WHAT IS A CHEMICAL BOND? It will take us the next two chapters to answer this question! Bonds are attractive forces that hold groups of atoms together and make them function as a unit. [Defined in 25 words or less, but leaves out LOTS of details!] Bonding relates to physical properties such as melting point, hardness and electrical and thermal conductivity as well as solubility characteristics. The system is achieving the lowest possible energy state by bonding. If you think about it, most of the chemical substances you can name or identify are NOT elements. They are compounds. That means being bound requires less energy than existing in the elemental form. It also means that energy was released from the system. This is a HUGE misconception most students have—it takes energy to break a bond, not make a bond! Energy is RELEASED when a bond is formed, therefore, it REQUIRES energy to break a bond.

Bond energy—energy required to break the bond

TYPES OF CHEMICAL BONDS
• **ionic bonds**—an electrostatic attraction between ions; usually produced by the reaction between a metal and nonmetal. Cause very high melting points and usually a solid state since the attraction is SO strong that the ions are VERY close together in a crystal formation.
• **covalent bonds**—electrons are shared by nuclei [careful, sharing is hardly ever 50-50!]
• **Coulomb’s Law**—used to calculate the Energy of an ionic bond.

\[ E = 2.31 \times 10^{-19} \text{ J} \cdot \text{nm} \left( \frac{Q_1 Q_2}{r} \right) \]

- \( r \) is the distance between the ion centers in nanometers [size matters!]
- \( J \) is the energy in Joules
- \( Q_1 \) and \( Q_2 \) are the numerical ion charges; don’t neglect their signs

There will be a negative sign on the Energy once calculated—it indicates an attractive force so that the ion pair has lower energy than the separated ions.

You can also use Coulomb’s Law to calculate the repulsive forces between like charges. What sign will that calculation have?

VALENCE ELECTRONS
• valence electrons—outermost electrons; focus on \( ns, np \) and \( d \) electrons of transition elements.
• Lewis dot structures—(usually main group elements) G.N. Lewis, 1916
• Emphasizes rare gas configurations, \( s^2p^6 \), as a stable state. All rare gasses except \( He \) have 8 valence electrons and follow the octet rule.

CHEMICAL BOND FORMATION
**Level 1**—When 2 hydrogen atoms approach each other 2 “bad” E things happen: electron/electron repulsion and proton/proton repulsion. One “good” E thing happens: proton/electron attraction. When the attractive forces offset the repulsive forces, the energy of the two atoms decreases and a bond is formed. Remember, nature is always striving for a LOWER ENERGY STATE.
• **bond length**—the distance between the 2 nuclei where the energy is minimum between the two nuclei.
• energy decrease is small--van der Waals IMFs [another chapter!]
• energy decrease is larger--chemical bonds

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Level 2—**Orbital Theory** — electrons and + nucleus of one atom strongly perturb or change the spatial distribution of the other atom’s valence electrons. A new orbital (wave function) is needed to describe the distribution of the bonding electrons **bond orbital**

- **bond orbital**—describes the motion of the 2 electrons of opposite spin
- **lone pair orbital**—the orbitals of electrons on a bonded atom that are distorted away from the bond region also have new descriptions (wave functions)

- The new bond orbital is “built” from the atomic orbitals of the two bonded atoms. Looks a lot like the original BUT, the bond orbital is concentrated in the region between the bonded nuclei.
- The energy of the electrons in a bond orbital, where the electrons are attracted by two nuclei, is lower than their energy in valence electron orbitals where the electrons are attracted to only one nucleus. [ZAPPED!!]
- **ionic bond**—the bonding orbital is strongly displaced toward one nuclei (metal from the left side of table + nonmetal from right side of the periodic table)
- **covalent bond**—bond orbital is more or less (polar or non-polar) evenly distributed and the electrons are shared by two nuclei. (elements lie close to one another on the periodic table)
- **Most chemical bonds are in fact somewhere between purely ionic and purely covalent.**

Recall the information you’ve already learned about electronegativity:

**ELECTRONEGATIVITY (En)**—The ability of an atom IN A MOLECULE [meaning it’s participating in a BOND] to attract shared electrons to itself. Think “tug of war”. Now you know why they teach you such games in elementary school!

- Linus Pauling’s scale—Nobel Prize for Chemistry & Peace
- Fluorine is the most En and Francium is the least En

![Electronegativity Chart]

- Why is F the most? Highest $Z_{eff}$ and smallest radius so that the nucleus is closest to the “action”.
- Why is Fr the least? Lowest $Z_{eff}$ and largest radius so that the nucleus is farthest from the “action”.
- We’ll use this concept a great deal in our discussions about bonding since this atomic trend is **only used when atoms form molecules**.

Use the difference in En to determine the type of bond formed.

- ionic—Electronegativity difference $> 1.67$
- covalent—Electronegativity difference $< 1.67$
- NONpolar En difference $< 0.4$
Exercise 1  Relative Bond Polarities
Order the following bonds according to polarity:  H—H, O—H, Cl—H, S—H, and F—H.

- **bond polarity and electronegativity**—En (χ) determines polarity since it measures a nucleus’ attraction or “pull” on the bonded electron pair.  En ranges from 0--4.0.  When 2 nuclei are the same, the sharing is equal ∴ the bond is described as NONPOLAR (a).  When the 2 nuclei are different the electrons are not shared equally, setting up slight +/- poles ∴ POLAR (b).  When the electrons are shared unequally to a greater extent ∴ IONIC (c).

- The polarity of a bond can be estimated from Δχ/Σχ.  Range is 0 for pure covalent bonds to 1 for completely ionic bonds.

### IONIC BONDING

The final result of ionic bonding is a solid, regular array of cations and anions called a **crystal lattice**.  At right, you can see the energy changes involved in forming LiF from the elements Li and F₂.

- Enthalpy of dissociation—energy required to decompose an ion pair (from a lattice) into ions ∴ a measure of the strength of the ionic bond
- from Coulomb’s law:

\[
E = \Delta H_{\text{dissociation}} \propto \frac{q_+q_-}{r}
\]

where \(q_+\) is the charge on the positive ion and \(q_-\) is the charge on the negative ion and \(r\) is the distance between the ion centers in the crystal lattice.

