Chapter 7: Chemical Bonding and Molecular Geometry

UNIT 38 Ionic Bonding

Question 38-1.

Does a cation gain protons to form a positive charge or does it lose electrons? **Solution** The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.

Question 38-2.

Iron(III) sulfate [$Fe_2(SO_4)_3$] is composed of Fe^{3+} and SO_4^{2-} ions. Explain why a sample of iron(III) sulfate is uncharged.

Solution

The Fe^{3+} ions and SO_4^{2-} ions are combined in a 2:3 ratio.

The positive and negative charges cancel, yielding a neutral compound: $[2 \times (+3)] + [3 \times (-2)] = 0$.

Question 38-3.

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co?

Solution

P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

Question 38-4.

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: Br, Ca, Na, N, F, Al, Sn, S, Cd?

Solution

Br, N, F, and S would form anions. Ca, Na, Al, Sn, and Cd would form cations.

Question 38-5.

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) P
(b) Mg
(c) Al
(d) O
(e) Cl
(f) Cs

Solution

(a) P^{3-}; (b) Mg^{2+}; (c) Al^{3+}; (d) O^{2-}; (e) Cl^{-}; (f) Cs^{+}

Question 38-6.

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) I
(b) Sr
(c) K
(d) N
(e) S
(f) In

Solution

(a) I^{-}; (b) Sr^{2+}; (c) K^{+}; (d) N^{3-}; (e) S^{2-}; (f) In^{+}

Question 38-7.

Write the electron configuration for each of the following ions:

(a) As^{3-}
(b) I^{-} (c) Be^{2+} (d) Cd^{2+}
(e) O^{2-} (f)
Ga^{3+}
(g) Li^{+}
(h) N^{3-} (i)
Sn^{2+}
(j) Co^{2+}
(k) Fe^{2+}
(l) As^{3+}

Solution

(a) $[Ar]4s^{2}3d^{10}4p^{6}$; (b) $[Kr]4d^{10}5s^{2}5p^{6}$; (c) $1s^{2}$; (d) $[Kr]4d^{10}$; (e) $[He]2s^{2}2p^{6}$; (f) $[Ar]3d^{10}$; (g) $1s^{2}$; (h) $[He]2s^{2}2p^{6}$; (i) $[Kr]d^{10}5s^{2}$; (j) $[Ar]3d^{7}$; (k) $[Ar]3d^{6}$; (l) $[Ar]3d^{10}4s^{2}$

Question 38-8.

Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):

(a) Cl

(b) Na
(c) Mg
(d) Ca
(e) K
(f) Br
(g) Sr
(h) F **Solution**

(a) Cl^-, [Ne]$3s^23p^6$; (b) Na^+, [Ne]; (c) Mg^{2+}, $1s^22s^22p^6$, [Ne]; (d) Ca^{2+}, [Ar]; (e) K^+, [Ar]; (f) Br^-, [Kr]; (g) Sr^{2+}, [Kr]; (h) F^-, [Ne] noble gas

Question 38-9.

Write out the full electron configuration for each of the following atoms and for the monatomic ion found in binary ionic compounds containing the element:

(a) Al
(b) Br
(c) Sr
(d) Li
(e) As
(f) S

Solution

(a) $1s^22s^22p^63s^23p^1$; Al^{3+}: $1s^22s^22p^6$; (b) $1s^22s^22p^63s^23p^63d^{10}4s^24p^5$; $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$; (c) $1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^2$; Sr^{2+}:$1s^22s^22p^63s^23p^63d^{10}4s^24p^6$; (d) $1s^22s^1$; Li^+ $1s^2$; (e) $1s^22s^22p^63s^23p^63d^{10}4s^24p^3$; $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$; (f) $1s^22s^22p^63s^23p^4$; $1s^22s^22p^63s^23p^6$

Question 38-10.

From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

Solution

Examples include sodium chloride (salt), NaCl; sodium hydrogen carbonate (baking soda), $NaHCO_3$; sodium hydroxide, NaOH; potassium chloride (a salt substitute), KCl; tin(II) fluoride (in toothpaste), SnF_2; calcium carbonate (antacid), $CaCO_3$; ammonium nitrate (fertilizer) NH_4NO_3.

UNIT 39 Covalent Bonding

Question 39-1.

Why is it incorrect to speak of a molecule of solid NaCl?

Solution

NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

Question 39-2.

What information can you use to predict whether a bond between two atoms is covalent or ionic?

Solution

If the elements in a compound are the same or close to one another in the periodic table, the compound is likely to be covalent; if they are far apart, then the compound will likely be ionic. If electronegativity values are available, the difference in electronegativity can indicate whether a bond is likely to be ionic or covalent.

Question 39-3.

Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

(a) Cl_2CO
(b) MnO
(c) NCl_3
(d) $CoBr_2$
(e) K_2S
(f) CO
(g) CaF_2
(h) HI
(i) CaO
(j) IBr
(k) CO_2

Solution

ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)

Question 39-4.

Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.

Solution

In an ionic bond, an electron or electrons are transferred from one atom to another, making one negative and the other positive. The electrostatic attraction holds them together. In a covalent bond, electrons are shared between the two atoms, resulting in a bond. A polar covalent bond is one in which the electrons are shared unequally. In this case, one atom has a greater electronegativity and a greater attraction for the electrons in the bond. In a pure covalent bond, the electrons are shared equally. In this case, the two atoms have very similar, if not the same, electronegativities and attract the electrons in the bond equally.

Question 39-5.

From its position in the periodic table, determine which atom in each pair is more electronegative:

(a) Br or Cl
(b) N or O
(c) S or O
(d) P or S
(e) Si or N
(f) Ba or P
(g) N or K

Solution

(a) Cl; (b) O; (c) O; (d) S; (e) N; (f) P; (g) N

Question 39-6.

From its position in the periodic table, determine which atom in each pair is more electronegative:

(a) N or P
(b) N or Ge
(c) S or F
(d) Cl or S
(e) H or C
(f) Se or P
(g) C or Si

Solution

(a) N; (b) N; (c) F; (d) Cl; (e) C; (f) P; (g) C

Question 39-7.

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

(a) C, F, H, N, O
(b) Br, Cl, F, H, I
(c) F, H, O, P, S
(d) Al, H, Na, O, P
(e) Ba, H, N, O, As

Solution

(a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O

Question 39-8.

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

- (a) As, H, N, P, Sb
- (b) Cl, H, P, S, Si
- (c) Br, Cl, Ge, H, Sr
- (d) Ca, H, K, N, Si
- (e) Cl, Cs, Ge, H, Sr

Solution

(a) H, Sb, As, P, N; (b) H, Si, P, S, Cl; (c) Sr, H, Ge, Br, Cl; (d) K, Ca, H, Si, N; (e) Cs, Sr, H, Ge, Cl

Question 39-9.

Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

Solution

N, O, F, and Cl

Question 39-10.

Which is the most polar bond?

(a) C --2
(b) C --2
(c) N --2
(d) O --2
(e) Se ---2

Solution O --- 9

Question 39-11.

Identify the more polar bond in each of the following pairs of bonds:

- (a) HF or HCl
- (b) NO or CO
- (c) SH or OH
- (d) PCl or SCl
- (e) CH or NH
- (f) SO or PO
- (g) CN or NN

Solution

(a) HF; (b) CO; (c) OH; (d) PCl; (e) NH; (f) PO; (g) CN

Question 39-12.

Which of the following molecules or ions contain polar bonds?

- (a) O_3
- (b) S_8

(c) O_2^{2-}

(d) NO_3^-

(e) CO_2

(f) H_2S

(g) BH_4^-

Solution

(d) NO_3^-; (e) CO_2; (f) H_2S; (g) BH_4^-

UNIT 40 Lewis Symbols and Structures

Question 40-1.

Write the Lewis symbols for each of the following ions:

(a) As^{3-}

(b) I^- (c) Be^{2+}

(d) O_{2-} (e)

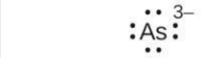
Ga^{3+}

(f) Li^+

(g) N^{3-}

Solution

(a) eight electrons:



;

(b) eight electrons:

;

(c) no electrons

Be^{2+};

(d) eight electrons:

;

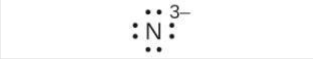
(e) no electrons

Ga^{3+};

(f) no electrons

Li^+;

(g) eight electrons:



Question 40-2.

Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:

(a) Cl

(b) Na
(c) Mg
(d) Ca
(e) K
(f) Br
(g) Sr
(h) F

Solution

(a)

:

(b) Na^+:
(c) Mg^{2+}:
(d) Ca^{2+}:
(e) K^+:
(f)

:

(g) Sr^{2+}:
(h)

Question 40-3.

Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

(a) MgS
(b) Al_2O_3
(c) $GaCl_3$
(d) K_2O
(e) Li_3N
(f) KF

Solution

(a)


:

(b)


:

(c)


:

(d)


:

(e)

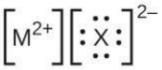

:

(f)

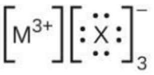
Question 40-4.

In the Lewis structures listed below, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:

(a)



(b)



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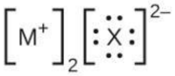

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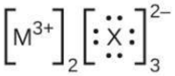


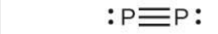
Solution

(a) MgS; (b) $AlCl_3$; (c) Na_2S; (d) Al_2S_3

Question 40-5.

Write the Lewis structure for the diatomic molecule P_2, an unstable form of phosphorus found in high-temperature phosphorus vapor.

Solution



Question 40-6.

