 04-186	506

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