Melting Point and Molecular Symmetry

R. J. C. Brown*

Department of Chemistry, Queen's University, Kingston, ON K7L 3N6, Canada; *brownrjc@chem.queensu.ca*

R. F. C. Brown

School of Chemistry, University of Melbourne, Victoria 3052, Australia

The melting point of a pure compound is a familiar property because the melting point is often used as evidence when identifying a compound and as an indicator of purity. But beyond that, little consideration is given in textbooks to the melting point and its relationship to the other properties of a substance. In part this is because there is no simple molecular-scale model for the liquid state, as there is for the gaseous and crystalline states. Even at the thermodynamic level, it is hard to find a useful rule, since the entropy change of fusion varies considerably from one crystal to another. By comparison, the entropy change of boiling is relatively constant for a wide range of liquids, as stated in Trouton's rule, and the exceptional cases of hydrogen-bonded liquids are readily accommodated by a slight modification to the rule.

The origin of the present discussion was a simple question about melting points: why does methane have such a high melting point compared to the higher alkanes? The simple answer is that methane is a highly symmetrical molecule. This paper is a consideration of that answer and the empirical rule on which it is based.

Carnelley's Rule, and Evidence in Support of It

For molecular substances, there is a simple and striking empirical rule relating the melting point to the symmetry of the molecules of the substance: *High molecular symmetry is associated with high melting point.*

The rule is counter-intuitive. Many highly symmetrical molecules have zero electric dipole moments, and in some cases zero quadrupole moments as well, so the forces holding the molecules together in the crystal should be weaker than for less symmetrical molecules. Weaker intermolecular forces should mean a lower melting point, since thermal motion can more easily overcome these forces holding the molecules in the crystal. For this reason, it is interesting to investigate

the range of validity of the rule and the underlying thermodynamics on which it is based.

The relationship between melting point and molecular symmetry has been known since the two-part paper published by Thomas Carnelley in 1882 (*1, 2*). Carnelley reviewed approximately 15,000 melting points and stated the rule in the following form:

> That of two or more isomeric compounds, those whose atoms are the *more symmetrically* and the *more compactly* arranged melt higher than those in which the atomic arrangement is asymmetrical or in the form of long chains.

It therefore seems reasonable to the call the rule Carnelley's rule. Despite its long history and potential usefulness, the rule does not appear to be well known at the present time. Carnelley also gave a similar rule relating solubility to molecular symmetry (*2*).

Further work was reported by Franchimont in 1897 (*3*) and by Michael in 1895 and 1918 (*4–6*). Hückel mentioned the rule in his 1931 textbook on organic chemistry (*7*). Timmermans discussed melting of molecular crystals in a brief review article in 1961 (*8*), but while there is considerable discussion of the entropy of fusion and the nature of crystals formed from globular molecules, the general rule relating melting point to molecular symmetry is not mentioned explicitly. Bondi reviewed the relationship between the entropy change of fusion and molecular structure (*9*). A number of authors of textbooks on organic chemistry, such as Noller (*10*), discuss melting points of alkanes briefly. Canceill et al. reported the melting points of some isomeric polyaromatic compounds and discussed the effects of molecular symmetry (*11*). Smith reviewed the orientational disorder and melting of disordered plastic crystals (*12*). Yalkowsky and coworkers discussed the estimation of entropy of fusion of organic compounds from molecular structure (*13*) and explicitly included

Table 1. Melting Points of Structural Isomers

Formula	Isomer					
	Name	mp/K	Name	mp/K	Name	mp/K
C_5H_{12}	pentane	143.5	methylbutane	113.3	2,2-dimethylpropane	256.6
C_8H_{18}	octane	216.4	3-methylheptane	152.7	hexamethylethane	373.9
C_6H_{12}	methylcyclopentane	130.7	2,3-dimethyl-2-butene	198.6	cyclohexane	279.8
C_7H_{14}	methylcyclohexane	146.6	1-heptene	153.5	cycloheptane	265.2
$C_2H_4Cl_2$	1,1-dichloroethane	176.2	1,2-dichloroethane	237.7	–	–
C_3H_7OH	1-propanol	147.1	2-propanol	183.7	–	–
C_4H_9OH	1-butanol	183.3	2-methyl-1-propanol	165	2-methyl-2-propanol	298.5
$C_6H_4Cl_2$	*o*-dichlorobenzene	256.5	*m*-dichlorobenzene	248.4	*p*-dichlorobenzene	325.9
C_8H_{10}	*o*-xylene	248.0	*m*-xylene	225.4	*p*-xylene	286.4
C_8H_{16}	ethylcyclohexane	161.9	1,1-dimethylcyclohexane	239.9	cyclooctane	288.0
C_8H_8	cyclooctatetraene	268.5	cubane	405	–	–
$C_{14}H_{10}$	phenanthrene	372.4	anthracene	488	–	–

a rotational pseudo-symmetry number in their method of statistical prediction of fusion point (*14*). Gavezzotti discussed the relationship between molecular symmetry, crystal packing, and melting point (*15*).

Empirical evidence supporting Carnelley's rule can be assembled from any extensive listing of melting points, such as the *Handbook of Chemistry and Physics* (*16*). Among similar substances, melting points generally increase with molar mass, and so the most convincing evidence for the effect of molecular symmetry is found among structural isomers. An extensive tabulation and analysis of data for a group of benzene derivatives is given in several of the above references.

In Table 1, the melting points of a number of pairs and triplets of structural isomers are compared. In every case the substance that, by common-sense criteria, has the highest molecular symmetry has the highest melting point, with differences of 100° or more in some cases.