Write Lewis structures for the following:

(a) H_2
(b) HBr (c) PCl_3
(d) SF_2
(e) H_2CCH_2
(f) HNNH
(g) H_2CNH
(h) NO^-
(i) N_2

(j) CO
(k) CN^-

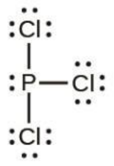
Solution

(a) H–H;

(b)


;

(c)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(d)


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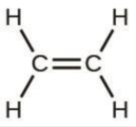
(e)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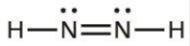
(f)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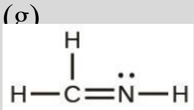
(g)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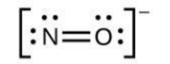
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(i)


;

(j)


;

(k)

Question 40-7.

Write Lewis structures for the following:

(a) O_2
(b) H_2CO (c) AsF_3
(d) ClNO
(e) $SiCl_4$

(f) H_3O^+

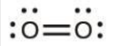
(g) NH_4^+ (h) BF_4^- (i) HCCH

(j) ClCN

(k) C_2^{2+}

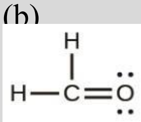
Solution

(a)



In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

(b)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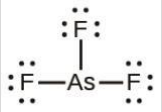
(c)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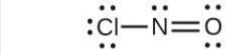
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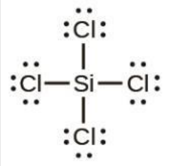
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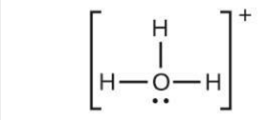
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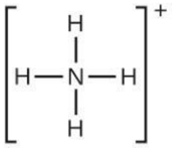

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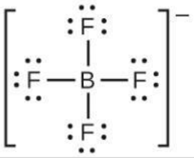

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(i)

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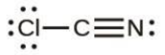
(j)



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(k)

Question 40-8.

Write Lewis structures for the following:

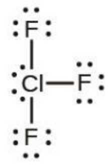
(a) ClF_3

(b) PCl_5

(c) BF_3
(d) PF_6^-

Solution

(a)



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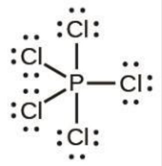
(b)



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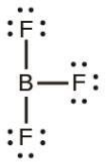

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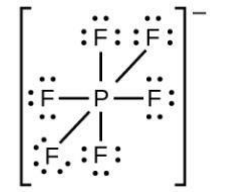


Question 40-9.

Write Lewis structures for the following:

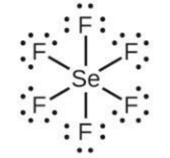
(a) SeF_6
(b) XeF_4

(c) $SeCl_3^+$

(d) Cl_2BBCl_2 (contains a B–B bond)

Solution

(a) SeF :



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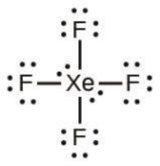
(b) XeF :



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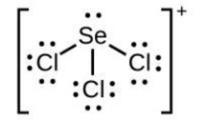
(c) $SeCl_3^+$:



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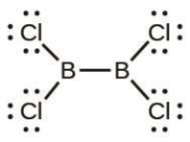
(d) Cl BBCl :



Question 40-10.

Write Lewis structures for:

(a) PO_4^{3-}

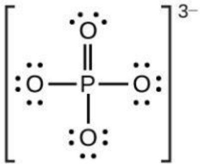
(b) ICl_4^-

(c) SO_3^{2-}

(d) HONO

Solution

(a)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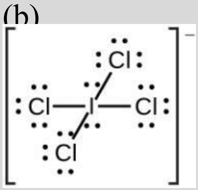
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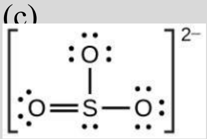
(c)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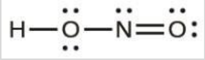


Question 40-11.

Correct the following statement: “The bonds in solid $PbCl_2$ are ionic; the bond in a HCl molecule is covalent. Thus, all of the valence electrons in $PbCl_2$ are located on the Cl^- ions, and all of the valence electrons in a HCl molecule are shared between the H and Cl atoms.”

Solution

Two valence electrons per Pb atom are transferred to Cl atoms; the resulting Pb^{2+} ion has a $6s^2$ valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

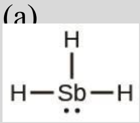
Question 40-12.

Write Lewis structures for the following molecules or ions:

(a) SbH_3
(b) XeF_2
(c) Se_8 (a cyclic molecule with a ring of eight Se atoms)

Solution

(a)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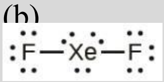
(b)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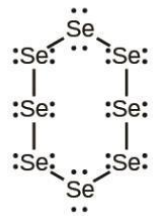
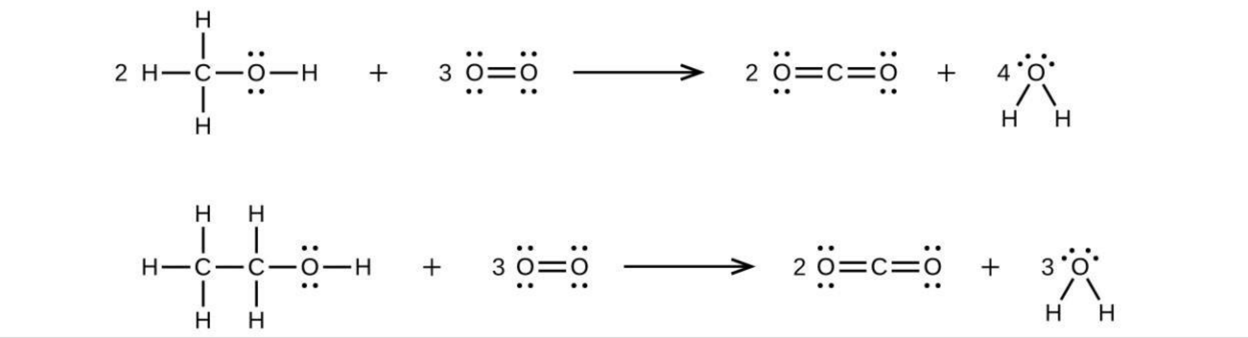
(c)



Question 40-13.

Methanol, H_3COH, is used as the fuel in some race cars. Ethanol, C_2H_5OH, is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas

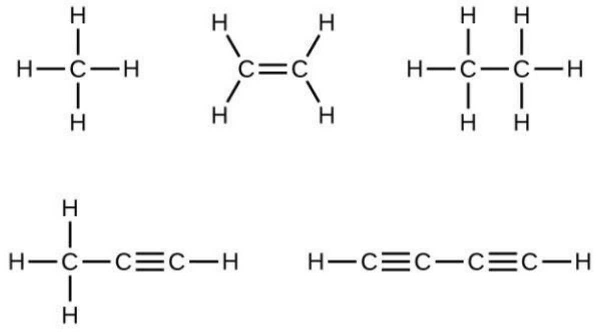
Solution



Question 40-14.

Many planets in our solar system contain organic chemicals including methane (CH_4) and traces of ethylene (C_2H_4), ethane (C_2H_6), propyne (H_3CCCH), and diacetylene ($HCCCCH$). Write the Lewis structures for each of these molecules.

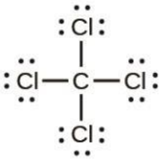
Solution

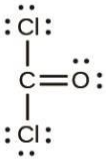


Question 40-15.

Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO. Write the Lewis structures for carbon tetrachloride and phosgene.

Solution





Question 40-16.

Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:

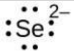
(a) $1s^22s^22p^5$
(b) $1s^22s^22p^63s^2$
(c) $1s^22s^22p^63s^23p^64s^23d^{10}$
(d) $1s^22s^22p^63s^23p^64s^23d^{10}4p^4$ (e) $1s^22s^22p^63s^23p^64s^23d^{10}4p^1$

Solution

(a) atom: F, common ion F^-, Lewis structure:

;

(b) atom: Mg, common ion Mg^{2+}, Lewis structure Mg^{2+}; (c) atom: Zn, common ion: Zn^{2+}, Lewis structure: Zn^{2+}; (d) atom: Se, common ion Se^{2-}, Lewis structure:



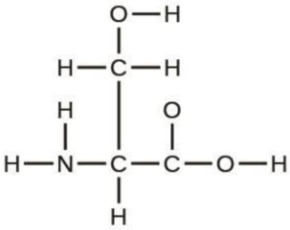
;

(e) atom: Ga, common ion: Ga^{3+}, Lewis structure: Ga^{3+}

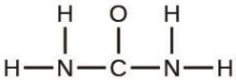
Question 40-17.

The arrangement of atoms in several biologically important molecules is given below. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

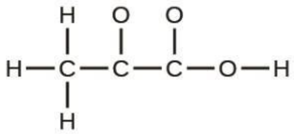
(a) the amino acid serine:



(b) urea:

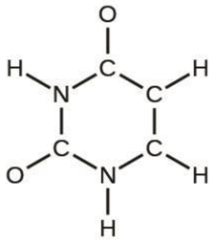


(c) pyruvic acid:

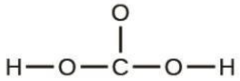


$$\mathrm{H{-}CH_2{-}C(O){-}C(O){-}O{-}H}$$

(d) uracil:

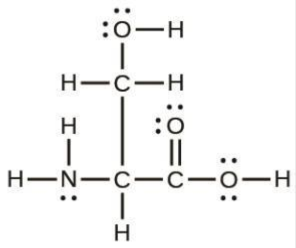


(e) carbonic acid:



Solution

(a)



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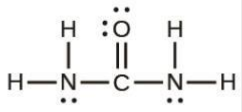
(b)



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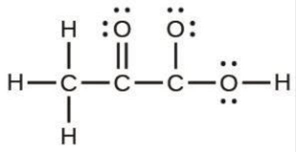
(c)



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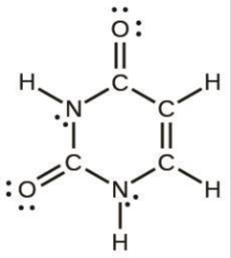
(d)



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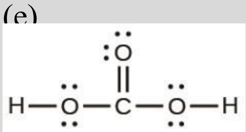
(e)



Question 40-18.

