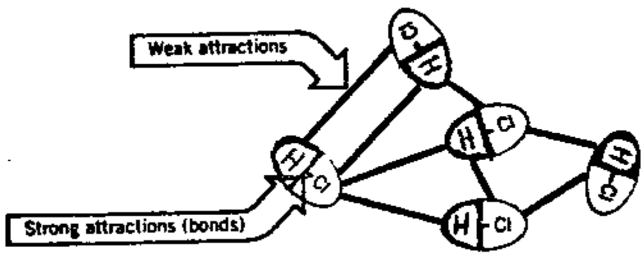
SOLIDS AND LIQUIDS

The physical properties of solids and liquids are strongly influenced by the forces of attraction between the particles within them, known as intermolecular forces. Therefore, to understand the differences in behaviour between various solids and liquids, one must learn about the kinds of forces of attraction and their relative strengths. Before considering the various types of solids and liquids and their forces of attraction, it should be pointed out that these forces of attraction are always much weaker than any of the types of intramolecular bonding (ionic, polar covalent or non-polar covalent).

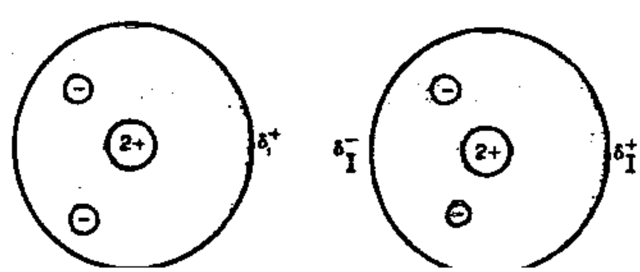


ATOMIC SOLIDS AND LIQUIDS

These types of solids and liquids are formed by the noble gases at very low temperatures. The noble gases are stable and unreactive. They already possess the electron configuration other elements achieve during chemical bonding. Because of the stability of noble gas atoms, one would expect that there is little attraction between one noble gas atom and another. This belief is supported by the fact that, at room temperature, these elements exist as gases, and that they can be liquefied or solidified only at extremely low temperatures. Although there is little attraction between one noble gas atom and another, there must be some attraction. If there were no forces of attraction, it would not be possible to solidify noble gases no matter how low the temperature was taken.

The forces of attraction between noble gas atoms are very weak and not very well understood. The currently accepted theory contends that the noble gas atoms are held together by what are called van der Waals forces. In a noble gas atom such as helium, an instantaneous charge imbalance can occur. That is, at a given instant, both helium electrons may be found on the same side of the atom. That side becomes slightly negative and the opposite side becomes slightly positive. These are caller instantaneous dipoles (δ_I). The atom with the instantaneous dipole can induce a dipole in a neighbouring atom and they can then attract each other. This idea may take some getting used to. To summarize things, in a mere instant of time, a helium atom has an imbalance of charge causing it to become polar. In that same instant, this polar atom induces a weaker dipole in a neighbouring atom, and the two polar atoms attract one another.

An instantaneous dipole in one helium atom (left) induces a smaller dipole (δ^+ and δ^- where I stands for induced) in a second helium atom (right).



The strength of the van der Waals forces depends upon the size of the atom. The larger the atom, the greater its number of electrons, the greater the chance for an instantaneous imbalance of electrons, and thus, the greater the strength of the van der Waals forces between that atom and a neighbouring one. This can be seen in the boiling point data for the noble gas elements (right).

Group 0	Boiling Point (°C)
He	-268.6
Ne	-245.9
Ar	-185.7
Kr	-152.3
Xe	-107.1
Rn	-61.8

In summary, atomic solids are soft and have low melting points. They do not conduct electricity because each electron in the solid belongs to an atom and is unable to move to any other atom. Atomic solids and liquids are formed by the noble gases. The weakness of the van der Waals forces explains why the solids are soft and why they only form at extremely low temperatures. Finally, the size of the van der Waals forces increases as the size of the atoms increases.

