Objectives

After completing this section, you should be able to

1. arrange a number of given straight-chain alkanes in order of increasing or decreasing boiling point or melting point.
2. arrange a series of isomeric alkanes in order of increasing or decreasing boiling point.
3. explain the difference in boiling points between a given number of alkanes.

Key Terms

Make certain that you can define, and use in context, the key term below.

- van der Waals force

Alkanes are not very reactive and have little biological activity; all alkanes are colorless and odorless.

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**Boiling Points**

The boiling points shown are for the "straight chain" isomers of which there is more than one. The first four alkanes are gases at room temperature, and solids do not begin to appear until about \( \text{C}_{17}\text{H}_{36} \), but this is imprecise because different isomers typically have different melting and boiling points. By the time you get 17 carbons into an alkane, there are unbelievable numbers of isomers!

Cycloalkanes have boiling points that are approximately 20 K higher than the corresponding straight chain alkane.

There is not a significant electronegativity difference between carbon and hydrogen, thus, there is not any significant bond polarity. The molecules themselves also have very little polarity. A totally symmetrical molecule like methane is completely non-polar, meaning that the only attractions between one molecule and its neighbors will be Van der Waals dispersion forces. These forces will be very small for a molecule like methane but will increase as the molecules get bigger. Therefore, the boiling points of the alkanes increase with molecular size.
Where you have isomers, the more branched the chain, the lower the boiling point tends to be. Van der Waals dispersion forces are smaller for shorter molecules and only operate over very short distances between one molecule and its neighbors. It is more difficult for short, fat molecules (with lots of branching) to lie as close together as long, thin molecules.

Example 3.5.1: Boiling Points of Alkanes

For example, the boiling points of the three isomers of \(\text{C}_5\text{H}_{12}\) are:

- pentane: 309.2 K
- 2-methylbutane: 301.0 K
- 2,2-dimethylpropane: 282.6 K

The slightly higher boiling points for the cycloalkanes are presumably because the molecules can get closer together because the ring structure makes them tidier and less "wriggly"!

Exercise 3.5.1

For each of the following pairs of compounds, select the substance which you expect to have the higher boiling point:

a. octane and nonane.

b. octane and 2,2,3,3-tetramethylbutane.

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**Solubility**

Alkanes are virtually insoluble in water, but dissolve in organic solvents. However, liquid alkanes are good solvents for many other non-ionic organic compounds.

**Solubility in Water**

When a molecular substance dissolves in water, the following must occur:

- break the intermolecular forces within the substance. In the case of the alkanes, these are the Van der Waals dispersion forces.
- break the intermolecular forces in the water so that the substance can fit between the water molecules. In water, the primary intermolecular attractions are hydrogen bonds.

Breaking either of these attractions requires energy, although the amount of energy to break the Van der Waals dispersion forces in something like methane is relatively negligible; this is not true of the hydrogen bonds in water.

As something of a simplification, a substance will dissolve if there is enough energy released when new bonds are made between the substance and the water to compensate for what is used in breaking the original attractions. The only new attractions between the alkane and the water molecules are Van der Waals forces. These forces do not release a sufficient amount of energy to compensate for the energy required to break the hydrogen bonds in water. The alkane does not dissolve.
Note

This is a simplification because entropic effects are important when things dissolve.

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**Solubility in organic solvents**

In most organic solvents, the primary forces of attraction between the solvent molecules are *Van der Waals* - either dispersion forces or dipole-dipole attractions. Therefore, when an alkane dissolves in an organic solvent, the Van der Waals forces are broken and are replaced by new Van der Waals forces. The two processes more or less cancel each other out energetically; thus, there is no barrier to solubility.

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**Exercises**

1. For each of the following pairs of compounds, select the substance you expect to have the higher boiling point.
   - a. octane and nonane.
   - b. octane and 2,2,3,3-tetramethylbutane.

**Answers:**

   a. Nonane will have a higher boiling point than octane, because it has a longer carbon chain than octane.

   b. Octane will have a higher boiling point than 2,2,3,3-tetramethylbutane, because it branches less than 2,2,3,3-tetramethylbutane, and therefore has a larger “surface area” and more van der Waals forces.

   **Note:** The actual boiling points are

   - nonane, 150.8°C
   - octane, 125.7°C
   - 2,2,3,3-tetramethylbutane, 106.5°C

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