

## Applying Inquiry Skills

### 29. Hypothesis

- (a) One might logically hypothesize that double bonds should be longer and stronger than single bonds, and triple bonds longer and stronger yet, because more electron orbital density is between the nuclei. More electron density might make the bonds longer with more space required for more electrons but make the bond stronger because there is more electrostatic attraction of electrons and nuclei.

### Analysis

- (b) According to the evidence provided, the order of bond length, from shortest to longest is triple, double, and then single bonds. The order of bond strength, from weakest to strongest is single, double, and then triple bonds. Single bonds are the longest but the weakest, and triple bonds are the shortest but the strongest.

### Evaluation

- (c) The hypothesis is verified for bond strength, but not for bond length. The reasoning based on electron density appears acceptable for bond strength but does not appear correct for bond lengths. (Note that the reasoning did not take into account the shapes and directions of the  $p$  orbitals forming the  $\pi$  bonds.)

## Making Connections

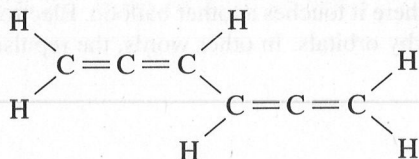
30. (Student reports should contain the following information.)

- (a) Infrared spectroscopy is based on the frequencies absorbed by the internal vibrations of molecules—that is, the vibration of atoms on either side of a bond.
- (b) Each type of bond has a specific vibrational frequency which varies slightly depending on the other atoms in the molecule. Therefore, a unique compound has a unique set of frequencies that it will absorb which allow it to be uniquely identified.
- (c) This technique is used in analysis in medical, pharmaceutical, sports, and industrial chemical laboratories, to name a few.

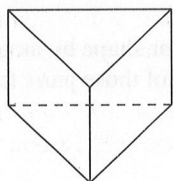
## CASE STUDY: THE STRANGE CASE OF BENZENE

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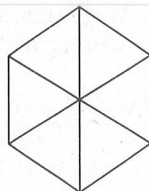
- (d) Benzene is found in coal tar and also in the combustion products of natural materials. Technologically, benzene is produced by the catalytic re-forming of petroleum and is also made from toluene ( $C_6H_5CH_3$ , or methylbenzene).
- (e) More than half of all benzene is used to produce styrene (phenylethene or vinyl benzene) which is the monomer for the plastic polystyrene. Benzene is also used to make detergents, pharmaceuticals, pesticides, and explosives.
- (f) Couper and Loschmidt proposed the following non-cyclic structure but could not provide any empirical support.



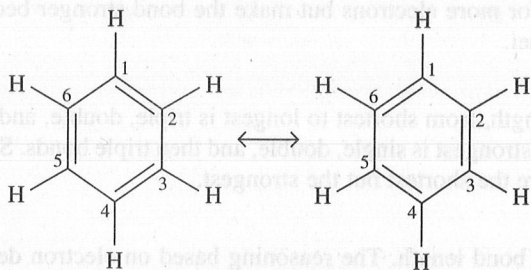
- Ladenburg tried to explain the chemical reactivity of benzene by proposing a prism-type structure.



- Clause also tried to explain the properties of benzene using a hexagon of carbon atoms with diagonal bonds between opposite carbon atoms.



- Kekulé initially proposed that a benzene molecule is a ring of six carbon atoms with alternating single and double covalent bonds. However, he later realized that the chemical reactivity of benzene could be better explained as two possible structures with their double bonds in different locations. Kekulé suggested that these two structures are in a very rapid equilibrium so that there is no fixed location for a particular double bond.



- (g) According to modern theory, each carbon atom in benzene is bonded to two adjacent carbons (in the ring) and one hydrogen using the three  $sp^2$  hybrid orbitals to form sigma bonds. Each of the six carbon atoms has a half-filled  $p$  orbital (perpendicular to the plane of the ring) which overlaps with adjacent  $p$  orbitals. The six  $p$  orbitals overlap above and below the plane of the carbon atoms. In modern terms, the  $p$  electrons are delocalized around the ring. This is a particularly stable arrangement. (This description actually describes only one of three molecular orbitals for benzene, each containing two paired electrons.)