- energy of attraction depends directly on the magnitude of the charges (higher the charges the greater the attractive energy) and inversely on the distance between them (greater the distance, the smaller the attractive energy).
- the larger the ion the smaller the \(\Delta H_{\text{dissociation}}\) (it’s a distance thing)
  - ion-ion attractions have a profound effect on melting points and solubilities.
  - Water must overcome the ion-ion attractions to dissolve an ionic substance.  Size affects this as does charge HOW??
  - The crystal lattice for LiF is shown at the left.
  - Lattice energy can be represented by a modified form of Coulomb’s Law: \(k\) is a proportionality constant that depends on the structure of the solid and the electron configurations of the ions.

\[
\text{Lattice Energy} = k \left( \frac{QO}{r} \right)
\]
COVALENT BONDING
Most compounds are covalently bonded, especially carbon compounds. We have 3 major bonding theories to discuss. Only one for this chapter though!
- **Localized Electron [LE] Bonding Model**—assumes that a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms. Electron pairs are assumed to be localized on a particular atom [lone pairs] or in the space between two atoms [bonding pairs].
  1. Lewis Structures describe the valence electron arrangement
  2. Geometry of the molecule is predicted with VSEPR
  3. Description of the type of atomic orbitals “blended” by the atoms to share electrons or hold lone pairs [hybrids—next chapter].
- **Number of Bond Pairs: The Octet Rule**—“noble is good”
  - predict # of bonds by counting the number of unpaired electrons in a Lewis structure
  - a dash is used to represent a pair of shared electrons, : is used to represent a lone pair

SINGLE AND MULTIPLE BONDS:
- single bond--one pair of electrons shared $\sigma$ sigma ($\sigma$) bond
- **MULTIPLE BONDS ARE MOST OFTEN FORMED** by C,N,O,P and S ATOMS—say “C-NOPS”
- double bond--two pairs of electrons shared $\sigma$ one $\sigma$ bond and one $\pi$ bond
- triple bond--three pairs of electrons shared $\sigma$ one $\sigma$ bond and two $\pi$ bonds
- obviously, combinations of $\sigma$ and $\pi$ are stronger than $\sigma$ alone. Pi bonds are weaker than sigma but never exist alone
- Multiple bonds increase the electron density between two nuclei and therefore decrease the nuclear repulsions while enhancing the nucleus to electron density attractions—either way, the nuclei move closer together and the bond length is shorter for a double than a single and triple is shortest of all!

COORDINATE COVALENT BONDS:
Some atoms such as N and P, tend to share a lone pair with another atom that is short of electrons, leading to the formation of a coordinate covalent bond: These bonds are in all coordination compounds and Lewis Acids/Bases

ammonium ion formation:

We show that N is sharing the lone PAIR of electrons by drawing an arrow from it to the H+, remember H+ has NO electrons to contribute to the bond. Note that all four bonds are actually identical in length and strength.

EXCEPTIONS TO THE OCTET RULE:
- **Fewer than eight**--H at most only 2 electrons (one bond)! BeH$_2$, only 4 valence electrons around Be (only two bonds)! Boron compounds, only 6 valence electrons (three bonds)!
  ammonia + boron trifluoride is a classic Lewis A/B reaction.
- **Expanded Valence**—can only happen if the central element has d-orbitals which means it is from the 3rd period or greater [periods 4, 5, 6…] and can thus be surrounded by more than four valence pairs in certain compounds. The number of bonds depends on the balance between the ability of the nucleus to attract electrons and the repulsion between the pairs.
- **odd-electron compounds**—A few stable cmpds. contain an odd number of valence electrons and thus cannot obey the octet rule. NO, NO$_2$, and ClO$_2$. 

HUGE concept CRITICAL stuff!
Drawing Lewis Structures: (VERY USEFUL when predicting molecular shape)

To predict arrangement of atoms within the molecule use the following rules:

1. H is always a terminal atom. ALWAYS connected to only one other atom!!
2. LOWEST En is central atom in molecule [not just the oddball element]
3. Find the total # of valence electrons by adding up group #’s of the elements. FOR IONS add for negative and subtract for positive charge. Divide by two to get the number of electron PAIRS.
4. Place one pair of electrons, a σ bond, between each pair of bonded atoms.
5. Subtract from the total the number of bonds you just used.
6. Place lone pairs about each terminal atom (EXCEPT H) to satisfy the octet rule. Left over pairs are assigned to the central atom. If the central atom is from the 3rd or higher period, it can accommodate more than four electron pairs, up to six pairs.
7. If the central atom is not yet surrounded by four electron pairs, convert one or more terminal atom lone pairs to pi bonds pairs. NOT ALL ELEMENTS FORM PI BONDS!! only C, N, O, P, and S!!

Exercise 6  Writing Lewis Structures
Give the Lewis structure for each of the following:

a. HF  d. CH₄
b. N₂  e. CF₄

Exercise 7  Lewis Structures for Molecules That Violate the Octet Rule I
Write the Lewis structure for PCl₅.

Exercise 8  Lewis Structures for Molecules That Violate the Octet Rule II
Write the Lewis structure for each molecule or ion.

a. ClF₃  b. XeO₃  c. RnCl₂  d. BeCl₂  e. ICl₄⁻
**RESONANCE STRUCTURES:**

Experiments show that ozone, O₃ has equal bond lengths and equal bond strengths, implying that there is an equal number of bond pairs on each side of the central O atom. When you draw the Lewis structure, that situation is NOT what you draw! So, we draw a resonance structure:

\[
\begin{array}{c}
\text{[O-O-O]} \\
\leftrightarrow \\
\text{[O=O]} \\
\end{array}
\]

We draw it as having a double bond and a single bond [the dashes are another way of representing lone pairs] BUT since there are equal bond lengths and strengths, they are clearly NOT as pictured above. The bonds are more equivalent to a “bond and \(\frac{1}{2}\)” in terms of length and strength. We use the double edged arrows to indicate resonance. We also bracket the structures just as we do for polyatomic ions.

In an attempt to improve the drawing, we sometimes use a single composite picture. The drawing at right better shows the bond angle. Focus on the central atom in either of the resonance structures above. The central atom is surrounded by three sites of electron density: a lone pair, a single \(\sigma\) bond and a double bond (consisting of one \(\sigma\) bond and one \(\pi\) bond). Three electron-dense sites surrounding a central point in a 3-dimensional space will orient themselves at 120° so that electron/electron repulsions are minimized.

