

Mechanism for entropy–enthalpy compensation in the fusion of organic molecules

Alwyn S. Gilbert

West Oak, Beckenham, Kent BR3 5EZ, UK

Received 5 March 2004; received in revised form 10 August 2004; accepted 12 September 2004

Available online 5 November 2004

Abstract

Contrary to Walden's Rule [P. Walden, *Z. Elektrochem.* 14 (1908) 713–728], the entropies of fusion of rigid organic molecules, ΔS_f , are linearly related (entropy–enthalpy compensation) to the enthalpies of fusion, ΔH_f , by an expression of the form $\Delta S_f = a + b\Delta H_f$ where a and b are constants [A.S. Gilbert, *Thermochim. Acta* 339 (1999) 131–142]. The compounds that show phase transitions in the solid state yield a value of the intercept a close to that expected (about $8 \text{ J K}^{-1} \text{ mol}^{-1}$) for the communal entropy of the liquid state. However, most compounds do not possess solid state transitions and for these the value of a is found to be much higher at around $30 \text{ J K}^{-1} \text{ mol}^{-1}$.

A simple statistical mechanical treatment has been applied to the way the external vibrational modes (translational and librational) might change on fusion and gives some success in describing the features of the compensation observed, in particular the values of the intercepts. This involves consideration of the enthalpy of vapourisation of the liquids, ΔH_v , as well as ΔH_f . It appears that the ratio between these two parameters, $\Delta H_f/\Delta H_v$ is a major determining factor so that compensation occurs more properly with this ratio than with ΔH_f alone.

The entropy and enthalpy changes for transitions in the solid state themselves also appear to be compensated in the same way as for fusion. © 2004 Elsevier B.V. All rights reserved.

Keywords: Entropy; Enthalpy; Fusion; Compensation; Organic

1. Introduction

The entropy of fusion, ΔS_f , is related to the melting point, T_{mp} , and the enthalpy of fusion, ΔH_f , according to the simple thermodynamic relation

$$\Delta S_f = \frac{\Delta H_f}{T_{\text{mp}}} \quad (1)$$

Both ΔH_f and T_{mp} are found experimentally, and thus, ΔS_f can be readily obtained.

It is often accepted that values of ΔS_f for non-spherical rigid organic molecules, that form isotropic melts, are not electrolytes and that do not exhibit solid–solid (s–s) transitions, are roughly constant at around $50\text{--}60 \text{ J K}^{-1} \text{ mol}^{-1}$. This is known as Walden's rule [1] after he observed 35 such compounds to have an average ΔS_f of 13.5 entropy units (i.e.

$\sim 56.5 \text{ J K}^{-1} \text{ mol}^{-1}$). The rule has provided the basis for some general schemes for prediction of ΔS_f in, for instance, cases where the organic molecules have flexible sub-units or are symmetrical [2]. However, it has been stated that Walden's empirical result is "strange" [3] and some theories of ΔS_f would expect variability (see [3] and references therein).

It has recently been shown [4], using literature compilations [5,6] of several hundred organics, that the ΔS_f values of rigid molecules are definitely not constant but dependent on ΔH_f . This dependency does not seem to have been recognised before. The relationship appears to be a very simple one of the kind

$$\Delta S_f = a + b\Delta H_f \quad (2)$$

where a and b are constants. As ΔH_f varies quite extensively, being very roughly dependent on molecular weight, Walden's rule cannot, therefore, be correct. Experimentally, values of ΔS_f are indeed found to cluster around about $55 \text{ J K}^{-1} \text{ mol}^{-1}$

E-mail address: alwyn.gilbert@tiscali.co.uk.

but this is because the set of known rigid organic molecules is severely clustered in terms of molecular weight and thereby ΔH_f , and therefore, random selections are also kurtosed in a similar manner [4].

Processes which exhibit a linear relationship between the entropy changes and enthalpy changes are said to show ‘entropy–enthalpy compensation’ and are widely observed in chemistry [7]. They are usually complex and often involve non-covalent binding, and thus, a change in free energy. The temperatures of the various chemical systems observed are generally invariant.

Fusion is a phase transition so that the free energy change is necessarily equal to zero (and thus constant). However, the apparent compensation observed [4] is not trivial as the temperatures (melting points), though clustered within the data set do vary by up to a factor of five or so. Also, compensation is not a requirement of Eq. (1) because if, for instance, T_{mp} was just linearly proportional to ΔH_f then ΔS_f would be a constant (and Walden’s rule valid).

The previous work [4] speculated that the compensation on fusion could be analogous to that observed in ligand binding processes [8]. The latter are theoretically expected to generate curved plots however [8], whereas the fusion relationships [4] appear to be linear.

Given that the compounds displaying entropy–enthalpy compensation on fusion are quite disparate in structure it should be possible to formulate a general and fairly simple, though inexact, theory to explain the behaviour. This is attempted below.

2. Selection of literature data

The compilations of data [5,6] utilised previously [4] have recently been updated [9]. In particular, there is now included values of ΔS and ΔH where s–s transitions (i.e. phase transitions below the melting point) have been observed and it was decided to use this new collection for the analysis below.