## 4.3 VSEPR THEORY

### Try This Activity: Electrostatic Repulsion Model

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- Two balloons are at about  $180^\circ$  to each other (a linear arrangement).
- Three balloons are at about  $120^\circ$  to each other and all in one plane (a trigonal planar arrangement).
- Four balloons are at about  $109^\circ$  to each other with each one pointing to one corner of a tetrahedron (a tetrahedral arrangement).
- Balloons let you visualize electron orbitals and how they might be arranged. The electrostatic repulsion is modelled by the balloons pushing equally against each other. A disadvantage of the balloon model is that electron orbitals are not physical objects of a fixed size. A balloon only contacts or “repels” where it touches another balloon. Electrostatic repulsion occurs to varying extents between all electrons in the two nearby orbitals. In other words, the repulsion is much more complicated than implied by the two touching balloons.

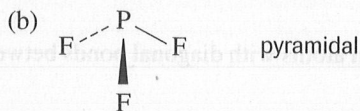
### PRACTICE

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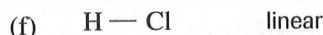
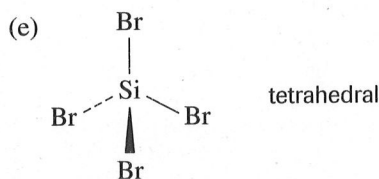
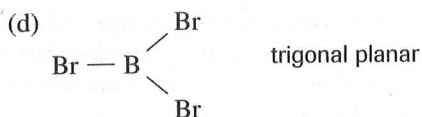
#### Understanding Concepts

- VSEPR is an acronym for valence shell electron pair repulsion — a theory that predicts molecular shape by assuming that repulsion between all pairs of electrons in the valence shell of an atom controls the direction of those pairs formed by bonding, and thus determines the shapes of molecules.

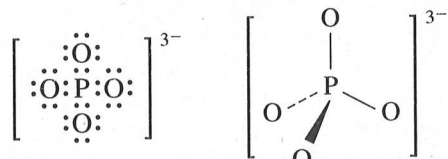
- (a)  $\text{I} - \text{Be} - \text{I}$  linear



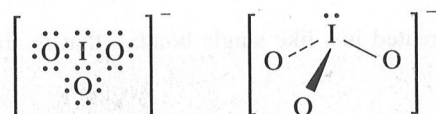
- (c) V-shape



3. (a)  $\text{PO}_4^{3-}$  will be tetrahedral in shape because it has four bond pairs around the P atom.



- (b)  $\text{IO}_3^-$  will be pyramidal in shape, having three bond pairs and one lone pair around the I atom.



4. (a) According to VSEPR theory, the shape around each carbon atom in cubane should be tetrahedral, since there are four bond pairs around each.  
 (b) If we assume an ideal cubic shape, three of the bond angles around each carbon have to be  $90^\circ$ .  
 (c) The normal tetrahedral angle is about  $109^\circ$ . To make these bonding orbitals bend to about  $90^\circ$  would greatly increase the repulsion of the electron pairs. This stress likely makes this molecule very unstable.

### Applying Inquiry Skills

5. VSEPR theory was created to explain known molecular shapes. It provided a simpler way to explain shapes and also to predict molecular shapes.  
 6. (Student reports may use a variety of criteria to evaluate sites. Typical criteria would involve the completeness of information, the opportunity for interaction, and the clarity and conciseness of information provided.)

