VOLUME 117, NUMBER 18
MAY 10, 1995

JOURNAL
OF THE
AMERICAN
CHEMICAL
SOCIETY

Empirical Correlations between Thermodynamic Properties and Intermolecular Forces

Martin S. Westwell, Mark S. Searle, David J. Wales, and Dudley H. Williams*

Contribution from University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW U.K.

Received January 2, 1995[⊗]

Abstract: We present a previously unknown correlation between the melting point of a substance and the magnitude of the intermolecular forces in terms of the enthalpy of sublimation. This correlation only becomes apparent after removing those substances which possess internal rotors, such as long-chain organic molecules. Other correlations between the melting point, boiling point, enthalpy of sublimation, and enthalpy of vaporization are also present in the same data set.

Trouton's rule is the well-known empirical observation that the entropy of vaporization for many liquids at the normal boiling point is roughly the same ($\Delta S_{vap} \approx 90$ J K^{-1} mol^{-1}),[1] reflecting, in part, the change in molar volume in passing from the liquid to the gas phase. This immediately implies that the enthalpy of vaporization is approximately proportional to the boiling point: $\Delta H_{vap} \approx 90T_b$ J mol^{-1}. Hence the boiling point of a liquid may be taken as a convenient measure of the strength of the interatomic or intermolecular forces. Not surprisingly, the correlation does not hold quite so well for associated liquids such as amines, alcohols and, of course, water, which have larger entropies of vaporization. It is also true that there is no corresponding rule for entropies of fusion at the melting point. Here we present data which show that there is a correlation between the melting point of a substance and its intermolecular force, if effects due to internal rotors in long-chain molecules are avoided. Such a correlation may provide further insight into the relation between intermolecular forces and phase changes.

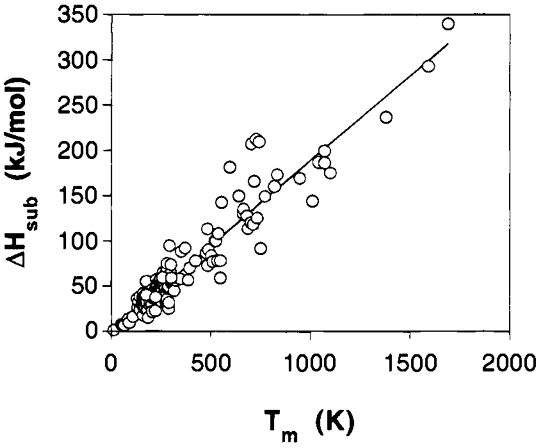

Figure 1. Plot of enthalpy of sublimation, ΔH_{sub} (determined directly or as $\Delta H_{fusion} + \Delta H_{vap}$), versus melting temperature, T_m.

Figure 1 shows the melting points of a wide variety of (organic and inorganic) crystals[2] plotted against the sublimation enthalpy (ΔH_{sub}), where known, or approximated by the sum

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[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1995.

(1) Trouton, F. *Philos. Mag.* **1884**, *18*, 54–57. See also: Dasent, W. E. *Inorganic Energetics—An Introduction*, 2nd ed.; Cambridge University Press: Cambridge, 1982; p124. Atkins, P. W. *Physical Chemistry*, 4th ed.; Oxford University Press: Oxford, 1990; p 90.