Firstly, so-called ‘flexible’ molecules were ignored, these being compounds that would be expected to take up multiple conformations in the liquid state that are not seen in the solid. Typical are the long chain alkanes with carbon numbers greater than three. The conformational disorder in the liquid causes ΔS_f to be higher than it might be if these molecules were rigid but not in a precisely predictable manner [10–12]. The criterion used for determining ‘flexibility’ was the same as in [2] so that hydrogens on substituents were ignored thus, for example, phenol was considered to be non-flexible.

Secondly, molecules having at least one axis of symmetry were also excluded. It has been pointed out [2] that such molecules show significantly lower values of ΔS_f compared to asymmetric ones; however, inspection of ΔS_f versus ΔH_f plots indicates that any decrement is minimal or non-existent. Nevertheless symmetrical molecules were ignored. It should be noted here that the definitions of symmetry in the present work differ slightly from [2] in the way hydrogen atoms

are treated. Thus, for symmetry purposes, only hydrogens on methyl groups have been considered invisible; therefore, toluene was regarded as possessing a two-fold axis while phenol was considered to be asymmetrical.

The above sifting yielded some 221 rigid and asymmetrical compounds which were divided into two sets. The minor set consisted of some 34 compounds, which show s–s transitions and the major set, some 187 compounds with no pre-melting transitions listed.

Fig. 1 shows a plot of ΔS_f against ΔH_f for the major set and it may be seen that, with the exception of three outliers, there is a very clear and apparently linear relationship. Linear regression yields

$$\Delta S_f = 29.91(1.129) + 0.0013\Delta H_f(0.000066) \quad (3)$$

where the correlation coefficient (r^2) = 0.677, the standard deviation (S.D.) = $6.5 \text{ J K}^{-1} \text{ mol}^{-1}$ and the figures in brackets are the standard errors on the coefficients. The two low entropy outliers are possibly compounds that possess unlisted s–s transitions.

It could be argued that compounds having methyl substituents (and also, e.g. NO_2 , NH_2 , etc.) should not have been included as these are technically not rigid. However, as long as the rotational status does not change on fusion, there should be no major consequence for ΔS_f . Many methyl groups freely rotate in the solid state while nitro groups for instance, when attached to unsaturated systems, can be expected to be held rigid by conjugation. These conclusions are confirmed by the observation that such compounds do not differ significantly

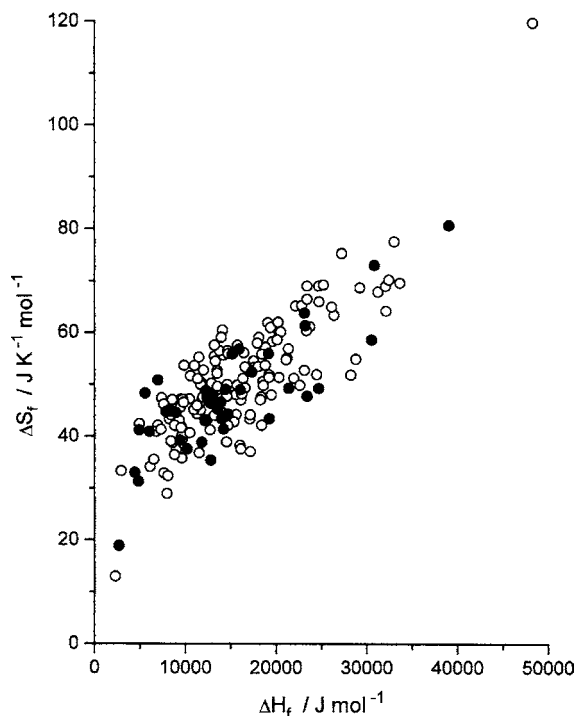


Fig. 1. Plot of ΔS_f against ΔH_f for the major set of 187 compounds: compounds with none or only halogen substituents (●) and others (○).

in their behaviour from truly rigid molecules, with none or only halogen substituents, shown highlighted (solid circles) in Fig. 1.

The large positive intercept a of Eq. (3) at around $30 \text{ J K}^{-1} \text{ mol}^{-1}$ is very similar to that found in the previous work [4]. It is, however, much higher than might be expected as the only enthalpy independent gain on melting should be the communal entropy [13] of just over $8 \text{ J K}^{-1} \text{ mol}^{-1}$ (i.e. equal to R , the molar gas constant). The communal entropy reflects the ability of each molecule to interchange position with any other in the liquid state.

Fig. 2 is the ΔS_f versus ΔH_f plot from the minor set which show s–s transitions. The relation also appears to be linear and regression yields

$$\Delta S_f = 10.97(2.76) + 0.00192\Delta H_f(0.0002) \quad (4)$$

with S.D. = $8.858 \text{ J K}^{-1} \text{ mol}^{-1}$ and correlation coefficient (r^2) = 0.746. Here, the intercept is much lower and actually quite near the expected value for the communal entropy.

Fig. 3 plots the actual values for the s–s transitions themselves from the minor set. The communal entropy should not be manifested here and it can be seen that the intercept is near zero.

It is evident from the foregoing that any general theory must not only explain the linear relationship between ΔS_f and ΔH_f but also the unusually high value of the intercept displayed in Fig. 1.

