

ENTROPY OF DISORDER AT MELTING OF SUBSTANCES WITH GENERAL SHAPE OF MOLECULES

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Abstract

Melting of substances with a general shape of rigid and nonrigid molecules is investigated. Different contributions to the entropy of melting are rigorously calculated by means of particular regularities found for liquid n-alkanes. A semiempirical correlation between the entropy of disorder and degrees of freedom of molecular motions, which significantly change at melting, is confirmed.

INTRODUCTION

A common entropy of disorder S_d at melting of simple substances with spherical-like¹⁻³ as well as with linear-like molecules³, has been established previously, to be about $0.7 R$ and $2.5 R$, respectively (R being the gas constant). Both values have been obtained from experimentally determined linear correlation between the entropy of melting S_m and the relative volume change $\Delta V/V$ at normal and high pressures¹⁻³. The entropy of disorder has been put in connection with numbers of rotational and translational degrees of freedom, r and t , respectively, corresponding to the particular types of molecular motions, activated at melting. It has been introduced

$$S_d = S_{op} = R \ln (1 + r) (1 + t) \quad (1)$$

from which one may obtain $R \ln 2$ and $R \ln 12$ for mentioned groups, respectively, in good agreement with experimentally deduced values³. Maximal entropy of such an orientational and positional disorder $S_{opm} = R \ln 16$ is expected for substances with rigid molecules of general shape, due to all combinations of their, more or less restricted, rotational and translational motions ($r = t = 3$) at melting. However, this third discrete value of S_d was experimentally (from melting under pressure) very poorly indicated⁴.

Therefore, a more detailed investigation of the substances with non-rigid molecules is included. Intra-molecular changes enlarge the entropy of disorder, but it may be possible, using certain regularities for similar compounds, to separate the basic inter-molecular disorder entropy term. An accurate extraction of this term is considered for n-alkanes, without any solid-to-solid (s-s) phase transition, though not from melting under pressure⁴⁾, because the necessary data are too scanty⁵⁾.

ANALYSIS OF EXPERIMENTAL DATA

A general definition of volume contribution to the entropy of melting $S_v = \int (\partial S / \partial V)_{T_m} dV$ will be used. By means of the thermal pressure coefficient γ_m of liquid at the temperature of melting T_m at normal pressure P_0 , S_v may be approximated by

$$S_v \cong \gamma_m \Delta V \tag{2}$$

using the equality: $(\partial S / \partial V)_T = (\partial P / \partial T)_V = \gamma^{3,4)}$. Due to the onset of internal hindered rotation around C-C bonds of chain molecules $C_n H_{2n+2}$ (further denoted as C_n), both disorder and volume terms of melting entropy for n-alkanes are expected to rise with n. For resolving these terms, very accurate determination of γ_m is necessary for each member of considered homologous series from C_5 to C_{20} . Unfortunately, experimental data for determining γ are also incomplete and related to temperatures equal or higher than the room temperature. From measured V-P isothermes^{6, 7)}, P-T isochores are evaluated, and from them $\gamma = f(T)_{P_0}$ and $\gamma = f(P)_{T_m}$ are deduced. By means of the extrapolations to T_m or P_0 , respectively, values of γ_m are obtained for $n = 7, 12, 18, 20$. Directly measured $\gamma = f(T)_{P_0}$, sufficiently accurate for the extrapolation to T_m , are available for C_{14} ⁸⁾, C_{16} ⁹⁾ and C_{20} ¹⁰⁾. For the remaining members ($n = 5, 6, 8, 10$), γ_m are determined by means of the adequate extra- and inter-polations, using particular regularities, which will be explained elsewhere. Values of γ_m are correlated with n^{-1} , and, as shown in Fig. 1, within the experimental accuracy, a straight line appears, i.e.

