

Making Sense of Boiling Points and Melting Points

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The boiling and melting points of a pure substance are characteristic physical constants of that substance in its pure state. Although it is not possible to predict these physical constants for a given substance, it is, however, possible to rationalize these values on a relative basis for given substances, taking into account the type of chemical bonding, the intermolecular forces and other factors.

It is known that physical constants like boiling and melting points of elements and compounds depend on the nature of bonding present in the substance and increase in the following order:

Non-polar → Polar → Electrovalent → Giant covalent structure
e.g. (hexane) (water) (sodium chloride) (diamond)

In the case of substances with electrovalent and giant covalent structures, melting/boiling involves breaking of ionic/covalent bonds, which involves high energy and hence high temperatures. Among the molecular covalent compounds (most organic compounds come under this category), it is possible, to some extent, to rationalize the trends in these physical constants based on non-covalent interactions and symmetry, which constitute the contents of this article.

If molecules have only paired electrons, which is the case with most compounds, magnetic forces are absent and only electrical forces operate between molecules; these are electrostatic, polarization and dispersion forces, collectively called non-covalent interactions. They are attractive at distances of ~ 1 nm. These interactions have energy comparable to thermal energy, $k_n T$ and hence are disrupted easily. They affect the bulk properties like melting point, boiling point, viscosity, surface tension, chromatographic



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separation, and molecular recognition. The magnitude of this interaction energy depends on the nature of the species involved, and their relative orientation.

Various types of non-covalent interactions, in decreasing order of magnitude, are:

- Ion-ion
- Ion-dipole
- Dipole-dipole, including H-bonding
- Dipole-induced dipole
- Instantaneous dipole-induced dipole

The last three types of interactions, namely, dipole-dipole, dipole-induced dipole and instantaneous dipole-induced dipole are together called van der Waals forces. Instantaneous dipole-induced dipole interactions are, more specifically, called 'London forces or dispersion forces'.

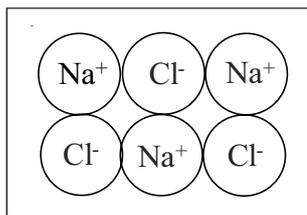


Figure 1.

We give below a brief description of these forces before we take up their effects on boiling points and melting points.

Ion-ion interactions are the strongest of these. Since a large amount of heat energy must be provided to disrupt these forces, ionic compounds typically have high melting and boiling points.

For example, NaCl, whose part structure is shown in *Figure 1*, has the melting and boiling point of 801°C and 1465°C respectively.

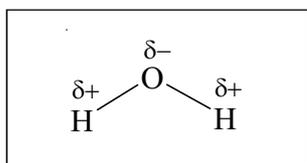
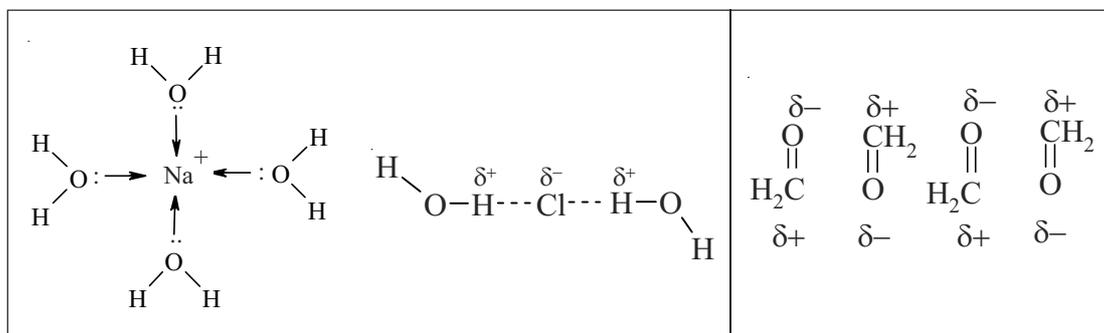


Figure 2.

Ion-dipole interaction is the force of attraction between an ion and a polar molecule. It is responsible for the solubility of ionic compounds like sodium chloride in a polar solvent like water. Water is a dipole because it has a permanent negative pole (oxygen) and a permanent positive pole (hydrogen), arising out of unequal sharing of the bonding electrons as shown in *Figure 2*.