A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

Solution

There are 85.7 g C and 14.3 g H in a 100.0-g sample:

$$\frac{85.7\ \text{g}}{12.011\ \text{g mol}^{-1}} = 7.14\ \text{mol C} \qquad \frac{7.14\ \text{mol}}{7.14\ \text{mol}} = 1 \qquad 1\ \text{C}$$

$$\frac{14.3\ \text{g}}{1.0079\ \text{g mol}^{-1}} = 14.19\ \text{mol H} \qquad \frac{14.19\ \text{mol}}{7.14\ \text{mol}} = 2 \qquad 2\ \text{H}$$

Question 40-19.

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

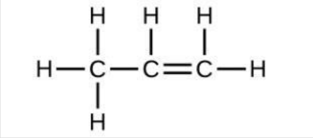
Solution

A 100.0-g sample of this compound would contain 85.7 g C and 14.3 g H:

$$\frac{85.7\ \text{g}}{12.011\ \text{g mol}^{-1}} = 7.14\ \text{mol C}$$

$$\frac{14.3\ \text{g}}{1.00794\ \text{g mol}^{-1}} = 14.19\ \text{mol H}$$

This is a ratio of 2 H to 1 C, or an empirical formula of CH_2 with a formula mass of approximately 14. As $\frac{42}{14} = 3$, the formula is 3 × CH_2 or C_3H_6. The Lewis structure is:



Question 40-20.

Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

Solution

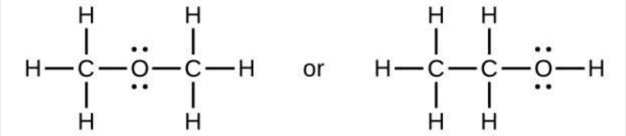
There are 52.2 g C, 13.1 g H, and 34.7 g O in a 100.0-g sample.

$$\frac{52.2}{12.011} = 4.346\ \text{mol} \qquad \frac{4.346\ \text{mol}}{4.346\ \text{mol}} = 2 \qquad 2\ \text{C}$$

$$\frac{13.1}{1.0079} = 12.997\ \text{mol} \qquad \frac{12.997\ \text{mol}}{2.1688\ \text{mol}} = 6 \qquad 6\ \text{H}$$

$$\frac{34.7}{15.9994} = 2.1668\ \text{mol} \qquad \frac{2.1688\ \text{mol}}{2.1688\ \text{mol}} = 1 \qquad 1\ \text{O}$$

Experimental formula = C_2H_6O; weight per formula unit = 46. The compound may be:



Question 40-21.

How are single, double, and triple bonds similar? How do they differ?

Solution

Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

UNIT 41 Formal Charges and Resonance

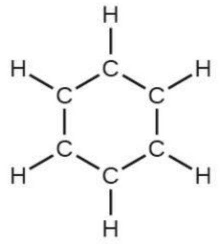
Question 41-1.

Write resonance forms that describe the distribution of electrons in each of the molecules or ions given below:

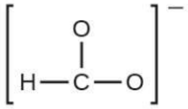
(a) selenium dioxide, OSeO

(b) nitrate ion, NO_3^-

(c) nitric acid, HNO_3 (N is bonded to an OH group and two O atoms) (d) benzene, C_6H_6:



(e) the formate ion:

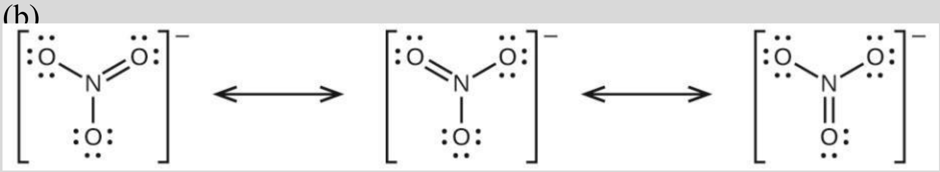


Solution

(a)


:

(b)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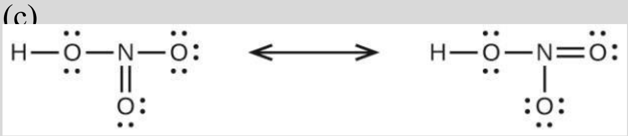
(c)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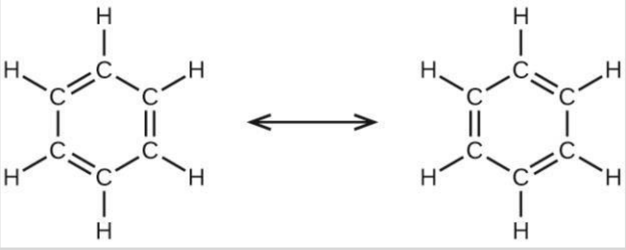
(d)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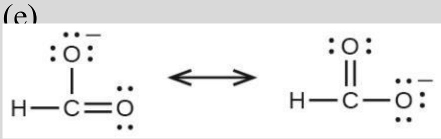
(e)



Question 41-2.

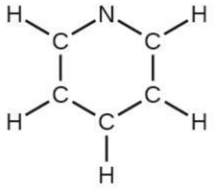
Write resonance forms that describe the distribution of electrons in each of the molecules or ions given below:

(a) sulfur dioxide, SO_2

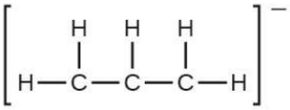
(b) carbonate ion, CO_3^{2-}

(c) hydrogen carbonate ion, HCO_3^- (C is bonded to an OH group and two O atoms)

(d) pyridine:

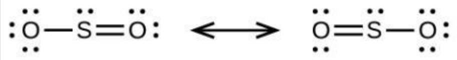


(e) the allyl ion:



Solution

(a)



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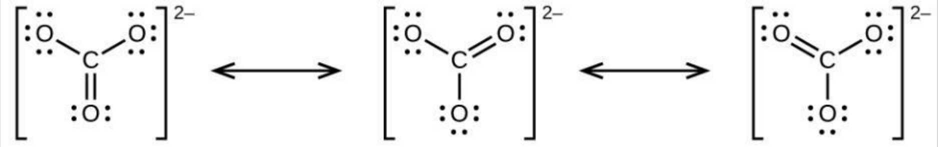
(b)

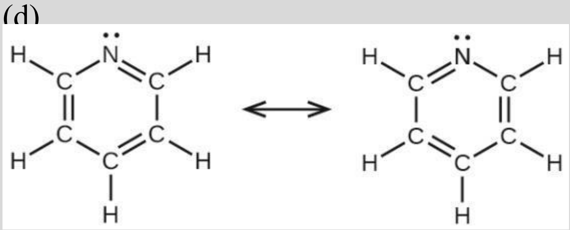


;

(c)

;

(d)



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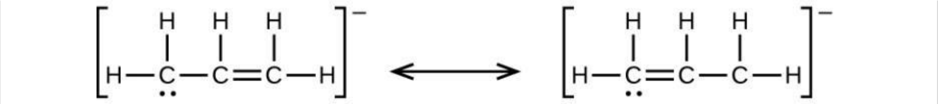
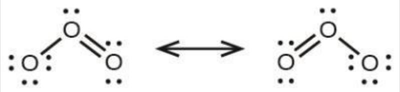
(e)



Question 41-3.

Write the resonance forms of ozone, O_3, the component of the upper atmosphere that protects the Earth from ultraviolet radiation.

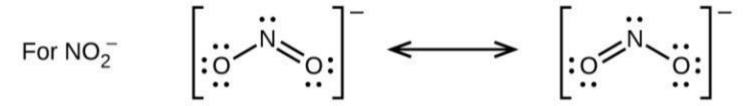
Solution



Question 41-4.

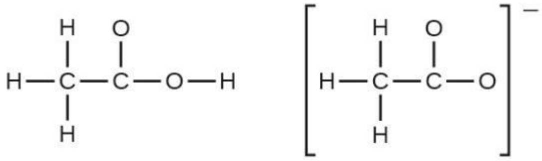
Sodium nitrite, which has been used to preserve bacon and other meats, is an ionic compound. Write the resonance forms of the nitrite ion, NO_2^-.

Solution



Question 41-5.

In terms of the bonds present, explain why acetic acid, CH_3CO_2H, contains two distinct types of carbon-oxygen bonds, whereas the acetate ion, formed by loss of a hydrogen ion from acetic acid, only contains one type of carbon-oxygen bond. The skeleton structures of these species are shown:



Solution

The acetic acid molecule contains a C–O double bond and a C–O single bond. The acetate ion is described by two resonance structures that average the two C–O bonds.

Question 41-6.

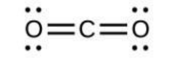
Write the Lewis structures for the following, and include resonance structures where appropriate. Indicate which of the three has the strongest carbon-oxygen bond.