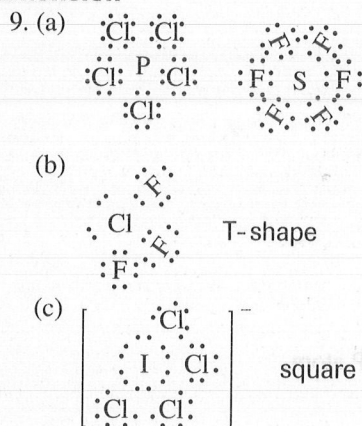
### Making Connections

7. Enzymes catalyze reactions. Their shape is critical, because they fit into precise spaces on the surface of other molecules to alter bond strengths—like a key fits precisely into a lock to allow it to operate.  
 8. Optical isomers are molecular structures that are identical except for their 3-D orientation. They are so named because the two isomeric structures of such a substance will rotate the plane of polarized light in opposite directions—called levorotary (counterclockwise), and dextrorotary (clockwise). Any central atom (such as carbon) to which are bonded four different atoms (or side groups) always has a “left-handed” and a “right-handed” orientation, which are mirror images of each other. That terminology, of course, comes from describing the human hand—which has a front, back, thumb side, and little finger side that can be arranged in space in two ways that are mirror images.



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**Extension**

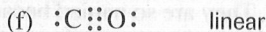
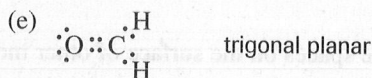
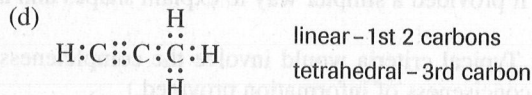
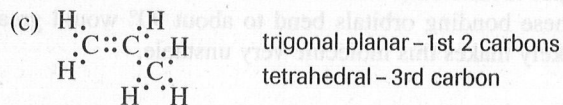
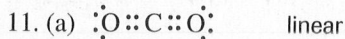


**PRACTICE**

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**Understanding Concepts**

10. To make the rules of VSEPR theory work, multiple bonds must be treated just like single bonds—that is, they are considered to be one bond, which involves 4 or 6 electrons.

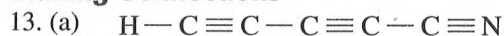


**Applying Inquiry Skills**

12. VSEPR is a very successful scientific theory. It successfully predicts the shapes of most molecular structures with a minimum of complexity—both being criteria for a “good” theory.



## Making Connections



linear shape

- (b) Astronomers detect molecules in space by spectroscopic analysis of electromagnetic radiation (light) absorbed and emitted by regions of space.

## Explore an Issue: Take a Stand: Linus Pauling and the Vitamin C Controversy

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- (a) It is claimed that large doses of vitamin C:
- reduce occurrence and severity of common cold,
  - lower the risk of heart disease and stroke,
  - reduce risk for most common types of cancer,
  - increase survival time and improve quality of life in terminal cancer patients,
  - improve blood vessel dilation, and
  - lower blood lead (Pb) levels.
- (b) The main criticism of Pauling's claims for the benefits of large doses of vitamin C are:
- The results of Pauling's studies using vitamin C to prevent the common cold are not reproducible. Numerous well-designed studies have shown that vitamin C does not prevent common colds; at best, vitamin C may slightly reduce cold symptoms.
  - Pauling's analyses of vitamin C therapy for the prevention and treatment of cancer is flawed. Independent analyses of the same studies show no significant effect.
  - The Linus Pauling Institute of Medicine is largely funded by the pharmaceutical company that produces most of the world's supply of vitamin C.
  - Pauling has lost scientific credibility by his association with the health food industry, which is notorious for making unsubstantiated claims.
- (c) To be scientifically valid, a claim must be experimentally testable. Then there must exist empirical evidence from well-designed experiments that have suitable controls and controlled variables. Finally, the evidence must be reproducible by independent investigators.
- (d) Pauling's fame was very likely a large factor in influencing public and scientific opinion about the benefits of vitamin C. Pauling's two Nobel Prizes represented significant achievements, and both involved contradicting conventional thinking of the time. It seemed plausible that once again Pauling knew more than his contemporaries.

A person unknown to the public and with no scientific training would not be taken seriously if he/she made the same claims about vitamin C, because the public would have no basis to believe the claims.