Carbonate ion:

NOTE: These all 3 need brackets and the charge shown in the upper right corner [like the composite at right] to gain full credit on the AP Exam!!!!

\[
\text{CO}_3^{2-}
\]

**THREE EQUIVALENT STRUCTURES**

**RESONANCE HYBRID**

Notice: 1) resonance structures differ only in the assignment of electron pair positions, NEVER atom positions. 2) resonance structures differ in the number of bond pairs between a given pair of atoms

<table>
<thead>
<tr>
<th>Exercise 9</th>
<th>Resonance Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Describe the electron arrangement in the nitrite anion (NO₂⁻) using the localized electron model.</td>
<td></td>
</tr>
</tbody>
</table>
BOND PROPERTIES

- **bond order**—simply the number of bonding electron pairs shared by two atoms in a molecule.
  - 1—only a sigma bond between the 2 bonded atoms
  - 2—2 shared pairs between two atoms; one sigma and one pi (CO₂ and ethylene)
  - 3—3 shared pairs between two atoms; one sigma and two pi (acetylene and CO and cyanide)
  - fractional—resonance; ozone 3/2; carbonate 2/3

  \[
  \text{bond order} = \# \text{ of shared pairs linking } X \text{ and } Y \\
  \text{number of } X-Y \text{ links}
  \]

- **bond length**—distance between the nuclei of two bonded atoms  
  \( C-N < C=C < C=P \)
  
The effect of bond order is evident when you compare bonds between the same two atoms

<table>
<thead>
<tr>
<th>Bond</th>
<th>C–O</th>
<th>C=O</th>
<th>C≡O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond order</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Bond length (pm)</td>
<td>143</td>
<td>122</td>
<td>113</td>
</tr>
</tbody>
</table>

The bond length is reduced by adding multiple bonds since it increases the electron density between the two nuclei. Variations in neighboring parts of a molecule can affect the length of a particular bond as much as 10%

- **bond energy**—the greater the number of electron pairs between a pair of atoms, the shorter the bond. This implies that atoms are held together more tightly when there are multiple bonds, so there is a relation between bond order and the energy required to separate them.

- **bond dissociation energy(D)**—gaseous atom; E supplied to break a chemical bond (bond energy for short!)
  - D is + and breaking bonds is *endothermic*. The converse is also true.
  - D in table 10.4 is +
  - D is an average with a +/- 10%
  - Gaseous atoms
  - What is the connection between bond energy and bond order???

- Calculating reaction energies from bond energies: Bonds in reactants are broken while bonds in products are formed. Energy released is greater than energy absorbed in EXOThermic reactions. The converse is also true.

\[
\Delta H^\circ_{\text{reaction}} = \Sigma mD \text{ (bonds broken)} - \Sigma nD\text{(bonds made)}
\]
\[ \Delta H^\circ_{\text{reaction}} = \text{reactants}(E \text{ cost}) - \text{products}(E \text{ payoff}) \]

NOTE THIS IS “BACKWARDS” FROM THE THERMODYNAMICS “BIG MAMMA” EQUATION. We’re back to that misconception if you are confused by this. It takes energy to break bonds NOT make bonds! First we must break the bonds of the reactants [costs energy] then subtract the energy gained by forming new bonds in the products.

Exercise 5

\[ \Delta H^\circ \text{ from Bond Energies} \]

Using the bond energies listed in Table 8.4, calculate \( \Delta H^\circ \) for the reaction of methane with chlorine and fluorine to give Freon-12 (CF\(_2\)Cl\(_2\)).

\[
\text{CH}_4(g) + 2\text{Cl}_2(g) + 2\text{F}_2(g) \rightarrow \text{CF}_2\text{Cl}_2(g) + 2\text{HF}(g) + 2\text{HCl}(g)
\]

\[ \Delta H = -1194 \text{ kJ/mol} \]

FORMAL CHARGE

Often, many nonequivalent Lewis structures may be obtained which all follow the rules. Use the idea of formal charge to determine the most favored structure. Physicists tell us that oxidation states of more than +/− two are pure fantasy and that formal charges are much more realistic.

- **formal charge**—The difference between the number of valence electrons on the free element and the number of electrons assigned to the atom in the molecule.

\[
\text{Atom’s formal charge} = \text{group number} - [\# \text{ of lone electrons} - 2 (\# \text{ of bonding electrons})]
\]

**THE SUM OF THE FORMAL CHARGES MUST EQUAL AN ION’S CHARGE!!**

- Use formal charges along with the following to determine resonance structure
  - Atoms in molecules (or ions) should have formal charges as small as possible—as close to zero as possible **[principle of electroneutrality]**
  - A molecule (or ion) is most stable when any negative formal charge resides on the most electronegative atom.
Example: Draw all possible structures for the sulfate ion. Decide which is the most plausible using formal charges.

**Caution** Although formal charges are considered closer to the atomic charges than the oxidation states, they are still only estimates and should not be taken as the actual atomic charges. Second, using formal charges can often lead to erroneous structures, so tests based on experiments must be used to make the final decisions on the correct description of bonding.

### Exercise 10
Give possible Lewis structures for XeO₃, an explosive compound of xenon. Which Lewis structure or structures are most appropriate according to the formal charges?

<table>
<thead>
<tr>
<th>Structures with the lower values of formal charge would be most appropriate</th>
</tr>
</thead>
</table>

**MOLECULAR SHAPE—MINIMIZE ELECTRON PAIR REPULSIONS!!!**

**VSEPR**—valence shell electron pair repulsion theory

- Molecular shape changes with the numbers of \( \sigma \) bonds plus lone pairs about the central atom

<table>
<thead>
<tr>
<th>( \sigma ) bonds + lone pairs on central atom</th>
<th>STRUCTURAL PAIR or ELECTRONIC GOMETRY (NOT to be confused with molecular geometry!)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
</tr>
<tr>
<td>3</td>
<td>Trigonal planar</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral (or pyramidal)</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramidal</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
</tr>
</tbody>
</table>

