Bonding / Molecular Shapes VSEPR

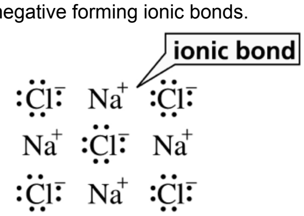
Dr. Ron Rusay

Ionic & Covalent Bonds

- *When a nonmetal and a metal form a compound: Valence electrons of the metal are lost and the nonmetal gains these electrons to achieve a Noble gas electron configuration and forming an Ionic Bond.*
- *When two nonmetals form a compound: They share electrons to achieve a Noble gas electron configuration and forming a Covalent Bond.*

Ionic Compounds

- Ionic compounds are formed when electron(s) are transferred.
- Electrons go from less electronegative element to the more electronegative forming ionic bonds.



sodium chloride

Bond Energy

- *It is the energy required to break a bond, i.e. overcome the force of attraction.*
- *The quantitative value provides information about the strength and nature of the bond.*

Bond Energies

- Bond breaking requires energy (endothermic).
- Bond formation releases energy (exothermic).
  - $\Delta H_{rxn} = \Sigma H(\text{bonds broken}) - \Sigma H(\text{bonds formed})$

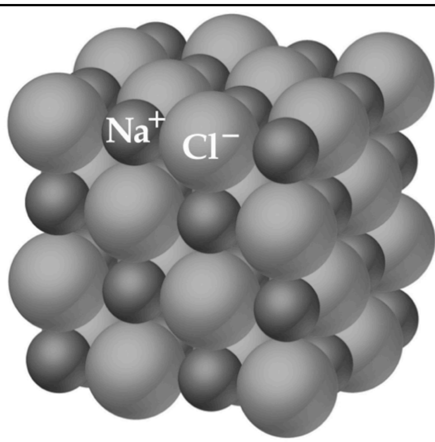
Lattice Energy

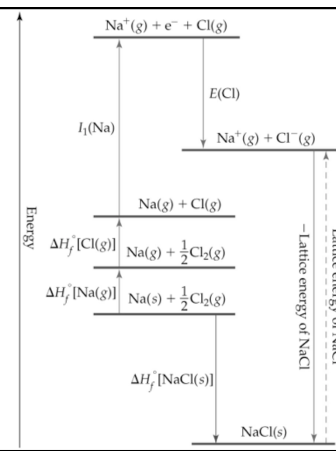
Hess's Law for ionic crystalline solids

- The change in energy when gaseous ions pack together to form an ionic solid.

$$M^{+}(g) + X^{-}(g) \rightarrow MX(s)$$

- Lattice energy is a negative value (exothermic).
- How can the Lattice energy be calculated?





Electronegativity

- The ability of an atom in a molecule to attract shared electrons to itself.

- $\Delta = (H - X)_{actual} - (H - X)_{expected}$

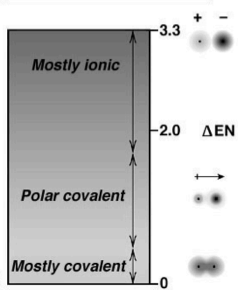
Electronegativity

Boundary Ranges for Classifying Ionic Character of Chemical Bonds

A

ΔEN	IONIC CHARACTER
>1.7	Mostly ionic
0.4-1.7	Polar covalent
<0.4	Mostly covalent
0	Nonpolar covalent

B



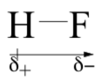
QUESTION

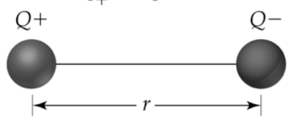
Atoms having greatly differing electronegativities are expected to form:

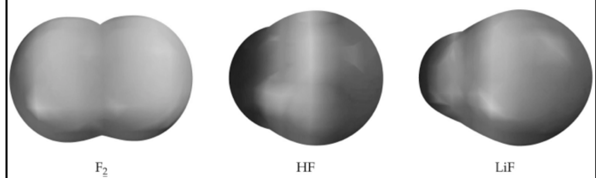
1) no bonds.
2) polar covalent bonds.
3) nonpolar covalent bonds.
4) ionic bonds.
5) covalent bonds.

Covalent Bond Polarity

- A molecule, such as HF, that has a center of positive charge and a center of negative charge is said to be polar, or to have a dipole moment.