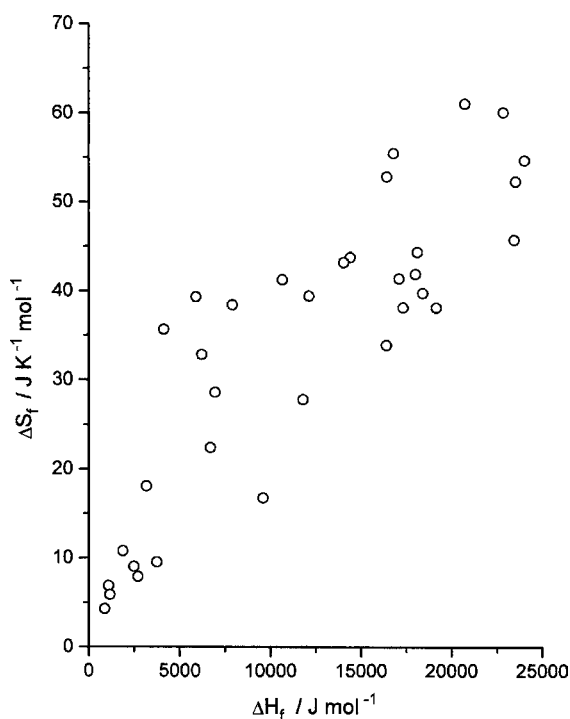


Fig. 2. Plot of ΔS_f against ΔH_f for the minor set of 34 compounds.

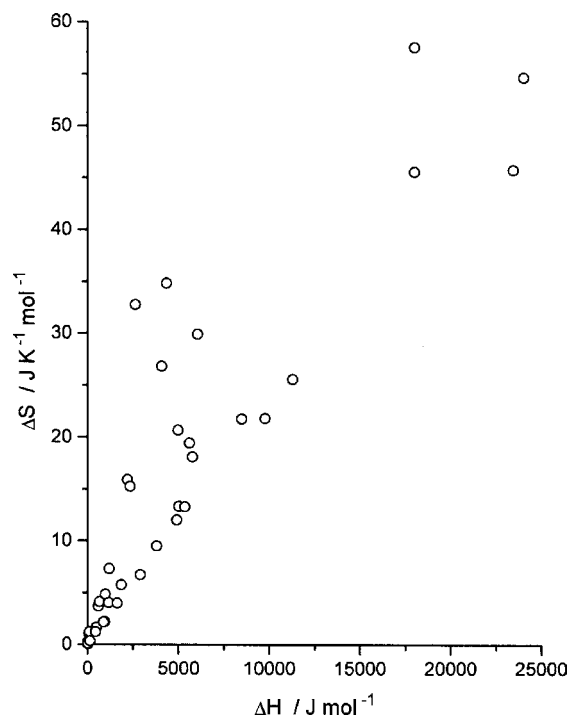


Fig. 3. Plot of ΔS against ΔH of the 43 s–s transitions for the minor set of 34 compounds.

3. The statistical mechanics description of entropy

The entropy change on fusion is of course the difference between the entropies of the solid and liquid states at the melting point. For a solid which has an ordered crystalline structure at absolute zero, the Third Law entropy is merely the sum of the entropies of the individual vibrational modes. Statistical mechanics yields the familiar expression

$$S = k \left[\frac{x}{(\exp(x) - 1)} + \ln \left(\frac{1}{(1 - \exp(-x))} \right) \right] \quad (5)$$

for each mode of vibration, with $x = \epsilon/kT$ where ϵ is the vibrational energy level spacing, k , the molecular gas constant, and T , the temperature. It is assumed that there is equal spacing of the energy levels (i.e. the harmonic approximation).

The total number of vibrational modes is $3nN$ where n is the number of atoms per molecule and N the number of molecules in the crystal. All but $6N$ ($5N$ for linear molecules and $3N$ for single atoms) are internal, the remainder are the external modes which are whole molecule (lattice) vibrations of either translational (acoustic modes) or librational (orientational) nature. In a molecular crystal, the forces that determine these vibrations are weak, often not specifically directional, and non-covalent. Both terms of Eq. (5) increase in value as x decreases.

On transition to a fluid there should be an immediate increase in entropy of Nk ($=R$, the molar gas constant), this being named the communal entropy [13]. This assumes that all molecules can and do exchange positions with each other.

The precise nature of the liquid state is uncertain but it seems likely that it should be treated more as a dynamically disordered solid rather than a highly compressed gas [14]. This might mean that the communal entropy is not as large as expected and varies from compound to compound due to ordering effects. Heat capacities drop sharply on transition from liquids to gases [15] which implies but by no means makes certain that the external modes largely retain their essential vibrational character in the liquid.

4. Mechanism for entropy–enthalpy compensation

Numerous observations of infra-red and Raman spectra demonstrate that internal vibrations are usually little affected by change of state (only a small percentage of ϵ). The values of ϵ are also mostly larger than kT (in spectroscopic terms about 200 cm^{-1} at room temperature) and vary widely with molecular structure. Therefore, most internal vibrations are unlikely to contribute significantly to ΔS_f and it is only necessary to look to the external modes for explanation.