Thus, water can stabilize a sodium ion by making use of the lone-pair of electrons on oxygen and chloride ion through H-bonding



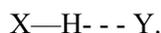
(see later) and these stabilizing forces cumulatively exceed the ion-ion interaction, thus leading to solubility (Figure 3).

Figure 3 (left).
Figure 4 (right).

Dipole-dipole interactions are the electrostatic attractions between polar molecules, which align in such a way that the opposite poles are in proximity, as shown in Figure 4 for formaldehyde.

In a multi-atomic molecule, every bond linking atoms of different electronegativities is a dipole and these molecules would tend to align all their dipoles in a way that enhances intermolecular attractive forces.

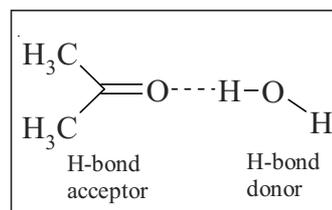
H-bonding is a special case of dipole-dipole interaction, where hydrogen is the positive end of the dipole. Prototypical H-bond is



where X and Y are, in most cases, O, N and F. Because of its small size and the lack of screening electrons, the magnitude of the positive charge on hydrogen in the dipole is high and hence H bonding is the strongest among dipole-dipole interactions.

In the H-bonding interaction between acetone and water shown in Figure 5, acetone is termed the H-bond acceptor, while water is termed the H-bond donor. Compounds like water, alcohols, carboxylic acids, amines, amides, where H is bonded to an electronegative atom, can act both as H-bond donors and H-bond acceptors. On the other hand, compounds like aldehydes, ketones,

Figure 5.



Polarisability is a measure of the propensity of the electrons to be displaced by external fields.

ethers, nitriles, esters which have electronegative atoms but no hydrogen bonded to an electronegative atom, can only act as H-bond acceptors.

Generally, molecules with a C-H bond are not H-bond donors through this bond, but in some exceptional cases like $\text{Cl}_3\text{C-H}$ (chloroform) and NC-H (hydrogen cyanide), there is evidence that they do act as H-bond donors.

The H-bond, as already mentioned, is the strongest of dipole-dipole interactions and is intermediate in strength between a covalent bond and other non-covalent interactions. The order of magnitude, at the high end of strengths, is

$$500 \text{ (covalent)} \longrightarrow 50 \text{ (H-bond)} \longrightarrow 0.5 \text{ kJ mol}^{-1} \text{ (non-bonded)}$$

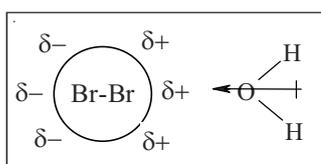
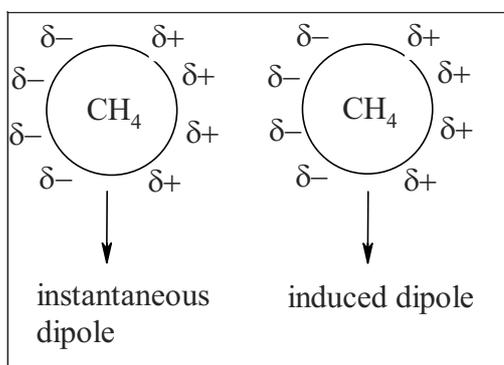


Figure 6.

Dipole-induced dipole interaction refers to a molecule with a permanent dipole (like water), inducing a dipole in an otherwise non-polar molecule (like bromine), as shown in *Figure 6*.

The extent of induction of dipole depends on the polarisability of the non-polar molecule. Polarisability is a measure of the propensity of the electrons to be displaced by external fields. Larger the size of the non-polar molecule, the softer and more deformable the electron cloud will be. For example, among the halogens, fluorine is the least and iodine the most polarisable.

Figure 7.



Instantaneous dipole-induced dipole (London forces or dispersion forces) refers to mutual deformation of electron clouds, thus creating a momentary dipole, which is shown in *Figure 7* for methane.

These forces are predominant in non-polar molecules. This concept was invoked by London to account for the cohesive forces operating in an inert gas like helium, which can be obtained in a condensed form. We expect a helium atom to

have its electron cloud spherically symmetric with zero polarisability, due both to its small size and closed shell electronic configuration. Helium should, therefore, be an ideal gas with zero intermolecular force at all temperatures and pressures, which, however, is not the case.

