Extension

8. • OF_2	b.p. –145°C	BeF_2	sublimes 800°C	This prediction was falsified.
• CH_3Cl	b.p. –24°C	C_2H_6	b.p. –89°C	This prediction was verified.
• NF_3	b.p. –129°C	Cl_2O	b.p. 2°C	No prediction was made.

Try This Activity: Floating Pins

(Page 263)

(a) The pin sits on the surface of the water but not on the surfaces of propanol or hexane. The evidence suggests that the intermolecular forces between water molecules are much greater than those between the molecules of either propanol or hexane. If the intermolecular forces are strong enough, the molecules at the surface act like a skin on the surface.

(b) The pin drops immediately into the water no matter which end is first. In this case, the entire weight of the pin is concentrated in a very small area. The surface tension is no longer able to support the pressure (force per unit area) exerted by the pin. When the pin is horizontal, the weight of the pin is spread out over a much larger area.

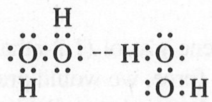
(c) The pin immediately falls through the water. The detergent must reduce the surface tension of the water perhaps by the detergent molecules coming between or separating the water molecules.

PRACTICE

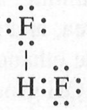
(Page 264)

Understanding Concepts

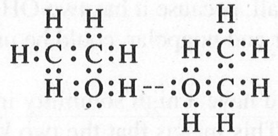
9. (a)



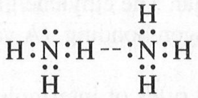
(b)



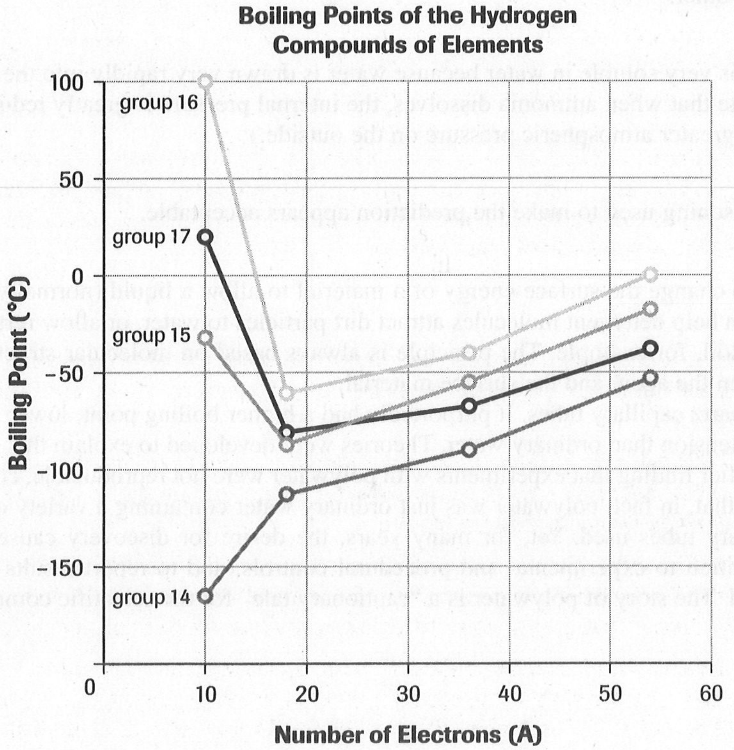
(c)



(d)



10. (a)



(b) The actual boiling points for water and ammonia (compared to an estimate from the graph) are about 170°C and 70°C higher, respectively.

(c) The actual boiling points are much higher for both water and ammonia because of hydrogen bonding between molecules in these substances.

(d) Likely, the difference is much greater for water (than for ammonia) because oxygen is a more electronegative central atom than nitrogen; and possibly also because of differences in molecular shape. Water molecules have more free lone pairs available for hydrogen bonding; and in ammonia, the third bond dipole acts to partially cancel the other two bond dipoles.

11. Water beading on a surface means that the surface material must have very low intermolecular attraction for water molecules. This would mean no polar areas on the surface molecules, and certainly no hydrogen bonding locations.

12. The two liquids must be something like water and oil—one polar and one nonpolar—so they will have no tendency to mix. The polar molecules attract each other more strongly and exclude the nonpolar molecules. The heat supply at the bottom makes the liquid there rise, so it must be just slightly denser than the other liquid. Thus, heating expansion causes the bottom liquid to become temporarily less dense than the other, and to rise until it cools, and falls again.