The description of the lattice modes of a crystalline solid is highly complex [16]. The observable infra-red and Raman frequencies are merely the extrema of frequency dispersions, caused by coupling between vibrational modes, all of which contribute to the entropy. It is simply not possible to consider all these vibrations. This problem can only be avoided by arbitrarily considering just six frequencies (representing say the maxima of the dispersion ranges) instead of $6N$ (or five instead of $5N$ in the case of linear molecules, etc.). The molecular constant k in front of the brackets in Eq. (5) is, therefore, replaced by the molar constant R .

For small values of the parameter x in Eq. (5), it can be approximated to

$$S = R[1 - \ln(x)] \quad (6)$$

which works surprisingly well even up to values of $x = 0.5$. Lattice modes are typically below 100 cm^{-1} and most melting points above room temperature so that values of x will generally be well below 0.5.

For a change of state altering the value of x , say $x_1 \rightarrow x_2$, then

$$\Delta S = R \ln \left(\frac{x_1}{x_2} \right) \quad (7)$$

and since kT and molecular mass terms or inertias cancel out then

$$\Delta S = 0.5R \ln \left(\frac{f_1}{f_2} \right) \quad (8)$$

where f_1, f_2 are the appropriate force constants. The factor of 0.5 arises because vibrational frequency (energy level spacing) is proportional to the square root of the force constant.

If it is assumed that the energy well profiles are the same and that they only differ, compound to compound, by their depths then the force constants for the external vibrations

may be taken as proportional to the appropriate dissociation energies (i.e. the enthalpies). If the change of state being considered is fusion then

$$f_s \propto \Delta H_f + \Delta H_v \quad (9)$$

$$f_l \propto \Delta H_v \quad (10)$$

where f_s and f_l are the force constants in the solid and liquid states, respectively, and ΔH_v is the enthalpy of vapourisation of the liquid at the T_{mp} . Technically, the latter should be corrected for the work of expansion but this is small at the vapour pressures encountered at the T_{mp} and so can be ignored.

With six external modes of vibration and including the communal entropy this gives

$$\Delta S_f = R \left[1 + 3 \ln \left(1 + \frac{\Delta H_f}{\Delta H_v} \right) \right] \quad (11)$$

4.1. Testing the initial theory

Table 1 includes data for some 53 compounds taken from the major set for which values of ΔH_v at the melting point were obtained. These were calculated from equations given in the McGraw-Hill Chemical Properties Handbook [15]. They appear to form a reasonably representative sub-set, linear regression yielding

$$\Delta S_f = 28.04(2.072) + 0.00154\Delta H_f(0.000156) \quad (12)$$

with S.D. = $5.48\text{ J K}^{-1}\text{ mol}^{-1}$ and correlation coefficient (r^2) = 0.654.

The form of Eq. (11) implies that the ratio of ΔH_f to ΔH_v determines ΔS_f and it may be seen by inspection of Table 1 that indeed the latter is quite nicely correlated with $\Delta H_f/\Delta H_v$; in fact, the linear fit is slightly better than that to ΔH_f alone.

A serious difficulty, however, is that Eq. (11) predicts entropy values that are several times too low. By contrast, the simple case of the noble gases yields predictions of the right order. Here, there are only three external vibration modes (all of translational nature) so that Eq. (11) must be modified by changing the factor in front of the natural logarithm to 1.5 instead of 3. For example, argon which has values for ΔH_f and ΔH_v of 1.12 and 6.524 kJ mol^{-1} , respectively, gives a predicted ΔS_f of $10.29\text{ J K}^{-1}\text{ mol}^{-1}$ compared to the experimental value of $13.19\text{ J K}^{-1}\text{ mol}^{-1}$. The other noble gases also predict slightly low.

5. Extension of theory

The data on the noble gases suggests that translational entropy is unlikely to change much in line with the relatively small volume increases on melting [3]. This indicates that the major contribution to ΔS_f is an increase in the re-orientational entropy.

This conclusion has been reached previously from a different viewpoint [13] and is supported by the fact that the