Dipole Moment

The terms polarity and dipole have been used as factors responsible for enhanced intermolecular attractions. Dipole moment is a term that quantifies the extent of the polarity. When a molecule contains positive and negative charges centered at points A and B, the product of distance d between the two points and the magnitude of charge e gives the magnitude of the dipole, called the dipole moment μ :

$$\mu = d \times e.$$

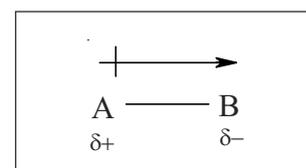
Since molecular distances are in the order of 10^{-8} cm and the charge of an electron is of the order of 10^{-10} esu, dipole moments will have an order of magnitude of 10^{-18} esu. cm.. This unit is called a *debye* (D).

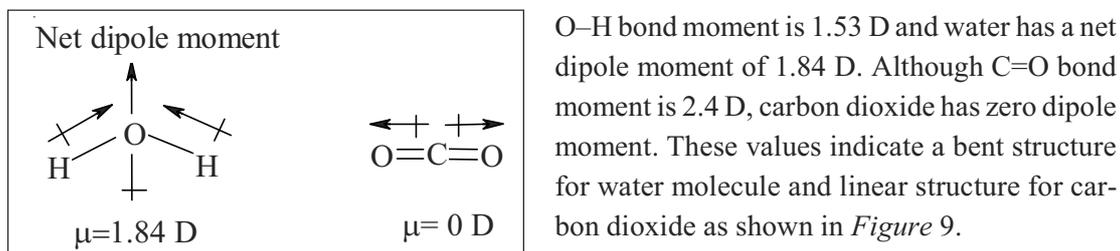
It should be noted that the dipole moment arises not from the net charge but from the separation of the centres of the opposite charges. Hence, if points A and B coincide, there is no dipole moment. Dipole moment is a vector quantity and chemists point the vector to the negative end of the dipole, with a cross on the line to indicate the positive end as shown in *Figure 8*.

Any bond between two different atoms or the same two atoms in different hybridization or oxidation states will have a bond moment due to differing electronegativities. Carbon in sp hybridization state is more electronegative than that in sp^2 state which is in turn more electronegative than that in sp^3 state. Similarly, higher the oxidation state of an element, the more electronegative it is.

Individual bond moments in a molecule add up in vector fashion to result in the net dipole moment for the molecule. For example,

Figure 8.



**Figure 9.**

Higher the dipole moment, more polar the molecule and greater the intermolecular force.

Using the concepts elucidated thus far, we try to rationalise the relative magnitudes of boiling points and melting points, among isomeric and analogous compounds. In the case of melting points, solid state properties also play an important role.

Boiling Point

Boiling point is the temperature at which the vapour pressure equals the ambient pressure which, in most cases, is the atmospheric pressure. A liquid boils when the cohesive forces are overcome by the kinetic energy of the molecules. Therefore, the greater the intermolecular forces, the higher the boiling point.

As the intermolecular force increases in the order

Dispersion or London forces < dipole – dipole < H - bonding,
the boiling point increases, as the cases in *Figure 10* illustrate.

In butane, weak London forces operate. In the next three cases, as we move from ethyl methyl ether to propanal to acetone, the dipole-dipole forces increase in magnitude. In the last two examples, propanol and acetic acid, H-bonding contributes more

Figure 10.

<i>n</i> -butane	ethyl methyl ether	propanal	acetone	propanol	acetic acid
–0.5 °C	16 °C	46 °C	56 °C	97 °C	118 °C

than the other forces. It may be noted that acetone has a higher b.p. than its functional isomer, propanal. This is true in general, i.e. ketones are higher boiling than the isomeric aldehydes.

The examples chosen above are such that the molecular weights of these compounds are comparable.

Dipole Moment

In isomeric structures where intermolecular forces are of the same nature, molecules with higher dipole moment are more polar, and hence have higher b.p. and this is illustrated by the examples in *Figure 11*.