**THE VSPER MODEL AND MOLECULAR SHAPE**

- **molecular geometry**—the arrangement in space of the atoms bonded to a central atom *not necessarily the same as the structural pair geometry* \( \sigma \) lone pairs have a different repulsion since they are experiencing an attraction or “pull” from only one nucleus as opposed to two nuclei. They also take up more space around an atom as you can see on the left.
- Each lone pair or bond pair repels all other lone pairs and bond pairs—they try to avoid each other making as wide an angle as possible.
  - works well for elements of the \( s \) and \( p \)-blocks
  - VSEPR does not apply to transition element compounds (exceptions)
• MOLECULAR SHAPES FOR CENTRAL ATOMS WITH NORMAL VALENCE: no more than 4 structural pairs if the atom obeys the octet rule. Since no lone pairs are present, the molecular and structural pair [or electronic] geometry is the same. 109.5° bond angle.
  - Ignore lone pairs AFTER you’ve determined the angles ∴ only the relative positions of the atoms are important in molecular geometry
  - Below is ammonia—3 sigma bonds and one lone pair—when lone pairs are present, the structural pair or electronic geometry are different!!
  - “electronic geometry”—tetrahedral while molecular geometry—trigonal pyramidal, 107.5° bond angle

- Water has 2 lone pairs and still obeys the octet rule. Again, the electronic and molecular geometries will be different. The electronic is still tetrahedral since the octet rule is obeyed BUT the molecular geometry is described as “bent” or V-shaped, 104.5° bond angle.

Now, let’s discuss the warping of the 109.5° bond angle. The lone pairs have more repulsive force than shared pairs and are “space hogs”. They force the shared pairs to squeeze together.

- To determine the geometry:
  1. Sketch the Lewis dot structure [DO NOT SKIP THIS STEP.]
  2. Describe the structural pair or electronic geometry
  3. Focus on the bond locations (ignore lone pairs) and assign a molecular geometry based on their locations
• MOLECULAR SHAPES FOR CENTRAL ATOMS WITH EXPANDED VALENCE—only elements with a principal energy level of 3 or higher can expand their valence and violate the octet rule on the high side. Why?

- *d* orbitals are needed for the expansion to a 5th or 6th bonding location—the combination of 1 *s* and 3 *p*’s provides the four bonding sites that make up the octet rule.

- seems to be a limit of 3 lone pairs about the central atom
- XeF₄; There are 2 lone pairs and 4 shared pairs. Two possible arrangements exist for this situation.
  - *equatorial*—shared pairs surround Xe. In both molecular arrangements the electronic geometry is octahedral with 90° angles. (a) has a molecular geometry known as “see saw”. This puts the lone pairs only 90° apart.
  - *axial*—lone pairs are located “top and bottom” This is preferred for this molecule since the lone pairs are 180° apart which minimizes their repulsion. Lone pairs prefer maximum separation—use this in your determinations! (b at upper right) has a molecular geometry that is more stable—square planar

Which of these arrangements do you predict to be the most stable for I₃⁻?

Remember to look at the lone pair-lone pair angles to make your determination.

---

**Exercise 11**

**Prediction of Molecular Structure I**

Describe the molecular structure of the water molecule.

Two bonding and two non-bonding pairs of electrons
Forming a V shape molecule

---

**Exercise 12**

**Prediction of Molecular Structure II**

When phosphorus reacts with excess chlorine gas, the compound phosphorus pentachloride (PCl₅) is formed. In the gaseous and liquid states, this substance consists of PCl₅ molecules, but in the solid state it consists of a 1:1 mixture of PCl₄⁻ and PCl₅²⁻ ions. Predict the geometric structures of PCl₃, PCl₄⁻, and PCl₅²⁻.
• RECAP including bond angles for all
• **structural pairs**—σ bond (π bond pairs occupy the same space) pairs about an atom
  - 2 @ 180° ∴ linear [and of course, planar]

- 3 @ 120° ∴ trigonal planar

- 4 @ 109.5° ∴ tetrahedral

- 3 @ 120 & 2 @ 90° with each other through central atom ∴ trigonal bipyramidal

- 6 @ 90° ∴ octahedral

The presence of lone pairs alters the six basic MOLECULAR geometries, but the *electronic or structural pair* geometry remains one of these six basic types.
MOLECULAR POLARITY

polar—bonds can be polar while the entire molecule isn’t and vice versa.

dipole moment—separation of the charge in a molecule; product of the size of the charge and the distance of separation

• align themselves with an electric field (figure b at right)
• align with each other as well in the absence of an electric field
• water—2 lone pairs establish a strong negative pole
• ammonia—has a lone pair which establishes a neg. pole
• note that the direction of the “arrow” indicating the dipole moment always points to the negative pole with the cross hatch on the arrow (looks sort of like we’re trying to make a + sign) is at the positive pole. Logical?

• IF octet rule is obeyed [which it is in both water and ammonia] AND all the surrounding bonds are the same [even if very polar] then the molecule is NONpolar since all the dipole moments cancel each other out.

• carbon dioxide, above is nonpolar since the dipole moments cancel. For those of you in physics, the dipole moments are vector quantities.

• Methane is a great example. Replace one H with a halogen and it becomes polar. Replace all and it’s nonpolar again!

Draw CH₄, CH₃Cl, CH₂Cl₂, CHCl₃, CCl₄. Indicate dipole moment(s) where necessary.
Exercise 2 Bond Polarity and Dipole Moment
For each of the following molecules, show the direction of the bond polarities and indicate which ones have a dipole moment: HCl, Cl₂, SO₃ (a planar molecule with the oxygen atoms spaced evenly around the central sulfur atom), CH₄ [tetrahedral (see Table 8.2) with the carbon atom at the center], and H₂S (V-shaped with the sulfur atom at the point).

Exercise 13 Prediction of Molecular Structure III
Because the noble gases have filled s and p valence orbitals, they were not expected to be chemically reactive. In fact, for many years these elements were called inert gases because of this supposed inability to form any compounds. However, in the early 1960s several compounds of krypton, xenon, and radon were synthesized. For example, a team at the Argonne National Laboratory produced the stable colorless compound xenon tetrafluoride (XeF₄). Predict its structure and whether it has a dipole moment.

Exercise 14 Structures of Molecules with Multiple Bonds
Predict the molecular structure of the sulfur dioxide molecule. Is this molecule expected to have a dipole moment?
ONCE MORE WITH FEELING…

CHEMICAL BONDS—Forces of attraction that hold groups of atoms together within a molecule or crystal lattice and make them function as a unit.