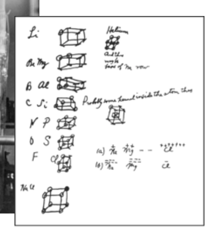




Lewis Structure

- Shows how valence electrons are arranged among atoms in a molecule.
- Reflects central idea that stability of a compound relates to noble gas electron configuration.
- Shows bonds in molecules and relates to 3-dimensional shapes in structures

G.N. Lewis
Photo Bancroft Library, University of California/LBNL Image Library



Footnote:
G.N. Lewis, despite his insight and contributions to chemistry, was never awarded the Nobel prize.

Notes from Lewis's notebook and his "Lewis" structure.

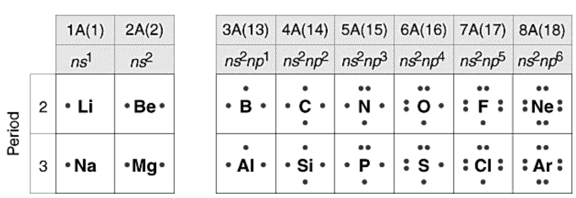
Octet Rule: General Comments

- *2nd row elements C, N, O, F observe the octet rule.*
- *2nd row elements B and Be often have fewer than 8 electrons around themselves - they are very reactive.*
- *3rd row and heavier elements CAN exceed the octet rule using empty valence d orbitals.*
- *When writing Lewis structures, satisfy octets first, then place electrons around elements having available d orbitals.*

QUESTION

Which of the following atoms cannot exceed the octet rule in a molecule?
A) N
B) S
C) P
D) I
E) All of the atoms (1–4) can exceed the octet rule.

Lewis Electron-Dot Symbols for Elements in Periods 2 & 3



Depicting ion formation with orbital diagrams and electron dot symbols

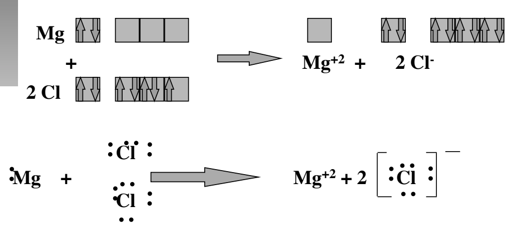
Problem: Use orbital diagrams and Lewis structures to show the formation of magnesium chloride from its ions starting with the respective atoms.

Step 1: Draw the orbital diagrams for Mg and Cl atoms.

To reach completely filled, stable electronic configurations each Mg atom loses 2 electrons, and each Cl atom gains 1 electron. Therefore there are two Cl^- ions for every one Mg^{2+} ion.

Step 2: Draw the orbital diagrams for the Mg^{2+} cation and 2 Cl^- anions.

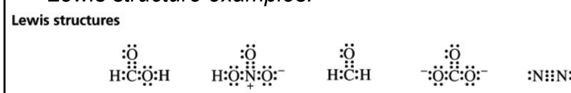
Depicting Ion Formation with Orbital Diagrams and Electron Dot Symbols



Remember chlorine is diatomic.

Covalent Compounds

- Share valence electrons.
- 1 pair = 1 bond; maximum # of atom-atom bonds = 3.
- Octet rule ("duet" for hydrogen)
- *Lewis structure examples:*



Notice the charges:
In one case they balance, can you name the compound?
In the other they do not.

It has a "Formal" charge. Can you name the polyatomic ion?

QUESTION

In the Lewis structure for SF_6, the central sulfur atom shares __________ electrons.

A) 4
B) 8
C) 10
D) 12
E) none of these, because SF_6 is an ionic compound

Important Bond Numbers

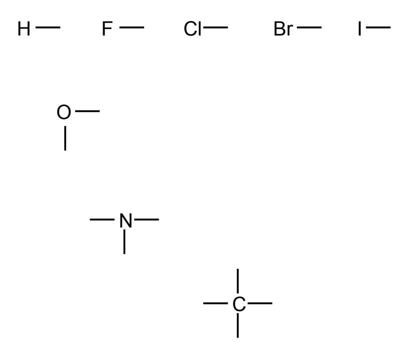
(Neutral Atoms!)

one bond

two bonds

three bonds

four bonds



QUESTION

In the Lewis structure for elemental nitrogen there is (are):

A) a single bond between the nitrogens.
B) a double bond between the nitrogens.
C) a triple bond between the nitrogens.
D) three unpaired electrons.
E) none of these.

