

## Ch.8:

12. Use Planck's equation (8.3) to determine
- the frequency, in hertz, of radiation having an energy of  $8.62 \times 10^{-21}$  J/photon;
  - the wavelength, in nanometers, of radiation with 360 kJ/mol of energy.

Ans:

(M)

$$(a) \quad \nu = \frac{E}{h} = \frac{8.62 \times 10^{-21} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 1.30 \times 10^{13} \text{ s}^{-1} = 1.30 \times 10^{13} \text{ Hz}$$

$$(b) \quad E = h\nu = \frac{hc}{\lambda}; \quad \lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m/s}}{360 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ photons}}} = 3.33 \times 10^{-7} \text{ m} = 333 \text{ nm}$$

24. High-pressure sodium vapor lamps are used in street lighting. The two brightest lines in the sodium spectrum are at 589.00 and 589.59 nm. What is the difference in energy per photon of the radiations corresponding to these two lines?

Ans:

(M)

$$E_1 = h\nu = \frac{hc}{\lambda} = \frac{6.62607 \times 10^{-34} \text{ J} \cdot \text{s} \times 2.99792 \times 10^8 \text{ m s}^{-1}}{589.00 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}}} = 3.3726 \times 10^{-19} \text{ J/Photon}$$

$$E_2 = \frac{6.62607 \times 10^{-34} \text{ J} \cdot \text{s} \times 2.99792 \times 10^8 \text{ m s}^{-1}}{589.59 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}}} = 3.3692 \times 10^{-19} \text{ J/Photon}$$

$$\Delta E = E_1 - E_2 = 3.3726 \times 10^{-19} \text{ J} - 3.3692 \times 10^{-19} \text{ J} = 0.0034 \times 10^{-19} \text{ J/photon} = 3.4 \times 10^{-22} \text{ J/photon}$$

26. The minimum energy required to cause the photoelectric effect in potassium metal is  $3.69 \times 10^{-19} \text{ J}$ . Will photoelectrons be produced when visible light shines on the surface of potassium? If 400 nm radiation is shone on potassium, what is the velocity of the ejected electrons?

**Ans:**

**(M)** We are given the work function of potassium in terms of the minimum energy required for photoelectron ejection. The minimum energy that an impinging photon must have to cause ejection of the photoelectron is:

$$eV_0 = h\nu_0 = 3.69 \times 10^{-19} \text{ J}$$

The photo frequency is therefore:

$$\nu_0 = 3.69 \times 10^{-19} \text{ J} / 6.6261 \times 10^{-34} \text{ J} \cdot \text{s}^{-1} = 5.57 \times 10^{14} \text{ s}^{-1}$$

And the wavelength of photon is:

$$\lambda = c/\nu_0 = (2.998 \times 10^8 \text{ m/s}) / (5.57 \times 10^{14} \text{ s}^{-1}) = 5.38 \times 10^{-7} \text{ m} = 538 \text{ nm}$$

Since the visible spectrum covers 390 to 750 nm, wavelengths covering the green to blue portion of the spectrum have enough energy to eject a photoelectron from potassium.

Provided that the energy of the impinging photo exceeds the minimum threshold, the extra energy is transferred to the photoelectron in form of kinetic energy. That is:

$$K_E = \frac{1}{2} m_e u^2 = h\nu - eV_0$$

Therefore, if potassium is exposed to light with  $\lambda = 400 \text{ nm}$ , the speed of the photoelectron is determined using the above equation. But first, determine the frequency of the photon:

$$\nu_0 = c/\lambda = (2.998 \times 10^8 \text{ m/s}) / (400 \times 10^{-9} \text{ m}) = 7.495 \times 10^{14} \text{ s}^{-1}$$

Then, enter the requisite information in the kinetic energy equation provided:

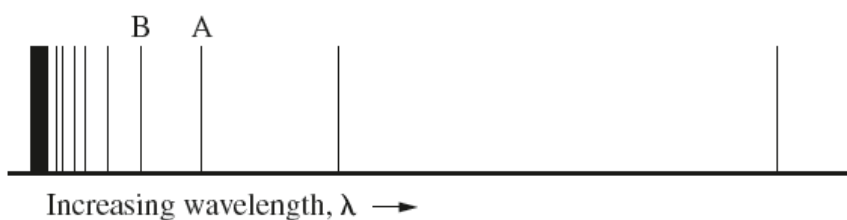
$$K_E = \frac{1}{2} m_e u^2 = h\nu - eV_0 = (6.6261 \times 10^{-34} \text{ J} \cdot \text{s}^{-1})(7.495 \times 10^{14} \text{ s}^{-1}) - 3.69 \times 10^{-19} \text{ J} = 1.28 \times 10^{-19} \text{ J}$$

$$\frac{1}{2} m_e u^2 = 1.28 \times 10^{-19} \text{ J}$$

so,

$$u = \sqrt{\frac{2 \times 1.28 \times 10^{-19} \text{ J}}{9.109 \times 10^{-31} \text{ kg}}} = 1.68 \times 10^7 \text{ m/s}$$

36. The emission spectrum below for a one-electron (hydrogen-like) species in the gas phase shows all the lines, before they merge together, resulting from transitions to the first excited state from higher energy states. Line A has a wavelength of 434 nm.



- (a) What are the upper and lower principal quantum numbers corresponding to the lines labeled A and B?  
 (b) Identify the one-electron species that exhibits the spectrum.

**Ans:**

**(M)**

- (a) Line A is for the transition  $n = 5 \rightarrow n = 2$ , while Line B is for the transition  $n = 6 \rightarrow n = 2$

- (b) This transition corresponds to the  $n = 5$  to  $n = 2$  transition. Hence,  $\Delta E = hc/\lambda$   
 $\Delta E = (6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1}) \div (434 \times 10^{-9} \text{ m}) = 4.577 \times 10^{-19} \text{ J}$   
 $\Delta E = -Z^2 R_H / n_1^2 - (-Z^2 R_H / n_2^2)$   
 $4.577 \times 10^{-19} \text{ J} = -Z^2 (2.179 \times 10^{-18}) / (5)^2 + Z^2 (2.179 \times 10^{-18}) / (2)^2$   
 $Z^2 = 1.00$  and  $Z = 1.00$  Thus, this is the spectrum for the hydrogen atom.

46. Show that the uncertainty principle is not significant when applied to large objects such as automobiles. Assume that  $m$  is precisely known; assign a reasonable value to either the uncertainty in position or the uncertainty in velocity, and estimate a value of the other.

**Ans:**

- (E)** Assume a mass of 1000 kg for the automobile and that its position is known to 1 cm (0.01 m).

$$\Delta v = \frac{h}{4\pi m \Delta x} = \frac{6.626 \times 10^{-34} \text{ J s}}{(4\pi)(1000 \text{ kg})(0.01 \text{ m})} = 5 \times 10^{-36} \text{ m s}^{-1}$$

This represents an undetectable uncertainty in the velocity.

52. An electron in a one-dimensional box requires a wavelength of 618 nm to excite an electron from the  $n = 2$  level to the  $n = 4$  level. Calculate the length of the box.

Ans:

(D)

$$618 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}} = 6.18 \times 10^{-7} \text{ m}$$

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ ms}^{-1})}{6.18 \times 10^{-7} \text{ m}}$$

$$\Delta E = 3.127 \times 10^{-19} \text{ J}$$

$$\Delta E = E_{\text{excited state}} - E_{\text{ground state}}$$

$$E = \frac{n^2 h^2}{8mL^2}$$

Where  $n$ =energy level,  $h$ =Planck's constant,  $m$ = mass,  $L$ =length of box

$$3.217 \times 10^{-19} \text{ J} = \left[ \frac{4^2 (6.626 \times 10^{-34} \text{ Js})^2}{8(9.109 \times 10^{-31} \text{ kg})(L)^2} \right] - \left[ \frac{2^2 (6.626 \times 10^{-34} \text{ Js})^2}{8(9.109 \times 10^{-31} \text{ kg})(L)^2} \right]$$

$$3.217 \times 10^{-19} \text{ J} = \frac{9.6397 \times 10^{-37}}{L^2} - \frac{2.410 \times 10^{-37}}{L^2}$$

$$L^2 = 2.247 \times 10^{-18}$$

$$L = 1.499 \times 10^{-9} \text{ m} \times \frac{1012 \text{ pm}}{1 \text{ m}} = 1499 \text{ pm} = 1.50 \times 10^3 \text{ pm}$$