Table 1
Fusion and vapourisation data for the major set

	ΔH_f (J mol ⁻¹)	ΔS_f (J K ⁻¹ mol ⁻¹)	T_{mp} (K)	ΔH_v (J mol ⁻¹)	$\Delta H_f/\Delta H_v$
Nitromethane	9700	39.62	244.8	40340	0.241
Methylamine	6130	34.14	179.7	31050	0.197
Chlorotrifluoroethylene	5550	48.28	115.0	27700	0.200
Trichloroethylene	8450	44.83	188.5	40030	0.211
Vinyl chloride	4920	41.21	119.3	30440	0.162
1,1-Dichloroethane	7870	44.77	176.2	36280	0.217
Chloroethane	4450	33.01	134.8	31050	0.143
Nitroethane	9850	53.64	183.7	45080	0.218
Acetamide	15600	44.19	353.0	60110	0.259
Beta-propiolactone	9410	39.22	239.9	53340	0.176
Acrylamide	15330	42.82	358.0	80280	0.191
Propene	2930	33.30	88.2	23640	0.124
2-Bromopropane	6530	35.50	184.1	34760	0.188
<i>N,N</i> -Dimethylformamide	8950	42.05	212.9	50980	0.176
Gamma-butyrolactone	9570	41.84	230.0	55690	0.172
2-Pyrrolidone	13920	46.56	299.0	65760	0.212
2-Methylthiophene	9470	45.57	207.8	42330	0.224
3-Methylthiophene	10540	51.62	204.2	42950	0.245
1,2-Chloronitrobenzene	19080	61.90	308.2	65810	0.290
1,3-Chloronitrobenzene	19370	60.99	317.6	63290	0.306
4-Chlorophenol	14070	44.54	315.9	54280	0.259
2-Nitroaniline	16110	47.00	342.5	83300	0.193
3-Nitroaniline	23680	61.16	387.0	82820	0.286
Phenol	11510	36.82	314.0	58610	0.196
Thiophenol	11300	44.30	258.3	50590	0.223
2-Methylpyridine	9720	47.10	206.5	47010	0.207
3-Methylpyridine	14180	55.62	255.0	46650	0.304
Phenylhydrazine	16430	56.11	292.8	61020	0.269
Benzotrifluoride	13950	59.11	236.0	53110	0.263
Benzotrifluoride	13770	56.45	244.1	40470	0.340
2,4-Di-nitrotoluene	20120	58.61	343.3	88990	0.226
3,4-Di-nitrotoluene	18830	57.15	329.5	89870	0.210
3-Nitrotoluene	19200	66.62	288.2	52550	0.366
<i>p</i> -Hydroxytoluene	12720	41.25	307.9	62150	0.205
<i>m</i> -Toluidine	8800	36.41	241.7	58280	0.151
<i>o</i> -Toluidine	8080	32.37	249.6	59670	0.135
2-Methylaniline	11660	45.10	258.0	59210	0.197
Benzothiophene	11820	38.82	304.5	53970	0.219
2,6-Dimethylphenol	18900	59.27	318.9	55120	0.343
3,5-Dimethylphenol	18000	53.44	336.8	63920	0.281
<i>N,N</i> -Dimethylaniline	11560	46.28	275.6	55150	0.209
2,4,6-Trimethylpyridine	9540	41.64	229.0	54470	0.175
2,4,4-Trimethyl-2-pentane	6780	40.9	166.0	45110	0.150
Isoquinoline	13540	45.21	299.6	59990	0.226
Indene	10200	37.54	271.7	52940	0.193
Indane	8600	38.77	221.8	52690	0.163
Alpha-methylstyrene	11920	47.55	250.8	48640	0.245
1,2,4-Trimethylbenzene	13190	57.23	229.3	49820	0.265
1-Chloronaphthalene	12900	47.65	270.7	66110	0.195
<i>t</i> -Butylbenzene	8400	39.10	215.0	53560	0.157
<i>t</i> -Butylphenol	14520	38.90	373.2	62370	0.233
2,4-Dinitrochlorobenzene	20200	62.00	325.2	86040	0.235
2,4,6-Trinitrotoluene	23400	66.50	352.2	65290	0.358

entropy of vapourisation ΔS_v is virtually constant (Trouton's rule), except for obvious and explicable exceptions. ΔS_v can be plausibly assigned almost entirely to increase in translational entropy because substances undergo a similar and several orders of magnitude increase in volume from liquid to gas. The rotational entropy of even small molecules in the gas phase is 50 J K⁻¹ mol⁻¹ or more [13] and if this is

not generated on vapourisation then it must largely appear at lower temperatures. In addition, s–s transitions can often be ascribed to changes in librational modes [17].

The crude assumption of strict proportionality between ΔH_f and ΔH_v , for the rotational modes must, therefore, be abandoned and a coefficient ($\ll 1$) put on ΔH_v to reduce it. This would imply that these external modes greatly diminish

in frequency on transition to the liquid to allow ΔS_f to rise significantly in magnitude.

However, the large increase in re-orientational entropy is probably not distinguishable as such in the liquid state as the external modes are likely to be highly mixed in character.

Eq. (11) can, therefore, be modified to give

$$\Delta S_f = R + 3 \ln \left(1 + \frac{\Delta H_f}{c\Delta H_v} \right) \quad (13)$$

with the grossly simplifying supposition that constant c is the same for all molecules and all modes, this assumption being made both because of mixing and in order to simplify matters as far as possible.

The value of c obtained by fitting data from the major set ($N=53$) to the above equation is 0.0582(0.00242) with an S.D. of 5.86 J K⁻¹ mol⁻¹. Thus, Eq. (13) can yield entropies of the right order but the predicted values of ΔS_f fall in a narrower range than the actual values (about 37–58 and 32–67 J K⁻¹ mol⁻¹, respectively). The predicted values are also slightly curved in a convex manner, due to the logarithm functionality, with regard to ΔH_f .

5.1. The predicted intercepts

While the detailed fit from Eq. (13) is not entirely satisfactory, it does describe the overall values of the intercepts.