Reproducible evidence from well-designed studies provides the most reliable basis for deciding which claims to believe. When the empirical evidence is unclear or contradictory, the claim is inconclusive or shown to be false.

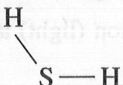

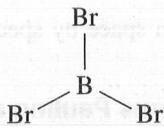
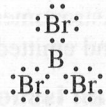

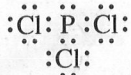
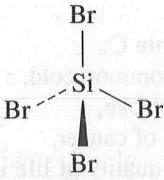
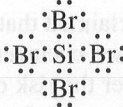
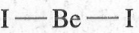
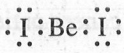
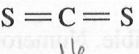
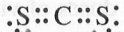
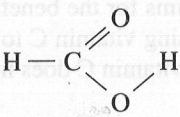
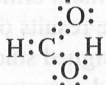
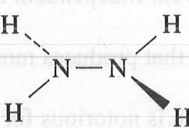
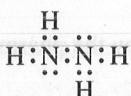
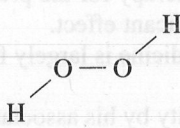

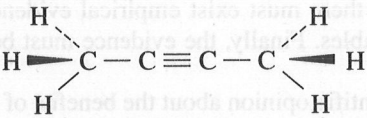
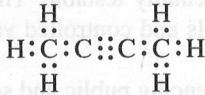
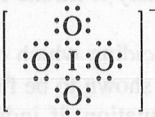

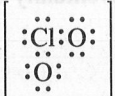
- (e) A scientist who goes against the rest of the scientific community risks his career and reputation, if independent research proves his claim to be wrong. On the other hand, if independent research supports his claim, he may enhance his career and receive much recognition.

The practice and work of science is not always completely objective, especially when new theories are proposed that contradict accepted knowledge. However, if continuing research consistently shows that the new theory is better than the old theory at explaining and predicting experimental evidence, the new theory will eventually be accepted (although this may occasionally take a long time).

## SECTION 4.3 QUESTIONS

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### Understanding Concepts

1. (a)  V-shape 
- (b)  trigonal planar 
- (c)  pyramidal 
- (d)  tetrahedral 
- (e)  linear 
2. (a)  linear 
- (b)  linear (C)  
V-shape (O) 
- (c)  pyramidal (both Ns) 
- (d)  V-shape (both Os) 
- (e)  linear (central Cs)  
tetrahedral (end Cs) 
3. (a)  tetrahedral
- (b)  pyramidal
- (c)  V-shape

### Making Connections

4. Dr. Bader's work has added to our understanding of molecules by applying quantum mechanics to the overall structure of a molecule. This gives a more comprehensive understanding of the structure and bonding, thus allowing for better predictions of molecular structures and ultimately, new substance properties.

5. Dr. Ronald Gillespie, the co-creator of VSEPR theory, is currently Professor Emeritus at McMaster University. He holds B.Sc. and Ph.D. degrees in science, and a D.Sc. from London University. He has won many significant awards, including the Chemical Institute of Canada Medal, the Henry Marshall Tory Medal of the Royal Society of Canada, and the Izaak Walter Killam Memorial Prize of the Canada Council for Pure Science, to name just a few. He is a visiting professor at nine international universities in Europe, Australia, and Asia, and has been awarded four honorary doctorates. His major topic of research, in cooperation with Dr. Richard Bader, is using calculated electron probability distributions to better understand the VSEPR model.
6. The sense of taste seems to be essentially built around the ability of taste receptors to form hydrogen bonds at specific locations with certain molecules. Thus, artificial sweeteners like saccharin and cyclamate and acesulfame-K are non-nutritive molecules with structural similarities to natural sugars. The molecular structure for sweetness involves part of the molecule being a small pentagon or hexagon of atom with the ability to hydrogen bond at a specific spot on the ring. Similarly, artificial compounds like Bitrex®—added as a safety precaution to many medications to make the taste extremely bitter—are structured to a shape that triggers human taste receptors for bitterness to react strongly.