Melting point usually increases with molar mass, except where the increase in molar mass is due to a substitution that makes the molecule less symmetrical. In Table 2, the melting points of benzene and some of its derivatives are listed. Singly substituted benzene derivatives have lower melting points than benzene itself despite the increase in molar mass. An exception is phenol, which is a hydrogen-bonded crystal. Among disubstituted derivatives of benzene, Table 1 shows that the melting point of the more symmetrical para compound is higher than those of the ortho and meta compounds.

Pyridine has a lower melting point than benzene, consistent with its lower symmetry. As compared with pyridine, the higher symmetry compounds diazine and triazine have increased melting points, as the order of the major symmetry axis increases.

Table 2. Melting Points of Benzene and Related Molecules

Formula	Name	mp/K
C_6H_6	benzene	278.7
$C_6H_5CH_3$	toluene	178.2
C_6H_5F	fluorobenzene	231
C_6H_5Cl	chlorobenzene	228.0
C_6H_5Br	bromobenzene	242.6
C_6H_5I	iodobenzene	241.9
C_6H_5OH	phenol	314.1
C_6F_6	hexafluorobenzene	278.5
C_6F_5H	pentafluorobenzene	225.9
C_5H_5N	pyridine	231.6
$C_4H_4N_2$	1,4-diazine	328.2
$C_3H_3N_3$	1,3,5-triazine	358.2

Table 3. Melting Points of Cage Molecules

Formula	Name	mp/K
$C_{10}H_{16}$	adamantane	543
$C_6H_{12}N_4$	hexamethylenetetramine	>523
C_{60}	buckminsterfullerene	high
C_8H_8	cubane	405
$C_{10}H_{16}O$	camphor	452

It is very striking that cage molecules have higher melting points than would be expected on the basis of molar mass, and some data are contained in Table 3. Many cage molecules, such as adamantane and cubane, are of high symmetry.

The Thermodynamics of Melting

Melting, or fusion, is the phase transition in which the crystalline phase changes to the liquid phase. At a fixed pressure, the melting point of a crystal of a pure substance is the temperature at which the crystalline and liquid phases are in thermodynamic equilibrium. The heat required to melt the crystal is absorbed at a constant (or nearly constant) temperature and is called the latent heat of melting, or latent heat of fusion. Since melting takes place at a fixed pressure, the latent heat of fusion is equal to the enthalpy change of fusion.

When a crystal melts, there is an increase in both the enthalpy and the entropy of the substance. The enthalpy change of fusion is a measure of the amount of energy required to convert the crystal to a liquid. The entropy change of fusion is a measure of the increase of randomness or disorder when the molecules are released from the constraints of the crystal into the relative freedom of the liquid. The enthalpy change and the entropy change are conveniently measured on a per mole basis, and the molar entropy change of fusion can be expressed as a multiple of the gas constant *R*.

Because the crystalline phase is converted reversibly to the liquid phase at the melting point, the molar entropy change of fusion ΔS_{fus} is equal to the molar enthalpy change of fusion ΔH_{fus} divided by the melting point temperature T_{fus} (*17*):

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_{fus}} \tag{1}$$

Equation 1 can be rearranged into the equivalent form

$$T_{fus} = \frac{\Delta H_{fus}}{\Delta S_{fus}} \tag{2}$$

From eq 2 it can be seen that the melting point can be expressed as the ratio of two quantities that are to some extent independent of each other and express different aspects of the melting process.

The Gibbs Energy

Equation 2 shows that a high melting point can be due to either a high enthalpy of fusion ΔH_{fus}, or a low entropy of fusion ΔS_{fus}, or both. It is useful to consider the reason for this in a little more detail. Melting occurs when the molar Gibbs energy of the crystal is equal to the molar Gibbs energy of the liquid. If the Gibbs energies of both the crystalline phase and the liquid phase are plotted as functions of temperature, the melting point is the temperature at which the two curves intersect.

The temperature dependence of the molar Gibbs energy *G* of a substance in a particular phase depends on the molar entropy *S* through the relationship (*17*)

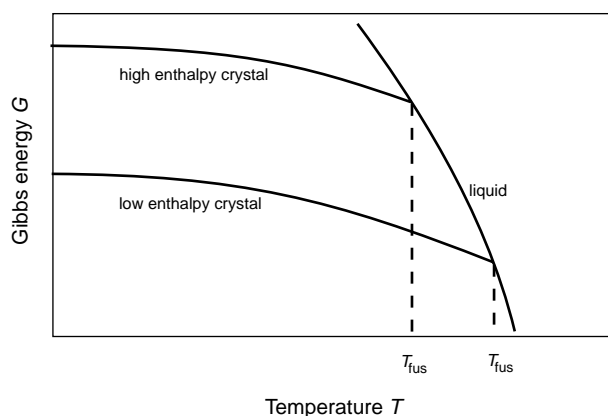$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{3}$$