Fig. 4 is a plot of $\Delta H_f/\Delta H_v$ versus ΔH_f for the major set which shows that it varies in an overall linear fashion. Significantly the plot has a positive value at zero ΔH_f . Linear

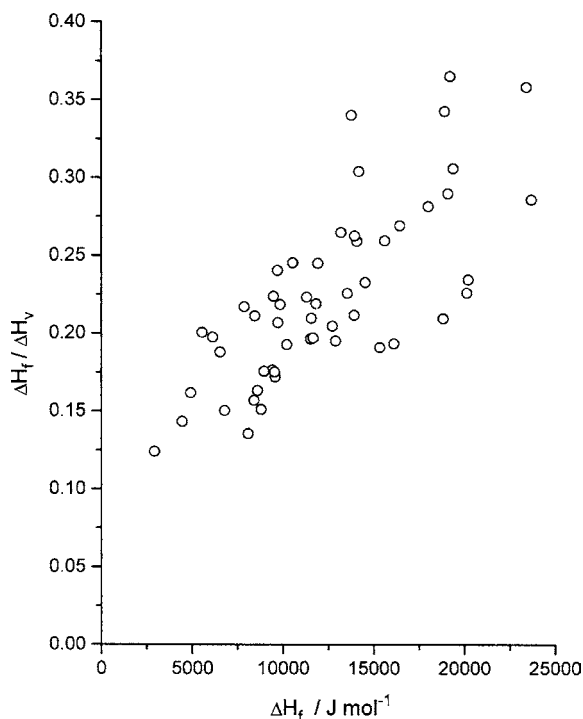


Fig. 4. Plot of $\Delta H_f/\Delta H_v$ against ΔH_f for the major set.

regression yields

$$\frac{\Delta H_f}{\Delta H_v} = 0.1156(0.0143) + 0.00000871\Delta H_f(0.0000011) \quad (14)$$

with S.D. = 0.0377 and correlation coefficient (r^2) = 0.562. Putting $\Delta H_f/\Delta H_v$ equal to 0.1156 and c equal to 0.0582 into Eq. (13) gives a value of $\Delta S_f = 35.6$ J K⁻¹ mol⁻¹ at ΔH_f equal to zero. This is of the same order, though higher, than the observed figure of around 30 J K⁻¹ mol⁻¹.

For the case of the compounds in the minor set, the ratios of $\Delta H_f/\Delta H_v$ are lower than for the major set (Table 2). This is because the ΔH_f values are lower than they would ordinarily be as a greater or lesser amount of the enthalpy change is ‘taken up’ by the s–s transitions. The values of ΔH_v are of course unchanged. The ratio $\Delta H_f/\Delta H_v$, therefore, tends to zero at zero ΔH_f , so the intercept of ΔS_f by Eq. (13) will simply be equal to the communal entropy as is nearly observed (Fig. 2). In fact, the limiting value of $\Delta H_f/\Delta H_v$ is found to be slightly positive at 0.0379 (standard error, 0.018) by linear regression but only 11 data values are available for these compounds.

5.2. The possible contribution from free translation and rotation

The general consensus seems to be that liquid molecules spend most of their time undergoing vibrational oscillations occasionally interrupted by short free translational and rotational excursions [14,18]. These are presumably mediated by thermal energy fluctuations. However, vibrational spectra of liquids do not show rotational features [19] though smoothed out rotational profiles can be seen sometimes in solution [20]. It should be noted that even if the presence of the free state is insufficient to register spectroscopically, it may still contribute significantly because its inherent entropy will be relatively higher.

If the existence of the free state is acknowledged, then another term is required such as $\ln((c\Delta H_v + \Delta H_f)/d)$, here the divisor being a simple constant d reflecting the fact the no force constant is involved in the free state. Thus,

$$\Delta S_f = R \left[1 + 3 \left[(1 - g) \ln \left(1 + \frac{\Delta H_f}{c\Delta H_v} \right) + g \ln \left(\frac{(c\Delta H_v + \Delta H_f)}{d} \right) \right] \right] \quad (15)$$

where g is a function of ΔH_f with maximum value of one.

The function g specifies the respective contributions from the vibrational and free states. The relative contributions will be determined by the ratio Z of thermal energy (R times T_{mp} per mole) to the height of the energy wells for vibration, this being proportional to $RT_{mp}/\Delta H_v$. The higher Z , the greater g .

The plot of Z versus ΔH_f appears to increase with ΔH_f in a linear manner but is noisy. Fortunately, it is possible to derive Z by combining and re-arranging Eqs. (3) and (14) to

Table 2
Fusion and vapourisation data for the minor set

	ΔH_f (J mol ⁻¹)	ΔS_f (J K ⁻¹ mol ⁻¹)	T_{mp} (K)	ΔH_v (J mol ⁻¹)	$\Delta H_f/\Delta H_v$
Chlorodifluoromethane	4120	35.85	115.7	25610	0.161
Methanol	3180	18.10	175.3	45030	0.071
Methanethiol	5900	39.33	150.2	29880	0.197
Pentafluorochloroethane	1880	10.79	173.7	22520	0.083
<i>t</i> -Butylmercaptan	2480	9.04	274.4	32040	0.077
<i>t</i> -Butylamine	880	4.28	206.2	33580	0.026
3,3-Dimethyl-1-butene	1090	6.87	158.4	33380	0.033
Cycloheptatriene	1160	5.86	198.0	45330	0.026
Quinoline	10660	41.27	258.4	61430	0.174
1-Methylnaphthalene	6950	28.62	242.7	62170	0.112
2-Methylnaphthalene	12130	39.43	307.4	59180	0.205

give

$$Z \propto R \frac{115.6 + 0.00871\Delta H_f}{1000(29.91 + 0.0013\Delta H_f)} \quad (16)$$

Inspection of Eq. (16) confirms that Z does indeed appear to increase with ΔH_f .