## 4.4 POLAR MOLECULES

### PRACTICE

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#### Understanding Concepts

1. (a)
 

$\delta^+$	$\delta^-$	
H	—	Cl
2.1		3.0

 polar covalent
  
  - (b)
 

$\delta^-$	$\delta^+$	
C	—	H
2.5		2.1

 polar covalent
  
  - (c)
 

$\delta^+$	$\delta^-$	
N	—	O
3.0		3.5

 polar covalent
  
  - (d)
 

$\delta^+$	$\delta^-$	
I	—	Br
2.5		2.8

 polar covalent
  
  - (e)
 

+	—	-
Mg	—	S
1.2		2.5

 ionic
  
  - (f)
 

P	—	H
2.1		2.1

 nonpolar covalent
2. (a) polar covalent  
 (b) ionic  
 (c) nonpolar covalent
  3. The list of the bonds in order of increasing bond polarity is assumed to be the same as the order of increasing difference in electronegativity of the bonded atoms. Thus, the orders are as follows:
    - (a) H—H, C—H, Be—H, N—H, Li—H, O—H, F—H
    - (b) I—I, I—Cl, P—Cl, (Li—I, Al—Cl), Rb—F (Note: Li—I and Al—Cl have equal dipoles.)
    - (c) C—H, C—O, O—H
    - (d) C—H, C—Cl, C—F



## Applying Inquiry Skills

4. Empirical (measured, observed) values change as new and better methods of determining values are found. As well, the electronegativity of an atom is not an exact concept. It also varies somewhat, depending on the bonded atoms. The new values could be described as more accurate values, but the word "true" cannot properly be applied to relative numerical values of this sort.

## Extension

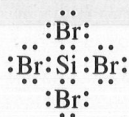
5. Pauling's electronegativity scale is derived from measurements of bond energies; the Mulliken-Jaffé scale is derived from the electron affinity and ionization potentials; and the Allred-Rochow scale is derived from the covalent radius and the effective charge on the electron (allowing for nuclear shielding). The relative values for electronegativity of the elements, and predictions made from these values, naturally vary slightly depending on which scale is used.

## PRACTICE

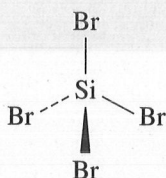
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### Understanding Concepts

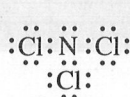
6. (a)



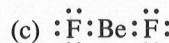
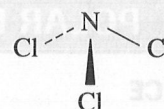
tetrahedral



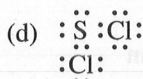
(b)



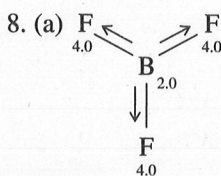
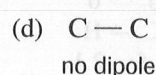
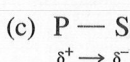
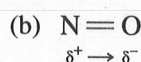
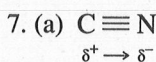
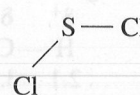
pyramidal



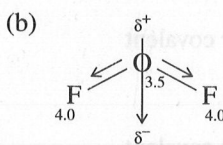
linear



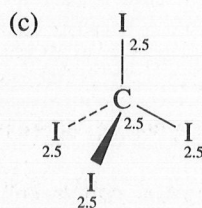
V-shape



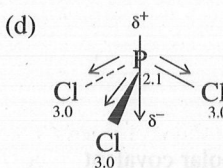
zero resultant



resultant dipole toward F side of molecule



no bond dipoles



resultant dipole toward Cl side of molecule

9. An octane,  $\text{C}_8\text{H}_{18(l)}$ , molecule should be nonpolar using the generalization that any molecule composed of carbons and only one other kind of atom is a nonpolar molecule.
10. For  $\text{N}_2\text{H}_4(l)$ , the molecular structure is symmetrical; thus, the molecule is nonpolar.