Lewis Structures of Simple Covalently Bonded Molecules

Draw Lewis Structures for the following:

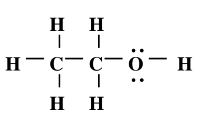
CH_3CH_2OH Ethyl alcohol (Ethanol)

CH_4 Methane

CF_4 Carbon Tetrafluoride

$KClO_3$ Potassium Chlorate

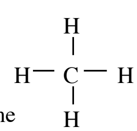
Lewis Structures of Simple Molecules

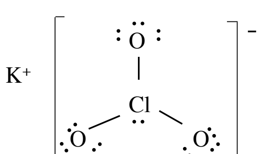


Ethyl Alcohol (Ethanol)

CH_4

Methane

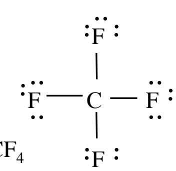




$KClO_3$

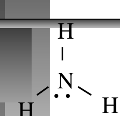
Potassium Chlorate

CF_4

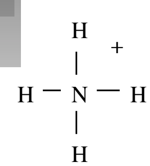


Carbon Tetrafluoride

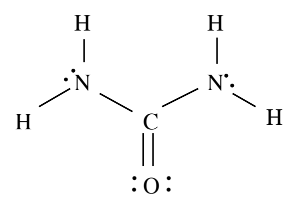
Lewis Structures of Simple Molecules



Ammonia



Ammonium Ion



Urea

QUESTION

The formaldehyde compound, also known as methanal, has been linked to indoor air pollution and related health effects. It can be used in some cases as a disinfectant and is found in some resins and glues. The correctly drawn Lewis structure of H_2CO would have how many unshared electrons?

A. Zero unshared e^-
B. One unshared e^-
C. Two unshared e^-
D. Four unshared e^-

QUESTION

Dinitrogen monoxide has several uses ranging from a dentistry anesthetic to automobile racing enhancement. Starting with two possible basic structures given here, diagram two different Lewis structures. If your first structure contains four unbonded electrons around oxygen and your second structure contains six unbonded electrons around oxygen, how many bonds would be between the N atoms in the first and second compounds?

N–N–O N–N–O

A. 2, 3
B. 1, 3
C. 2, 2
D. 1, 2

Formal Charge

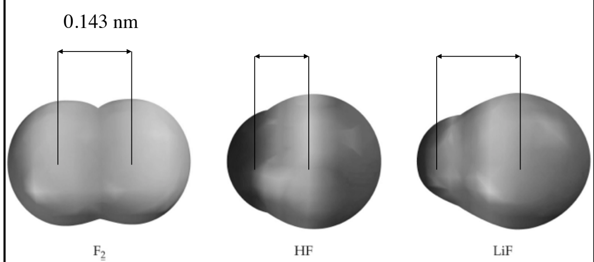
- *Equals the number of valence electrons of the free atom minus [the number of unshared valence electrons in the molecule + 1/2 the number of shared valence electrons in the molecule].*

QUESTION

The N_2O molecule has sometimes found use as an aerosol propellant. One structure that satisfies the Lewis electron dot rules is N=N=O. In this case, what would be the formal charge of the middle N atom?

A. Zero
B. +1
C. −1
D. I am not sure how to determine the formal charge on an atom in a compound.

Visual Interpretation



Color coded electron density distribution:
blue-lowest, red highest, green balanced

Determining Bond Polarity from Electronegativity Values

Draw arrows to represent the dipole moment of each using ENs:

a) the EN of O = 3.5 and of H = 2.1**: O - H**
the EN of O = 3.5 and of Cl = 3.0**: O - Cl**
the EN of C = 2.5 and of P = 2.1**: C - P**
the EN of P = 2.1 and of N = 3.0**: P - N**
the EN of N = 3.0 and of S = 2.1**: N - S**
the EN of C = 2.5 and of Br = 2.8**: C - Br**
the EN of As = 2.0 and of O = 3.5**: As - O**

b) Rank the bonds in increasing order of polarity.