IONIC

Characteristics of ionic substances usually include:
- electrons that are transferred between atoms having high differences in electronegativity (greater than 1.67)
- compounds containing a metal and a nonmetal (Remember that metals are located on the left side of the periodic table and nonmetals are to the right of the “stairs”.)
- strong electrostatic attractions between positive and negative ions
- formulas given in the simplest ratio of elements (empirical formula; NaCl, MgCl₂)
- crystalline structures that are solids at room temperature
- ions that form a crystal lattice structure as pictured in Figure 1
- compounds that melt at high temperatures
- substances that are good conductors of electricity in the molten or dissolved state

COVALENT

Characteristics of covalent substances usually include:
- the sharing of electrons between atoms having small differences in electronegativities (less than 1.67)
- nonmetals attracted to other nonmetals
- formulas that are given in the true ratios of atoms (molecular formulas; C₆H₁₂O₆)
- substances that may exist in any state of matter at room temperature (solid, liquid, or gas)
- compounds that melt at low temperatures
- substances that are nonconductors of electricity

METALLIC

Characteristics of metallic substances usually include:
- substances that are metals
- a “sea” of mobile or delocalized electrons surrounding a positively charged metal center
- an attraction between metal ions and surrounding electrons
- formulas written as a neutral atom (Mg, Pb)
- solids with a crystalline structure at room temperature
- a range of melting points—usually depending on the number of valence electrons
- substances that are excellent conductors of electricity since the electrons in the “sea” are free to move
Most chemical bonds are in fact somewhere between purely ionic and purely covalent.

**DRAW THE DANG LEWIS STRUCTURE**

when answering bonding multiple choice or free-response questions.
<table>
<thead>
<tr>
<th>HYBRIDIZATION</th>
<th>REGIONS OF ELECTRON DENSITY</th>
<th>GEOMETRIES ANGLES POLARITIES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>Remember that in molecules where the outside atoms are different, shapes that tend to be nonpolar usually become polar</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Remember to count the number of regions of electron density. Lone pairs, double and triple bonds are all only one region</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

Lone pairs and atoms with higher electronegativities cause a bond to have a dipole moment towards them.
Lone pairs have more energy and thus occupy more space, they repel bonded pairs therefore decreasing bond angles.
1996

Explain each of the following in terms of the electronic structure and/or bonding of the compounds involved.

(a) At ordinary conditions, HF (normal boiling point = 20°C) is a liquid, whereas HCl (normal boiling point = -114°C) is a gas.

(b) Molecules of AsF₃ are polar, whereas molecules of AsF₅ are nonpolar.

(c) The N-O bonds in the NO₂⁻ ion are equal in length, whereas they are unequal in HNO₂.

(d) For sulfur, the fluorides SF₂, SF₄, and SF₆ are known to exist, whereas for oxygen only OF₂ is known to exist.

1999

Answer the following questions using principles of chemical bonding and molecular structure.

(a) Consider the carbon dioxide molecule, CO₂, and the carbonate ion, CO₃²⁻.

(i) Draw the complete Lewis electron-dot structure for each species.

(ii) Account for the fact that the carbon-oxygen bond length in CO₃²⁻ is greater than the carbon-oxygen bond length in CO₂.

(b) Consider the molecules CF₄ and SF₄.

(i) Draw the complete Lewis electron-dot structure for each molecule.

(ii) In terms of molecular geometry, account for the fact that the CF₄ molecule is nonpolar, whereas the SF₄ molecule is polar.

2002B

Using principles of chemical bonding and molecular geometry, explain each of the following observations. Lewis electron-dot diagrams and sketches of molecules may be helpful as part of your explanations. For each observation, your answer must include references to both substances.

(a) The bonds in nitrite ion, NO₂⁻, are shorter than the bonds in nitrate ion, NO₃⁻.
(b) The CH₃F₂ molecule is polar, whereas the CF₄ molecule is not.
(c) The atoms in a C₂H₄ molecule are located in a single plane, whereas those in a C₂H₆ molecule are not.
(d) The shape of a PF₅ molecule differs from that of an IF₅ molecule.
(e) HClO₃ is a stronger acid than HClO.
2003

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Compound Formula</th>
<th>$\Delta H^{\circ}_{\text{vap}}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>CH$_3$CH$_2$CH$_3$</td>
<td>19.0</td>
</tr>
<tr>
<td>Propanone</td>
<td>CH$_3$COCH$_3$</td>
<td>32.0</td>
</tr>
<tr>
<td>1-propanol</td>
<td>CH$_3$CH$_2$CH$_2$OH</td>
<td>47.3</td>
</tr>
</tbody>
</table>

Using the information in the table above, answer the following questions about organic compounds.

(a) For propanone,
   (i) draw the complete structural formula (showing all atoms and bonds);
   (ii) predict the approximate carbon-to-carbon-to-carbon bond angle.

(b) For each pair of compounds below, explain why they do not have the same value for their standard heat of vaporization, $\Delta H^{\circ}_{\text{vap}}$. (You must include specific information about both compounds in each pair.)
   (i) Propane and propanone
   (ii) Propanone and 1-propanol

(c) Draw the complete structural formula for an isomer of the molecule you drew in part (a) (i).

(d) Given the structural formula for propyne below,

```
H

H—C—C≡C—H

H
```

   (i) indicate the hybridization of the carbon atom indicated by the arrow in the structure above;
   (ii) indicate the total number of sigma ($\sigma$) bonds and the total number of pi ($\pi$) bonds in the molecule.
QUESTION 9
(5 points)

9. Explain each of the following observations in terms of the electronic structure and/or bonding of the compounds involved.

(a) In ordinary conditions, HF (normal boiling point = 20°C) is a liquid, whereas HCl (normal boiling point = -84°C) is a gas.

(b) Molecules of Al₂O₃ are polar, whereas molecules of Al₂Cl₄ are nonpolar.

(c) The N-O bond in the NO₂⁻ ion is equal in length, whereas they are unequal in NO₂.

(d) For sulfur, the fluorides SF₂, SF₃, and SF₄ are known to exist, whereas for oxygen only SO₃ is known to exist.

Scoring Guide

(a) Hydrogen bonding (or dipole–dipole attraction) in HF to greater than it is in HCl.

(b) Al₂O₃ has a trigonal pyramidal shape and bond dipoles do not cancel (or, asymmetric molecule).