Applying Inquiry Skills

13. To investigate hydrogen bonding, you should control the other intermolecular forces, London and dipole–dipole forces, by controlling the number of electrons per molecule and the polarity. You should probably control the shapes of the molecules as well.

14. (a) Equal volumes of various liquids will be exposed to the atmosphere in a fume hood at constant temperature. The remaining volume of liquid will be measured at set time intervals. The independent variable is the substance; the dependent variable is the volume remaining; and the controlled variables include the time intervals, the temperature, the initial volume, the surface area, and the air movement (draft).

(b) Some liquids to be used might include ethanol, acetic acid (ethanoic acid), and ethylene glycol (1,2-ethanediol). Assuming the hydrogen bonding from OH groups is the most significant intermolecular force, we would predict the acetic acid to be less volatile than the ethanol, because acetic acid molecules have more lone pairs available to form H-bonds, and are also more polar. The ethylene glycol should be least volatile of all, because it has two OH groups and thus overall stronger hydrogen bonding. (A variety of liquids, including polar and nonpolar, could be used.)

15. **Prediction/Hypothesis**

(a) According to the concepts and rules of intermolecular bonding, ammonia should have a high solubility in water. Both ammonia and water are polar and have multiple hydrogen bonding sites. This means that the two kinds of molecules should easily attract each other.

Analysis

(b) Based upon the evidence, ammonia is very soluble in water because water is drawn very rapidly into the flask to replace the dissolved ammonia. (Note that when ammonia dissolves, the internal pressure is greatly reduced and water is forced into the flask by the greater atmospheric pressure on the outside.)

Evaluation

(c) The prediction is verified, so the reasoning used to make the prediction appears acceptable.

Making Connections

16. Wetting agents are substances that act to change the surface energy of a material to allow a liquid (normally, water) to spread easily over the surface. This can help detergent molecules attract dirt particles to water, or allow fertilizer to penetrate more readily and deeply into soil, for example. The principle is always based on molecular structure and enhanced intermolecular bonding between the agent and the surface material.

17. Polywater was believed to form inside quartz capillary tubes. It purportedly had a higher boiling point, lower freezing point, higher density, and higher surface tension than ordinary water. Theories were developed to explain this in terms of especially strong hydrogen bonding. After finding that experiments with polywater were not reproducible, continued study with better technology established that, in fact, polywater was just ordinary water containing a variety of impurities—mostly absorbed from the capillary tubes used. Yet, for many years, the desire for discovery caused many reputable scientists to pay too little attention to experimental and procedural controls, and to report results without determining that they could be duplicated. The story of polywater is a "cautionary tale" for the scientific community.

SECTION 4.5 QUESTIONS

(Page 266)

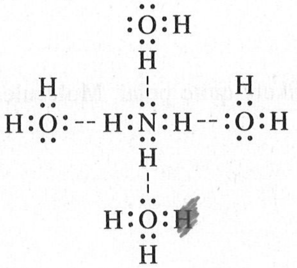
Understanding Concepts

1. (a) London forces

(b) hydrogen bonding, dipole–dipole and London forces

(c) dipole–dipole and London forces
(d) hydrogen bonding, dipole–dipole and London forces
(e) dipole–dipole and London forces
(f) hydrogen bonding, dipole–dipole and London forces
(g) hydrogen bonding, dipole–dipole and London forces
(h) dipole–dipole and London forces
(i) dipole–dipole and London forces

2.



The very high solubility of ammonia in water is due to the high number of hydrogen bonding sites (see diagram). Every ammonia molecule can hydrogen bond at least four times, as can every water molecule in the solution.