(2) Data collected for the following materials (in order of increasing melting point); H_2, F_2, O_2, N_2, carbon monoxide, SiH_4, methane, NO, methylcyclopentane, isobutane, spiropentane, cyclopropane, BF_3, methylcyclohexane, trimethylamine, HCl, PCl_3, carbon disulfide, ethylcyclohexane, THF, BCl_3, cyclohexene, Cl_2, propylbenzene, methanol, dichloromethane, toluene, propylcyclohexane, acetone, cyclopentane, bromomethane, methylamine, dimethylamine, N_2O, *trans*-1,3-dimethylcyclohexane, *trans*-1,2-dimethylcyclohexane, *cis*-1,4-dimethylcyclohexane, HBr, H_2S, HF, NH_3, *cis*-1,3-dimethylcyclohexane, SO_2, *m*-difluorobenzene, $SiCl_4$, *tert*-butylamine, 2-methylpyridine, 2,2,4,4-tetramethylpentane, H_2Se, chloroform, BrF_5, pyrrolidine, HI, $GeCl_4$, *cis*-1,2-dimethylcyclohexane, *m*-xylene, pentafluorobenzene, chlorobenzene, mesitylene, 1,2,4-trimethylbenzene, fluorobenzene, pyridine, HNO_3, thiophene, *trans*-1,4-dimethylcyclohexane, 1,1-dimethylcyclohexane, $SnCl_4$, bromobenzene, pentafluorotoluene, VCl_4, 1,2,3-trimethylbenzene, *o*-xylene, $TiCl_4$, *m*-dichlorobenzene, pyrrole, carbon tetrachloride, 3-methylpyridine, *o*-dichlorobenzene, $AsCl_3$, benzyl alcohol, benzenethiol, quinoline, piperidine, N_2O_4, Br_2, aniline, AsF_3, H_2O_2, H_2O, $POCl_3$, WF_6, hexafluorobenzene, benzene, nitrobenzene, cyclohexane, cyclohexylbenzene, formic acid, *m*-cresol, 1,4-dioxane, *p*-xylene, acetic acid, SO_3, MoF_6, VF_5, cyclohexanol, isoquinoline, *o*-cresol, $SnBr_4$, $AsBr_3$, *p*-cresol, $TiBr_4$, OsO_4, phenol, IrF_6, *p*-dichlorobenzene, $SbCl_3$, NbF_5, phenanthrene, I_2, SiI_4, TiI_4, $NbCl_5$, $WOCl_3$, GaI_3, $TaCl_5$, $BiCl_3$, $HgBr_2$, $SnCl_2$, $NbBr_5$, HgI_2, $TaBr_5$, WCl_6, $HgCl_2$, $ZnCl_2$, NaOH, $PbBr_2$, CdI_2, $ZnBr_2$, PbI_2, $BeCl_2$, TlCl, AgBr, TlI, Tl_2S, AgCl, TlBr, LiOH, BeI_2, $PbCl_2$, LiBr, $CdCl_2$, $FeCl_2$, $CaBr_2$, $ThCl_4$, NaCl, MoO_3, PbF_2, CdF_2, BaF_2, CaF_2.

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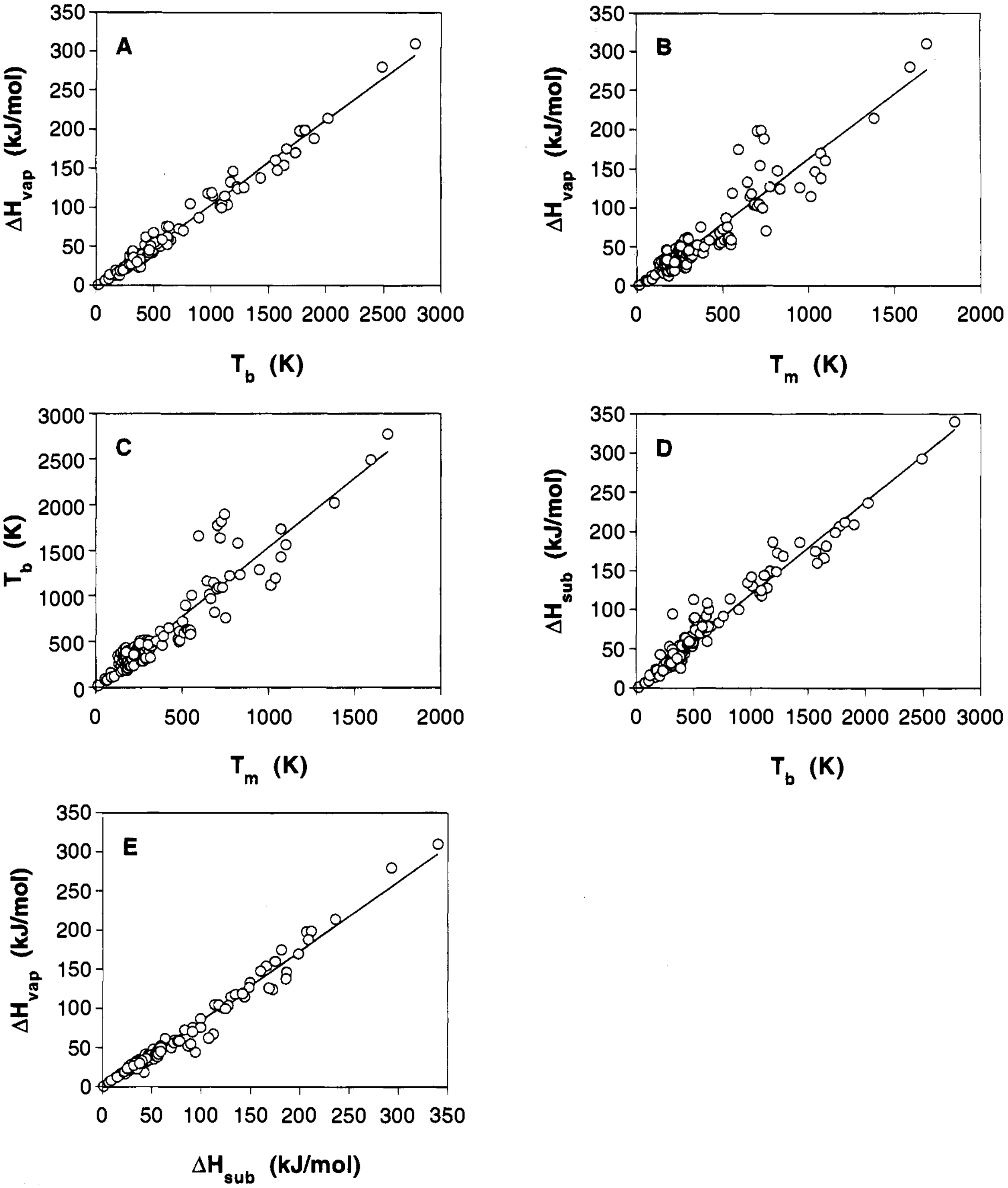

