

Intermolecular Forces, Boiling and Melting Points

The molecule is the smallest observable group of uniquely bonded atoms that represent the composition, configuration and characteristics of a pure compound. Our chief focus up to this point has been to discover and describe the ways in which atoms bond together to form molecules. Since all observable samples of compounds and mixtures contain a very large number of molecules (ca. 10^{20}), we must also concern ourselves with interactions between molecules, as well as with their individual structures. Indeed, many of the physical characteristics of compounds that are used to identify them (e.g. boiling points, melting points and solubilities) are due to intermolecular interactions. All atoms and molecules have a weak attraction for one another, known as **van der Waals** attraction. This attractive force has its origin in the electrostatic attraction of the electrons of one molecule or atom for the nuclei of another. If there were no van der Waals forces, all matter would exist in a gaseous state, and life as we know it would not be possible. It should be noted that there are also smaller repulsive forces between molecules that increase rapidly at very small intermolecular distances.

Boiling & Melting Points

For general purposes it is useful to consider temperature to be a measure of the kinetic energy of all the atoms and molecules in a given system. As temperature is increased, there is a corresponding increase in the vigor of translational and rotation motions of all molecules, as well as the vibrations of atoms and groups of atoms within molecules. Experience shows that many compounds exist normally as liquids and solids; and that even low-density gases, such as hydrogen and helium, can be liquified at sufficiently low temperature and high pressure. A clear conclusion to be drawn from this fact is that intermolecular attractive forces vary considerably, and that the boiling point of a compound is a measure of the strength of these forces. Thus, in order to break the intermolecular attractions that hold the molecules of a compound in the condensed liquid state, it is necessary to increase their kinetic energy by raising the sample temperature to the characteristic boiling point of the compound.

The following table illustrates some of the factors that influence the strength of intermolecular attractions. The formula of each entry is followed by its formula weight in parentheses and the boiling point in degrees Celsius. First there is molecular size. Large molecules have more electrons and nuclei that create van der Waals attractive forces, so their compounds usually have higher boiling points than similar compounds made up of smaller molecules. It is very important to apply this rule only to like compounds. The examples given in the first two rows are similar in that the molecules or atoms are spherical in shape and do not have permanent dipoles. Molecular shape is also important, as the second group of compounds illustrate. The upper row consists of roughly spherical

molecules, whereas the isomers in the lower row have cylindrical or linear shaped molecules. The attractive forces between the latter group are generally greater. Finally, permanent molecular dipoles generated by polar covalent bonds result in even greater attractive forces between molecules, provided they have the mobility to line up in appropriate orientations. The last entries in the table compare non-polar hydrocarbons with equal-sized compounds having polar bonds to oxygen and nitrogen. Halogens also form polar bonds to carbon, but they also increase the molecular mass, making it difficult to distinguish among these factors.

Boiling Points (°C) of Selected Elements and Compounds

Increasing Size

Atomic	Ar (40) -186	Kr (83) -153	Xe (131) -109	
Molecular	CH ₄ (16) -161	(CH ₃) ₄ C (72) 9.5	(CH ₃) ₄ Si (88) 27	CCl ₄ (154) 77

Molecular Shape

Spherical:	(CH ₃) ₄ C (72) 9.5	(CH ₃) ₂ CCl ₂ (113) 69	(CH ₃) ₃ CC(CH ₃) ₃ (114) 106
Linear:	CH ₃ (CH ₂) ₃ CH ₃ (72) 36	Cl(CH ₂) ₃ Cl (113) 121	CH ₃ (CH ₂) ₆ CH ₃ (114) 126

Molecular Polarity

Non-polar:	H ₂ C=CH ₂ (28) -104	F ₂ (38) -188	CH ₃ C≡CCH ₃ (54) -32	CF ₄ (88) -130
Polar:	H ₂ C=O (30) -21	CH ₃ CH=O (44) 20	(CH ₃) ₃ N (59) 3.5	(CH ₃) ₂ C=O (58) 56
	HC≡N (27) 26	CH ₃ C≡N (41) 82	(CH ₂) ₃ O (58) 50	CH ₃ NO ₂ (61) 101

The melting points of crystalline solids cannot be categorized in as simple a fashion as boiling points. The distance between molecules in a crystal lattice is small and regular, with intermolecular forces serving to constrain the motion of the molecules more severely than in the liquid state. Molecular size is important, but shape is also critical, since individual molecules need to fit together cooperatively for the attractive lattice forces to be large. Spherically shaped molecules generally have relatively high melting points, which in some cases approach the boiling point. This reflects the fact that spheres can pack together more closely than other shapes. This structure or shape sensitivity is one of the reasons that melting points are widely used to identify specific compounds. The data in the following table serves to illustrate these points.

Compound	Formula	Boiling Point	Melting Point
pentane	CH ₃ (CH ₂) ₃ CH ₃	36°C	-130°C
hexane	CH ₃ (CH ₂) ₄ CH ₃	69°C	-95°C
heptane	CH ₃ (CH ₂) ₅ CH ₃	98°C	-91°C
octane	CH ₃ (CH ₂) ₆ CH ₃	126°C	-57°C
nonane	CH ₃ (CH ₂) ₇ CH ₃	151°C	-54°C
decane	CH ₃ (CH ₂) ₈ CH ₃	174°C	-30°C
tetramethylbutane	(CH ₃) ₃ C-C(CH ₃) ₃	106°C	+100°C

Notice that the boiling points of the unbranched alkanes (pentane through decane) increase rather smoothly with molecular weight, but the melting points of the even-carbon chains increase more than those of the odd-carbon chains. Even-membered chains pack together in a uniform fashion more compactly than do odd-membered chains. The last compound, an isomer of octane, is nearly spherical and has an exceptionally high melting point (only 6° below the boiling point).

Source : <http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/physprop.htm#exp3>