3. (a) 2-chloropropane should have low or medium solubility, because it is polar and water is also polar.
   (b) 1-propanol should have high solubility, because it is not only polar but can hydrogen bond with water molecules.
   (c) Propanone should have medium solubility, because it is quite polar, and so is water.
   (d) Propane should have low solubility, because it is a nonpolar substance and water is polar.
4. (a) Bromine should have stronger intermolecular attractions. Both molecules are nonpolar but bromine has larger molecules with a greater number of electrons, so it should have the stronger London force.
   (b) Hydrogen chloride should have stronger intermolecular attractions. Hydrogen chloride and fluorine are isoelectronic which means the London force should be the same. However, HCl has polar molecules so it should have additional dipole–dipole force.
   (c) Ammonia should have stronger intermolecular attractions. Ammonia and methane are isoelectronic so the London force should be the same. Unlike methane, ammonia is polar and has hydrogen bonding. Ammonia therefore has additional attractions, dipole–dipole force, and hydrogen bonds.
   (d) Water should have stronger intermolecular attractions. Both molecules are polar but hydrogen sulfide is less polar. Although hydrogen sulfide has a greater number of electrons and stronger London forces, water has hydrogen bonding. This is likely much more significant than the difference in London forces.
   (e) Silicon tetrahydride should have stronger intermolecular attractions. Both substances are nonpolar and silicon tetrahydride has more electrons per molecule, so it should have more London force.
   (f) Ethanol should have stronger intermolecular attractions. The two substances are isoelectronic which means the London force should be the same. Both are polar but ethanol has hydrogen bonding and chloromethane does not.
5. Ethanol should have the greater surface tension because it has the stronger intermolecular attractions. Propane and ethanol molecules are isoelectronic so the London force is the same for both. There are no other intermolecular attractions between propane molecules because they are nonpolar. However, ethanol has additional dipole–dipole and hydrogen bonds between its molecules.
6. When water freezes it expands, unlike most substances. This occurs because hydrogen bonding causes the molecules to arrange in a specific three-dimensional pattern (lattice). Water left to freeze in a pipe may break the pipe open.
7. The property that creates a meniscus curve is commonly called "surface tension," (but is more correctly termed "surface energy").This results because the molecules on a surface are attracted both sideways and downward, but not upward, by other molecules. This unbalanced attraction causes the surface to act as though it has a "skin" and can contain slightly more water than the level of the top of the glass.
8. A LeRoy radius for a molecule represents a theoretical boundary first calculated and used by Dr. R. J. LeRoy of Waterloo University. Within this boundary, the energies of molecular changes are primarily quantum mechanical and chemical (involving electron exchange energies) and beyond it, the energies of molecular changes are classic intermolecular (involving van der Waals forces). This theoretical boundary proved so useful to the scientific community that the term "LeRoy Radius" was coined to describe it.

Applying Inquiry Skills

9. Two liquids such as diethyl ether, $CH_3CH_2OCH_2CH_{3(l)}$, and butanol, $CH_3CH_2CH_2CH_2OH_{(l)}$, are placed in a beaker and a thin wire (or pin) is placed horizontally on the surface of each liquid. The independent variable is the substance;

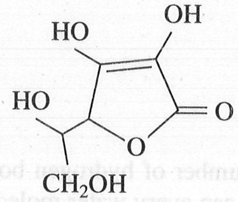
the dependent variable is the action of the wire; and controlled variables include the molecular size, polarity, and temperature of the substance, and mass and size of the wire or pin.
(Some variations include: other combinations of liquids with isoelectronic molecules, several different densities of wires of the same length to determine the mass supported by the liquid surface, measure the force required to lift a specific wire or disk from the surface.)

10. This experiment design is judged unacceptable because it does not stipulate or make clear that comparisons must be done for different liquids using the same kind of capillary tubes of equal diameters. As well, the design does not identify the variables for the experiment.

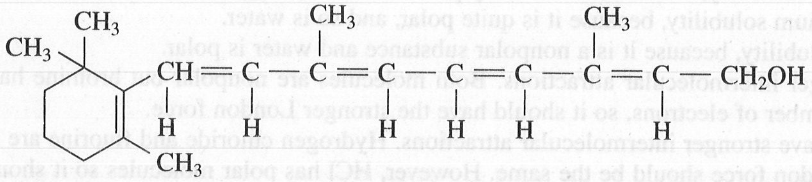
Making Connections

11. (a) Molecules of water-soluble vitamins probably have hydrogen bonding, and are likely quite polar. Molecules of fat-soluble vitamins are probably nonpolar.

(b)



vitamin C



vitamin A

(c) Vitamins are complex substances that react in very complicated ways with many other chemical substances in the body. A balanced diet is essential to ensure that taking vitamins can be of any benefit to an individual. Using vitamins to replace any elements of a normal diet is often ineffective, and may be very dangerous.