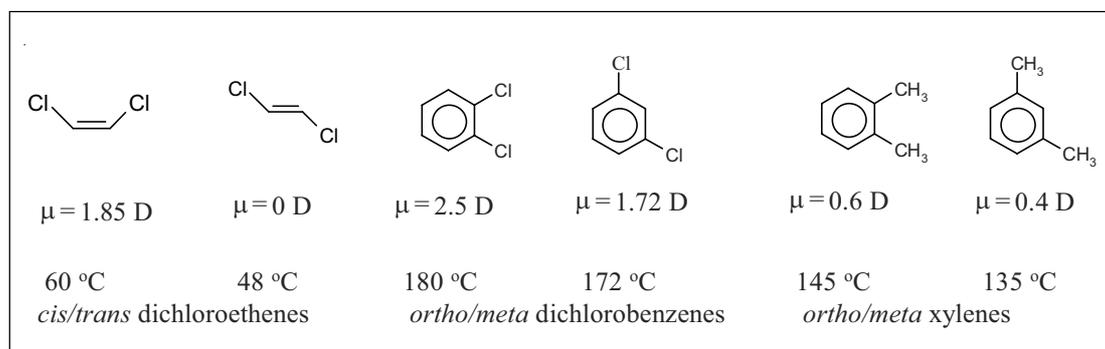
Since dipole moment is a vector quantity, in the examples given in *Figure 11*, *cis* and *ortho* isomers have higher dipole moments than *trans* and *meta* isomers.

Higher dipole moments of ketones compared to those of isomeric aldehydes is responsible for the higher b.p. of the former, as noted earlier.

Molecular Weight

This, as a factor, is important for non-polar compounds like hydrocarbons, where only London forces operate. As already mentioned, London forces increase with increase in polarisability, which in turn shows an increase as the size of the molecule increases. The examples in *Figure 12* are self explanatory.

Figure 11.



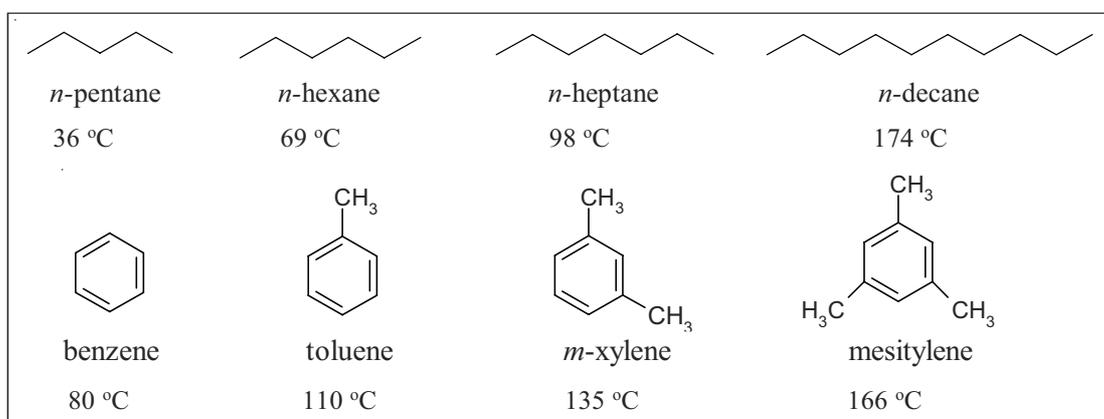


Figure 12.

Cyclic vs Acyclic and Linear vs Branched (Effective Surface Area) Structures

Greater the surface area of a molecule, greater is the intermolecular interaction, because of enhanced “contact” points. Cyclic structure enhances effective surface area by drastically reducing the conformational freedom. Conformations have a profound influence on how effectively two molecules interact. Take the example of *n*-hexane in two different conformations shown in Figure 13.

It can be seen that a given hexane molecule in *zig-zag* conformation can have maximum points of contact with another hexane molecule, also in *zig-zag* conformation, and not with that in *syn* conformation. Since billions of different conformations are possible, the probability of molecules interacting in the same conformation is low. On the other hand, going from acyclic *n*-hexane to cyclohexane, due to drastically curtailed conformational possibilities, it is easy to see that any given cyclohexane molecule will

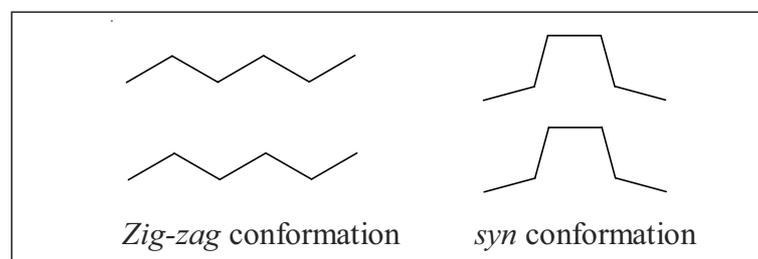


Figure 13.



always encounter another cyclohexane molecule in conformations favourable for interaction as given in *Figure 14*.