Figure 2. Plots showing correlations between the thermodynamic parameters for the 160 "normal" substances. (A) T_b vs ΔH_{vap} (representing Trouton's rule); (B) T_m vs ΔH_{vap}; (C) T_m vs T_b; (D) T_b vs ΔH_{sub}; (E) ΔH_{sub} vs ΔH_{vap}.

of the enthalpies of fusion and vaporization (data from refs 3 and 4). The linear correlation coefficient (0.95) gives the empirical relationship $\Delta H_{sub} \approx 188T_m$ J mol^{-1} (Table 1). Although the trend is clear, there is sufficient scatter that ΔH_{sub} is only a crude guide to the melting point (T_m). However, it is striking that although only a small and variable fraction (0.04–0.1) of the binding energy of the solid is lost upon melting (reflecting the ratio $\Delta H_{fusion}/\Delta H_{sub}$), the melting point ($T_m$) correlates with the strength of the intermolecular forces (ΔH_{sub}).

It is important to note that all long-chain organic molecules (with more than two internal rotations) have been excluded from the data set together with the 12 compounds which were found to deviate from Trouton's rule.[5] For the long-chain organic molecules, the deviation is expected, since the associated configurational entropy will contribute to the total entropy change so as to lower the melting temperature. In some of the cases listed,[5] the reason for the deviation is less obvious, and may need further investigation.

The correlation of sublimation energy (ΔH_{sub}) and melting point (T_m) carries with it some further implications. Since the enthalpy of fusion is generally an order of magnitude smaller than the enthalpy of vaporization, and neglecting the integrated

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(3) Lide, D. R. *Handbook of Chemistry and Physics*, 74th ed.; CRC Press Inc.: Boca Raton, FL, 1993.

(4) Dasent, W. E. *Inorganic Energetics—An Introduction*, 2nd ed.; Cambridge University Press: Cambridge, 1982; pp 95 and 123.

(5) Materials for which the collected data gave large deviations from Trouton's Rule (in order of increasing melting point); 2,6-xylenol, 3,4-xylenol, 3,5-xylenol, $GaCl_3$, $AlBr_3$, $GaBr_3$, AlI_3, $MoCl_5$, AgI, $MgCl_2$, $CrCl_2$, LiF

Table 1. Correlations Observed between Various Thermodynamic Parameters Fitted Using Linear Regression Analysis to the Relationship $y = mx + c$[a]

y	x	m	c	R
ΔH_{sub}	T_m	0.188	0.522	0.95
ΔH_{vap}	T_b	0.108	−5.08	0.99
ΔH_{vap}	T_m	0.166	−3.99	0.93
T_b	T_m	1.52	14.6	0.93
ΔH_{sub}	T_b	0.119	1.38	0.98
ΔH_{vap}	ΔH_{sub}	0.889	−4.75	0.99