(a) CO_2

(b) CO

Solution

(a)



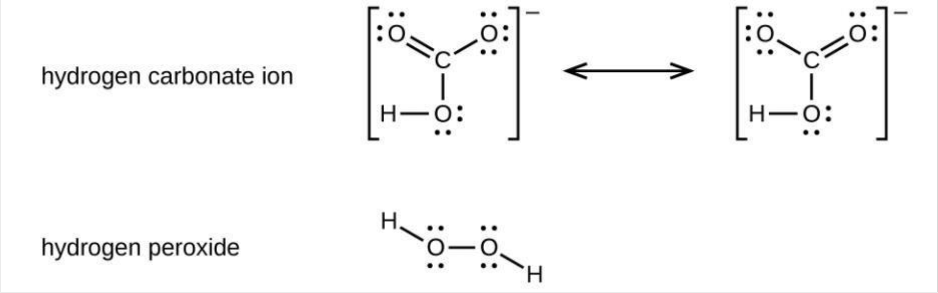
(b)

CO has the strongest carbon-oxygen bond, because there are is a triple bond joining C and O. CO_2 has double bonds, and carbonate has 1.3 bonds.

Question 41-7.

Toothpastes containing sodium hydrogen carbonate (sodium bicarbonate) and hydrogen peroxide are widely used. Write Lewis structures for the hydrogen carbonate ion and hydrogen peroxide molecule, with resonance forms where appropriate.

Solution



Question 41-8.

Determine the formal charge of each element in the following:

(a) HCl (b)
CF_4
(c) PCl_3
(d) PF_5

Solution

	Element	Bonding Electrons	Nonbonded Electrons	Valence Electrons	Formal Charge
(a)	H Cl	1 1	0 6	1 7	0 0
(b)	C F	4 1	0 6	4 7	0 0
(c)	P Cl	3 1	2 6	5 7	0 0
(d)	P F	5 1	0 6	5 7	0 0

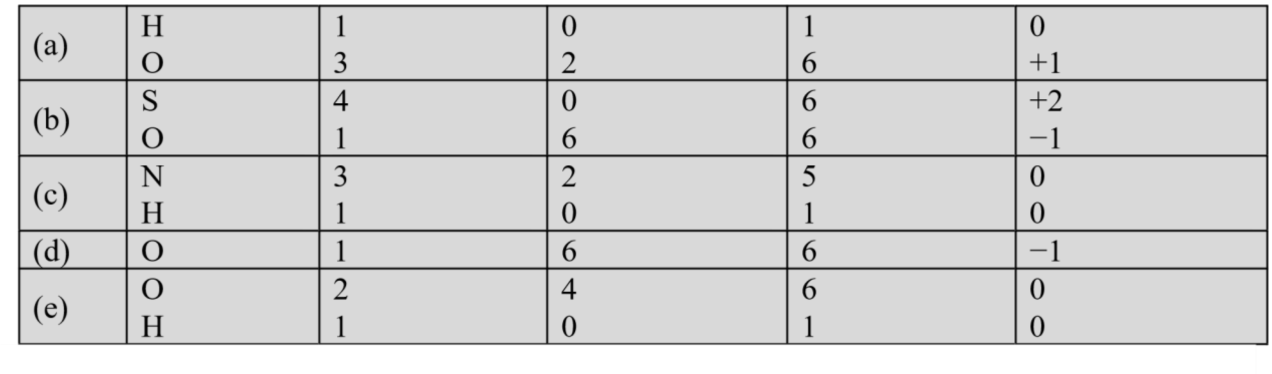
Question 41-9.

Determine the formal charge of each element in the following:

(a) H_3O^+
(b) SO_4^{2-}
(c) NH_3
(d) O_2^{2-}
(e) H_2O_2

Solution

	Element	Bonding Electrons	Nonbonded Electrons	Valence Electrons	Formal Charge



(a)	H O	1 3	0 2	1 6	0 +1
(b)	S O	4 1	0 6	6 6	+2 −1
(c)	N H	3 1	2 0	5 1	0 0
(d)	O	1	6	6	−1
(e)	O H	2 1	4 0	6 1	0 0

Question 41-10.

Calculate the formal charge of chlorine in the molecules Cl_2, $BeCl_2$, and ClF_5.

Solution

	Element	Bonding Electrons	Nonbonded Electrons	Valence Electrons	Formal Charge
Cl_2	Cl	1	6	7	0
$BeCl_2$	Be Cl	2 1	0 6	2 7	0 0
ClF_5	Cl F	5 1	2 6	7 7	0 0

Question 41-11.

Calculate the formal charge of each element in the following compounds and ions:

(a) F_2CO
(b) NO^- (c) BF_4^- (d) $SnCl_3^-$

(e) H_2CCH_2
(f) ClF_3

(g) SeF_6
(h) PO_4^{3-}

Solution

	Element	Bonding Electrons	Nonbonded Electrons	Valence Electrons	Formal Charge
(a)	F	1	6	7	0
	C	4	0	4	0
	O	2	4	6	0
(b)	N	2	4	5	−1
	O	2	4	6	0
(c)	B	4	0	3	−1
	F	1	6	7	0
(d)	Sn	3	2	4	−1
	Cl	1	6	7	0
(e)	C	4	0	4	0
	H	1	0	1	0
(f)	Cl	3	4	7	0
	F	1	6	7	0
(g)	Se F	6	0	6	0
		1	6	7	0
(h)	P	4	0	5	+1
	O	1	6	6	−1

Question 41-12.

Draw all possible resonance structures for each of the compounds below. Determine the formal charge on each atom in each of the resonance structures:

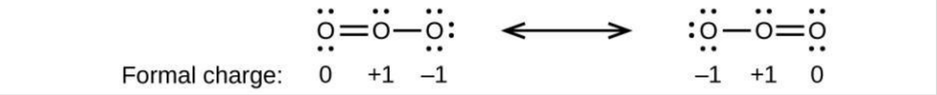
(a) O_3
(b) SO_2

(c) NO_2^-

(d) NO_3^-

Solution

(a)



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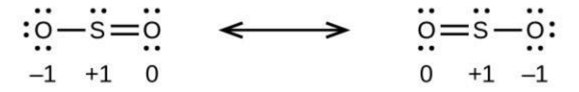
(b)



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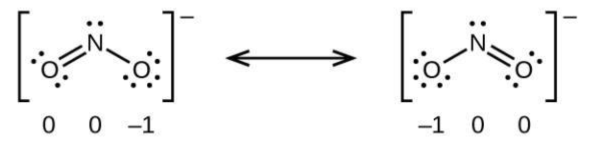
(c)



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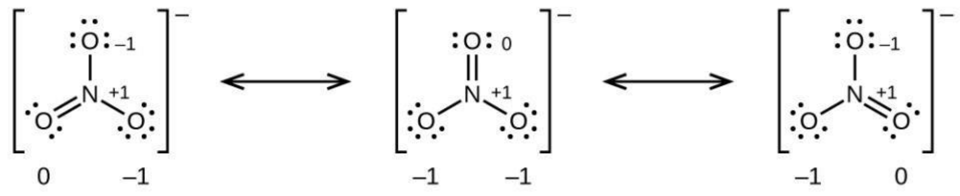
(d)

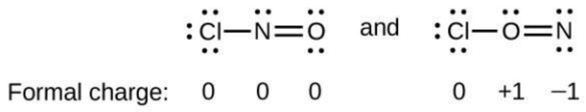


Question 41-13.

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in nitrosyl chloride: ClNO or ClON?

Solution

Two possibilities exist:

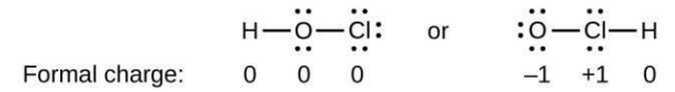


The first representation, having no formal charges, is more likely to occur than the second representation, which has formal charges at both N and O. The latter arrangement is even less favored because the formal negative charge is on the more electropositive ion.

Question 41-14.

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in hypochlorous acid: HOCl or OClH?

Solution



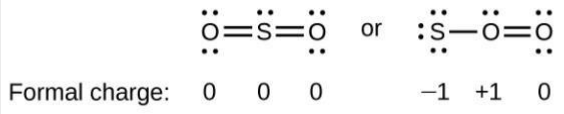
The structure with formal charges of 0 is the most stable and would therefore be the correct arrangement of atoms.

Question 41-15.

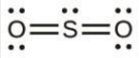
Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in sulfur dioxide: OSO or SOO?

Solution

Formal charge:



Correct arrangement:



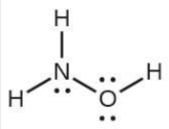
This form has no formal charges. The second form has a positive charge on the more electronegative element, an unfavorable situation.

Question 41-16.

Draw the structure of hydroxylamine, H_3NO, and assign formal charges; look up the structure. Is the actual structure consistent with the formal charges?

Solution

The structure that gives zero formal charges is consistent with the actual structure:

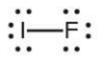


Question 41-17.

Iodine forms a series of fluorides (listed below). Write Lewis structures for each of the four compounds and determine the formal charge of the iodine atom in each molecule: (a) IF
(b) IF_3
(c) IF_5
(d) IF_7

Solution

(a) formal charge 0: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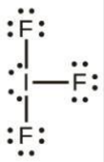
(b) formal charge 0: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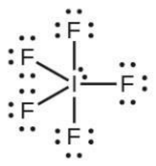
(c) formal charge 0: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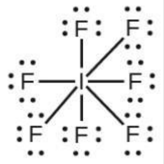
(d) formal charge 0:



Question 41-18.