Hence, it makes sense to say that a cyclic structure has a more *effective surface area* for interaction than analogous acyclic structure. Similar is the situation when a linear structure is compared to isomeric branched structure. Branching leads to more compactness, and hence decreases surface area.

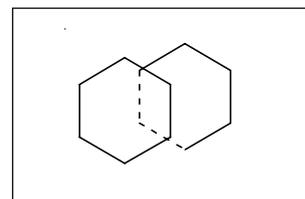


Figure 14.

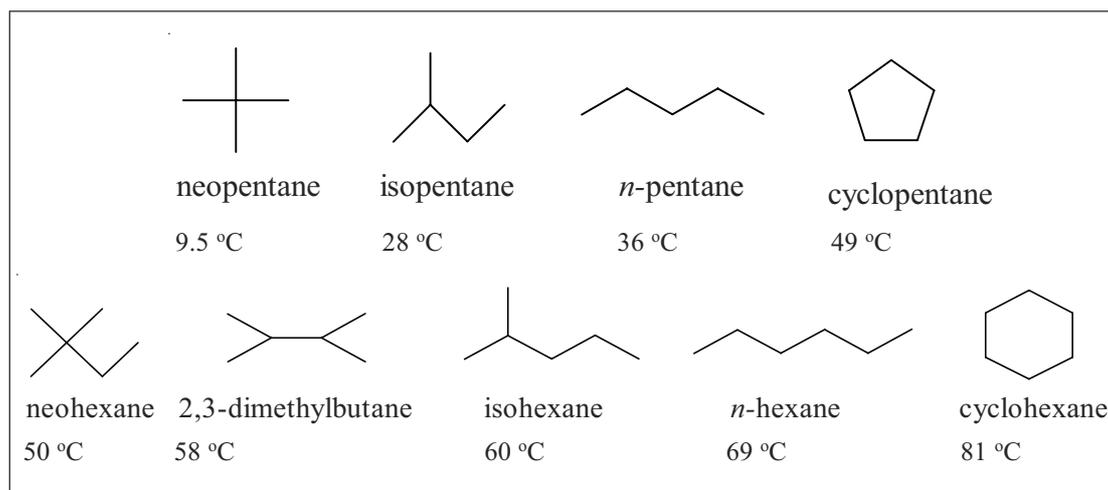
The examples given in *Figure 15* are in support of what is discussed above.

It has been found that double branching on the same carbon has more effect in decreasing the boiling point than two separate branchings, as illustrated by the boiling points of neohexane and 2,3-dimethylbutane.

Some more examples of different functional classes are presented in *Figure 16*.

Among the hydrocarbons, boiling points of alkanes, alkenes and alkynes with the same number of carbon atoms have comparable values, because the differing factor is the number of hydrogens, which does not contribute significantly, either to molecular weight or to polarity.

Figure 15.