Determining Bond Polarity from Electronegativity Values

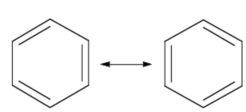
Solutions:

a) the EN of O = 3.5 and of H = 2.1**: O - H**
the EN of O = 3.5 and of Cl = 3.0**: O - Cl**
the EN of C = 2.5 and of P = 2.1**: C - P**
the EN of P = 2.1 and of N = 3.0**: P - N**
the EN of N = 3.0 and of S = 2.1**: N - S**
the EN of C = 2.5 and of Br = 2.8**: C - Br**
the EN of As = 2.0 and of O = 3.5**: As - O**

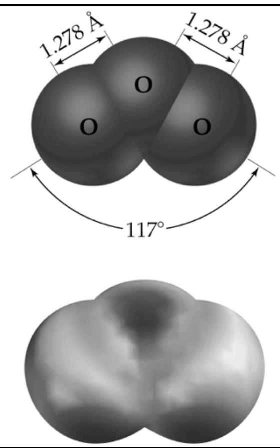
b) C - Br < C - P < O - Cl < P - N < N - S < O - H < As - O
0.3 < 0.4 < 0.5 < 0.9 < 0.9 < 1.4 < 1.5

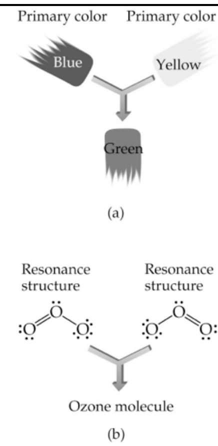
Resonance

- *Occurs when more than one valid Lewis structure can be written for a particular molecule.*



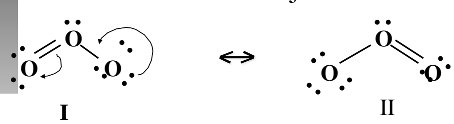
- *These are resonance structures. The actual structure is an average of the resonance structures.*



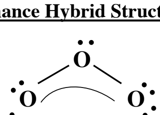


Resonance: Delocalized Electron-Pairs

Ozone : O_3

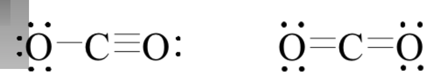


Resonance Hybrid Structure



One pair of electron's resonates between the two locations!!

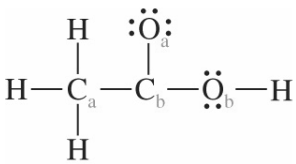
Resonance and Formal Charge



(-1) (0) (+1) — *Not as good*

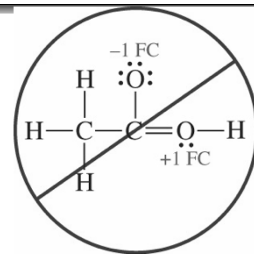
(0) (0) (0) — *Better*

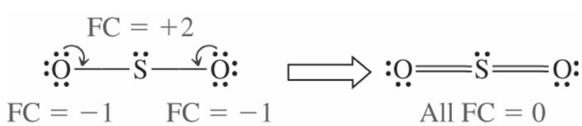
Acetic acid



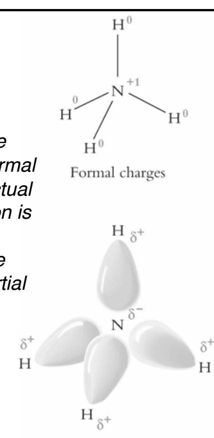
Complete the Lewis Structure.

Acetic acid





The nitrogen atom in the ammonium ion has a formal charge of +1, but the actual positive charge of the ion is distributed around the hydrogen atoms and the nitrogen atom has a partial negative charge.



Localized Electron Model

- *1. Description of valence electron arrangement (Lewis structure).*
- *2. Prediction of geometry (VSEPR model).*
- *3. Description of atomic orbital types used to share electrons or for lone pairs.*

Coupled with molecular orbital theory, highly reliable conceptual images of molecular shape can be obtained.

QUESTION

Biologically the NO molecule plays several important roles in human physiology. Of particular importance and interest is its role in maintaining blood flow and pressure. A properly diagramed Lewis structure of NO would have how many e^- not involved in bonding?

A. Zero
B. Three
C. Five
D. Seven

Formal Charge

- *Equals the number of valence electrons of the free atom minus [the number of unshared valence electrons in the molecule + 1/2 the number of shared valence electrons in the molecule].*
- *Adding/subtracting atoms and electrons.*

Formal charge = number of valence electrons –
(number of lone pair electrons +1/2 number of bonding electrons)

Formal charge = 5 – (3+1/2 4) = 0

VSEPR Model
Valence Shell Electron Pair Repulsion

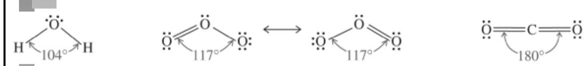
VSEPR Model

- The molecular structure which surrounds a given atom is determined principally by minimizing electron pair repulsions through maximizing separations.