(d) Vitamin C is water soluble, so it is easily excreted from the body and does not accumulate in humans. Humans are naturally adapted to handle fairly large amounts of this vitamin. Omnivores often ingest significant amounts of it from fruits and vegetables in their diets. Vitamin E is quite another matter. It is not water soluble and cannot be excreted readily. It tends to accumulate quickly to dangerous (toxic) levels if there is too much in the diet. (Large carnivores like polar bears and lions can have so much vitamin E stored in their livers that eating the organ can be fatal to humans.)

12. The structure of a "fuzzyball," $C_{60}F_{60(s)}$, molecule is essentially a "buckyball" (see p. 238) with a fluorine bonded (on the exterior of the sphere) to each carbon. It is hypothesized that a material made of such molecules would be the slipperiest possible substance—an ideal nonreactive lubricant. As in the polymer Teflon®, the fluorine atoms would bond to the carbons very strongly, preventing any other atom from reacting at that site. The only attractions between fuzzyball molecules and any other matter would be relatively weak London forces.

13. Hard lens polymers do not absorb or attract water. Oxygen moves through holes in the polymer to the eye surface. Soft lenses are made of hydrogel polymers that absorb and attract water. In these lenses, oxygen is carried through by water flow. The polymers in soft lenses must have many surface locations that are very polar and/or allow hydrogen bonding, whereas hard lens polymer surfaces will be nonpolar.

14. Plastic cling wrap is made with a significant amount of a softening material, called a plasticizer, added to the polyvinyl chloride polymer. This causes the film to be very soft and flexible; consequently, it moulds well to any smooth surface (including itself), and the closeness of contact combined with large surface area makes the London force quite significant—the plastic wrap is "clingy." (It is also likely that this plastic easily acquires an electrostatic charge that helps it cling to itself and nonmetallic objects.)

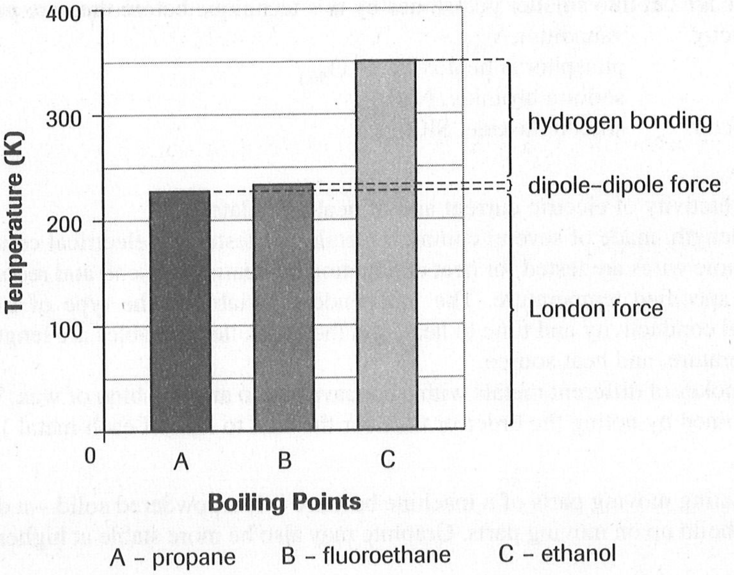
Some plasticizers, particularly di-(2-ethylhexyl) adipate (DEHA), have come under fire because of suspicions that they may act as endocrine disruptors, with possible long-term harmful effects on the body. These compounds can be dissolved out of the wrap if the wrapped food contains fats (cheese is a prime example).

The plasticizer molecules are liquid and nonpolar, so London forces will make them soluble in nonpolar fats.

Extensions

15. The London force is affected by the shape and structure of adjacent molecules. The key variables are the distance between charge points, and the number of charge points that can approach closely. Molecules that have a shape that allows them to pack closely together have attractions that are stronger because the distances separating charges are less. Molecules with shapes closer to planar (like a sheet of paper) than spherical (like a ball) will attract more strongly.

16. (a)



(b) Based on the boiling point graph for these isoelectronic liquids, London force contributes most to intermolecular attraction, hydrogen bonding is usually less significant (about one-half in this example), and dipole–dipole force is almost insignificant.

4.6 THE STRUCTURE AND PROPERTIES OF SOLIDS

PRACTICE

(Page 273)

Understanding Concepts

1. The main factors that determine the hardness of a solid are the strength and direction of bonds between its entities.

2.