Al₂Cl₄ has a trigonal pyramidal shape and bond dipoles cancel (or, symmetric molecule).

(c) NO₂⁻ has resonance structures.

NO₂⁻ has no resonance structures.

(d) Sulfur has no orbitals in its valence shell.

Sulfur has a larger size, can accommodate more bonds.

Question 8

8 points

(a) (i) 2 points

[Diagram of Lewis electron-dot structure of CO₃⁻]

One point earned for each Lewis electron-dot structure.

Indication of lone pairs of electrons are required on each structure.

Resonance forms of CO₃⁻ are not required.

(ii) In CO₂, the C-O interactions are double bonds, OR in CO₃⁻ the C-O interactions are resonance forms (or figures below.)

1 point

The carbon-oxygen bond length is greater in the resonance forms than in the double bonds.

1 point

• 1st point earned for indicating double bonds are present in CO₂ OR resonance occurs in CO₃⁻

• 2nd point earned for BOTH of the above AND indicating the relative lengths of the bond types.

(b) (i) 2 points

[Diagram of Lewis electron-dot structure of CF₄]

One point earned for each Lewis electron-dot structure.

Lone pairs of electrons are required on each structure.

[Diagram of Lewis electron-dot structure of SF₄]

One point earned for each Lewis electron-dot structure.

Lone pairs of electrons are required on each structure.

Question 8 (cont.)

(ii) CF₄ has a tetrahedral geometry, so the bond dipoles cancel, leading to a nonpolar molecule.

With five pairs of electrons around the central S atom, SF₄ exhibits a trigonal bipyramidal electronic geometry, with two lone pairs of electrons. In this configuration, the bond dipoles do not cancel, and the molecule is polar.

(a) The bonds in nitrite ion, NO₂⁻, are shorter than the bonds in nitrate ion, NO₃⁻.

According to the Lewis electron-dot diagram, two resonance structures are required to represent the bonding in the NO₂⁻ ion. The effective number of bonds between N and O is 1.5.

Three resonance structures are required to represent the bonding in the NO₃⁻ ion. The effective number of bonds between N and O is 1.33.

The greater the effective number of bonds, the shorter the N–O bond length.

(b) The CH₂F₂ molecule is polar, whereas the CF₄ molecule is not.

The molecular geometry in both CH₂F₂ and CF₄ is tetrahedral (or the same). The C-F bond is polar. In CH₂F₂, the molecule geometry arranges the C-F dipoles so that they cancel out and the molecule is nonpolar. The C-H bond is less polar than the C-F bond. The two C-H dipoles do not cancel the two C-F dipoles in CH₂F₂.
(c) The atoms in a C₃H₆ molecule are located in a single plane, whereas those in a C₃H₅O molecule are not.

The carbon atoms in C₃H₆ have a molecular geometry around each carbon atom that is trigonal planar (AX₃), so all six atoms are in the same plane. The carbon atoms in C₃H₅O have a molecular geometry that is tetrahedral (AX₅), so the atoms are not all in the same plane.

OR

The carbon-carbon double bond in C₃H₆ results in a planar molecule whereas the carbon-carbon single bond in C₃H₅O results in a non-planar (tetrahedral) type of each carbon atom.

(d) Given the structural formula below,

The shape of a PF₅ molecule differs from that of an IF₅ molecule.

In PF₅, the molecular geometry is trigonal bipyramidal because the phosphorus atom has five bonding pairs of electrons and no lone pairs of electrons.

In IF₅, the molecular geometry is tetrahedral because the central iodine atom has five bonding pairs of electrons and one lone pair of electrons.

The presence of the additional lone pair of electrons on the central iodine atom means the molecular geometry is different.

(e) HOCl is a stronger acid than HClO.

According to the IUPAC rules, HClO₂ is named hypochlorous acid whereas HOCl₂ is named hypochlorous acid.

The result is to reduce the electrostatic attraction between the H⁺ and ClO₂⁻ ions. The weaker the H-O bond, the stronger the acid.

(f) Using the information in the table above, answer the following questions about organic compounds.

(a) For propane,

(i) draw the complete structural formula (showing all atoms and bonds);

(ii) predict the approximate carbon-to-carbon-to-carbon bond angle.

(b) For each pair of compounds below, explain why they do not have the same value for their standard heat of vaporization, ΔH°vap. (You must include specific information about both compounds in each pair.)

(i) Propane and 1-propanol

(ii) Propyne and propane

The intermolecular attractive forces in propane are dispersion forces only. The IMFs in propane are dispersion and dipole-dipole. Since the intermolecular attractive forces differ in the two substances, the enthalpy of vaporization will differ.

1 point earned for the structure
1 point earned for the bonding
1 point earned for the shape of the two molecules
1 point earned for the hybridization
1 point earned for bond angle
1 point earned for intermolecular forces
1 point earned for bond angle
1 point earned for intermolecular forces
1 point earned for bond angle
1 point earned for intermolecular forces
Practice Test I.1 Bonding & Geometry

1. The correct Lewis symbol for ground state for atomic carbon is
   a. C:  
   b. :C:  
   c. C:  
   d. :C:  
   e. C:

2. Using the picture below, what process (or its reverse) corresponds to the lattice energy?

3. Which of the atoms below is least likely to violate the octet rule by having less than 8 in its octet?
   a. Be  
   b. P  
   c. S  
   d. B  
   e. F

4. How many valence electrons are shown in the Lewis structure of perchlorate ion, ClO₄⁻?
   a. 30  
   b. 31  
   c. 32  
   d. 50  
   e. 51

5. Which of the following bonds is most polar?
   a. N – F  
   b. C – N  
   c. S – S  
   d. Br – Br  
   e. F – O

6. What is the size of the C-C-O bond angle in
   a. 90  
   b. 109.5  
   c. 120  
   d. <120  
   e. >120

7. Which of the following contains a central atom that is an exception to the octet rule?
   a. NO₃⁻  
   b. H₂O  
   c. O₂  
   d. CO₂  
   e. none of these

8. Which of the following is the correct Lewis structure for SOCl₂?

9. Which one of the following molecules is a polar molecule?
   a. Cl₂  
   b. CO₂  
   c. NF₃  
   d. CO₂  
   e. H₂S

10. Which of the following molecular shapes has six atoms joined to a central atom?
    a. octahedral  
    b. linear  
    c. trigonal bipyramidal  
    d. tetrahedral  
    e. planar trigonal