Write the Lewis structure and chemical formula of the compound with a molar mass of about 70 g/mol that contains 19.7% nitrogen and 80.3% fluorine by mass, and determine the formal charge of the atoms in this compound.

Solution

There are 19.7 g N and 80.3 g F in a 100.0-g sample:

$$\frac{19.7\text{ g}}{14.0067\text{ g mol}^{-1}} = 1.406\text{ mol}$$

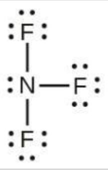
$$\frac{1.406\text{ mol}}{1.406\text{ mol}} = 1\text{ N}$$

$$\frac{80.3\text{ g}}{18.9984\text{ g mol}^{-1}} = 4.2267\text{ mol}$$

$$\frac{4.2267\text{ mol}}{1.406\text{ mol}} = 3\text{ F}$$

The empirical formula is NF_3 and its molar mass is 71.00 g/mol, which is consistent with the stated molar mass.

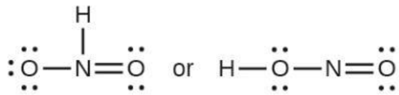
Oxidation states: N = +3, F = –1.



Formal charges: N = 0, F = 0:

Question 41-19.

Which of the following structures would we expect for nitrous acid? Determine the formal charges:



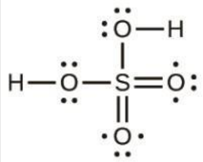
Solution

The second form, having all zero formal charges, is more likely:

Question 41-20.

Sulfuric acid is the industrial chemical produced in greatest quantity worldwide. About 90 billion pounds are produced each year in the United States alone. Write the Lewis structure for sulfuric acid, H_2SO_4, which has two oxygen atoms and two OH groups bonded to the sulfur.

Solution



UNIT 42 Strengths of Ionic and Covalent Bonds

Question 42-1.

Which bond in each of the following pairs of bonds is the strongest?

(a) C–C or C = C

(b) C–N or C≡N

(c) C≡O or C = O

(d) H–F or H–Cl

(e) C–H or O–H

(f) C–N or C–O

Solution

In general, a multiple bond between the same two elements is stronger than a single bond. The greater the electronegativity difference between two similar elements, the greater the bond energy.

(a) C=C; (b) C≡N; (c) C≡O; (d) H–F; (e) O–H; (f) C–O

Question 42-2.

Using the bond energies in Table 7.2, determine the approximate enthalpy change for each of the following reactions:

(a) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

(b) $CH_4(g) + I_2(g) \longrightarrow CH_3I(g) + HI(g)$

(c) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$

Solution

$$\Delta H^\circ_{298} = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}}$$

(a)
$$= D_{H-H} + D_{Br-Br} - 2D_{H-Br};$$
$$= 436 + 190 - 2(370) = -114\ \text{kJ}$$

$$\Delta H^\circ_{298} = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}}$$

(b)
$$= 4D_{C-H} + D_{I-I} - 3D_{C-H} - D_{C-I} - D_{H-I};$$
$$= 4(415) + 150 - 3(415) - 240 - 295 = 30\ \text{kJ}$$

$$\Delta H^\circ_{298} = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}}$$

(c)
$$= D_{C=C} + 4D_{C-H} + 3D_{O=O} - 4D_{C=O} - 4D_{O-H}$$
$$= 611 + 4(415) + 3(498) - 4(741) - 4(464)$$
$$= -1055\ \text{kJ}$$

Question 42-3.

Using the bond energies in Table 7.2, determine the approximate enthalpy change for each of the following reactions:

(a) $Cl_2(g) + 3F_2(g) \longrightarrow 2ClF_3(g)$

(b) $H_2C{=}CH_2(g) + H_2(g) \longrightarrow H_3CCH_3(g)$

(c) $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(g)$

Solution

$$\Delta H^\circ = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}}$$

(a)
$$= 2D_{Cl-Cl} + 3D_{F-F} - 6D_{Cl-F};$$
$$= -564\ \text{kJ}$$

$$\Delta H^\circ = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}}$$

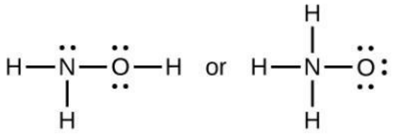
(b)
$$= D_{C-C} + 4D_{C-H} + D_{H-H} - D_{C-C} - 6D_{C-H};$$
$$= 611 + 4(415) + 436 - 345 - 6(415)$$
$$= -128\ \text{kJ}$$

$$\Delta H^\circ = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}}$$

(c)
$$= 2D_{C-C} + 12D_{C-H} + 7D_{O-O} - 8D_{C-O} - 12D_{O-H}$$
$$= 2(345) + 12(415) + 7(496) - 8(741) - 12(464) = -2354\ \text{kJ}$$

Question 42-4.

When a molecule can form two different structures, the structure with the stronger bonds is usually the more stable form. Use bond energies to predict the correct structure of the hydroxylamine molecule:



Solution

(a)
2 N−H bonds = 2(390)
1 N−O bond = 200
1 O−H bond = 464
1444 kJ

; (b)
3 N−H bonds = 3(390)
1 N−O bond = 200
1370 kJ

; the greater bond energy is for (a), and it is more stable

Question 42-5.

How does the bond energy of HCl(*g*) differ from the standard enthalpy of formation of HCl(*g*)?

Solution

The bond energy involves breaking HCl into H and Cl atoms. The enthalpy of formation involves making HCl from H_2 and Cl_2 molecules.

Question 42-6.

Using the standard enthalpy of formation data in Appendix G, show how can the standard enthalpy of formation of HCl(*g*) can be used to determine the bond energy.

Solution

$$\mathrm{HCl}(g) \longrightarrow \frac{1}{2}\mathrm{H_2}(g) + \frac{1}{2}\mathrm{Cl_2}(g) \qquad \Delta H^\circ_1 = -\Delta H^\circ_{\mathrm{f[HCl}(g)]}$$

$$\frac{1}{2}\mathrm{H_2}(g) \longrightarrow \mathrm{H}(g) \qquad \Delta H^\circ_2 = \Delta H^\circ_{\mathrm{f[H}(g)]}$$

$$\frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{Cl}(g) \qquad \Delta H^\circ_3 = \Delta H^\circ_{\mathrm{f[Cl}(g)]}$$

$$\mathrm{HCl}(g) \longrightarrow \mathrm{H}(g) + \mathrm{Cl}(g) \qquad \Delta H^\circ_{298} = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3$$

$$\begin{aligned} D_{\mathrm{HCl}} = \Delta H^\circ_{298} &= -\Delta H^\circ_{\mathrm{f[HCl}(g)]} + \Delta H^\circ_{\mathrm{f[H}(g)]} + \Delta H^\circ_{\mathrm{f[Cl}(g)]} \\ &= -(-92.307\ \mathrm{kJ}) + 217.97\ \mathrm{kJ} + 121.3\ \mathrm{kJ} \\ &= 431.6\ \mathrm{kJ} \end{aligned}$$

Question 42-7.

Using the standard enthalpy of formation data in Appendix G, calculate the bond energy of the carbon-sulfur double bond in CS_2.

Solution

$$\mathrm{CS}\,(\ )\ {}_{2}g \longrightarrow \mathrm{C(graphite)} + 2\mathrm{S}(\ )s \qquad \Box = \Box H_1^{\Box}\ \ H_{\mathrm{f[(CS\,(\ )]}}^{\Box}\ \ {}_{2}g$$

$$\mathrm{C(graphite)} \longrightarrow \mathrm{C}(\ )g \qquad \Box = \Box H_{2}\Box\ \ H_{\mathrm{f\,C(\,)}\Box\,g}$$

$$2\mathrm{S}(\ )\ s \longrightarrow 2\mathrm{S}(\ )g \qquad 2\Box = \Box H_3^{\Box}\ \ 2\ H_{\mathrm{f\,S(\,)}}^{\Box}\ g$$

$$D_{\mathrm{CS_2}} = \Box H\!\!\!\!\Box = -\Box\ \ H^{\Box}_{\mathrm{f[(CS_2(\,}g\mathrm{)]}} + \Box H^{\Box}_{\mathrm{f\,C(}g\mathrm{)}} + 2\,\Box H^{\Box}_{\mathrm{f\,S(}g\mathrm{)}}$$

$$= -\ 116.9 + 716.681 + 2(278.81)$$

$$= 1157.4\ \mathrm{kJ\ mol}^{-1}$$

$$D_{\mathrm{C\,S}} = \frac{1157.4}{2} = 578.7\ \mathrm{kJ\ mol}^{1}\ \mathrm{of\ C} = \mathrm{S\ bonds}$$

Question 42-8.

Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the S–F bond in $SF_4(g)$ or in $SF_6(g)$?