Figure 1. The molar Gibbs energy of a pure substance in its crystal-line and liquid states as a function of temperature, starting at absolute zero. The melting point is the temperature T_{fus} at which the curve for the crystal crosses the curve for the liquid. To illustrate the effect of the molar enthalpy of the crystal on the melting point, two curves are shown for the crystalline phase, corresponding to different hypothetical values of the molar enthalpy but with equal values of the molar entropy at all temperatures. The crystal with lower molar enthalpy is "more stable" than the other crystal; it has a larger molar enthalpy change of fusion, and a higher melting point.
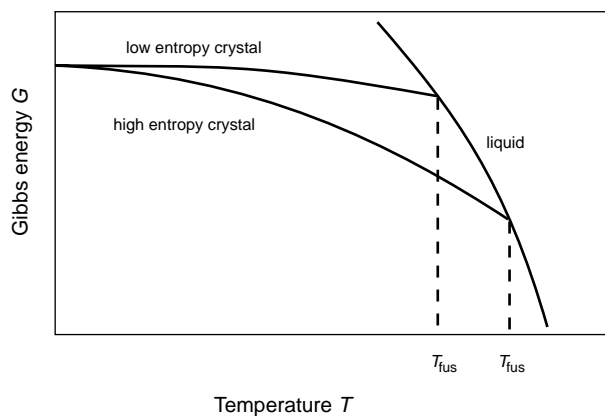

Figure 2. The molar Gibbs energy of a pure substance in its crystal-line and liquid states as a function of temperature, starting at absolute zero. To illustrate the effect of the molar entropy of the crystal on the melting point, two curves are shown for the crystalline phase, corresponding to different hypothetical values of the molar entropy but with equal values of the molar enthalpy at absolute zero. The crystal with the higher molar entropy is more disordered than the other crystal; it has a smaller molar entropy change of fusion and a higher melting point.

Since the molar entropy S is positive, the graph of molar Gibbs energy G as a function of temperature T has a negative slope, and the larger the entropy, the steeper the slope. By the third law of thermodynamics, the entropy of a crystal approaches zero at very low temperatures, and the slope of the graph of Gibbs energy approaches zero as the temperature approaches absolute zero. As the temperature increases, the entropy increases and the slope of the curve becomes more negative. The curve is therefore concave downwards.

As the temperature is increased, the Gibbs energy of a liquid decreases more rapidly than that of the same substance in the crystalline phase because the entropy of the liquid is higher. Equilibrium between crystalline and liquid phases is reached when the molar Gibbs energies of the two phases are equal. Hence at the melting point, the graphs of the molar Gibbs energies of the crystalline and liquid phases cross with different slopes because the entropies of the two phases are different.

Consider a hypothetical substance for which the enthalpy of the crystal can be varied while holding constant three other quantities: the entropy of the crystal and both the enthalpy and the entropy of the liquid. In a graph of Gibbs energy as a function of temperature, changing the enthalpy of the crystal (but not the entropy) corresponds to shifting the curve for the crystal up and down without change of shape. Figure 1 shows the graph of Gibbs energy for the liquid and two graphs for the crystal corresponding to two hypothetical values of the enthalpy. The figure shows that decreasing the enthalpy of the crystal increases the temperature at which the crystal curve intersects the liquid curve, and hence increases the melting point. Decreasing the enthalpy of the crystal while holding the enthalpy of the liquid constant increases the enthalpy change of fusion. Hence the higher melting point is consistent with eq 2 and with the intuitive idea that a high

temperature is needed to melt a crystal that is tightly bound relative to the liquid.

It should be noticed that in Figure 1 the curves for the crystal do not extend above the melting point, since it is impossible to "superheat" a crystal above its melting point. However, the liquid curve extends to temperatures below the melting point, since liquids can be "supercooled" in many cases.

Now consider the effect of the entropy change of fusion on the melting point. Consider another hypothetical substance, for which the entropy of the crystalline phase can be varied while holding constant the enthalpy of the crystal and both the enthalpy and the entropy of the liquid. In a graph of Gibbs energy as a function of temperature, changing the entropy changes the slope of the curve.

Figure 2 shows the graph of Gibbs energy for the liquid and two graphs for the crystal corresponding to two hypothetical values of the entropy. The figure shows that increasing the entropy of the crystal increases slope of the Gibbs energy curve for the crystal, increases the temperature at which the curve for the crystal intersects the curve for the liquid, and hence increases the melting point.

Increasing the entropy of the crystal while holding the entropy of the liquid constant decreases the entropy change of fusion. Hence the higher melting point is consistent with eq 2. However, the effect on the melting point of varying the entropy change of fusion is less easy to reconcile with intuition than the effect of varying the enthalpy change of fusion, which was discussed above.

The entropy change of fusion is equal to the difference, at the melting point, between the slopes of the graphs of Gibbs energy for the crystalline and liquid phases. Figure 2 shows that the change of slope at the melting point is smaller for the crystal with the higher entropy.

Symmetry and Disorder in Crystals and Liquids

An important distinction between the crystalline and liquid states is based on symmetry. Macroscopically, a liquid is isotropic, which means that its physical properties are the same in all directions. Another way of saying this is that a liquid is symmetric under all rotations. The molecules in a liquid are not restricted to fixed positions or orientations, and so every direction in the liquid is equivalent to every other direction. A liquid is isotropic because of the translational and rotational disorder of the molecules in it.

Although the molecules in a liquid are largely disordered, there is some short-range order that extends over distances of approximately several molecular diameters. This is because the molecules tend to stay close together and line up with each other.

In a crystal, the molecules are arranged in a repetitive pattern that extends over long distances through the crystal. The order in a crystal is described as long range. The ordered arrangement of the molecules in a crystal has characteristic symmetry, which is described by the space group of the crystal. The molecules are located at sites of specific symmetry, which must be consistent with the space group and usually matches the symmetry of the molecules. However there is no unique relationship between the space group of a crystal and the point group of the molecules. This complicates any attempt to provide a theoretical microscopic model for the relationship between molecular symmetry and melting point (*15*).