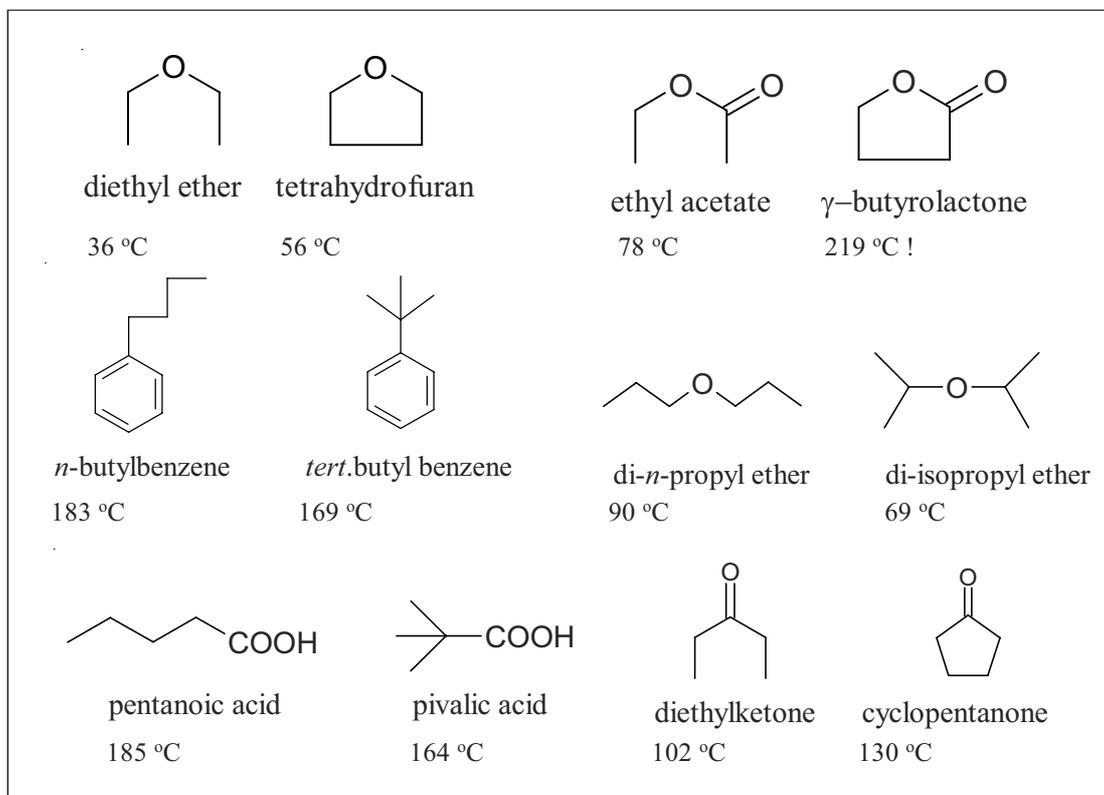
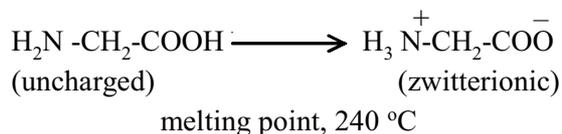


Figure 16.

Special Classes of Compounds

Amino acids: These bifunctional compounds are special in the context of physical properties because of the complementary nature of the two functional groups, namely, the basic amino group and the acidic carboxylic group (or any other acid functional group like a sulphonic acid group). As a consequence, amino acids exist in zwitterionic form due to intramolecular proton transfer which results in very strong intermolecular forces, as shown below for glycine.



The boiling point for glycine is expected to be so high that the

compound will decompose (i.e. the covalent bonds break) before it has a chance to boil.

Carbohydrates: These are by definition, polyhydroxy compounds, which have extensive intermolecular H-bonding. Here again, we do not talk of boiling point, but only melting point. For example, glucose has a melting point of 150 °C.

Fluoro compounds: Fluorine, by virtue of its high electronegativity and low polarisability, provides a negative environment around the molecule in which it is present and this results in a decrease of intermolecular forces, despite increased bond polarity. As a result, fluoro compounds have low boiling points compared to analogous compounds as exemplified below.

$\text{Cl}_3\text{C-COOH}$	$\text{H}_3\text{C-COOH}$	$\text{F}_3\text{C-COOH}$
Trichloroacetic acid	Acetic acid	Trifluoroacetic acid
196 °C	118 °C	72 °C
CHBr_3	CHCl_3	CHF_3
Bromoform	Chloroform	Fluoroform
149 °C	62 °C	-84 °C !

Melting Point

Melting point is the temperature at which the solid phase changes over to the liquid phase. Melting point, unlike boiling point, is a solid state property and hence is influenced by properties of solids such as amorphous or crystalline nature, allotropy, polymorphism, molecular symmetry, as additional and more important factors than intermolecular forces. In this article, the molecular symmetry aspect is highlighted.

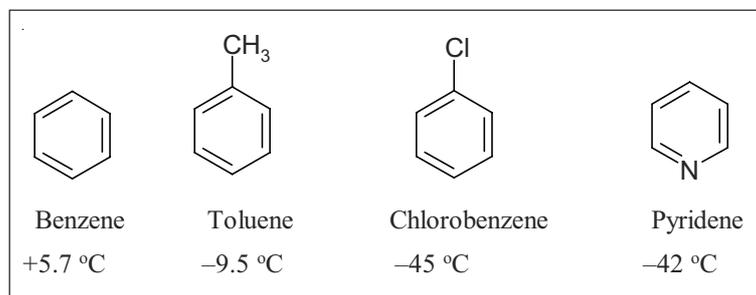
Molecular symmetry determines the packing coefficient in a crystal, which is the ratio of occupied space to the free space in a crystal. Higher the packing coefficient, more the number of molecules in a unit cell and hence higher the melting point.