Solution

$$\mathrm{SF}_4(g) \longrightarrow \frac{1}{8}\mathrm{S}_8(s) + 2\mathrm{F}_2(g) \qquad \Box H_1^{\Box} = -\Box\ \ H_{\mathrm{f[SF}_4(g)]}$$

$$\frac{1}{8}\mathrm{S}_8(s) \longrightarrow \mathrm{S}(g) \qquad \Box H_2^{\Box} = \Box H^{\Box}_{\mathrm{f\,S(}g\mathrm{)}}$$

$$2\mathrm{F}_2(g) \longrightarrow 4\mathrm{F}(g) \qquad 4\ \ \Box H_3^{\Box} = 4\Box H^{\Box}_{\mathrm{f\,F(}g\mathrm{)}}$$

$$D_{\mathrm{SF_4}} = \Box H^{\Box}_{298} = -\Box H_{\mathrm{f[SF_4(}g\mathrm{)]}} + \Box H^{\Box}_{\mathrm{f\,S(}g\mathrm{)}} + 4\Box H^{\Box}_{\mathrm{f\,F(}g\mathrm{)}}$$

$$= 728.43 + 278.81 + 4(79.4) = 1369.7\ \mathrm{kJ}$$

$$D_{\mathrm{S\,F}} = \frac{1324.84\ \mathrm{kJ}}{4\ \mathrm{S-F}} = 331.21\ \mathrm{kJ}$$

Proceeding in the same manner, $-\Box H_{\mathrm{f[SF_6(}g\mathrm{)]}} = 1220.5\ \mathrm{kJ\ mol}^{-1}$. The 6F($g$) and S($g$) contribute 755.21 kJ; then $\mathrm{DF}_{\mathrm{SF_6}} = 1962.7\ \mathrm{kJ}$ and $D_{\mathrm{S\,F}} = \frac{1975.71}{6} = 392.3\ \mathrm{kJ\ mol}^{-1}$ per mole of bonds. The S–F bond in SF is stronger.

Question 42-9.

Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the P–Cl bond in $PCl_3(g)$ or in $PCl_5(g)$?

Solution

$$\mathrm{PCl_3}(g) \longrightarrow \tfrac{1}{4}\mathrm{P_4}(s) + \tfrac{3}{2}\mathrm{Cl_2}(g) \qquad \Delta H_1^\circ = -\Delta H_{\mathrm{f}[\mathrm{PCl_3}(g)]}^\circ$$

$$\tfrac{1}{4}\mathrm{P_4}(s) \longrightarrow \mathrm{P}(g) \qquad \Delta H_2^\circ = \Delta H_{\mathrm{f\,P}(g)}^\circ$$

$$\tfrac{3}{2}\mathrm{Cl_2}(g) \longrightarrow 3\mathrm{Cl}(g) \qquad 3\Delta H_3^\circ = 3\Delta H_{\mathrm{f\,Cl}(g)}^\circ$$

$$D_{\mathrm{PCl_3}} = □\;□ = -\Delta H_{\mathrm{f}[\mathrm{PCl_3}(g)]}^\circ + \Delta H_{\mathrm{f\,P}(g)}^\circ + 3\Delta H_{\mathrm{f\,Cl}(g)}^\circ$$

$$= 287.0 + 314.64 + 3(121.3) = 965.54\ \mathrm{kJ\ mol^{-1}}$$

$$D_{\mathrm{PCl_3}} = \frac{965.54\ \mathrm{kJ}}{3} = 321.8\ \text{kJ per mol of bonds}^{-1}$$

Proceeding in the same manners, $-\Delta H_{\mathrm{f}[\mathrm{PCl_5}(g)]} = 374.9\ \mathrm{kJ\ mol^{-1}}$. The P($g$) and the 5Cl($g$) contribute 921.14 kJ; then $\mathrm{DF_{PCl_5}} = 1296.04$ kJ and $D_{\mathrm{P\,Cl}} - = \frac{1296.04\ \mathrm{kJ/mol}}{5} = 259.2$ kJ/mol of bonds. The P–Cl bond in $\mathrm{PCl_3}$ is stronger.

Question 42-10.

Complete the following Lewis structure by adding bonds (not atoms), and then indicate the longest bond:

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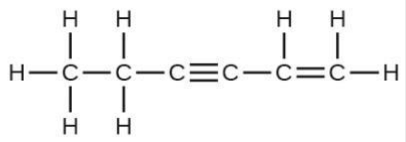
     H   H           H   H