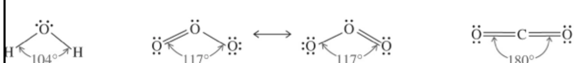
VSEPR Model

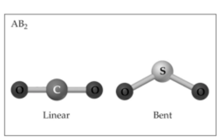
The molecular structure of a given atom is determined principally by minimizing electron pair (bonded & free) repulsions through maximizing separations.

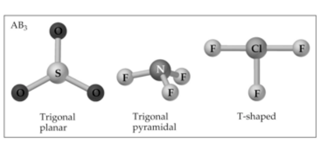
Some examples of minimizing interactions.



Some examples of minimizing interactions.







Predicting a VSEPR Structure

- 1. Draw Lewis structure.
- Using your imagination in 3 dimensions:
- 2. Put pairs as far apart as possible.
- 3. Determine positions of atoms from the way electron pairs are shared.
- 4. Select the geometrical name of the molecular structure from positions of the atoms, or……. skip 2 &3 and match to the names:

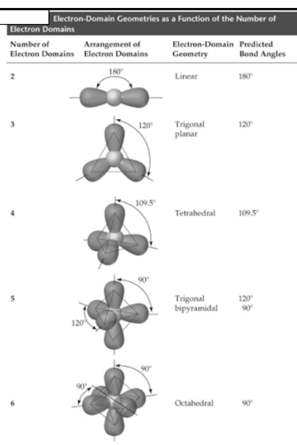
http://chemconnections.org/VSEPR-jmol/

	Orbital Geometry	Molecular Geometry	Bond Angle	# of lone pairs
Important in Organic Compounds	Linear	Linear	180°	0
	Trigonal Planar	Trigonal Planar	120°	0
	Trigonal Planar	Bent	<120°	1
	Tetrahedral	Tetrahedral	109.5°	0
	Tetrahedral	Trigonal Pyramidal	[illegible]°	1
	Tetrahedral	Bent	<109.5°	2
	Trigonal Bipyramidal	Trigonal Bipyramidal	120°, 90°	0
	Trigonal Bipyramidal	Seesaw	<120°, <90°	1
	Trigonal Bipyramidal	T-shape	<90°	2
	Trigonal Bipyramidal	Linear	180°	3
	Octahedral	Octahedral	90°	0
	Octahedral	Square Pyramidal	[illegible]°	1
	Octahedral	Square Planar	90°	2

QUESTION

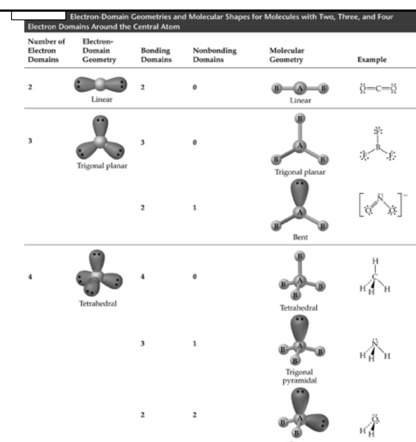
The compound BF_3 can react with silicon to help etch computer chips. After diagraming the complete Lewis structure for this compound, determine its shape and provide one of the following names for the shape you drew.

A. Trigonal planar
B. Trigonal bipyramidal
C. T–shaped
D. Linear



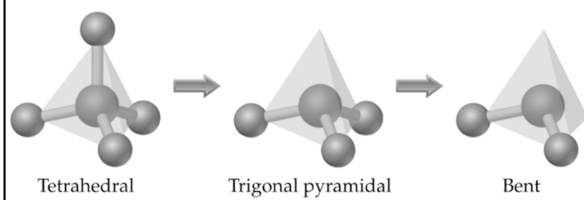
Electron-Domain Geometries as a Function of the Number of Electron Domains

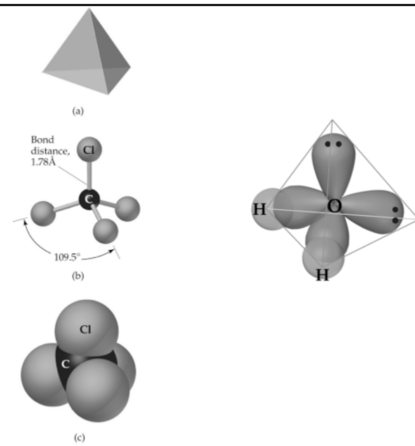
Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