Fluorine, by virtue of its high electronegativity and low polarisability, provides a negative environment around the molecule in which it is present.

Melting point is the temperature at which the solid phase changes over to the liquid phase.



Figure 17.



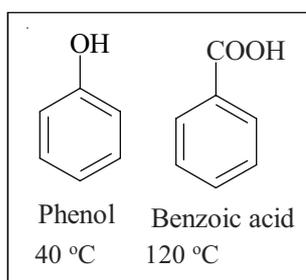
Molecular symmetry, in our context, can be measured in terms of number of chemically different carbon atoms in the given structures. For example, benzene has six carbon atoms of one single chemical type, unlike toluene, which has seven carbon atoms in five chemically different types – one methyl carbon, one *ipso* carbon, two *ortho* carbons, two *meta* carbons and one *para* carbon. Hence, we can say that benzene is more symmetric than toluene.

Where intermolecular forces are not too strong (like H-bonding), molecular symmetry plays an overwhelmingly important role. The empirical rule is stated as follows.

“High molecular symmetry is associated with high melting point.”

This statement was made by Carnelley as long ago as in 1882, after determining the melting points of about 15,000 compounds. Some single substituted benzenes have lower melting points than benzene itself, despite the increase in molar mass and polarity and this is due to higher symmetry of benzene compared to the substituted ones. The melting points of benzene, toluene and chlorobenzene given in *Figure 17* are indicative.

Figure 18.



Pyridine, as an example, further highlights the symmetry aspect. However, if the substituent brings in strong polar interactions like H – bonding as in phenol and benzoic acid, symmetry as a factor becomes less important. Both phenol and benzoic acid have higher melting points than benzene as given in *Figure 18*.

Among disubstituted benzene derivatives, melting points of the

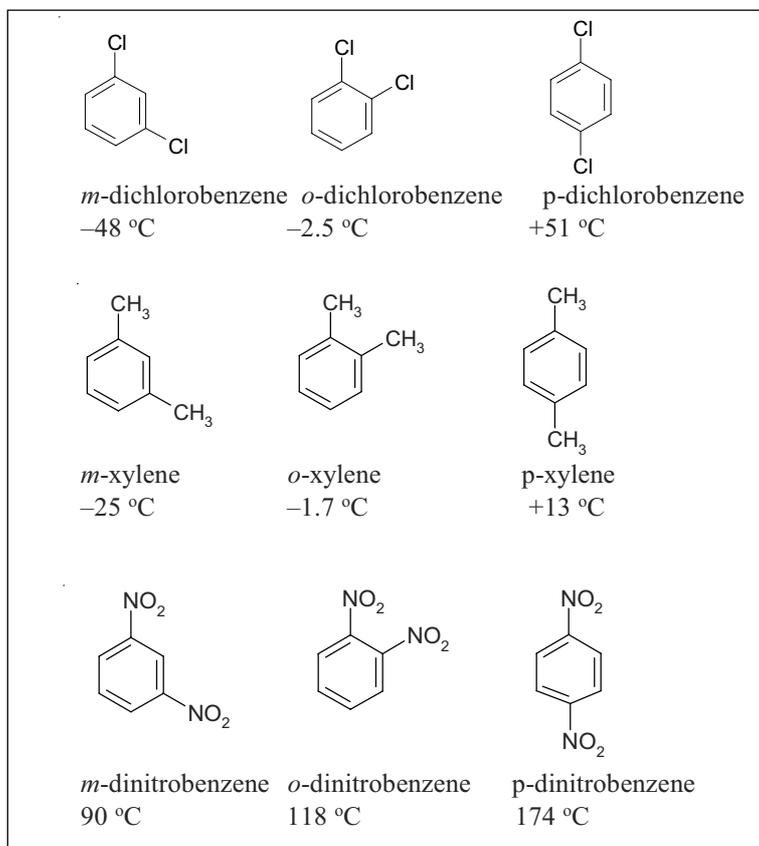
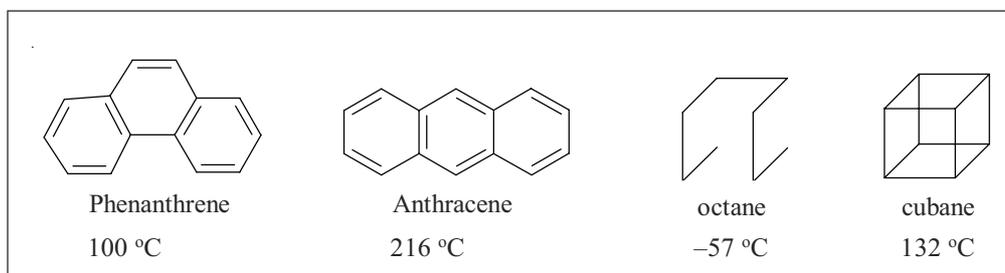