MOLECULAR SOLIDS AND LIQUIDS

These types of solids and liquids are formed by molecules whose atoms are held together by covalent (non-polar) or polar covalent bonds. H_2, CCl_4 and H_2S are three examples of the millions of substances that form molecular solids and liquids.

With non-polar molecules (i.e. no molecular dipole), the forces of attraction actually are the van der Waals forces that were previously discussed. This is because the atoms in these molecules have filled energy levels just like noble gas atoms. Thus, the only force of attraction that can exist between molecules of this type is one which results from instantaneous charge imbalances in the atoms which make up the molecules.

When comparing non-polar molecules with the same number of atoms, the size of the forces of attraction depends on the size of the atoms. As the size of the atoms increases and thus the size of the molecules increases, the number of electrons also increases. Thus, there is a greater chance of an instantaneous charge imbalance arising which makes the forces of attraction stronger.

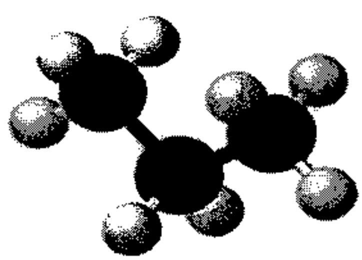
Group 17 (VIIA)	Boiling Point (°C)
F_2	-188.1
Cl_2	-34.6
Br_2	58.8
I_2	184.4

BOILING POINTS OF RELATED MOLECULAR COMPOUNDS OF GROUP 14 (IVA)		
Formula	Number of Electrons	Boiling Point (°C)
CH_4	10	-161
SiH_4	18	-112
GeH_4	36	-90
SnH_4	54	-52

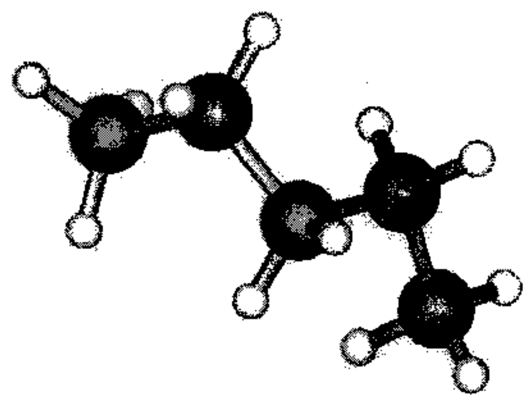
When comparing non-polar molecules in which the atoms are the same size but there are a different number of them, the forces of attraction are greater between molecules with the greatest number of atoms. This is because if there are more atoms, there are more locations for van der Waals forces to occur between adjacent molecules.

Boiling Points of Hydrocarbons

	Molecular Formula	Boiling Point (°C)	State at STP
	CH_4	-161.5	gas
	C_2H_6	-88.6	
$CH_3-CH_2-CH_3$	C_3H_8	-42.1	↓
	C_4H_{10}	-0.5	
	C_5H_{12}	36.1	liquid
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$	C_6H_{14}	68.7	
$CH_3-CH_2-CH_2-CH_2-CH_2$ / $CH_3-CH_2-CH_2-CH_2-CH_2$	$C_{10}H_{22}$	174.1	↓
	$C_{22}H_{46}$	327	solid

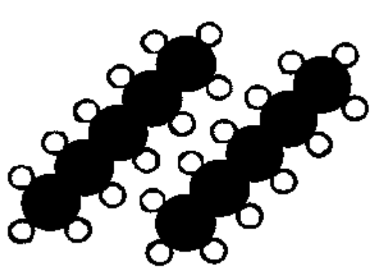


Propane (C_3H_8)

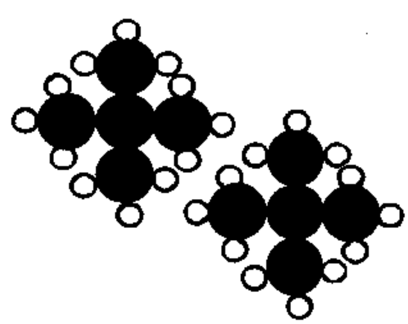


Pentane (C_5H_{12})

When comparing non-polar molecules in which the same number and type of atoms are present (i.e. structural isomers), the forces of attraction are greater between molecules with the shape that allows for more places where forces of attraction can arise between adjacent molecules.