There are two kinds of order in a crystal: translational order, which describes the relative positions of the molecules, and orientational order, which describes their relative orientations. When a normal crystal melts, both the rotational order and the translational order of the molecules are lost. However, in some cases the translational order and the rotational order are lost at different temperatures. Many crystals consisting of nearly spherical, or globular, molecules become rotationally disordered below the melting point, while the translational order is retained. Such crystals are called plastic crystals because they are soft and easily deformed (*8, 12, 18*). On the other hand, if the translational order is lost at a lower temperature than the orientational order, then a liquid crystal is formed.

In plastic crystals the molecules rotate rapidly at temperatures below the melting point. In a few special cases, such as methane, molecules rotate in the crystal by means of quantum tunneling even at the lowest temperatures, but at ordinary temperatures rotation takes place by thermally activated jumps over an energy barrier. The rate of thermally activated rotation increases with increasing temperature according to the Arrhenius equation.

In some cases there is a phase transition at a sharply defined temperature, from an ordered crystalline phase in which the molecules do not rotate to a disordered crystalline phase in which they rotate rapidly. Usually the high-temperature phase has higher symmetry than the low-temperature phase; often the high-temperature phase is face-centered cubic or hexagonal close-packed if the molecules are rotating nearly freely. The transition from one crystalline phase to another involves a latent heat of transition or an increased heat capacity in the neighborhood of the transition. Changes in rotational and translational order are readily followed by

NMR line width and relaxation time, as long as suitable nuclei are available, or by heat capacity measurements (*18*).

In some crystals there is an order–disorder transformation close to the melting point, examples being ethane, with a transition only 0.5 K below the melting point at 90 K (*19*), and cubane, with a transition 11 K below the melting point of 405 K (*20*).

The onset of rotational disorder may also occur gradually over a range of temperatures, without a phase transition. An example of a compound that shows this behavior is 1,2-dichloroethane, which disorders over a range of temperature without passing through a phase transition, whereas 1,2-dibromoethane disorders at a phase transition (*21*).

Whether or not there is a phase transition, the existence of rotational molecular motion in a crystal increases molecular disorder and increases the entropy of the crystal. Since at the melting point the molecules have already gained their rotational entropy, only the translational degrees of freedom contribute to the entropy change of fusion. Hence, in a rotationally disordered crystal, the entropy change of fusion is smaller than expected when both rotational and translational order are lost at the melting point.

The effect of rotational disorder is therefore to increase the melting point by lowering the entropy change of fusion. For disordered crystals formed from highly symmetrical or globular molecules, Carnelley's rule works because of a low entropy change of fusion.

Symmetry and Flexibility of Molecules

All the information about the symmetry of a molecule is summarized by giving its point group. But two structural isomers may have totally unrelated point groups, and the point group may not be very useful in deciding which of two molecules is the more symmetrical. One possible measure is the rotational symmetry number that appears in the rotational partition function in statistical mechanics; but this takes no account of inversion-center or mirror-plane symmetry, which influence molecular properties such as electric dipole moment. Abramowitz and Yalkowsky used a rotational pseudo-symmetry number based on the assumption that groups or atoms of nearly equal size are sterically equivalent for the purpose of determining the symmetry number (*14*).

We also have to consider the possibility that a molecule may be flexible, with a number of different conformations that are accessible thermally at the melting point. The symmetry of a flexible molecule with internal degrees of freedom may be described in terms of group theory (*22*), but this may not be easy except for small molecules.

A flexible molecule with internal degrees of freedom is usually constrained to a single conformation in the crystal but can adopt various conformations in the liquid, where there are no constraints imposed on the molecule by the presence of stationary neighbors. Hence such a crystal will have a higher than usual entropy of fusion. The straight-chain hydrocarbons are the good examples and are discussed below.

Hence in some cases the relationship between molecular symmetry and melting point must be based on a qualitative judgement in comparing the symmetry of molecules.

The Enthalpy/Entropy Diagram

When considering trends in melting points, it is instructive to consider separately the enthalpy change and the entropy change of fusion, in place of the melting point itself. One way to do this is to plot the enthalpy change and the entropy change of fusion for each substance on a graph. If the entropy change is plotted horizontally, as abscissa, and the enthalpy change is plotted vertically, as ordinate, then the melting point is equal to the slope of the line from the origin to the point representing the data. The higher the melting point, the steeper the slope of the line. In such a graph, compounds with equal melting points lie on a single line passing through the origin. This diagram will be referred to as an enthalpy/entropy diagram.

Figure 3 shows an enthalpy/entropy diagram for three hypothetical compounds, which are indicated by the letters A, B, and C. Compounds B and C melt at the same temperature and compound A melts at a lower temperature. The graph illustrates how enthalpy and entropy effects can independently affect the melting point. Compound B melts at a higher temperature than compound A because the enthalpy change of fusion is higher, although the entropy changes for the two compounds are equal. Compound C melts at a higher temperature than compound A because the entropy change of fusion is lower. Other compounds that have the same melting points as compounds B and C may have different combinations of enthalpy change and entropy change, as long as the ratio $\Delta H_{fus}/\Delta S_{fus}$ is the same.

The Application of Carnelley's Rule to Various Classes of Crystal

We now apply these observations to the question of the relationship between molecular symmetry and melting point. For this purpose, it is useful to discuss the various types of crystal separately. Four classes of molecular crystal can be distinguished. In addition, recently developed low-melting ionic materials that are liquid at room temperature are included in the discussion. Each type of crystal has a characteristic entropy change of fusion. We will see that Carnelley's rule relating melting point to symmetry applies in different cases for rather different reasons.