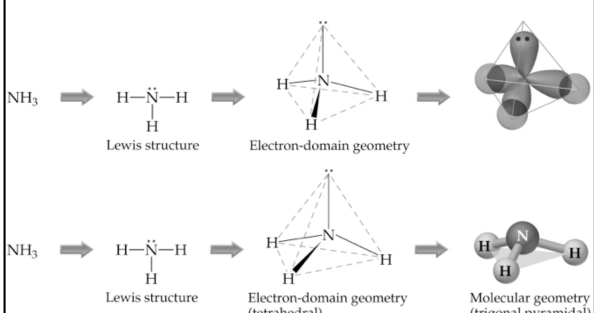


Electron-Domain Geometries and Molecular Shapes for Molecules with Two, Three, and Four Electron Domains Around the Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	Linear	2	0	Linear	O=C=O
3	Trigonal planar	3	0	Trigonal planar	BF_3
		2	1	Bent	$[NO_2]^-$
4	Tetrahedral	4	0	Tetrahedral	CH_4
		3	1	Trigonal pyramidal	NH_3
		2	2	Bent	H_2O



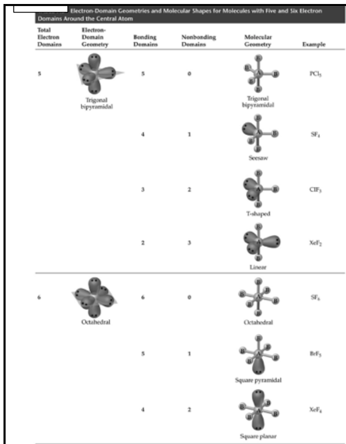




QUESTION

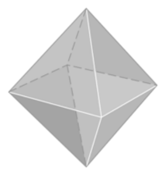
The bond angle in H_2Se is about:

A) 120°.
B) 60°.
C) 180°.
D) 109°.
E) 90°.



Electron-Domain Geometries and Molecular Shapes for Molecules with Five and Six Electron Domains Around the Central Atom

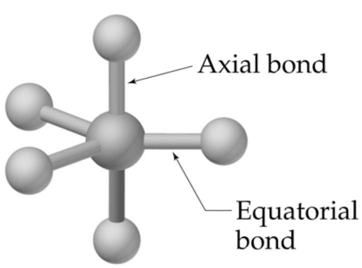
Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl_5
		4	1	Seesaw	SF_4
		3	2	T-shaped	ClF_3
		2	3	Linear	XeF_2
6	Octahedral	6	0	Octahedral	SF_6
		5	1	Square pyramidal	BrF_5
		4	2	Square planar	XeF_4



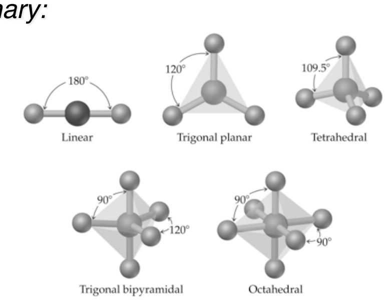
QUESTION

According to VSEPR theory, which of the following species has a square planar molecular structure?

A) $TeBr_4$
B) BrF_3
C) IF_5
D) XeF_4
E) SCl_2



Summary:



http://chemconnections.org/VSEPR-jmol/

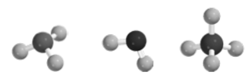
http://chemconnections.org/general/chem120/VSEPR/index.html

Representing Molecules

Formulas, Structures & Models

Lewis Structures / VSEPR Molecular Models

- *Using all of the tools.*
- *Computer Generated Models*



Covalent Compounds

•Equal sharing of electrons: nonpolar covalent bond, same electronegativity (e.g., H_2)
• Unequal sharing of electrons between atoms of different electronegativities: polar covalent bond (e.g., HF)

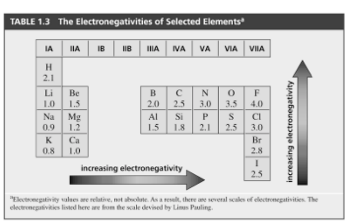


TABLE 1.3 The Electronegativities of Selected Elements[a]

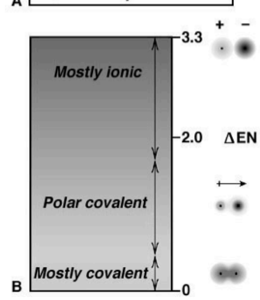
IA	IIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA
H 2.1								
Li 1.0	Be 1.5			B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2			Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0							Br 2.8
								I 2.5

[a]Electronegativity values are relative, not absolute. As a result, there are several scales of electronegativities. The electronegativities listed here are from the scale devised by Linus Pauling.