## Applying Inquiry Skills

11. Hydrogen sulfide,  $\text{H}_2\text{S}_{(g)}$ , has a V-shaped molecule, with bond dipoles directed toward the sulfur. Thus, the molecular dipole should be slightly negative on the sulfur side, and slightly positive on the hydrogen side.

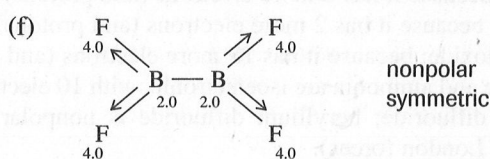
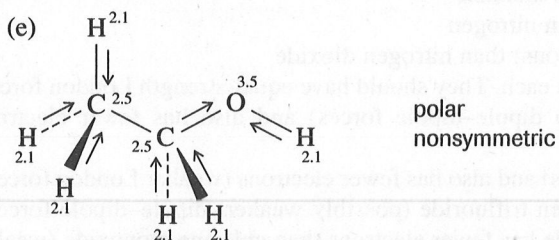
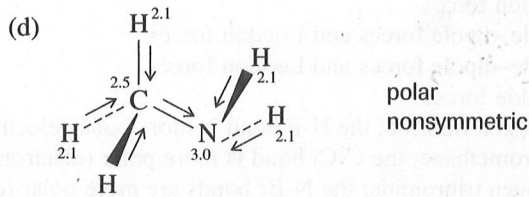
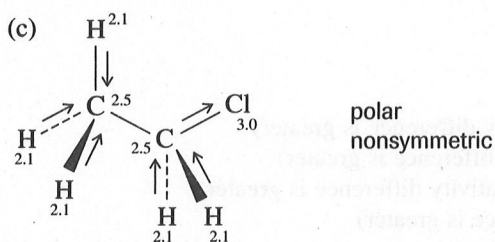
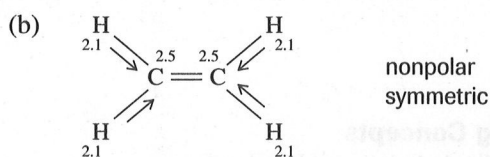
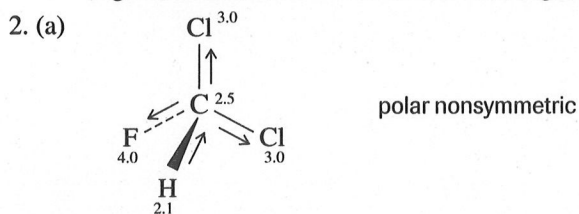
The hydrogen sulfide will be cooled to the liquid state, and a thin stream of the liquid allowed to flow downward past a strong electric charge. Molecular polarity should cause deflection of the liquid stream.

## SECTION 4.4 QUESTIONS

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### Understanding Concepts

- Beryllium bromide is nonpolar because it is symmetrical. Therefore, the bond dipoles add up to zero for the whole molecule.
  - Nitrogen trifluoride is polar because it has polar bonds and is not symmetrical. The sum of all of the bond dipoles produces a non-zero dipole for the whole molecule.
  - Methanol is polar because it has polar bonds and is not symmetrical. The sum of all of the bond dipoles produces a non-zero dipole for the whole molecule.
  - Hydrogen peroxide is nonpolar because it has polar bonds and is assumed to be symmetrical. The sum of all of the bond dipoles produces a zero dipole for the whole molecule. (Note that this answer ignores any rotation about the O-O bond and considers only the most stable arrangement.)
  - Ethylene glycol is nonpolar because it has polar bonds and is symmetrical. The bond dipoles have a zero resultant. (Again, this assumes the most stable arrangement.)



- Based upon polarity, water is a candidate for use in a capacitor, because it is a V-shaped (nonsymmetrical) molecule with high molecular polarity.
  - Other considerations for choosing a liquid inside a capacitor might be toxicity, corrosiveness, cost, ease of fabrication, and effectiveness as a storage material.



### 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.