It is unfortunately not possible to use Z to derive a simple function for g without making too many assumptions about the details of the energy levels. If g is simply assumed to be directly proportional to Z then fitting the data to Eq. (15) yields values for c and d of 0.0392(0.135) and 4.953(13.87), respectively, with somewhat improved values for the S.D. of 5.204 J K⁻¹ mol⁻¹ and intercept at $\Delta H_f=0$ of 31.29 J K⁻¹ mol⁻¹ for ΔS_f though compared to the results from Eq. (13), the improvement in significance of fit is less clear because of the greater number of parameters used. The standard errors on the fitted values for d and g are particularly large. The predicted values of ΔS_f now range from 30 to 60 J K⁻¹ mol⁻¹ and form a slightly straighter progression.

6. Discussion

It is evident that the above theory implies that ΔS_f is determined not only by ΔH_f but also ΔH_v and in particular the ratio, modified by the constant c , between these two parameters. Because $\Delta H_f/\Delta H_v$ increases in line with ΔH_f (Fig. 4), ΔS_f also rises with ΔH_f . The fact that this ratio is significantly positive at zero ΔH_f is responsible for the high value of the intercept a in the simple compensation relationship (Eq. (2)).

In fact, the linear fit of ΔS_f with $\Delta H_f/\Delta H_v$ is even better than that for ΔH_f alone. Thus, for the relationship

$$\Delta S_f = a' + b' \frac{\Delta H_f}{\Delta H_v} \quad (17)$$

the correlation coefficient (r^2) for the major set ($N=53$) is 0.677 compared to 0.654 (see Eq. (12)) the intercept at $\Delta H_f=0$ coming out at 32.53 J K⁻¹ mol⁻¹ for ΔS_f . The improvement for the minor set ($N=11$) is even greater with r^2 going from 0.806 to 0.914 when ΔH_v is included. It would seem, therefore, that compensation of ΔS_f is more properly

with the ratio of the two enthalpies rather than with ΔH_f alone.

It would appear from Eq. (16) that the degree of free translation and rotation increases with ΔH_f , i.e. that larger molecules with higher melting points spend more time in the free state. If the free state is not relevant then the logarithm functionality forces the fit to be convexly curved as long as c is indeed a constant. However, if the free state is significant and if g indeed rises with ΔH_f , then the line of predicted points can be straightened out somewhat.

6.1. The problem of the liquid state

A fundamental difficulty in developing any theory of fusion is undoubtedly the present lack of understanding of the precise nature of the liquid state. For instance, the ephemeral nature of the intermolecular contacts lends uncertainty to the assumption and character of external vibrations. Moreover, local order effects could mean that the use of the communal entropy may not be entirely sound. Hydrogen bonding is known to yield lower than expected values for ΔS_f [4,21].

Then, there is the possibility that free translation and rotation may contribute significantly to the entropy but as mentioned above this cannot be properly evaluated [19,20].

It is a pity that it is not possible to find out if the values obtained for the constant c (Eq. (13)) are reasonable. This ought to be possible by comparing vibrational frequencies in the different states. Unfortunately while organic liquids yield infra-red absorptions in the appropriate regions these are typically broad and featureless and can be attributed to a number of different mechanisms such as dipolar relaxation effects [22]. Both infra-red and Raman spectroscopic analyses of the band shapes of internal vibrational modes can give information on re-orientational processes but librational frequencies cannot be obtained [23].

6.2. The solid–solid transitions

The plot of the s–s transitions themselves (Fig. 3) shows that here the enthalpy and entropy changes do not seem to

Table 3
Data for the s–s transitions from the minor set: for explanation of ΔH_f and ΔH_t , see text

	ΔH (J mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)	T_{mp} (K)	ΔH_f (J mol ⁻¹)	$\Delta H/\Delta H_t$
Chlorodifluoromethane	70	1.13	59.0	4120	0.002
Methanol	64	4.00	157.3	3180	0.013
Methanethiol	2200	15.90	137.6	5900	0.061
Pentafluorochloroethane	2630	32.76	80.2	1880	0.108
<i>t</i> -Butylmercaptan	4070	26.83	151.6	4100	0.113
	650	4.13	157.0	3450	0.018
	970	4.87	199.4	2480	0.028
<i>t</i> -Butylamine	110	1.24	91.3	6930	0.003
	6050	29.92	202.3	880	0.176
3,3-Dimethyl-1-butene	4350	34.84	124.9	1090	0.126
Cycloheptatriene	2350	15.24	154.0	1160	0.051
Quinoline	70	0.31	220.0	10660	0.001
1-Methylnaphthalene	4980	20.69	240.7	6950	0.072
2-Methylnaphthalene	5610	19.43	288.5	12130	0.079

be related in the same way as those for fusion. Instead of a strict narrow line relationship, the points fan-out from the origin as ΔH increases. This is of course required as if there was perfect linearity then all transitions would take place at the same temperature (equal to the reciprocal of the slope) because there is no intercept.