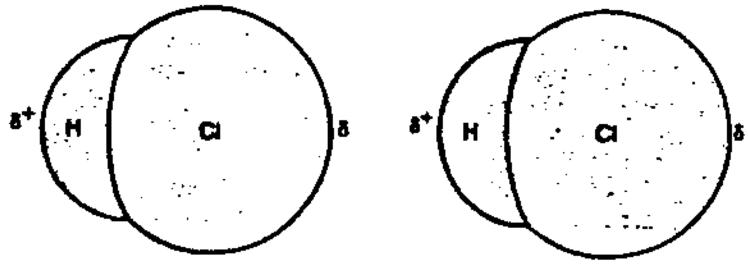


n-pentane (boiling point = 36.2°C)



neopentane (boiling point = 9.5°C)
(2,2-dimethylpropane)

With polar molecules (containing polar covalent bonds and a molecular dipole), the forces of attraction consist of the van der Waals forces and a stronger force called the dipole-dipole force of attraction. Polar molecules such as HCl have a permanent dipole. Thus, the slightly negative end of one molecule can attract the slightly positive end of a neighbouring molecule. This force is called the dipole-dipole force of attraction.



When comparing polar molecules and the forces of attraction between them, one considers the same factors as were discussed with non-polar molecules. It should be noted that the forces of attraction between polar molecules are stronger than those between similar non-polar molecules because there is the dipole-dipole force of attraction in addition to the van der Waals forces.

Boiling Points of Some Polar and Nonpolar Substances

Substance		Boiling Point (°C)	Molar Mass (g/mol)	Number of Electrons
HCl	polar	-84.9	36	18
H_2S		-60.7	34	18
F_2	nonpolar	-188.1	38	18
Ar		-185.7	40	18

In summary, molecular solids are soft and often have fairly low melting points. However since the forces of attraction increase as the size of a molecule increases, and some molecules are large, some molecular solids have fairly high melting temperatures. Molecular solids and liquids do not conduct electricity because each electron in the solid belongs to a molecule and is unable to move to any other molecule.

Read p. 257 – 262 of the textbook *Chemistry 12*.

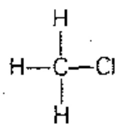
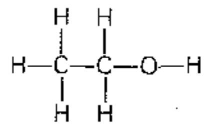
READ LAB EXERCISE 4.5.1 (p.278)

1) Create a Hypothesis/Prediction for the trend you expect to observe.
2) Complete the Analysis section by plotting a graph of boiling point (y-axis) vs. Electron Number (x). Connect data points for each set of elements in the same group (14, 15, 16, 17).
3) Evaluate your prediction by examining the evidence. Explain any general trends that are observed and any anomalies that are also present.

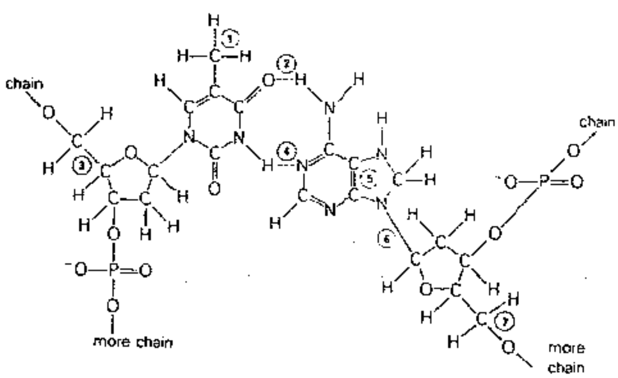
EXERCISE – ATOMIC AND MOLECULAR SUBSTANCES

1. Rank the following bonds and forces from the strongest to the weakest: covalent, London forces, hydrogen bonds, dipole-dipole forces.