H    C   C   C   C   C   C   H

     H   H
```

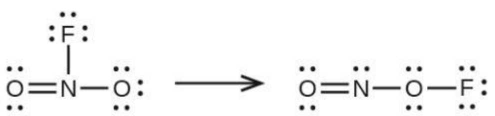
Solution



The C–C single bonds are longest.

Question 42-11.

Use the bond energy to calculate an approximate value of ΔH for the following reaction. Which is the more stable form of $\mathrm{FNO_2}$?



Solution

the left hand arrangement: $O=N$ not listed. N–F 270. N–O 200; the right hand arrangement: $O=N$ not listed. N–O 200. O–F 185; the bond energy of $O=N$ does not matter because it must be the same in both cases. the form on the right has a bond energy of $X + 470$; that on the right, $X + 385$; the form on the left is more stable.

Question 42-12.

Use principles of atomic structure to answer each of the following:[1]

(a) The radius of the Ca atom is 197 pm; the radius of the Ca^{2+} ion is 99 pm. Account for the difference.

(b) The lattice energy of CaO(s) is –3460 kJ/mol; the lattice energy of K_2O is –2240 kJ/mol. Account for the difference.

(c) Given these ionization values, explain the difference between Ca and K with regard to their first and second ionization energies.

Element	First Ionization Energy (kJ/mol)	Second Ionization Energy (kJ/mol)
K	419	3050
Ca	590	1140

(d) The first ionization energy of Mg is 738 kJ/mol and that of Al is 578 kJ/mol. Account for this difference.

Solution

(a) When two electrons are removed from the valence shell, the Ca radius loses the outermost energy level and reverts to the lower *n* = 3 level, which is much smaller in radius.

(b) The +2 charge on calcium pulls the oxygen much closer compared with K, thereby increasing the lattice energy relative to a less charged ion.

(c) Removal of the 4*s* electron in Ca requires more energy than removal of the 4*s* electron in K, because of the stronger attraction of the nucleus and the extra energy required to break the pairing of the electrons. The second ionization energy for K requires that an electron be removed from a lower energy level, where the attraction is much stronger from the nucleus for the electron. In addition, energy is required to unpair two electrons in a full orbital. For Ca, the second ionization potential requires removing only a lone electron in the exposed outer energy level.

(d) In Al, the removed electron is relatively unprotected and unpaired in a *p* orbital. The higher energy for Mg mainly reflects the unpairing of the 2*s* electron.

Question 42-13.

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 200.8 pm. NaF crystallizes in the same structure as LiF but with a Na–F distance of 231 pm. Which of the following values

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[1] This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

most closely approximates the lattice energy of NaF: 510, 890, 1023, 1175, or 4090 kJ/mol? Explain your choice.

Solution

The lattice energy is given by $U = C\left(\frac{Z_+Z_-}{R_o}\right)$, where R_o is the interatomic distance. The charges are the same in both LiF and NaF. The major difference is expected to be the interatomic distance 2.008 Å versus 2.31 Å. From the data for LiF, with $Z^+Z^- = -1$,

$$C = \frac{UR_o}{Z_+Z_-} = \frac{1023 \times 2.008}{-1} = -2054 \text{ kJ Å mol}^{-1}.$$

Then,

$$U_{\text{NaF}} = \frac{-2054 \text{ kJ Å mol}^{-1}(-1)}{2.31 \text{ Å}} = 889 \text{ kJ mol}^{-1} \text{ or } 890 \text{ kJ mol}^{-1}.$$

Question 42-14.

For which of the following substances is the least energy required to convert one mole of the solid into separate ions?

(a) MgO
(b) SrO
(c) KF
(d) CsF
(e) MgF_2

Solution

The lattice energy, *U*, is the energy required to convert the solid into separate ions. *U* may be calculated from the Born-Haber cycle.

The values in kJ/mol are approximately (a) 3791; (b) 3223; (c) 821; (d) 740; and (e) 2957. The answer is (d), which requires about 740 kJ/mol.

Question 42-15.

The reaction of a metal, M, with a halogen, X_2, proceeds by an exothermic reaction as indicated by this equation: $M(s) + X_2(g) \longrightarrow MX_2(s)$. For each of the following, indicate which option will make the reaction more exothermic. Explain your answers.

(a) a large radius vs. a small radius for M^{+2}
(b) a high ionization energy vs. a low ionization energy for M
(c) an increasing bond energy for the halogen
(d) a decreasing electron affinity for the halogen
(e) an increasing size of the anion formed by the halogen **Solution**

In each case, think about how it would affect the Born-Haber cycle. Recall that the more negative the overall value, the more exothermic the reaction is. (a) The smaller the radius of the cation, the shorter the interionic distance and the greater the lattice energy would be. Since the lattice energy is negative in the Born-Haber cycle, this would lead to a more exothermic reaction. (b) A lower ionization energy is a lower positive energy in the Born-Haber cycle. This would make the reaction more exothermic, as a smaller positive value is "more exothermic." (c) As in part (b), the bond energy is a positive energy. The lower it is, the more exothermic the reaction will be. (d) A higher electron affinity is more negative. In the Born-Haber cycle, the more negative the electron affinity, the more exothermic the overall reaction. (e) The smaller the radius of the anion, the shorter the interionic distance and the greater the lattice energy would be. Since the lattice energy is negative in the Born-Haber cycle, this would lead to a more exothermic reaction.

Question 42-16.

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 201 pm. MgO crystallizes in the same structure as LiF but with a Mg–O distance of 205 pm. Which of the following values most closely approximates the lattice energy of MgO: 256 kJ/mol, 512 kJ/mol, 1023 kJ/mol, 2046 kJ/mol, or 4090 kJ/mol? Explain your choice.

Solution

4008 kJ/mol; both ions in MgO have twice the charge of the ions in LiF; the bond length is very similar and both have the same structure; a quadrupling of the energy is expected based on the equation for lattice energy

Question 42-17.

Which compound in each of the following pairs has the larger lattice energy? Note: Mg^{2+} and Li^{+} have similar radii; O^{2-} and F^{-} have similar radii. Explain your choices.

(a) MgO or MgSe
(b) LiF or MgO
(c) Li_2O or LiCl
(d) Li_2Se or MgO

Solution

(a) MgO; selenium has larger radius than oxygen and, therefore, a larger interionic distance and thus, a larger smaller lattice energy than MgO;

(b) MgO; the higher charges on Mg and O, given the similar radii of the ions, leads to a larger lattice energy;

(c) Li_2O; the higher charge on O^{2-} leads to a larger energy; additionally, Cl^{-} is larger than O^{2-} ; this leads to a larger interionic distance in LiCl and a lower lattice energy; (d) MgO; the higher charge on Mg leads to a larger lattice energy

Question 42-18.

Which compound in each of the following pairs has the larger lattice energy? Note: Ba^{2+} and K^{+} have similar radii; S^{2-} and Cl^{-} have similar radii. Explain your choices.

(a) K_2O or Na_2O

(b) K_2S or BaS
(c) KCl or BaS
(d) BaS or $BaCl_2$

Solution

(a) Na_2O; Na^+ has a smaller radius than K^+; (b) BaS; Ba has a larger charge than K; (c) BaS; Ba and S have larger charges; (d) BaS; S has a larger charge

Question 42-19.

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

(a) MgO
(b) SrO
(c) KF
(d) CsF
(e) MgF_2

Solution

MgO

Question 42-20.

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

(a) K_2S
(b) K_2O
(c) CaS
(d) Cs_2S
(e) CaO

Solution

CaO

Question 42-21.

The lattice energy of KF is 794 kJ/mol, and the interionic distance is 269 pm. The Na–F distance in NaF, which has the same structure as KF, is 231 pm. Which of the following values is the closest approximation of the lattice energy of NaF: 682 kJ/mol, 794 kJ/mol,924 kJ/mol, 1588 kJ/mol, or 3175 kJ/mol? Explain your answer.

Solution

924 kJ/mol

UNIT 43 Molecular Structure and Polarity

Question 43-1.

Explain why the HOH molecule is bent, whereas the HBeH molecule is linear. **Solution** The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

Question 43-2.

What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?

Solution

The presence or absence of lone pairs on the central atom.

Question 43-3.

Explain the difference between electron-pair geometry and molecular structure. **Solution** Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

Question 43-4.

Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4? Why is the H–N–H angle in NH_4^+ identical to the H–C–H bond angle in CH_4?

Solution

NH_3 contains three bonding pairs of electrons and a lone pair of electrons. The lone pair takes up more room than the bonding pairs. Both CH_4 and NH_4^+ contain four bonding pairs and no lone pairs.

Question 43-5.

Explain how a molecule that contains polar bonds can be nonpolar. **Solution** As long as the polar bonds are compensated (for example. two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

Question 43-6.

As a general rule, MX_n molecules (where M represents a central atom and X represents terminal atoms; n = 2 – 5) are polar if there is one or more lone pairs of electrons on M. NH_3 (M = N, X = H, n = 3) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?

Solution

MX_2E_3 (linear) and MX_4E_2 (square planar), where E represents an unshared pair of electrons; XeF_2 and XeF_4 are examples

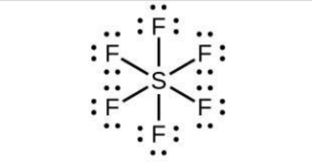
Question 43-7.

Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

(a) SF_6
(b) PCl_5
(c) BeH_2
(d) CH_3^+

Solution

(a) Number of valence electrons: S = 6, F = 7 each, total 48. A single line bond represents two electrons:



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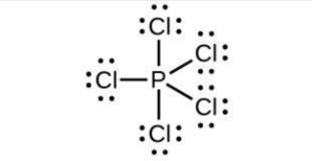
The total number of electrons used is 48; six bonds are formed and no nonbonded pairs exist. Therefore the molecule includes six regions of electron density and, from the table, the electron geometry is octahedral. Since no lone pairs exist, the electron geometry and molecular structure are the same.

(b) Number of valence electrons: P = 5, Cl = 7 each, total 40:



.

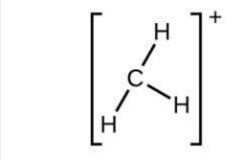
The total number of electrons is 40; there are five regions of electron density and, from the table, the geometry is trigonal bipyramid. Since no lone pairs exist on P, the electron geometry and molecular structure are the same.

(c) Number of valence electrons: Be = 2, H = 1 each, total 4:

H:Be:H.

There are only two regions of electron density and they must have a linear arrangement. These regions also correspond to the location of the bonds. Both the electron and molecular structures are linear.

(d) Number of valence electrons: C = 4, H = 1 each, less one electron because of the positive charge, for a total of six electrons:



There are three regions of electron density coincident with the three bonds. Therefore the shape is trigonal planar for both the electron geometry and molecular structure.

