

4.2: PHYSICAL PROPERTIES OF ALKANES

Learning Objective

- explain & predict the physical properties of alkanes including relative bp and solubility in a mixture

Overview

Alkanes are not very reactive and have little biological activity; all alkanes are colorless and odorless non-polar compounds. The relative weak London dispersion forces of alkanes result in gaseous substances for short carbon chains, volatile liquids with densities around 0.7 g/mL for moderate carbon chains, and solids for long carbon chains. The differences in the physical states occurs because there is a direct relationship between the size and shape of molecules and the strength of the intermolecular forces (IMFs).

Because alkanes have relatively predictable physical properties and undergo relatively few chemical reactions other than combustion, they serve as a basis of comparison for the properties of many other organic compound families. Let's consider their physical properties first.

BOILING POINTS

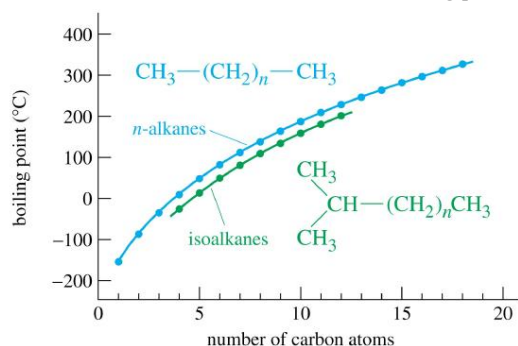
Table 4.2.1 describes some of the properties of some of the first 10 straight-chain alkanes. Because alkane molecules are nonpolar, they are insoluble in water, which is a polar solvent, but are soluble in nonpolar and slightly polar solvents. Consequently, alkanes themselves are commonly used as solvents for organic substances of low polarity, such as fats, oils, and waxes. Nearly all alkanes have densities less than 1.0 g/mL and are therefore less dense than water (the density of H₂O is 1.00 g/mL at 20°C). These properties explain why oil and grease do not mix with water but rather float on its surface.

Table 4.2.1: Physical Properties of Some Alkanes

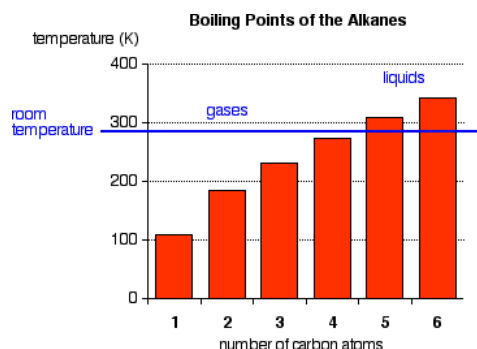
Molecular Name	Formula	Melting Point (°C)	Boiling Point (°C)	Density (20°C)*	Physical State (at 20°C)
methane	CH ₄	-182	-164	0.668 g/L	gas
ethane	C ₂ H ₆	-183	-89	1.265 g/L	gas
propane	C ₃ H ₈	-190	-42	1.867 g/L	gas
butane	C ₄ H ₁₀	-138	-1	2.493 g/L	gas
pentane	C ₅ H ₁₂	-130	36	0.626 g/mL	liquid
hexane	C ₆ H ₁₄	-95	69	0.659 g/mL	liquid
octane	C ₈ H ₁₈	-57	125	0.703 g/mL	liquid
decane	C ₁₀ H ₂₂	-30	174	0.730 g/mL	liquid

*Note the change in units going from gases (grams per liter) to liquids (grams per milliliter). Gas densities are at 1 atm pressure.

The boiling points for the "straight chain" isomers and isoalkanes isomers are shown to demonstrate that branching decreases the surfaces area, weakens the IMFs, and lowers the boiling point.



This next diagrams summarizes the physical states of the first six alkanes. The first four alkanes are gases at room temperature, and solids do not begin to appear until about C₁₇H₃₆, 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.

For example, the boiling points of the three isomers of C_5H_{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 "wiggly"!

SOLUBILITY

Alkanes (both alkanes and cycloalkanes) 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:

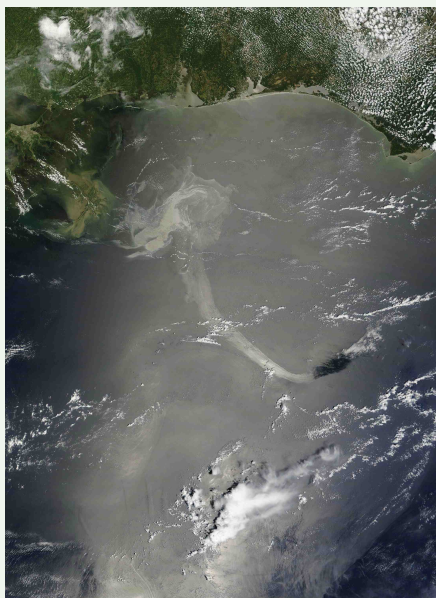
- break the intermolecular forces within the substance. In the case of the alkanes, these are the Van der Waals dispersion forces.
- break the intermolecular forces in the water so that the substance can fit between the water molecules. In water, the primary intermolecular attractions are hydrogen bonds.