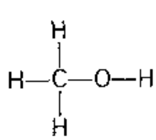
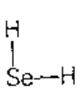
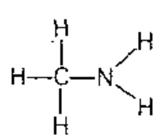
2. What type of intermolecular attraction (hydrogen bonds, London forces, dipole-dipole forces) would you expect for each of the following substances?

a. NH_3
b. BF_3
c. 
d. HCl
e. C_2H_6
f. 

3. DNA (deoxyribonucleic acid) is the main information-bearing molecule in a cell. Molecules of DNA contain the kinds of bonds you have been studying in this chapter. Below is a portion of a DNA molecule in which certain bonds have been labeled. Identify each bond as a covalent, polar covalent, or hydrogen bond.



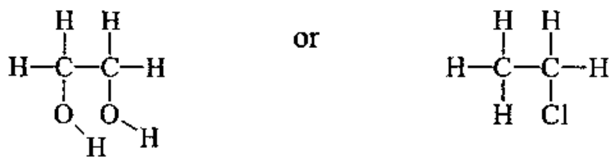
4. Which of these molecules would you expect to be hydrogen-bonded in the liquid or solid state?

a. 
b. CH_4
c. 
d. 
e. H—O—Cl

II)

Atomic and Molecular Substances

1. Which of the following would you expect to form a solid with a higher melting point? Explain your choice.



2. What kinds of intermolecular attractive forces (van der Waals; dipole-dipole, hydrogen bonding) are present in the following substances?

   a) HF b) CS_2 c) PCl_3 d) SF_6

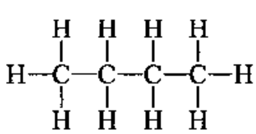
3. What compound in each pair has the higher boiling point? Explain your choice based on the strength of the intermolecular forces.

   a) NH_3 or PCl_3
   b) C_2H_6 or C_4H_{10}
   c) sulfur (S_8 allotrope) or chlorine (Cl_2)

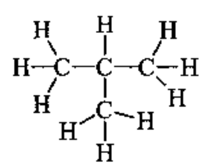
4. Which should have the higher boiling point, krypton or neon? Explain.

5. The two isomers of butane (C_4H_{10}) have boiling points of 0 °C and -12 °C. Their molecular structures are:

(a)



(b)



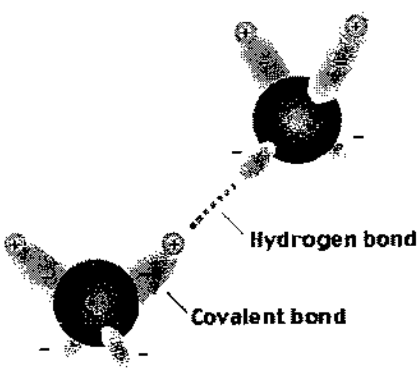
Which boiling point would you assign to isomer (a), and which would you assign to isomer (b)? Explain your answer.

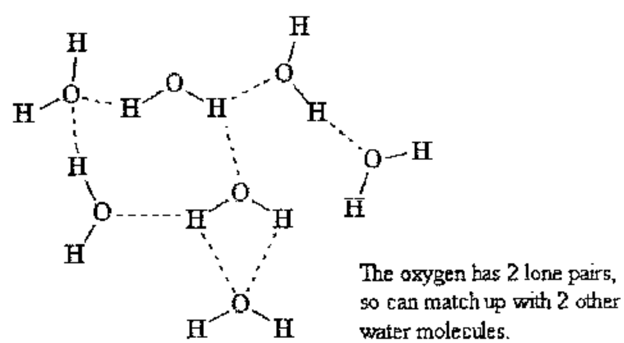
6. The compound CH_4 boils at -161 °C while H_3CF boils at -68 °C. Write a reasonable explanation for this difference in physical properties.

HYDROGEN BONDING

Hydrogen bonding is the name given to the additional force of attraction that can exist between polar molecules in molecular solids and liquids. When hydrogen is covalently bonded to a very small highly electronegative atom such as fluorine, oxygen or nitrogen, unusually strong dipole-dipole attractions are often observed. The existence of this additional force of attraction becomes apparent when one examines boiling point data (*Refer to the Boiling Points Lab Exercise, p. 278*).

