

### Applying Inquiry Skills

4. Cis-1,2-dichloroethene is a nonsymmetrical molecule that should have a resultant molecular dipole; thus, the substance should be polar. The other stereoisomer, trans-1,2-dichloroethene, is symmetrical, and should not be a polar substance. Thin streams of each liquid are allowed to flow downward past a strong electric charge. Any stream deflection is noted. (The polar substance should deflect.)

### Making Connections

5. The entire field of cleaning and stain removal is based on a knowledge of polar and nonpolar substances. Stains may be polar or nonpolar substances. Nonpolar substances pose particular problems because the common liquid for washing is water, which is very polar. Soaps and detergents are molecules selected or designed to have both polar and nonpolar regions so that they can dissolve oily or greasy dirt from a stain, and also dissolve in water to carry the material away.

## 4.5 INTERMOLECULAR FORCES

### PRACTICE

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### Understanding Concepts

- (a) dipole–dipole forces and London forces  
(b) London forces  
(c) London forces  
(d) dipole–dipole forces and London forces  
(e) dipole–dipole forces and London forces  
(f) London forces
- (a) hydrogen fluoride; the H-F bond is more polar (electronegativity difference is greater)  
(b) chloromethane; the C-Cl bond is more polar (electronegativity difference is greater)  
(c) nitrogen tribromide; the N-Br bonds are more polar (electronegativity difference is greater)  
(d) water; the O-H bonds are more polar (electronegativity difference is greater)
- (a) ethane; because it has 8 more electrons (and protons) than methane  
(b) oxygen; because it has 2 more electrons (and protons) than nitrogen  
(c) sulfur dioxide; because it has 18 more electrons (and protons) than nitrogen dioxide  
(d) Methane and ammonia are isoelectronic, with 10 electrons each. They should have equal-strength London forces.
- (a) oxygen difluoride; beryllium difluoride is nonpolar (no dipole–dipole forces) and also has fewer electrons (weaker London forces).  
(b) chloromethane; ethane is nonpolar (no dipole–dipole forces) and also has fewer electrons (weaker London forces).
- Chlorine monoxide bonds are less polar than bonds in nitrogen trifluoride (possibly weaker dipole–dipole forces), and there are fewer bonds per molecule, but nitrogen trifluoride has fewer electrons than chlorine monoxide (weaker London forces). Therefore, no simple prediction is possible in this case.

### Applying Inquiry Skills

6. Some patterns found in Table 4 include:
- In the homologous series for the alkanes, alkenes, and alkynes, the boiling point increases proportionally to the number of electrons per molecule. Because these are all nonpolar molecules, the pattern can be explained as an increase in the strength of the London force.
  - In the comparison of alkanes with their corresponding alkenes (same number of carbons), we find the boiling point of the alkene is slightly lower. This is what we might expect because the molecules are nonpolar and the London force should decrease when the number of electrons is reduced by two.
  - Interestingly, the alkynes have higher boiling points than corresponding alkenes, even though they have fewer electrons. Since polarity is not a factor, there is obviously some other factor involved that has not yet been studied. (Note that the effect of molecular shape on the strength of intermolecular forces has not been considered.)
7. Look up in a reference, or determine experimentally, the melting points of the hydrocarbons listed in Table 4. Possible complications of this proposed experiment include the equipment needed if it is necessary to determine the melting points of substances that have freezing points well below 0°C. The interpretation of the results may also be complicated by the fact that the bonding changes between solid and liquid forms are not as clear as the change between liquid and gas states. With boiling points, we usually assume that no intermolecular bonding forces exist between molecules in a gas.

### Extension

8. • $\text{OF}_2$	b.p. $-145^\circ\text{C}$	$\text{BeF}_2$	sublimes $800^\circ\text{C}$	This prediction was falsified.
• $\text{CH}_3\text{Cl}$	b.p. $-24^\circ\text{C}$	$\text{C}_2\text{H}_6$	b.p. $-89^\circ\text{C}$	This prediction was verified.
• $\text{NF}_3$	b.p. $-129^\circ\text{C}$	$\text{Cl}_2\text{O}$	b.p. $2^\circ\text{C}$	No prediction was made.

### Try This Activity: Floating Pins

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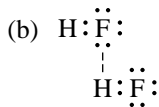
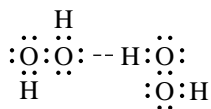
- The pin sits on the surface of the water but not on the surfaces of propanol or hexane. The evidence suggests that the intermolecular forces between water molecules are much greater than those between the molecules of either propanol or hexane. If the intermolecular forces are strong enough, the molecules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

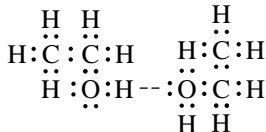
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#### Understanding Concepts

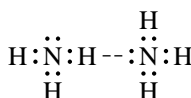
9. (a)