In the following the entropy change of fusion will be quoted in the form $\Delta S_{fus}/R$, so as to give the entropy change in a dimensionless form.

Class 1. Ordered Crystals of Rigid Molecules

This is the normal case of melting, and a survey of tabulated data shows that for this class of crystal the entropy change of fusion is approximately $\Delta S_{fus}/R \approx 7$. Walden stated this rule in 1908 (23). Walden's rule may be compared with Trouton's rule, which states that the entropy change of boiling lies in the range $\Delta S_b/R \approx 9$ for non-hydrogen-bonded liquids (17, 24). As discussed below, Walden's rule can be relied on only for ordered crystals of rigid molecules.

Figure 4 shows the enthalpy/entropy diagram for two groups of isomers that form ordered crystals. In both the dichlorobenzenes and the xylenes, the highest-melting-point isomer is the para compound, which is the most symmetrical. In the case of the xylenes, the methyl groups are rotationally
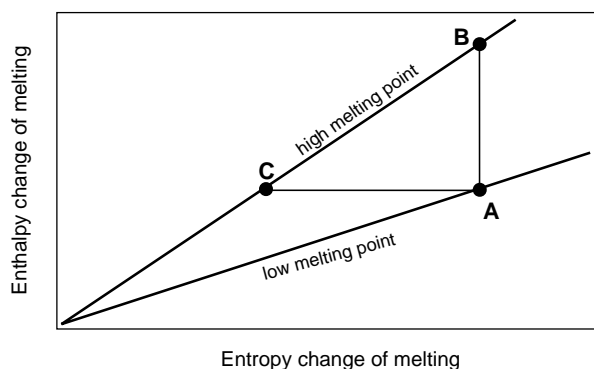
Figure 3. In this graph, the enthalpy change of fusion is plotted as a function of the entropy change of fusion for three compounds, which are identified by the letters A, B, and C. Each compound is represented by a single point, and the melting point is the slope of the line from the origin to that point, according to eq 2. All compounds with a particular melting point lie on a single straight line. The melting point of compound A is lower than the melting points of compounds B and C, which are equal.
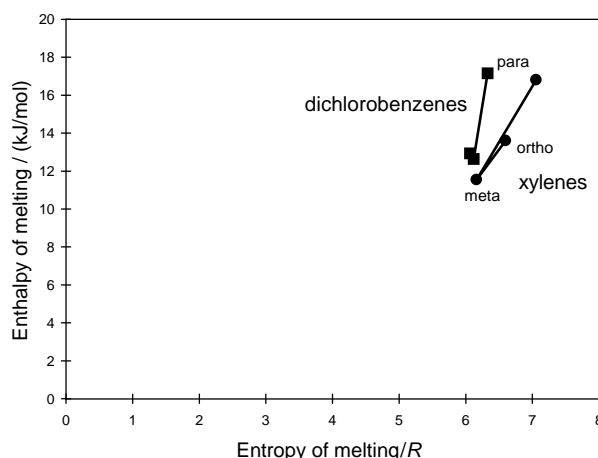
Figure 4. The enthalpy/entropy diagram for dichlorobenzenes and xylenes.
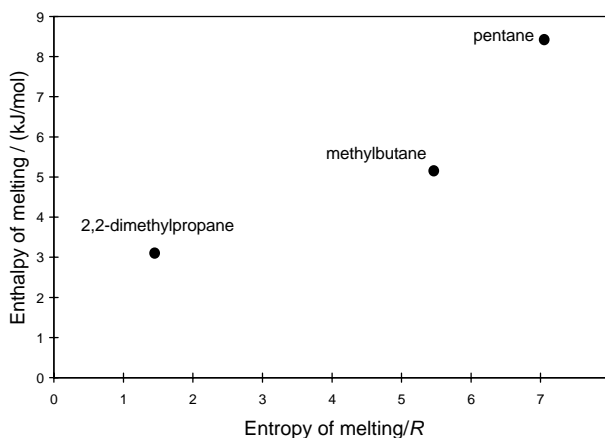
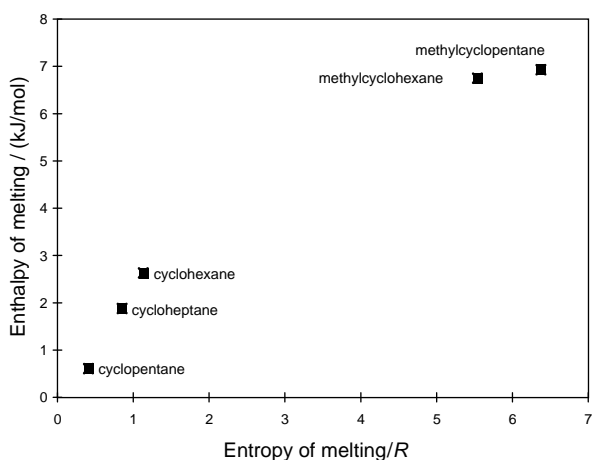Figure 5. The enthalpy/entropy diagram for pentane isomers.