[a] Parameters y, x, m, c, and R are listed. There are 160 data points in each plot.[2]

heat capacity, we can approximate:

$$\Delta H_{sub} \approx \Delta H_{vap} + \Delta H_{fusion}$$

$\Delta H_{vap} \gg \Delta H_{fusion}$

$$\Delta H_{sub} \approx \Delta H_{vap}$$

using Trouton's rule

$$\Delta H_{sub} \approx 90 T_b \text{ J mol}^{-1}$$

and from Figure 1, there is a rough proportionality between ΔH_{sub} and T_m.

Hence, for compounds which obey Trouton's rule, have few or zero internal rotors, and do not possess the high symmetry which allows an overall rotation in the crystal, we would expect correlations between all four of the following parameters: T_m, T_b, ΔH_{sub}, and ΔH_{vap}. Indeed, good linear plots for these relationships are found (Figure 2) and the correlation coefficients for linear regression between all six possible pairs are given in Table 1.

The validity of Trouton's rule reflects the fact that the entropy of vaporization is approximately constant for many substances. If the entropy of melting were constant we would expect a correlation between ΔH_{fusion} and T_m. However, as shown in Figure 3, this correlation is very poor. Linear regression gives a best fit of $\Delta H_{fusion} = 0.0216 T_m + 4.52$ kJ mol^{-1} with a correlation coefficient of only 0.603.

In conclusion, we have shown that there are significant correlations between the fundamental thermodynamic properties of boiling point, enthalpy of vaporization, enthalpy of sublimation, and also melting point for a remarkably wide range of materials. One reasonable interpretation of this result is that all four properties provide a measure of the strength of the intermolecular forces, remarkably so in the case of the melting point since so little of the expression of the intermolecular force is lost upon melting. How can these observations be reconciled?

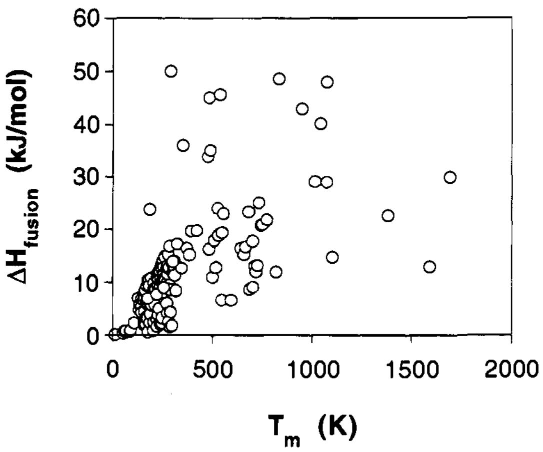

Figure 3. Plot of enthalpy of fusion (ΔH_{fusion}) versus melting temperature (T_m).

We suggest that the onset of diffusive motion is determined by some relatively constant fraction of the intermolecular potential. In the crystal, below the melting temperature, there is a large barrier to positional exchange, and each particle is confined to its own lattice site. Above the melting temperature, the liquid has only local, quasicrystalline structure as shown by X-ray diffraction studies.[6] This positional disorder is entropically favorable and enables the enthalpic barrier to be overcome at sufficiently high temperature. The transition between the crystal and the liquid is a cooperative one because any local disruption in the structure gives the nearby particles more freedom to move. Hence, at a temperature below, but very close to, the melting temperature the enthalpic barrier to positional exchange, averaged over the large-amplitude vibrations of individual molecules, starts to fall rapidly. Increase in motion and reduction in average potential energy are cooperatively linked, and this results in the sharp melting transition. That is, the thermodynamic descriptions just below and above T_m are related to the rate of exchange of adjacent particles since the increased occupancy of higher potential energy configurations leading to particle exchange is weighted by the thermodynamic parameters. Hence, it is not unreasonable that the melting point itself should also reflect the magnitude of the intermolecular forces.

Acknowledgment. M.S.W., M.S.S., and D.H.W. thank EPSRC and Glaxo (UK) for financial support. D.J.W. is a Royal Society Research Fellow.

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(6) Guinier, A.; Jullien, R. *The Solid State—from superconductors to super alloys*; Oxford University Press: Oxford, 1989; pp 254−256