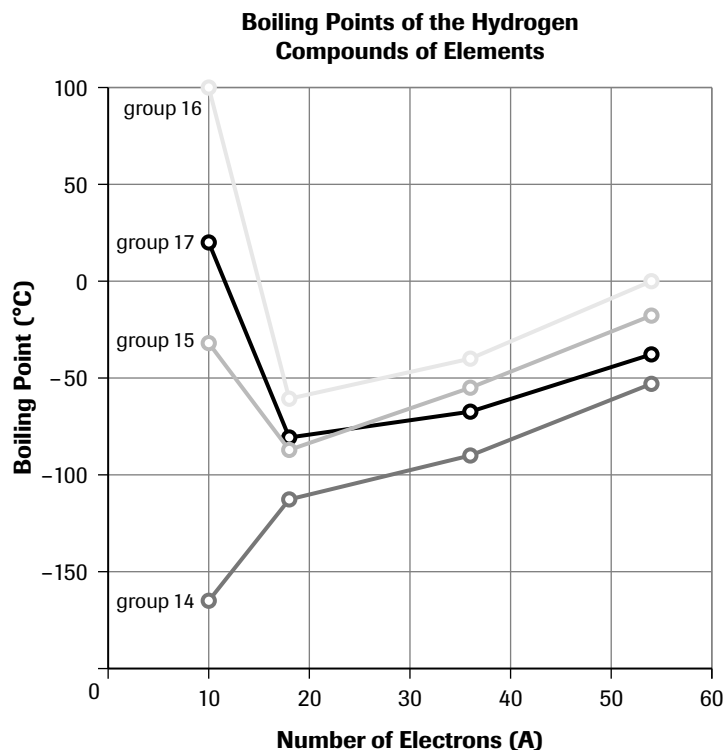
(c)



(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.

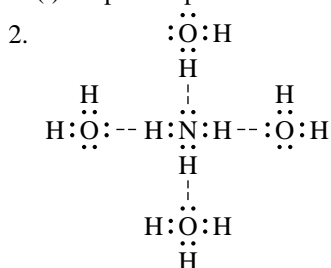
## SECTION 4.5 QUESTIONS

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### 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



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,  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3(l)$ , and butanol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}(l)$ , 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.

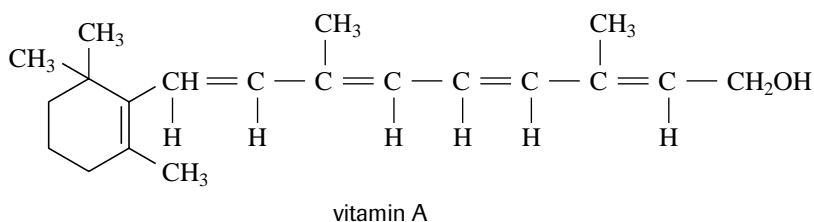
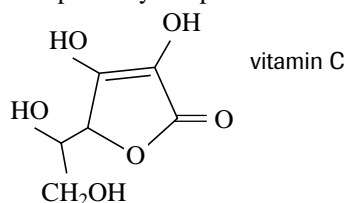
(Some variations include: other combinations of liquids with isoelectronic molecules, several different densities of wires of the same length to determine the mass supported by the liquid surface, measure the force required to lift a specific wire or disk from the surface.)

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)



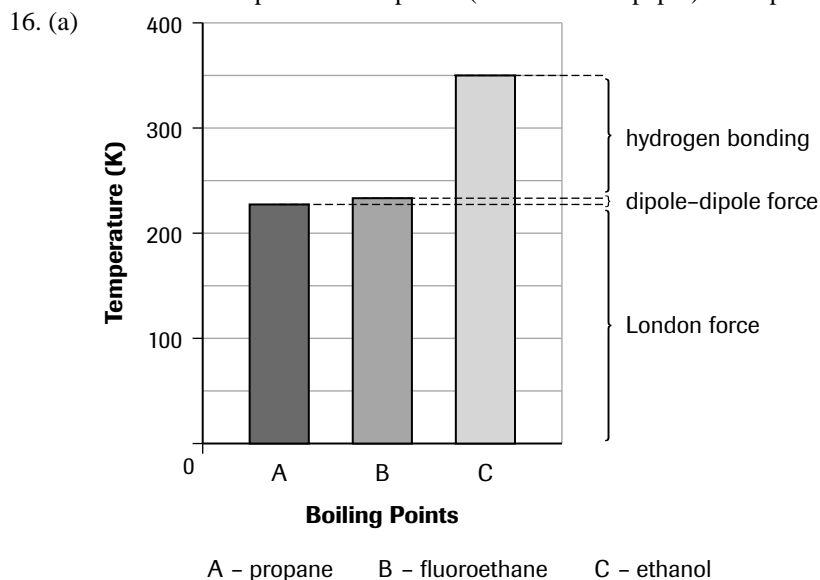
- (c) Vitamins are complex substances that react in very complicated ways with many other chemical substances in the body. A balanced diet is essential to ensure that taking vitamins can be of any benefit to an individual. Using vitamins to replace any elements of a normal diet is often ineffective,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



(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

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#### Understanding Concepts

- The main factors that determine the hardness of a solid are the strength and direction of bonds between its entities.
- covalent bonding    covalent network crystal
  - ionic bonding    ionic crystal
  - covalent bonding    molecular crystal
  - covalent bonding    covalent network crystal
  - metallic bonding    metallic crystal
  - ionic bonding    ionic crystal
- 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.
- 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.
- 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.
  - 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.