Figure 6. The enthalpy/entropy diagram for cyclic hydrocarbons and derivatives. The cyclic molecules are globular and rotationally disordered below the melting point. Addition of a methyl group to the ring is enough to prevent molecular reorientation.
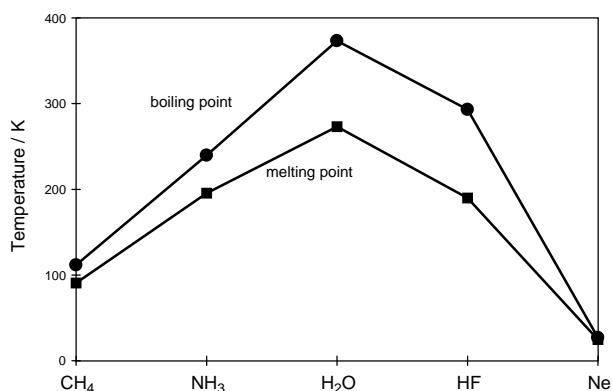

Figure 7. Melting points and boiling points of the second-row hydrides XH_n and Ne plotted as a function of increasing group number of the element X.
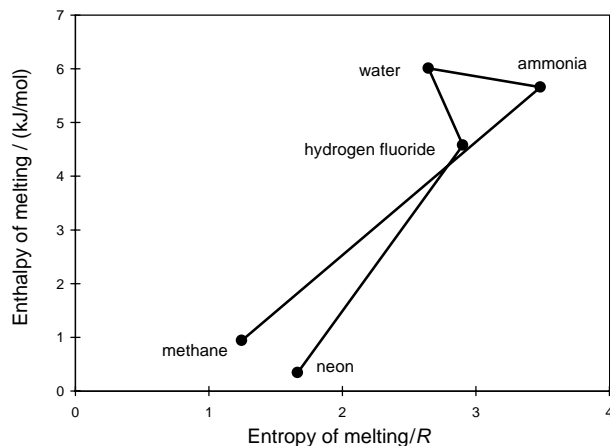

Figure 8. The enthalpy/entropy diagram for the melting points of the second-row hydrides.

disordered in both the liquid and crystalline phases, and this does not affect the melting point. The figure shows that for each group of isomers, the points are arranged in a nearly vertical pattern, which shows that the higher melting point of the para compounds is due almost completely to the higher enthalpy change of fusion.

Carnelley's rule works for ordered crystals through a high enthalpy change of fusion rather than through a low entropy change of fusion. This point has been made previously by Gavezzotti (*15*) in a broad survey of similar compounds.

It is not clear why high molecular symmetry should result in low enthalpy of the crystal. Higher-symmetry molecules might be expected to pack together better, but Gavezzotti remarks that there are substantial variations in density between different phases of a given compound (*15*). In addition, high symmetry favors low dipole moment, so dipole–dipole forces would be reduced. Hence this simplest class of crystals remains unexplained at the molecular level.

Class 2. Disordered Crystals of Rigid Molecules

For these crystals the entropy change of fusion is reduced by the rotational disorder already existing in the crystal at the melting point. Typically, $\Delta S_{fus}/R \approx 0.5$ to 2 for highly disordered crystals (*9*) and 2 to 5 for partially disordered crystals. The reduced entropy change of fusion tends to lead to increased melting point. This is observed for both highly symmetrical small molecules and for larger globular and cage molecules.

Figure 5 shows the enthalpy/entropy diagram for isomers of pentane. The most symmetrical molecule, 2,2-dimethyl-propane, has a low entropy change of fusion because the crystal is rotationally disordered, and a high melting point relative to its isomers that are not disordered in this way.

The molecules of cyclic alkanes, such as cyclohexane, are nearly spherical and form crystals that are orientationally disordered. These substances have small entropy changes of fusion and high melting points. However, replacement of a single hydrogen atom by a methyl group decreases the orientational disorder and increases the entropy change of fusion. As a result, the melting point is reduced. Figure 6 demonstrates the effect on the melting point of methyl group substitution in cyclic hydrocarbons.

Class 3. Crystals with Intermolecular Hydrogen Bonds

Experimental data show that intermolecular hydrogen bonding increases the melting point. Furthermore, intuition suggests that hydrogen-bonded crystals should have high melting points because the hydrogen bonds hold the molecules together in the crystal. However, it is important to keep several other factors in mind. For these substances, the liquid state is also hydrogen bonded to some extent, and so the orientational order may persist in the liquid. As a result, the entropy change of fusion may be lower than for substances where the liquid is not so structured (*9*). Typically the entropy change of fusion of simple hydrogen bonded crystals is in the range $\Delta S_{fus}/R \approx 3$ to 6. It is notable that hydrogen bonding reduces the entropy change of fusion but increases the entropy change of boiling (*17*), in comparison with non-hydrogen-bonded substances. However, the enthalpy change of fusion may also be reduced, so it is necessary to turn to experimental data to find out what actually happens.

The second-row hydrides of the nonmetals nitrogen, oxygen, and fluorine are hydrogen-bonded substances, and in plotting trends in properties it is useful to include methane and neon, which do not form hydrogen bonds. Figure 7 shows that for this group of substances the trend in the melting points is similar to that of the boiling points. Water has both the highest melting point and the highest boiling point of the whole group. The enthalpy/entropy diagram in Figure 8 shows that although the melting points in Figure 7 follow a systematic trend, the trend in the enthalpy/entropy diagram is more complicated.

One may speculate that $\Delta S_{fus}/R$ of ammonia is larger than might be expected, bearing in mind that ammonia forms much weaker hydrogen bonds than water (25). Another explanation is that crystalline methane is orientationally disordered, whereas the hydrogen-bonded crystals are not, so for the purposes of comparison it would be reasonable to "assign" a value of about 3 or 4 to $\Delta S_{fus}/R$, similar to the values for propane and butane. If that were done, then at least the lines joining the points would not cross. In any case, the main difference between the hydrogen-bonded and non-hydrogen-bonded crystals lies in the enthalpy change of fusion, not the entropy change.