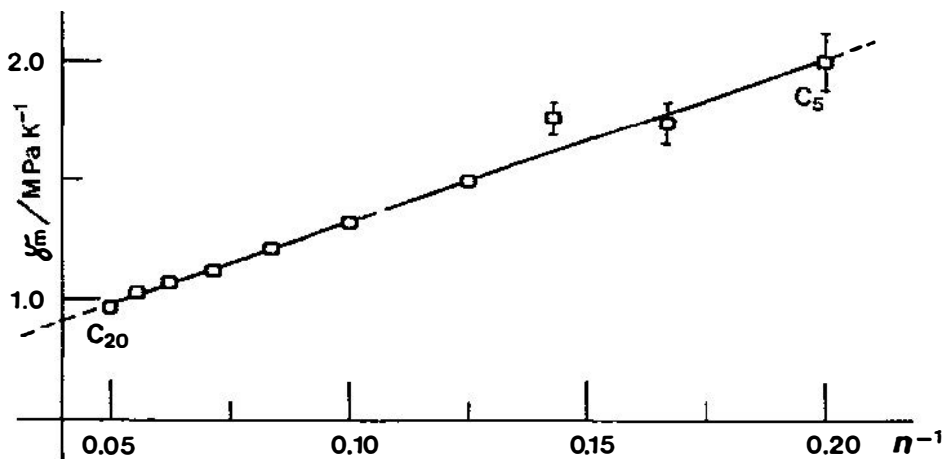


Fig. 1. Thermal pressure coefficient γ_m of n-alkanes $C_n H_{2n+2}$ in dependence of n^{-1} .

$$\gamma_m = \gamma_0 + a n^{-1} \quad (3)$$

which has not been verified before. Mean values of $\gamma_m(n)$, obtained by the least-square (1-s) method, are used for the calculation of $S_v(n)$, according to eq. (2), together with directly measured volume changes ΔV ^{5, 11-13}. Interpolated values of ΔV are used for C_{10} , C_{14} and C_{16} . From systematized experimental melting data¹⁴, the entropy of melting S_m is calculated. The entropy of disorder follows then from $S_d = S_m - S_v$. This procedure is shown in Fig. 2. A linear increase of melting entropy S_m with n , as well as of its both components, S_d and S_v , is evident. Some deviations of S_v appear only for shorter members with $n < 8$, which do not crystallize in the triclinic form, as do all the other considered members¹⁴. The rotations around the and C-C bonds cannot change the conformation of molecule. Thus, only $(n-3)$ bonds remain effective for conformational contribution S_{cd} to the entropy of disorder, i.e.

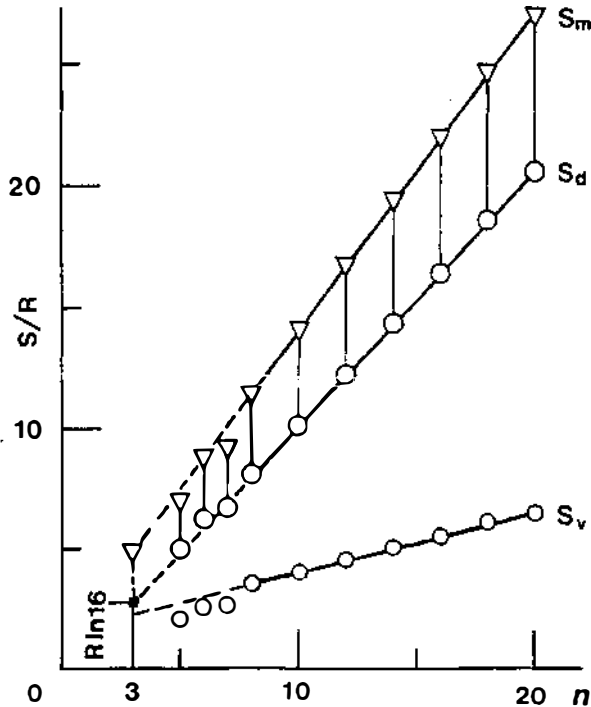


Fig. 2. Dependence of the entropy of melting S_m , and its components S_d and S_v , on the number n of C atoms in C_nH_{2n+2} .

$$S_d(n) = S_{opm} + S_{cd}(n) = S_{opm} + (n-3) S'_{cd} \quad (4)$$

where S'_{cd} is specific contribution per monomer.

CONCLUSION

The significant result of such an approach is an arising of a common entropy of disorder S_{opm} . This entropy corresponds to the total entropy of disorder for propane ($n = 3$) with unchanged molecules after melting. The $(1 - s)$ method gives $S_{\text{opm}} = 2.78 R$ with rms error $\pm 0.07 R$, which is in surprising agreement with the expected value $R1n16 = 2.77 R$, according to eq. (1). Thus, preliminary estimations of $S_{\text{opm}}^{(4)}$ are now more exactly confirmed.

Finally, it should be emphasized, that a general theoretical approach to the melting entropy is not found until now. Therefore, it is interesting and useful to know that an essential part of the disorder entropy may be deduced, at last, for the substances belonging to a definite group. Discrete values of entropy $R1n2$, $R1n12$ and $R1n16$ for substances with spherical, linear and general shape of molecules, characterize fundamental orientational and positional disorder, in accordance with eq. (1).

Further experimental verification will be extended by n -alkanes with (s-s) transitions for which promising preliminary results are yet obtained¹⁵⁾, together with some other appropriate organic compounds. Also, the eq. (1) requires a theoretical explanation, which is a still open problem.

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