(a)	covalent bonding	covalent network crystal
(b)	ionic bonding	ionic crystal
(c)	covalent bonding	molecular crystal
(d)	covalent bonding	covalent network crystal
(e)	metallic bonding	metallic crystal
(f)	ionic bonding	ionic crystal

3. The melting point of a solid is proportional to the attractive forces between the entities of the solid. Strong bonds like covalent bonds will result in very high melting points, while much weaker bonds like London forces will result in lower melting points.

4. Metals are generally malleable, ductile, and flexible because the bonding between atoms in metals is nondirectional—so changing the position of the atoms (shape of the solid) does not “break” the bonding.

5. (a) Aluminum is a light, soft, flexible, silvery metal solid, with a fairly low melting point for metals. Aluminum oxide is a very hard network crystalline solid with an extremely high melting point. In aluminum, the bonding is metallic bonds of a lower-than-average strength for metals. In aluminum oxide, very strong ionic bonds lock the aluminum and oxygen ions in a rigid three-dimensional network.

   (b) Carbon dioxide is a soft molecular solid with a very low boiling point. Silicon carbide is a very hard network crystal solid with an extremely high boiling point. In carbon dioxide, the molecules are held together by relatively weak nondirectional London forces only. In silicon carbide, the silicon and carbon atoms are locked in a three-dimensional network by very strong covalent bonds.

6. (a) The blade must be oriented in the same direction as the plane of the atoms (or ions) in the crystal because the crystal can only break along these "cleavage" planes.
   (b) To cleave a sodium chloride crystal, the knife blade should be perpendicular to a crystal face because the crystal is a cube and planes of ions are at 90° to each other.
   (c) The crystal will shatter into small pieces if struck incorrectly.
   (d) Diamonds and other precious stones are cut into smaller gemstones by this technique before they are polished.

7.

(a)	high melting point, conducts electricity	vanadium, $V_{(s)}$
(b)	low melting point, soft	phosphorus pentoxide, $P_2O_{5(s)}$
(c)	high melting point, soluble in water	sodium bromide, $NaBr_{(s)}$
(d)	very high melting point, non-conductor	silicon dioxide, $SiO_{2(s)}$

Applying Inquiry Skills

8. (a) It seems logical to assume that conductivity of electric current and of heat are related.
   (b) Thick wires of equal diameter and length, made of several common metals, are tested for electrical conductivity with an electrical multimeter. The same wires are tested for heat conduction by heating one end and recording the time for the other end to reach a specified temperature. The independent variable is the type of metal; the dependent variables are the electrical conductivity and time to heat; and the controlled variables are length, diameter, initial temperature, final temperature, and heat source.
   (A common laboratory device has spokes of different metals with a concave end to attach a blob of wax. The relative heat conductivity can be determined by noting the order or time for the wax to fall off each metal.)

Making Connections

9. Graphite may be better than oil in lubricating moving parts of a machine because it is a powdered solid—a dry lubricant that will not stick to dirt, or cake or build up on moving parts. Graphite may also be more stable at higher temperatures than an oil.
10. Nitinol is a nickel-titanium mixture in about a 55%–45% proportion by mass. It has two distinct crystalline structures, called martensitic and austenitic after crystal structure first observed in steels. It exhibits unique properties of "shape memory" and "superelasticity." It can be deformed easily in the martensitic form, and will return to its original shape upon heating. In its austenitic form, it is extremely elastic, allowing it to be bent severely without breaking or changing the shape to which it returns. Superelasticity is used in making eyeglass frames, cell phone antennas, orthodontic wires and surgical probes that are far more flexible than if made with other metals. Thermal "memory" has a host of medical applications for devices that take final shape only after they are inserted in the body, like vertebral spacers, and heart valve instruments that can be shaped to a patient for an operation, and then returned to original shape later for reuse.
11. (a) Moissanite has a refractive index of 2.67±2, dispersion of 0.104, hardness of 9.25, and specific gravity of 3.21. Diamond has a refractive index of 2.42, dispersion of 0.044, hardness of 10, and specific gravity of 3.52.
    (b) In theory, any of these properties could distinguish the two materials, given precise measuring equipment and time. Finding specific gravity, for example, requires very precise measure of mass and volume for very small objects.
    (c) Jewellers normally distinguish diamonds from other stones by thermal conductivity, but this doesn't work with moissanite. The only device that can currently distinguish diamond from moissanite uses absorption of UV light as its operating principle. The stone is first tested for thermal conduction to ensure that it is either diamond or moissanite, and then is tested with the UV sensor device. Diamond transmits certain UV frequencies which moissanite absorbs.