Question 43-8.

Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:

(a) IF_6^+

(b) CF_4
(c) BF_3
(d) SiF_5^-

(e) $BeCl_2$

Solution

		Regions of High Electron Density		Structure	
Formula	Electrons	Total	Lone pairs	Electron	Molecular
(a) IF_6^+	48	6	0	octahedral	octahedral
(b) CF_4	32	4	0	tetrahedral	tetrahedral
(c) BF_3	24	3	0	trigonal	trigonal
(d) SiF_5^-	40	5	0	trigonal bipyramidal	trigonal bipyramidal
(e) $BeCl_2$	16	2	0	linear	linear

Question 43-9.

What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

(a) ClF_5
(b) ClO_2^- (c) $TeCl_4^{2-}$

(d) PCl_3
(e) SeF_4
(f) PH_2^-

Solution

		Regions of High Electron Density		Structure	
Formula	Electrons	Total	Lone pairs	Electron	Molecular
(a) ClF_5	42	6	1	octahedral	square pyramidal
(b) ClO_2^-	20	4	2	tetrahedral	bent
(c) $TeCl_4^{2-}$	36	6	2	octahedral	square planar
(d) PCl_3	26	4	1	tetrahedral	trigonal pyramidal
(e) SeF_4	34	5	1	trigonal bipyramidal	seesaw
(f) PH_2^-	8	4	2	tetrahedral	bent (109°)

Question 43-10.

Predict the electron pair geometry and the molecular structure of each of the following ions:

(a) H_3O^+
(b) PCl_4^- (c) $SnCl_3^+$

(d) $BrCl_4^-$ (e)

ICl_3

(f) XeF_4
(g) SF_2

Solution

		Regions of High Electron Density		Structure	
Formula	Electrons	Bonding pairs	Lone pairs	Electron	Molecular
(a) H_3O^+	8	3	1	tetrahedral	trigonal pyramidal
(b) PCl_4^-	34	4	1	trigonal bipyramidal	sawhorse
(c) $SnCl_3^+$	24	3	0	trigonal planar	trigonal planar
(d) $BrCl_4^-$	36	4	2	octahedral	square planar
(e) ICl_3	28	3	2	trigonal bipyramidal	T-shaped
(f) XeF_4	36	4	2	octahedral	square planar
(g) SF_2	20	2	2	tetrahedral	bent (109°)

Question 43-11.

Identify the electron pair geometry and the molecular structure of each of the following molecules:

(a) ClNO (N is the central atom)
(b) CS_2
(c) Cl_2CO (C is the central atom)
(d) Cl_2SO (S is the central atom)
(e) SO_2F_2 (S is the central atom)
(f) XeO_2F_2 (Xe is the central atom)
(g) $ClOF_2^+$ (Cl is the central atom)

Solution

		Regions of High Electron Density		Structure	
Formula	Electrons	Total	Lone pairs	Electron	Molecular
(a) ClNO	18	3	1	trigonal planar	bent (120°)
(b) CS_2	16	2	0	linear	linear
(c) Cl_2CO	24	3	0	trigonal planar	trigonal planar
(d) Cl_2SO	26	4	1	tetrahedral	trigonal pyramidal
(e) SO_2F_2	32	4	0	tetrahedral	tetrahedral
(f) XeO_2F_2	34	5	1	trigonal bipyramidal	seesaw
(g) $ClOF_2^+$	26	4	1	tetrahedral	trigonal pyramidal

Question 43-12.

Predict the electron pair geometry and the molecular structure of each of the following:

(a) IOF_5 (I is the central atom)
(b) $POCl_3$ (P is the central atom)
(c) Cl_2SeO (Se is the central atom)
(d) $ClSO^+$ (S is the central atom) (e) F_2SO (S is the central atom)
(f) NO_2^-
(g) SiO_4^{4-}

Solution

		Regions of High Electron Density		Structure	
Formula	Electrons	Bonding pairs	Lone pairs	Electron	Molecular
(a) IOF_5	48	6	0	octahedral	octahedral
(b) $POCl_3$	32	4	0	tetrahedral	tetrahedral
(c) Cl_2SeO	26	3	1	tetrahedral	trigonal pyramidal
(d) $ClSO^+$	18	2	1	trigonal	Bent (120°)
(e) F_2SO	26	3	1	tetrahedral	trigonal pyramidal
(f) NO_2^-	18	2	1	trigonal planar	bent (120°)
(g) SiO_4^{4-}	32	4	0	tetrahedral	tetrahedral

Question 43-13.

Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

(a) ClF_5
(b) ClO_2^- (c) $TeCl_4^{2-}$
(d) PCl_3
(e) SeF_4
(f) PH_2^-
(g) XeF_2

Solution

All of these molecules and ions contain polar bonds. Only ClF_5, ClO_2^-, PCl_3, SeF_4, andPH_2^- have dipole moments.

Question 43-14.

Which of these molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

(a) H_3O^+
(b) PCl_4^- (c) $SnCl_3^-$
(d) $BrCl_4^-$

(e) ICl_3
(f) XeF_4
(g) SF_2

Solution

All of these molecules and ions contain polar bonds. Only H_3O^+, PCl_4^-, and SF_2 have dipole moments.

Question 43-15.

Which of the following molecules have dipole moments?

(a) CS_2
(b) SeS_2
(c) CCl_2F_2
(d) PCl_3 (P is the central atom)
(e) ClNO (N is the central atom)

Solution

(a) CS_2 is linear and has no dipole moment. (b) SeS_2 is bent. This leads to an overall dipole moment. (c) The C–Cl and C–F bonds are not balanced—that is, the dipoles do not completely cancel. Therefore, it has a dipole moment. (d) PCl3 is trigonal pyramidal. Due to this shape, the dipoles of the bonds do not cancel and there is an overall dipole moment. (e) The ClNO molecule is bent, leading to a dipole moment.

Question 43-16.

Identify the molecules with a dipole moment:

(a) SF_4
(b) CF_4
(c) Cl_2CCBr_2
(d) CH_3Cl
(e) H_2CO

Solution

(a) SF_4; (c) Cl_2CCBr_2; (d) CH_3Cl; (e) H_2CO

Question 43-17.

The molecule XF_3 has a dipole moment. Is X boron or phosphorus?

Solution

P

Question 43-18.

The molecule XCl_2 has a dipole moment. Is X beryllium or sulfur?

Solution

X is sulfur because XCl_2 is bent; $BeCl_2$ does not have a dipole moment because it is linear.

Question 43-19.

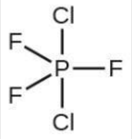
Is the Cl_2BBCl_2 molecule polar or nonpolar?

Solution
nonpolar

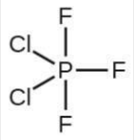
Question 43-20.

There are three possible structures for PCl_2F_3 with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.

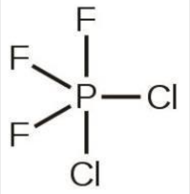
Solution
(a) The dipole moments resulting from the P–F and P–Cl bonds cancel one another so that no dipole moment is expected:



(b) The two F atoms, at 180° cancel one another's effects. The two Cl atoms at 120° will have less influence on the dipole moment than the two F atoms at 120° in (c):



(c) The two P–F bond dipoles at 120° are only partially cancelled by the single P–Cl bond dipole at 120°. Likewise, the P–F bond 180° to the P–Cl bond only results in a minor cancellation of the dipole along the axis.



Question 43-21.

Describe the molecular structure around the indicated atom or atoms:

(a) the sulfur atom in sulfuric acid, H_2SO_4 [$(HO)_2SO_2$]
(b) the chlorine atom in chloric acid, $HClO_3$ [$HOClO_2$]
(c) the oxygen atom in hydrogen peroxide, HOOH
(d) the nitrogen atom in nitric acid, HNO_3 [$HONO_2$]
(e) the oxygen atom in the OH group in nitric acid, HNO_3 [$HONO_2$]
(f) the central oxygen atom in the ozone molecule, O_3
(g) each of the carbon atoms in propyne, CH_3CCH
(h) the carbon atom in Freon, CCl_2F_2
(i) each of the carbon atoms in allene, H_2CCCH_2 **Solution**

(a) tetrahedral; (b) trigonal pyramidal; (c) bent (109°); (d) trigonal planar; (e) bent (109°); (f) bent (109°); (g) $\underline{C}H_3CCH$ tetrahedral, $CH_3\underline{C}\underline{C}H$ linear; (h) tetrahedral, (i) $H_2C\underline{C}CH_2$ linear; $H_2\underline{C}C\underline{C}H_2$ trigonal planar

Question 43-22.

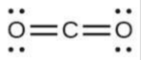
Draw the Lewis structures and predict the shape of each compound or ion:

(a) CO_2
(b) NO_2^-

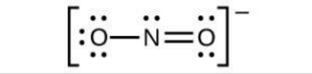
(c) SO_3
(d) SO_3^{2-}

Solution

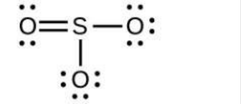
(a) linear:


;

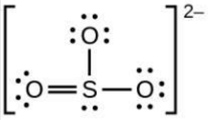
(b) bent:


;

(c) trigonal planar:


;

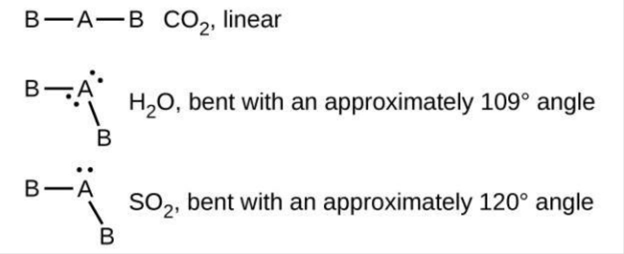
(d) trigonal pyramidal:



Question 43-23.

A molecule with the formula AB_2, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

Solution



CO_2, linear

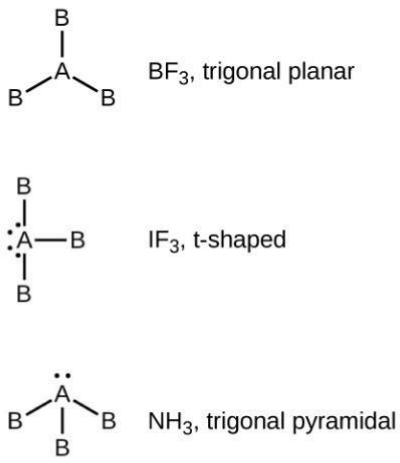
H_2O, bent with an approximately 109° angle

SO_2, bent with an approximately 120° angle

Question 43-24.

A molecule with the formula AB_3, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.

Solution



Question 43-25.

Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:

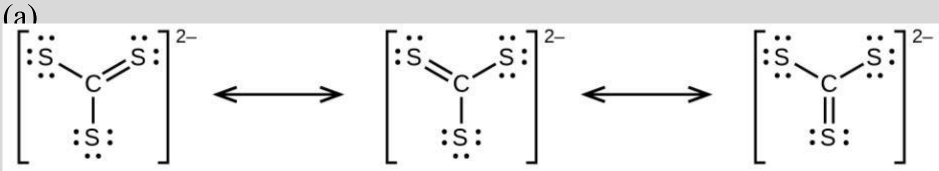
(a) CS_3^{2-}

(b) CS_2 (c) CS

(d) predict the molecular shapes for CS_3^{2-} and CS_2 and explain how you arrived at your predictions

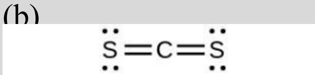
Solution

(a)



;

(b)



;

(c)

;

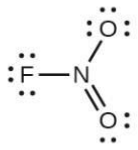
(d) CS_3^{2-} includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar; CS_2 has only two regions of electron density (all bonds with no lone pairs); the shape is linear

Question 43-26.

What is the molecular structure of the stable form of FNO_2? (N is the central atom.)

Solution

The Lewis dot structure is:


.

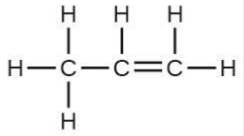
There are three regions of electron density and three bonds. The molecule is trigonal planar.

Question 43-27.

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure?

Solution

The empirical formula is CH_2 with a unit mass of14. $\frac{42}{14} = 3$. Therefore, the Lewis structure is made from three units, but the atoms must be rearranged:



Question 43-28.

Use this link: http://phet.colorado.edu/en/simulation/molecule-polarity to perform the following exercises for a two-atom molecule:

(a) Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.

(b) With a partial positive charge on A, turn on the electric field and describe what happens.

(c) With a small partial negative charge on A, turn on the electric field and describe what happens.

(d) Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.

Solution

(a) The electronegativity of A must be greater than B. (b) Nothing happens. (c) The molecule slowly rotates to align with the field. (d) The molecule quickly rotates to align with the field.

Question 43-29.

Use this link: http://phet.colorado.edu/en/simulation/molecule-polarity to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.

(a) Sketch the bond dipoles and molecular dipole (if any) for O_3. Explain your observations.

(b) Look at the bond dipoles for NH_3. Use these dipoles to predict whether N or H is more electronegative.

(c) Predict whether there should be a molecular dipole for NH_3 and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.

Solution

The molecular dipole points away from the hydrogen atoms.

Question 43-30.

Use this link: http://phet.colorado.edu/en/simulation/molecule-shapes to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers. **Solution** electron group geometry: trigonal planar; molecular structure: bent, bond angle 120°

Question 43-31.

Use this link: http://phet.colorado.edu/en/simulation/molecule-shapes to explore real molecules. On the Real Molecules tab, select H_2O. Switch between the “real” and “model” modes. Explain the difference observed.

Solution

The structures are very similar. In the model mode, each electron group occupies the same amount of space, so the bond angle is shown as 109.5°. In the “real” mode, the lone pairs are larger, causing the hydrogens to be compressed. This leads to the smaller angle of 104.5°.

Question 43-32.

Use this link: http://phet.colorado.edu/en/simulation/molecule-shapes to explore real molecules. On the Real Molecules tab, select “model” mode and S_2O. What is the model bond angle? Explain whether the “real” bond angle should be larger or smaller than the ideal model angle.

Solution

The model angle is 120°, as expected for a trigonal planar electron-group geometry. The real angle should be smaller, because the lone pair occupies more space and compresses the bonds to 119°.