Boundary Ranges for Classifying Ionic Character of Chemical Bonds

A

ΔEN	IONIC CHARACTER
>1.7	Mostly ionic
0.4-1.7	Polar covalent
<0.4	Mostly covalent
0	Nonpolar covalent



Bond Dipole & Dipole Moment

- Dipole moments are experimentally measured.
  - Polar bonds have dipole moments.

dipole moment (D) = $\mu = e \times d$

(e) : magnitude of the charge on the atom

(d) : distance between the two charges

Table 1.4 The Dipole Moments of Some Commonly Encountered Bonds

Bond	Dipole moment (D)	Bond	Dipole moment (D)
H—C	0.4	C—C	0
H—N	1.3	C—N	0.2
H—O	1.5	C—O	0.7
H—F	1.7	C—F	1.6
H—Cl	1.1	C—Cl	1.5
H—Br	0.8	C—Br	1.4
H—I	0.4	C—I	1.2

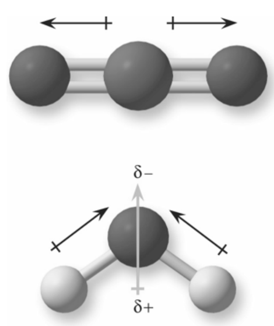
Bond Polarity

A molecule, such as HF, that has a center of positive charge and a center of negative charge is polar, and has a dipole moment. The partial charge is represented by δ and the polarity with a vector arrow.

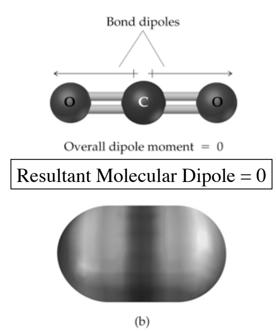
H—F

δ+ ⟶ δ−

Molecular Polarity & Dipole Moment



When identical polar bonds point in opposite directions, the effects of their polarities cancel, giving no net dipole moment. When they do not point in opposite directions, there is a net effect and a net molecular dipole moment, designated δ.



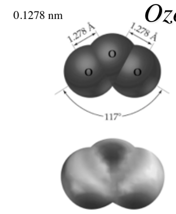
QUESTION

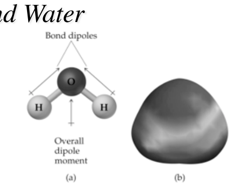
The bonds between carbon and oxygen in CO_2 and the bonds between carbon and oxygen in acetic acid have exactly the same difference in electronegativity. Yet CO_2 is a non-polar gas, whereas acetic acid is polar. Which statement provides a factual reason for this difference?

A. CO_2 has no dipole moment because the symmetry of the C–O bonds places them 180°C apart; thus, the polarity predicted in the bonds is cancelled by molecular shape. Since acetic acid is polar, the shape must not allow for canceling the bond polarity.
B. Polarity in a bond does not always predict polarity in a molecule because the dipole moment could be increased causing the molecule to be less polar.
C. The partial negative charge of each oxygen, compared to carbon, is decreased in CO_2 because it gets shared among two atoms.
D. The C–O bond in acetic acid remains polar because the other parts of the molecule form a tetrahedron.

Molecular Size, Shape & Properties

Ozone and Water





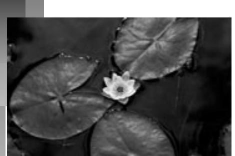
- Resultant Molecular Dipoles > 0
- Solubility: Polar molecules that dissolve or are dissolved in like molecules

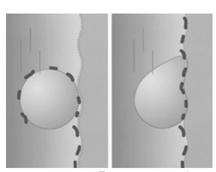
- The Lotus flower
- Water & dirt repellancy

The "Lotus Effect"

Biomimicry

http://www.bfi.org/Trimtab/spring01/biomimicry.htm





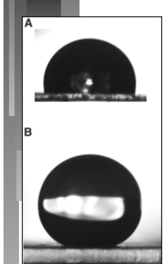
Wax

- *Lotus petals have micrometer-scale roughness, resulting in water contact angles up to 170°*
- *See the Left image in the illustration on the right.*

The "Lotus Effect"