The least symmetrical of these molecules, water, has the highest melting point, and the most symmetrical, methane and neon, have the lowest melting points. Hence Carnelley's rule relating melting point to molecular symmetry does not apply to this group of substances because the differences between them are too great.

Figure 9 shows the enthalpy/entropy diagram for some short-chain alcohols and provides several interesting comparisons. Of the isomers of propanol, 2-propanol is more symmetrical than 1-propanol and has the higher melting point purely because of a lower entropy change of fusion. The globular molecule 2-methyl-2-propanol has a much higher melting point than its less symmetrical isomer 1-butanol, again due entirely to a lower entropy change of fusion. Of the straight-chain alcohols, 1-pentanol has a higher melting point than 1-butanol because of a higher enthalpy change of fusion.

Class 4. Crystals of Nonrigid Molecules

In the crystalline state, long-chain molecules such as the straight chain alkanes are usually locked into a fixed conformation in the crystal but are able to flex into many different conformations in the liquid state. Melting permits additional randomness due to flexing of the molecules, and the entropy change of fusion of flexible molecules may be larger than is usual for rigid molecules. Methyl group rotation is nearly free in both the crystalline and liquid states, and so does not contribute significantly to the entropy change at melting. Typically $\Delta S_{fus}/R \geq 6$ and increases with chain length.

Broadhurst (26) has discussed the dependence of the melting point on the chain length for very long chains; both the enthalpy change and the entropy change of fusion increase approximately linearly with chain length. Figure 10 shows the melting points and boiling points of the straight-chain alkanes C_nH_{2n+2} for $n = 1$ up to 12. The boiling point is a smooth function of chain length, but the melting point shows two interesting features: the high melting points of methane and ethane compared with higher members of the series, and
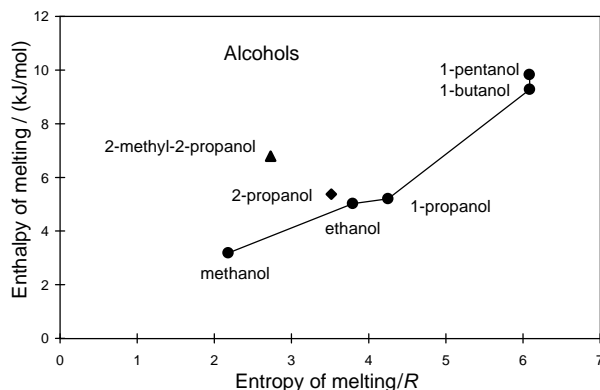

Figure 9. The enthalpy/entropy diagram for the melting points of some short-chain alcohols.
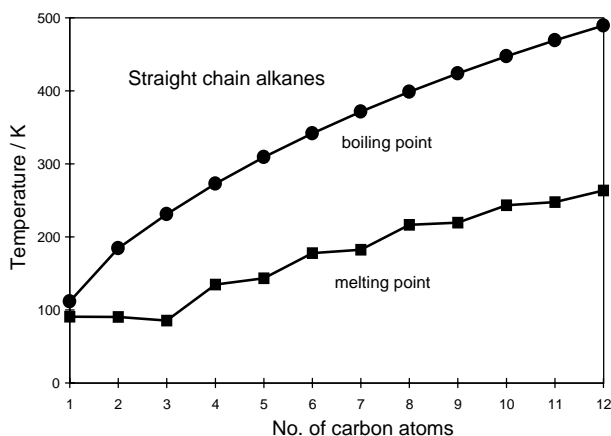

Figure 10. The melting and boiling points of straight-chain hydrocarbons.
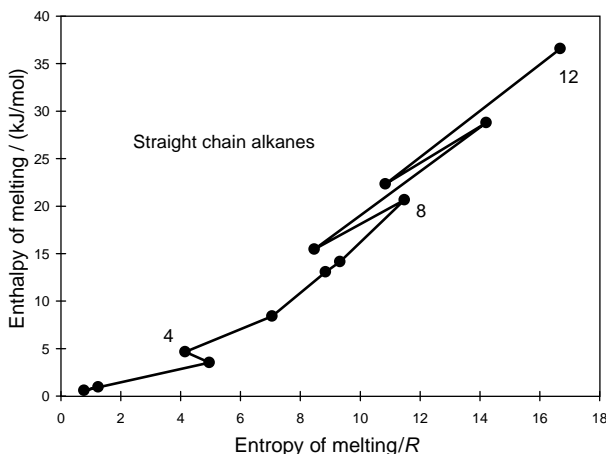

Figure 11. The enthalpy/entropy diagram for the straight chain alkanes from $n = 1$ up to $n = 12$.

the regular stepwise increase in the melting point with increasing chain length.

Figure 11 shows the enthalpy/entropy diagram for the straight chain alkanes up to $n = 12$. The high values of the entropy change of fusion for the longer chain lengths is clear. Straight-chain alkanes in the crystalline state may be rotationally disordered about their long axes. The striking alternation in the entropy change of fusion beginning at $n = 9$ is due to the formation of an orientationally disordered phase for odd values of $n = 9, 11, 13, …$, but not for even values (26). This decreases the entropy change of fusion for the odd alkanes relative to *both* the adjacent even alkanes. It is notable that the graph of melting point in Figure 10 gives no hint of this phenomenon for odd values of n beginning at $n = 9$.