11. Which molecular shape has bond angles which are not all the same?
    a. linear  
    b. planar trigonal  
    c. tetrahedral  
    d. trigonal bipyramidal  
    e. octahedral

12. What is the geometry of the electron domains in the molecule XeF₂?
    a. linear  
    b. planar trigonal  
    c. tetrahedral  
    d. trigonal bipyramidal  
    e. octahedral

13. The molecule BrF₃ has how many lone pairs of electrons on the central atom?
    a. 0  
    b. 1  
    c. 2  
    d. 3  
    e. 4

14. What is the geometrical arrangement of electron domains in H₃O⁺?
    a. linear  
    b. trigonal bipyramidal  
    c. bent  
    d. tetrahedral  
    e. none of these

15. What is the shape of BrF₃?
    a. square planar  
    b. pyramidal  
    c. T-shaped  
    d. bent  
    e. distorted tetrahedral

16. What type of hybridization is associated with a square planar molecular shape?
    a. sp²  
    b. sp³  
    c. sp³  
    d. sp³d  
    e. sp³d²

17. What is the shape of the Br⁻ ion?
    a. square planar  
    b. octahedral  
    c. tetrahedral  
    d. T-shaped  
    e. square pyramidal

18. Which of the following is a polar species?
    a. CO₂  
    b. PCl₅  
    c. ICl₃  
    d. TeCl₅  
    e. CCl₄

19. Among those listed below, which element will have the strongest tendency to form double bonds?
    a. Br  
    b. B  
    c. F  
    d. O  
    e. Mg

20. Which hybridization is associated with 3 domains?
    a. sp  
    b. sp²  
    c. sp³  
    d. sp³d  
    e. sp³d²

21. The molecule SF₆ has how many electron domains on the central atom?
    a. 2  
    b. 3  
    c. 4  
    d. 5  
    e. 6

22. What is the hybridization of Br in BrF₃?
    a. sp³  
    b. sp²  
    c. sp³d  
    d. sp³d²  
    e. none of these

23. What shape for electron pairs is associated with sp³ hybridization?
    a. linear  
    b. tetrahedral  
    c. square planar  
    d. octahedral  
    e. trigonal planar

24. What hybridization is predicted for phosphorus in the PCl₅ molecule?
    a. sp³  
    b. sp³  
    c. sp³d  
    d. sp³d²  
    e. none of these

25. A double bond contains ___ sigma bond(s) and ___ pi bond(s).
    a. 0, 2  
    b. 1, 2  
    c. 2, 0  
    d. 1, 1  
    e. 0, 1

26. What angle exists between domains in an octahedral structure?
    a. 90.0°  
    b. 120.0°  
    c. 180.0°  
    d. 78.5°  
    e. 109.5°

27. Which of the following elements is most likely to display sp³ hybridization?
    a. oxygen  
    b. carbon  
    c. nitrogen  
    d. boron  
    e. phosphorus

28. How many sigma (σ) and pi (π) bonds are in a carbon dioxide molecule?
    a. four σ and zero π  
    b. two σ and four π  
    c. three σ and two π  
    d. one σ and three π  
    e. two σ and two π
29. What is the hybridization of the oxygen atoms in CH$_3$OH and CO$_2$, respectively?
   a. sp, sp
   b. sp$^3$, sp$^3$
   c. sp$^3$, sp$^3$
   d. sp, sp
   e. sp$^3$, sp$^3$

30. All of the following species contain two $\pi$-bonds except:
   a. SCN$^-$
   b. OCS
   c. CO
   d. NO
   e. HCCO

31. How many unshared pair of electrons on the central atom in the molecule, XeF$_2$?
   a. 1
   b. 2
   c. 3
   d. 4
   e. 5

32. Which of the following are true about BF$_3$?
   i. trigonal planar
   ii. one unshared pair of electrons on B
   iii. polar molecule
   a. i only
   b. i and ii only
   c. i and iii only
   d. ii and iii only
   e. i, ii, and iii

33. Consider the chemical reaction below:
   BF$_3$ + NH$_3$ $\rightarrow$ BF$_4$NH$_2$
   During this chemical reaction, the geometry around the boron atom changes from:
   a. trigonal planar to tetrahedral
   b. trigonal planar to octahedral
   c. trigonal pyramidal to trigonal bipyramidal
   d. actually its geometry doesn’t change at all
   e. (none of the above)

34. The melting point of CaS is higher than that of KCl. Explanations for this observation include which of the following?
   I. Ca$^{2+}$ is more positively charged than K$^{+}$
   II. S$^{2-}$ is more negatively charged than Cl$^{-}$
   III. The S$^{2-}$ ion is smaller than the Cl$^{-}$ ion
   IV. The Ca$^{2+}$ ion is smaller than the K$^{+}$ ion
   a. I only
   b. II, IV only
   c. III and IV only
   d. II and III only
   e. I, II, III, and IV

35. Types of hybridization exhibited by the three C atoms in propane, CH$_3$CH=CH$_2$, include which of the following?
   I. sp$^3$
   II. sp$^3$
   III. sp
   a. I only
   b. II only
   c. I and II only
   d. II and III only
   e. I, II, and III

36. Of the following molecules, which has the largest dipole moment?
   a. NH$_3$
   b. CO$_2$
   c. ClF$_3$
   d. H$_2$O
   e. CF$_3$O

37. The molecular geometry of SF$_6$ is:
   a. tetrahedral
   b. trigonal bipyramidal
   c. trigonal planar
   d. octahedral
   e. tetrahedron

38. In the molecule shown with the formula AFI$_4$, which element could be in position A?
   a. S
   b. O
   c. Xe
   d. P
   e. It could be either a or b

39. In order to exhibit delocalized $\pi$ bonding, a molecule must have:
   a. at least two $\pi$ bonds
   b. at least two resonance structures
   c. at least three $\sigma$ bonds
   d. at least four atoms
   e. a and c are both true

40. In ozone, O$_3$, the formal charge on the central atom is:
   a. 0
   b. +1
   c. -1
   d. +2
   e. -2

41. The Lewis structure of HCN shows that _____ has ____ nonbonding electron pairs.
   a. C, 1
   b. N, 1
   c. H, 1
   d. N, 2
   e. C, 2

42. According to the VSEPR model, the progressive decrease in the bond angles in the series of molecules CH$_4$, NH$_3$, and H$_2$O is best accounted for by:
   a. increasing strength of bonds
   b. decreasing size of the central atom
   c. increasing the electronegativity of the central atom
   d. increasing number of unshared pairs of electrons
   e. decreasing repulsion between hydrogen atoms

43. The hybridization of the carbon atom in methane, CH$_4$ is:
   a. sp$^3$
   b. sp$^2$
   c. sp$^2$
   d. sp$^3$
   e. sp$^3$-

44. The molecule whose central atom’s electron domains are not tetrahedral.
   a. CO$_2$
   b. H$_2$O
   c. NH$_3$
   d. CH$_4$
   e. None of the molecules above satisfy the statement.