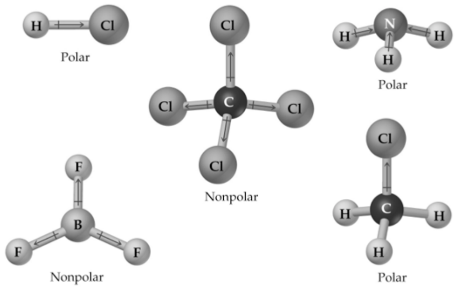
Biomimicry

http://www.sciencemag.org/cgi/content/full/299/5611/1377/DC1



- *Isotactic polypropylene (i-PP) melted between two glass slides and subsequent crystallization provided a smooth surface. Atomic force microscopy tests indicated that the surface had root mean square (rms) roughness of 10 nm.*
- *A) The water drop on the resulting surface had a contact angle of 104° ± 2*
- *B) the water drop on a superhydrophobic i-PP coating surface has a contact angle of 160°.*

Science, 299, (2003), pp. 1377-1380, H. Yldrm Erbil, A. Levent Demirel, Yonca Avc, Olcay Mert

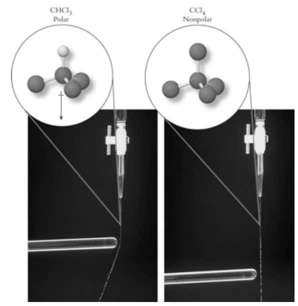


http://chemconnections.org/COT/VSEPR1/

BONUS: Questions #2, 3, & 4

DVC Student Project Group

http://chemconnections.org/COT/VSEPR1/VSEPR/VSEPR-WKS-I-12.pdf



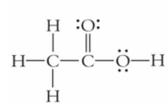
An electrically charged rod attracts a stream of chloroform but has no effect on a stream of carbon tetrachloride.

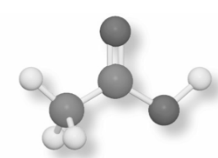
QUESTION

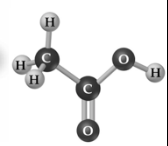
Which of the following molecules has a dipole moment?

A) BCl_3
B) $SiCl_4$
C) PCl_3
D) Cl_2
E) none of these

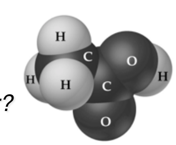
Acetic acid







- *Is acetic acid polar or non-polar?*
- *Will acetic acid be miscible in water?*



QUESTION

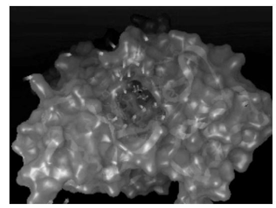
How many of the following molecules possess dipole moments?

BH_3, CH_4, PCl_5, H_2O, HF, H_2

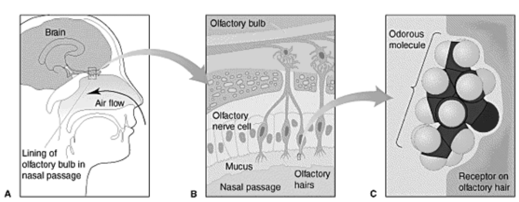
A) 1
B) 2
C) 3
D) 4
E) 5

Proteins & Small Molecules

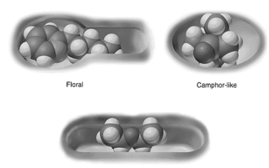
The interaction of a large protein bio-polymer, acetylcholinesterase, with a relatively small molecule of acetylcholine. A general process similar to the way that scientists think we smell.



Molecular Shape & Smell Theory



Historical view of a few smell receptors.



4 October 2004

The Nobel Assembly at Karolinska Institutet has today decided to award

The Nobel Prize in Physiology or Medicine for 2004

jointly to

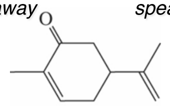
Richard Axel and **Linda B. Buck**

for their discoveries of

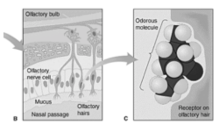
"odorant receptors and the organization of the olfactory system"

S-(+)-d-carvone *caraway*

R-(-)-l-carvone *spearmint*



Carvone ($C_{10}H_{14}O$)



They discovered a large gene family, comprised of some 1,000 different genes (three per cent of our genes) that give rise to an equivalent number of olfactory receptor types. These receptors are located on the olfactory receptor cells, which occupy a small area in the upper part of the nasal epithelium and detect the inhaled odorant molecules.

Odorant Receptors and the Organization of the Olfactory System