For alkanes higher than $n = 8$, the difference between the values of $\Delta S_{fus}/R$ for C_n and C_{n+2} alkanes is approximately $2 \ln 3 = 2.19$, corresponding to the threefold nature of the rotation about each of two C–C single bonds (9, 13).

Methane and ethane have very low values of the entropy change of fusion owing to rotational disorder in the crystalline state, and the relatively high melting points of methane and ethane are due to this disorder. This is the basis for the answer to the original question from which this whole discussion arose. Ethane has an order–disorder phase transition only 0.5 K below the melting point (19), which caused some confusion in the earlier literature.

The melting points of branched-chain alkanes do not seem to vary systematically with the degree of branching except where the branching leads either to an increase in symmetry or to a globular molecular shape that facilitates rotational disorder in the crystal (10). This is illustrated in Table 1 by the isomers of octane.

Class 5. Molten Salts

Most salts are high-melting-point ionic crystals, but salts that are ionic liquids at room temperature have been prepared (27). These ionic liquids show promise as solvents in the development of "clean" industrial processes. The anions are the tetrahedral tetrachloroaluminate(III) ion, but the cations are large organic ions of low symmetry. The more unsymmetrical the cation, the lower the melting point, it appears. For example, the 1-ethyl-3-methylimidazolium ion is less symmetrical than the 1-butylpyridinium ion and the corresponding salt has a melting point about 100 K lower, which suggests that Carnelley's rule for molecular materials may also apply to these salts.

Conclusions

Compounds of high molecular symmetry have, as a general rule, high melting points. The rule originates in a two-part paper published in 1882 by Thomas Carnelley, summarizing a survey of the melting points of a large number of compounds. The rule is potentially useful to organic chemists.

From a thermodynamic point of view, a high melting point may be the result of a high enthalpy change of fusion, a low entropy change of fusion, or a combination of these two factors. The origin of variations of the melting point can be demonstrated effectively on an enthalpy/entropy diagram. In many cases the high melting points of ordered crystals of highly symmetrical molecules are due to enthalpic effects, while the high melting points of disordered crystals are due to entropic effects. In the cases of hydrogen-bonded crystals and straight-chain alkanes, the enthalpy/entropy diagram reveals some interesting trends that are not apparent in the bare melting point data.

The wide range of validity of Carnelley's rule is due to the fact that high symmetry of the molecules can cause either a high enthalpy change of fusion (if the crystal is ordered) or a low entropy change of fusion (if the crystal is disordered). Both these factors increase the melting point.

Acknowledgments

Literature Cited

1. Carnelley, T. *Philos. Mag.* 5th series **1882,** *13,* 112–130.
2. Carnelley, T. *Philos. Mag.* 5th series. **1882,** *13,* 180–193.
3. Franchimont, A. P. N. *Rec. Trav. Chim.* **1897,** *16,* 126–161.
4. Michael, A. *J. Prakt. Chem.* **1895,** *52,* 344–372.
5. Michael, A. *J. Am. Chem. Soc.* **1918,** *40,* 704–723.
6. Michael, A. *J. Am. Chem. Soc.* **1918,** *40,* 1674–1707.
7. Hückel, W. *Theoretische Grundlagen der organischen Chemie;* Akademische Verlagsgesellschaft: Leipzig, 1931; Vol II, p 185.
8. Timmermans, J. *J. Phys. Chem. Solids* **1961,** *18,* 1–8.
9. Bondi, A. *Chem. Rev.* **1965,** *65,* 565–580.
10. Noller, C. R. *Chemistry of Organic Compounds,* 3rd ed.; Saunders: Philadelphia, 1965; p 72.
11. Canceill, J.; Jacques J.; Perucaud-Brianso, M. *Bull. Soc. Chim. France* **1974,** *12,* 2833–2838.
12. Smith, G. W. *Comments Solid State Phys.* **1978,** *9,* 21–35.
13. Yalkowsky, S. H. *Ind. Eng. Chem. Fund.* **1979,** *18,* 108–111.
14. Abramowitz, R.; Yalkowsky, S. H. *Pharm. Res.* **1990,** *7,* 942–947.
15. Gavezzotti, A. *J. Chem. Soc., Perkin Trans. 2* **1995,** 1399–1404.
16. *Handbook of Chemistry and Physics,* 77th ed.; Lide, D. R., Ed.; CRC: Boca Raton, FL, 1996.
17. Atkins, P. *Physical Chemistry,* 6th ed.; Freeman: New York, 1998.
18. Parsonage, N. G.; Staveley, L. A. K. *Disorder in Crystals;* Clarendon: Oxford, 1978.
19. Arake, T.; Chihara, H. *Chem. Lett.* **1976,** 683–688.
20. White, M. A.; Wasylishen, R. E.; Eaton, P. E.; Xiong, Y.; Pramod, K.; Nodari, N. *J. Phys. Chem.* **1992,** *96,* 421–425.
21. Pitzer, K. *J. Am. Chem. Soc.* **1940,** *62,* 331–335.
22. Longuet-Higgins, H. C. *Mol. Phys.* **1963,** *6,* 445–460.
23. Walden, P. *Z. Elektrochemie* **1908,** *14,* 713–724.
24. Trouton, F. T. *Philos. Mag.* 5th series, **1884,** *18,* 54–57.
25. Nelson, D. D.; Fraser G. T.; Klemperer, W. *Science* **1987,** *238,* 1670–1674.
26. Broadhurst, M. G. *J. Chem. Phys.* **1962,** *36,* 2578–2582.
27. Seddon, K. R. *Molten Salt Forum* **1998,** *5–6,* 53–62.