Extension

12. If graphite did not conduct electricity, one might assume that it was composed of double sheets of carbons bonded together, explaining why there are no free electrons. The double sheets should slide over each other still, because they would not be bonded except by London forces.

CAREERS IN CHEMISTRY

PRACTICE

(Page 275)

Making Connections

1. (Reports will vary, but almost all universities provide excellent web site biographical information on faculty members. In Ontario, Dr. LeRoy (Waterloo) and Drs. Gillespie and Bader (McMaster) are examples already used in this course.)

SECTION 4.6 QUESTIONS

(Page 276)

Understanding Concepts

1. Ionic substances do not conduct while solid because all ions are locked in position. Upon melting, the ions are free to move and the substance conducts freely. In aqueous solution, the ions are also free to move and the solution will conduct more or less well, depending on concentration.
2. A substance conducts electricity when its particles have a charge and are free to move, meaning the particles must be held only by weak forces.
3. In calcium oxide, the ions have double the charge that the ions in sodium chloride have, creating a significantly greater interionic attraction.
4. In solid carbon dioxide, the bonding consists of London forces between molecules. These relatively weak forces result in very low melting and boiling points, and make the solid a soft substance. By contrast, in silicon dioxide, the bonding consists of a continuous network of covalent bonds between atoms. These very strong forces result in very high melting and boiling points, and make the solid a very hard, brittle substance.
5. Most metals have a relatively high density because their atoms are closely packed together in solid form, held together strongly by mobile valence electrons that are dispersed throughout a structure of positive ions.
6. Covalent network structures have the highest hardnesses and also the highest melting and boiling points, indicating that covalent bonds are the strongest. Molecular structures have the lowest values for these properties, indicating that intermolecular bonding forces are the weakest. Metals and ionic compound properties fall between these first two, but the values for both metals and ionic compounds vary widely, depending on the specific substance.
7. Rubbing your zipper with your pencil will coat it with graphite which will act as a lubricant. Graphite crystals form in layers one atom thick held to each other only by very weak London force, so they slide very easily over each other.
8. Diamond is composed of carbon atoms bonded four times each in a three-dimensional covalent network. It is a colourless solid, extremely hard, and a nonconductor. Its main use is as an abrasive; pure crystals are used as gemstones.

   Graphite is composed of carbon atoms bonded three times each in a two-dimensional covalent network resulting in layers one atom thick which are held to each other by London force. It is a grey-black solid, very soft and slippery, and a good electrical conductor because of the mobility of the delocalized, unbonded fourth electron of each carbon atom. It has a myriad of uses in industry, most of which have to do with its high melting point and lubricant properties.

Applying Inquiry Skills

9. XCl_a must be an ionic compound. The high melting point suggests that it has very strong bonding holding the entities together, but is water soluble, so it is not likely a covalent network crystal.

   YCl_b must be a molecular compound. The melting and boiling points are low, indicating London forces holding the entities together. The solubility argues that the molecules are nonpolar.

Making Connections

10. (Note: Many answers are possible.)

    Molecular research in the medical and pharmaceutical fields has produced materials such as human insulin for diabetics, and diagnostic devices such as MRI scans. The plastics industry has produced new contact lens materials and many new fabrics and containers and construction materials. The electronics industry has created new products like rechargeable NiMH batteries, fuel cells, and LEDs for traffic lights.
11. Clay is a term that refers to a general class of minerals produced by long-term weathering of igneous rock into very tiny particles—usually less than a few micrometres in size. The predominant compound present (of a very complex mixture)—in the clays that can be heated to produce pottery—is normally kaolinite, $Al_2Si_2O_5(OH)_{4(s)}$. In general, all clays may be thought of as hydrated aluminum silicates with varying amounts of other atoms, such as K, Mg, Fe, and Ca included in the mineral's crystal structure. All clays contain at least some tiny particles of SiO_2 and Al_2O_3.

    Ceramic is a term that refers to any manufactured materials that have essentially a network crystalline structure. This includes abrasives, porcelain, china, refractories (heat-shielding materials), structural clay products (brick and pottery), electrical ceramics (for electronics), and glasses. Glasses account for nearly half of all ceramic production.