45. The molecule with only one double bond.
   a. CH$_2$=CH$_2$
   b. H$_2$O
   c. CO$_2$
   d. NO$_2$
   e. HCCO

46. The molecule with the largest dipole moment.
   a. CH$_3$OH
   b. CO$_2$
   c. F$_2$O
   d. H$_2$O
   e. SF$_6$

47. The molecule that has more than one pi bond.
   a. CH$_3$=CH$_2$
   b. CO$_2$
   c. H$_2$O
   d. H$_2$S
   e. SF$_6$

48. The molecule with no non-bonded electron pairs.
   a. CH$_4$
   b. H$_2$O
   c. CO$_2$
   d. NH$_3$
   e. SF$_6$

49. Of the following, ______ cannot accommodate more than an octet of electrons.
   a. P
   b. Xe
   c. N
   d. S
   e. I

50. A valid Lewis structure of ______ cannot be drawn without violating the octet rule.
   a. PO$_2$F$_2$
   b. SF$_4$
   c. CF$_4$
   d. SeF$_4$
   e. NF$_5$
66. The electron-domain geometry and molecular geometry of iodine trichloride are ______ and ______ respectively.
   a. trigonal planar, trigonal planar  
b. tetrahedral, trigonal pyramidal  
c. trigonal bipyramidal, T-shaped  
d. octahedral, trigonal planar  
e. T-shaped, trigonal planar

67. If the electron-domain geometry of some sulfur-centered compound is trigonal bipyramidal, then the hybridization of the central sulfur atom must be ______
   a. sp  
b. sp²  
c. sp³  
d. sp³d  
  e. sp³d²

68. There are ______ unhybridized p atomic orbitals on an sp hybridized carbon atom
   a. 0  
b. 1  
c. 2  
d. 3  
e. 4

69. If the hybridization of orbitals on the central atom of a molecule is sp. The electron-domain geometry around this central atom must be ______
   a. octahedral  
b. linear  
c. trigonal planar  
d. trigonal bipyramidal  
e. tetrahedral

70. The shortest F-Xe-F bond angle in the XeF₄ molecule is about ______
   a. 60°  
b. 90°  
c. 109.5°  
d. 120°  
e. 180°

71. A ____ covalent bond is the longest
   a. single  
b. double  
c. triple  
d. they are all the same length  
e. nonpolar

72. When counting domains, a triple bond
   a. Should not be counted as a domain  
b. Depends on the geometry as to how many domains it should be counted as  
c. Should be counted as three domains  
d. Should be counted as two domains due to the 2 π bonds  
e. Should be counted as only one domain

73. The electron-domain geometry and the molecular geometry of a molecule of the general formula ABₓ will be the same if
   a. there are no unshared electron pairs on the central atom  
b. there is more than one central atom  
c. x is greater than 4  
d. x is less than 4  
e. the octet rule is obeyed

74. Of the molecules below, only ______ is nonpolar.
   a. BF₃  
b. NF₃  
c. IF₃  
d. PF₃  
e. BrF₃

75. The molecular geometry of the H₂O⁺ ion is ______
   a. linear  
b. tetrahedral  
c. bent  
d. trigonal pyramidal  
e. trigonal planar

76. Draw the Lewis structure for carbonate: CO₃²⁻.
   a. What is the shape of the electron domains around the central carbon?  
b. What is the shape of the carbonate ion?  
c. What are the bond angles in carbonate?  
d. Does the carbonate ion exhibit resonance?  
e. Does delocalization occur? What does this term mean?  
f. Comment on the bond lengths in carbonate.

77. Bond enthalpy values can be used to calculate and estimation for ΔHrx when the ΔHf° values are not available for all the compounds in the reaction. Use bond enthalpy values from the back of your ΔHf° tables to calculate the ΔHrx for the reaction below.
   Do your work in the space below. Circle your final answer. Be sure and label it appropriately.

   H₂CNH + H₂O → CH₂O + NH₃
AP Chemistry Bonding Multiple Choice

Name: ________________________________

1. A B C D  
2. A B C D  
3. A B C D  
4. A B C D  
5. A B C D  
6. A B C D  
7. A B C D  
8. A B C D  
9. A B C D  
10. A B C D 
11. A B C D 
12. A B C D 
13. A B C D 
14. A B C D 
15. A B C D 
16. A B C D 
17. A B C D 
18. A B C D 
19. A B C D 
20. A B C D 
21. A B C D 
22. A B C D 
23. A B C D 
24. A B C D 
25. A B C D 
26. A B C D 
27. A B C D 
28. A B C D 
29. A B C D 
30. A B C D 
31. A B C D 
32. A B C D 
33. A B C D 
34. A B C D 
35. A B C D 
36. A B C D 
37. A B C D 
38. A B C D 
39. A B C D 
40. A B C D 
41. A B C D 
42. A B C D 
43. A B C D 
44. A B C D 
45. A B C D 
46. A B C D 
47. A B C D 
48. A B C D 
49. A B C D 
50. A B C D 
51. A B C D 
52. A B C D 
53. A B C D 
54. A B C D 
55. A B C D 
56. A B C D 
57. A B C D 
58. A B C D 
59. A B C D 
60. A B C D 
61. A B C D 
62. A B C D 
63. A B C D 
64. A B C D 
65. A B C D 
66. A B C D 
67. A B C D 
68. A B C D 
69. A B C D 
70. A B C D 
71. A B C D 
72. A B C D 
73. A B C D 
74. A B C D 
75. A B C D