Figure 19.

most symmetric *para* compound is higher than those of the *ortho* and *meta* isomers. Between *ortho* and *meta* isomers, the former is more symmetric. The examples in Figure 19 of the three isomers of dichlorobenzenes, xylenes and dinitrobenzenes clearly show that the molecule with the highest symmetry has the highest melting point. Some more examples are given in (Figure 20).

Crystal packing is dependant also on whether the molecule has Figure 20.



Molecules with even number of carbon atoms pack, apparently, more compactly in the crystal lattice and hence have higher melting points than those with odd number of carbon atoms.

odd or even number of carbon atoms and on the geometry of the molecules. One of the most pronounced odd-even effects is seen with α,ω -alkanedioic acids, which show differences in melting points upto 90 °C between successive members. The following examples illustrate these aspects.

Compound	m.p.	Compound	m.p.
(C ₂) Oxalic acid	189 °C	(C ₃) Malonic acid	135 °C
(C ₄) Succinic acid	186 °C	(C ₅) Glutaric acid	95 °C
(C ₆) Adipic acid	154 °C	(C ₇) Pimelic acid	105 °C

Molecules with even number of carbon atoms (left column) pack, apparently, more compactly in the crystal lattice and hence have higher melting points than those with odd number of carbon atoms (right column).

If the geometry of the molecule results in steric crowding, the packing coefficient in the crystal decreases, which, results in a decrease in the melting point.

Stilbenes offer an example (*Figure 21*). In *cis* stilbene, the two phenyl rings cannot be coplanar, unlike in *trans* stilbene, which packs more compactly and hence has higher melting point.

Isomeric ethanedioic acids shown in *Figure 22* owe their large melting points differences to both geometry (as discussed for stilbenes before) and H-bonding parameters.

In maleic acid, intramolecular H-bonding is partly responsible for its lower melting point compared to fumaric acid, which can have a network of intermolecular H-bonding.

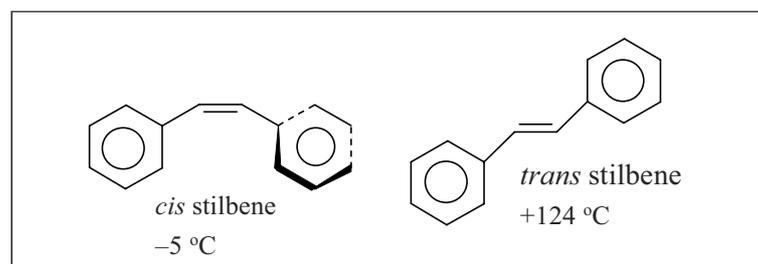


Figure 21.

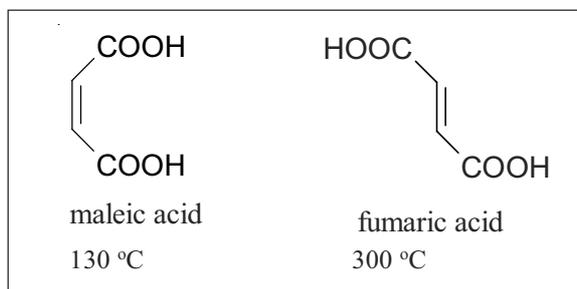


Figure 22.

Conclusion

Dipole–dipole, H–bonding, dipole – induced dipole and London forces are the important factors that determine the physical properties of covalent compounds. In simple molecules, there clearly are trends in boiling and melting points which can be rationalized in terms of basic chemical bonding, intermolecular forces and solid state properties. However, it should be kept in mind that no single factor, all by itself, can account for the differences in these physical constants. There are always exceptions under each category discussed, which happens whenever we try to generalize.

Suggested Reading

- [1] The physical data have been taken from *CRC Handbook of Chemistry and Physics*, 79th edition.
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