    Clay, when wet, is a soft, slippery plastic material. It is easily moulded into shapes, because the tiny particles are attracted to each other by low-strength London forces and hydrogen bonds. By heating these silicaceous minerals at very high temperatures, new bonds form to change the material into a very hard, brittle network solid. The networks are mostly covalent—but also somewhat ionic—in crystalline character. The bonding structure is extremely complex, but may be thought of as a tetrahedral silicon-oxygen network modified with many substituted atoms and ions, all held together within an overall glass structure. All glasses have a crystal structure that is unique—the arrangement of atoms in glasses is like the arrangement in liquids—because there is no regular repetitive pattern to the structure.

12. Boron nitride, $BN_{(s)}$, is a network covalent compound with unique properties. It has very high melting and boiling points, conducts heat well, is a soft slippery solid like graphite, but unlike graphite, is a nonconductor of electricity. It is used as an additive to plastics, ceramic mixes, and lubricants, where it adds lubricating and thermal transmission properties and, to ceramics, increased strength. It can be used as a dry lubricant in powdered form. The network structure is planar hexagonal sheets, much like graphite, except that the hexagon corners are alternating B and N atoms. As in graphite, the atoms within a single crystal sheet of boron nitride are strongly bonded with covalent bonds, while each sheet is attracted to the next only by London force.
13. Biological computers have been a scientific dream for years. The progressive technology of miniaturization is driven by the fact that the more transistors one can place on a microchip, the faster and more powerful the processor will be. The logical limit to miniaturization is at the level where individual switches would be molecular (or even atomic) in size. Current mechanical computers depend on a huge number of possible circuits through microscopic transistor "switches" engraved photographically on silicon-based semiconducting microchips.

    Recently, Dr. Ehud Shapiro, working at the Weismann Institute in Israel, constructed a different kind of mechanical computer that is designed along the theoretical lines of proposed biological computers. The key point here is that such a computer operates as a continuous ribbon of individual information "cells." These cells are scanned by a read/write head that moves along the ribbon from cell to cell, reading symbols, writing symbols, and changing its control state as it goes. Alan Turing created such a concept on paper in 1936, and the system has been called a Turing Machine ever since. Biologists believe that ribosomes operate in a somewhat similar fashion—they may be thought of as biological computers preprogrammed by messenger RNA to assemble proteins.

    Scientists theorize that someday the ability to build such computers from biological components might result, for example, in microscopic devices that could be programmed to adjust any desired chemical levels within the body. Perhaps they might also produce needed proteins on demand, and replace many or most medical treatments now in existence. The possibilities seem endless, and will certainly include applications not yet dreamed of.

CHAPTER 4 LAB ACTIVITIES

ACTIVITY 4.3.1 SHAPES OF MOLECULES

(Page 277)

Prediction

(a) According to the VSEPR theory,

CCl_4 should be tetrahedral, with 4 bond pairs around the carbon atom.

C_2Cl_4 should be trigonal planar at each end, with three groups of electrons (one double bond and two single bonds) around each carbon atom. The overall molecule should be flat (i.e., in one plane).

C_2F_2 should be linear around each carbon atom, with two groups of electons (a triple bond and a single bond) around each carbon atom. The overall shape of the molecule should also be linear.

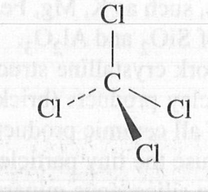
NCl_3 should be pyramidal, with 3 bond pairs and 1 lone pair around the nitrogen atom.

OF_2 should be V-shaped, with 2 bond pairs and 2 lone pairs around the oxygen atom.

NH_2OH should be pyramidal around the nitrogen, with 3 bond pairs and 1 lone pair around the nitrogen atom; and V-shaped around the oxygen, with 2 bond pairs and 2 lone pairs around the oxygen atom. There is no simple description of the overall shape of the whole molecule.

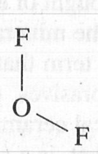
Evidence/Analysis

(b)

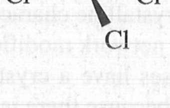


tetrahedral

$F—C\equiv C—F$ linear

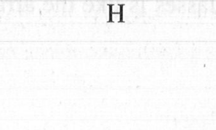


V-shape



pyramidal

trigonal planar



pyramidal (N)
V-shape (O)