Of particular interest is whether there is a well-defined envelope to the ‘fan-out’ because if so, this would imply some type of compensation. However, it is possible that the distribution of points merely reflects the kurtosis of the sample set in terms of various parameters already mentioned.

The two edges of the envelope make up two isotherms corresponding to approximately 125 and 440 K for the higher and lower bounds of the plot respectively. The lack of higher temperature transitions than 440 K could well reflect a cut-off in the number of high molecular weight compounds available for analysis though such materials should appear well to the right hand side because of their high expected values of ΔH_f . The low temperature bound is more difficult to refute. Thus, compensation does appear to be genuine for s–s transitions.

For the 11 compounds of the minor set, where values of ΔH_v can be calculated, linear regression of the fourteen s–s transitions listed (Table 3) yields

$$\Delta S = 3.063(2.99) + 0.00485\Delta H(0.000924) \quad (18)$$

and

$$\Delta S = 1.794(1.77) + 218.8 \frac{\Delta H}{\Delta H_t}(22.1) \quad (19)$$

Here, $\Delta H_t = \Delta H_v + \Delta H_f$ where the latter term represents the remaining enthalpy change before fusion. The difference in correlation coefficients (r^2) is quite striking being 0.696 and 0.891, respectively. In particular, the plot of Eq. (19) does not exhibit the ‘fan-out’ seen in Fig. 3. This indicates that the entropy and enthalpy changes for s–s transitions are indeed compensated in the same way as for fusion.

Finally, it should be noted that if the s–s data are added to the ΔS_f and ΔH_f values from the minor set, a plot similar

to that from compounds without pre-melting transitions (the major set) is obtained.

7. Conclusion

Using various approximations, a simple statistical mechanical treatment of the way the external vibrational modes should change on fusion is able to explain certain features of the observed entropy–enthalpy compensation. The predicament is that the relation between ΔS_f and ΔH_f is predicted as slightly curved whereas the observed plots appear to be linear. It is likely that deficiencies in the treatment can be attributed to the assumptions made about the nature of the liquid state.

References

- [1] P. Walden, *Z. Elektrochem.* 14 (1908) 713–728.
- [2] R.-M. Dannenfelser, S.H. Yalkowsky, *Ind. Eng. Chem. Res.* 35 (1996) 1483–1486.
- [3] A. Bondi, *Physical Properties of Molecular Crystals, Liquids and Gases*, Wiley, New York, 1968.
- [4] A.S. Gilbert, *Thermochim. Acta* 339 (1999) 131–142.
- [5] W.E. Acree Jr., *Thermochim. Acta* 189 (1991) 37–56.
- [6] W.E. Acree Jr., *Thermochim. Acta* 219 (1993) 97–104.
- [7] L. Liu, Q.-X. Guo, *Chem. Rev.* 101 (2001) 673–695.
- [8] D.H. Williams, M.S. Westwell, *Chem. Soc. Rev.* 27 (1998) 57.
- [9] J.S. Chickos, W.E. Acree Jr., J.F. Liebman, *J. Phys. Chem. Ref. Data* 28 (1999) 1535–1672.
- [10] A. Turturro, U. Bianchi, *J. Chem. Phys.* 62 (1975) 1668–1673.
- [11] R.S. Cantor, K.A. Dill, *Macromolecules* 18 (1985) 1875–1882.
- [12] J. Baturic-Rubic, A. Rubic, *Fizika* 15 (1983) 385–399.
- [13] J. Hirschfelder, D. Stevenson, H. Eyring, *J. Chem. Phys.* 5 (1937) 896.
- [14] J.N. Murrell, A.D. Jenkins, *Properties of Liquids and Solutions*, John Wiley and Sons, Chichester, 1994.
- [15] C.L. Yaws, *Chemical Properties Handbook*, McGraw-Hill, New York, 1999.

- [16] O. Schnepp, N. Jacobi, in: G.K. Horton, A.A. Maradudin (Eds.), *Dynamical Properties of Solids*, vol. II, North Holland, Amsterdam, 1975, pp. 151–204.
- [17] G.B. Guthrie, J.P. McCullough, *J. Phys. Chem. Solids* 18 (1961) 53–61.
- [18] W.G. Rothschild, *J. Chem. Phys.* 53 (1970) 3265–3271.
- [19] A.I. Burshtein, S.I. Temkin, *Spectroscopy of Molecular Rotation in Gases and Liquids*, Cambridge University Press, Cambridge, 1994.
- [20] G. Turrell, *Spectrosc. Eur.* 9 (1997) 8–15.
- [21] P.L. Huyskens, G.G. Siegel, *Bull. Soc. Chim. Belg.* 97 (1988) 821–824.
- [22] J.R. Durig, A.W. Cox, in: J.R. Ferraro, L.J. Basile (Eds.), *Fourier Transform Infrared Spectroscopy*, vol. 1, Academic Press, New York, 1978, pp. 215–274.
- [23] W.G. Rothschild, R.M. Cavagnat, *J. Chem. Phys.* 100 (1994) 3869–3871.