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.

The energy only description of solvation is an oversimplification because entropic effects are also important when things dissolve.

The lack of water solubility can lead to environmental concerns when oils are spilled into natural bodies of water as shown below.



Oil Spills. Crude oil coats the water's surface in the Gulf of Mexico after the Deepwater Horizon oil rig sank following an explosion. The leak was a mile below the surface, making it difficult to estimate the size of the spill. One liter of oil can create a slick 2.5 hectares (6.3 acres) in size. This and similar spills provide a reminder that hydrocarbons and water don't mix. Source: Photo courtesy of NASA Goddard / MODIS Rapid Response Team, <http://www.nasa.gov/topics/earth/features/oilspill/oil-20100519a.html>.

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.

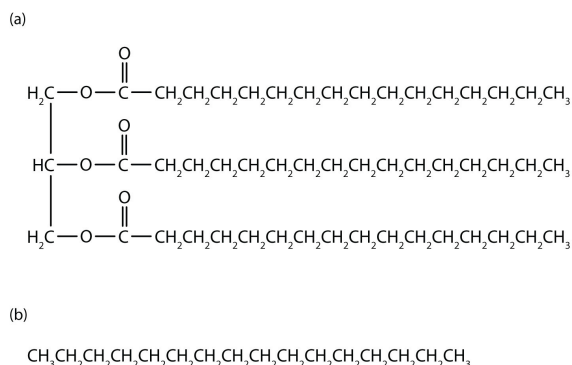
LOOKING CLOSER: GAS DENSITIES AND FIRE HAZARDS

Table 4.2.1 indicates that the first four members of the alkane series are gases at ordinary temperatures. Natural gas is composed chiefly of methane, which has a density of about 0.67 g/L. The density of air is about 1.29 g/L. Because natural gas is less dense than air, it rises. When a natural-gas leak is detected and shut off in a room, the gas can be removed by opening an upper window. On the other hand, bottled gas can be either propane (density 1.88 g/L) or butanes (a mixture of butane and isobutane; density about 2.5 g/L). Both are much heavier than air (density 1.2 g/L). If bottled gas escapes into a building, it collects near the floor. This presents a much more serious fire hazard than a natural-gas leak because it is more difficult to rid the room of the heavier gas.

Also shown in Table 4.2.1 are the boiling points of the straight-chain alkanes increase with increasing molar mass. This general rule holds true for the straight-chain homologs of all organic compound families. Larger molecules have greater surface areas and consequently interact more strongly; more energy is therefore required to separate them. For a given molar mass, the boiling points of alkanes are relatively low because these nonpolar molecules have only weak dispersion forces to hold them together in the liquid state.

LOOKING CLOSER: AN ALKANE BASIS FOR PROPERTIES OF OTHER COMPOUNDS

An understanding of the physical properties of the alkanes is important in that petroleum and natural gas and the many products derived from them—gasoline, bottled gas, solvents, plastics, and more—are composed primarily of alkanes. This understanding is also vital because it is the basis for describing the properties of other organic and biological compound families. For example, large portions of the structures of lipids consist of nonpolar alkyl groups. Lipids include the dietary fats and fatlike compounds called **phospholipids** and **sphingolipids** that serve as structural components of living tissues. These compounds have both polar and nonpolar groups, enabling them to bridge the gap between water-soluble and water-insoluble phases. This characteristic is essential for the selective permeability of cell membranes.



Tripalmitin (a), a typical fat molecule, has long hydrocarbon chains typical of most lipids. Compare these chains to hexadecane (b), an alkane with 16 carbon atoms.

Exercise

- Without referring to a table, predict which has a higher boiling point—hexane or octane. Explain.
- If 25 mL of hexane were added to 100 mL of water in a beaker, which of the following would you expect to happen? Explain.
 - Hexane would dissolve in water.
 - Hexane would not dissolve in water and would float on top.
 - Hexane would not dissolve in water and would sink to the bottom of the container.
- Without referring to a table or other reference, predict which member of each pair has the higher boiling point.
 - pentane or butane
 - heptane or nonane
- For which member of each pair is hexane a good solvent?
 - pentane or water
 - sodium chloride or soybean oil

Answer

- octane because of its greater molar mass
- b; Hexane is insoluble in water and is less dense than water so it floats on top.
- a) pentane
b) nonane
- a) pentane
b) soybean oil

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