There are two reasons for this additional attraction. First, because of the large electronegativity difference, the F-H, O-H or N-H bonds are very polar. Thus, the ends of these dipoles carry a substantial fraction of one charge. Second, because of the small size of the atoms involved, the charge on the end of a dipole is also highly concentrated. This makes it particularly effective at attracting the end of opposite charge on a neighbouring dipole. These two factors combine to produce attractions called hydrogen bonds. They are about one-tenth as strong as covalent bonds but about ten times stronger than normal van der Waals forces.





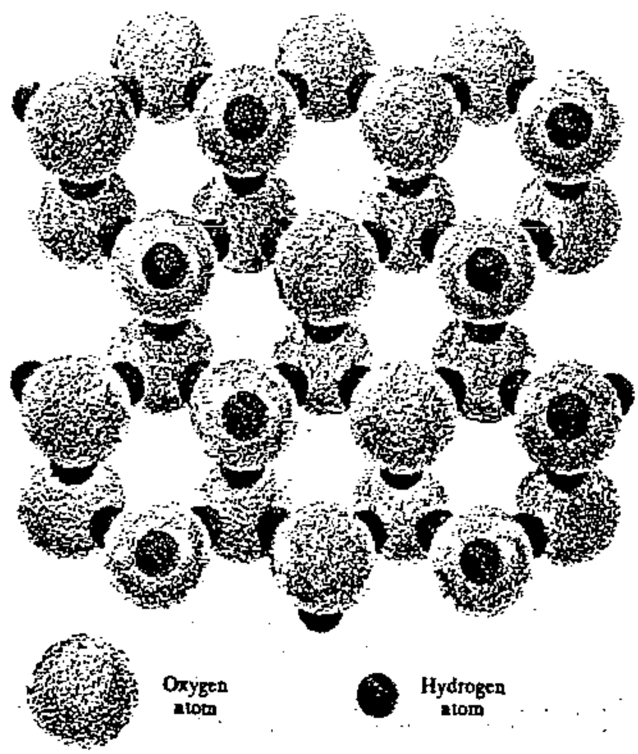
Hydrogen bonding in water

The strength of hydrogen bonds causes molecules that experience them to have some very unusual properties. If a substance has molecules with hydrogen bonds between them, it tends to have a higher melting point, boiling point, heat capacity, heat of fusion and heat of vapourization than other similar substances do.

As is shown in the diagram below, hydrogen bonding also causes substances to form unusual structures in the solid state. When water freezes, it forms a rather open expanded structure. As a result, water "expands" when it freezes and ice has a lower density than liquid water. This permits ice to float on water. For most substances, the solid state is more dense than the liquid.

Hydrogen bonding in water has a number of important consequences. When ice forms in cold weather, it covers the top of the water, thereby insulating the water below. If ice were more dense than water, ice forming at the top of a lake would fall to the bottom and the lake could freeze solid. Most aquatic life could not survive under these circumstances. The expansion of water upon freezing is also what causes water pipes to break in freezing weather. In addition, the high heat capacity of water means that a relatively large amount of heat must be added to raise the temperature of liquid water and conversely, a large amount of heat is released when it cools. Thus water prevents temperature extremes in the surroundings and acts as a modifier of the planet's climate.

There are many examples of the widespread occurrence and importance of hydrogen bonds. All living organisms contain hydrogen-bonded substances. The structure of proteins, the building blocks of animal tissue, is controlled by hydrogen bonding. Furthermore, hydrogen bonding is one of the chief factors which determines the structure of DNA. Also, plant fibres are more rigid than animal tissue because of the greater amount of hydrogen bonding in plants. In addition, much of our clothing and food is composed of hydrogen-bonded materials.



In ice, hydrogen atoms are located between oxygen atoms, and by forming hydrogen bonds with oxygen, bind the whole structure together into a vast network of atoms. Throughout the network there are four hydrogen atoms arranged tetrahedrally about each oxygen atom, and two oxygen atoms on either side of each hydrogen atom.