62. Concerning the concept of subshells and orbitals,
- How many subshells are found in the  $n = 3$  level?
  - What are the names of the subshells in the  $n = 3$  level?
  - How many orbitals have the values  $n = 4$  and  $\ell = 3$ ?
  - How many orbitals have the values  $n = 3$ ,  $\ell = 2$ , and  $m_\ell = -2$ ?
  - What is the total number of orbitals in the  $n = 4$  level?

Ans:

(E)

(a) 3 subshells

(b) 3s, 3p, 3d

(c) 7 orbitals

(d) 1 orbital

(e) 16 orbitals

80. Use orbital diagrams to show the distribution of electrons among the orbitals in (a) the  $4p$  subshell of Br; (b) the  $3d$  subshell of  $\text{Co}^{2+}$ , given that the two electrons lost are  $4s$ ; (c) the  $5d$  subshell of Pb.

Ans:

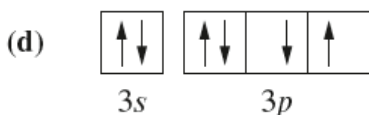
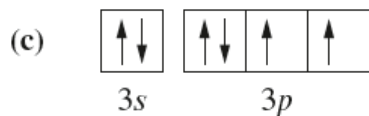
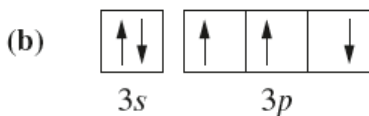
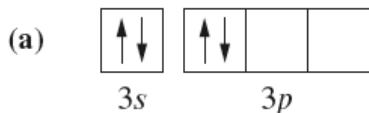
(E)

(a) The  $4p$  subshell of Br contains 5 electrons:  $[\text{Ar}] 3d \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow 4s \uparrow\downarrow 4p \uparrow\downarrow \uparrow$

(b) The  $3d$  subshell of  $\text{Co}^{2+}$  contains 7 electrons:  $[\text{Ar}] 3d \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow 4s \square$

(c) The  $5d$  subshell of Pb contains 10 electrons:  
 $[\text{Xe}] 4f \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow 5d \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow 6s \uparrow\downarrow 6p \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$

84. To what neutral atom do the following valence-shell configurations correspond? Indicate whether the configuration corresponds to the ground state or an excited state.



Ans:

(E)

(a) This is an excited state silicon atom ( $3p$  electrons should remain unpaired with same spin).

(b) This is an excited state phosphorus atom; the three  $3p$  orbital electrons should have the same spin (violates Hund's rule).

(c) This is a ground state sulfur atom.

(d) This is an excited state sulfur atom. The two unpaired electrons should have the same spin.

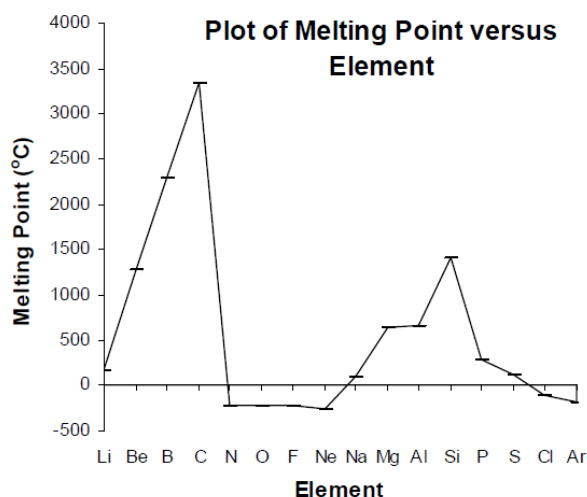
## Ch.9:

4. The following melting points are in degrees Celsius. Show that melting point is a periodic property of these elements: Al, 660; Ar, -189; Be, 1278; B, 2300; C, 3350; Cl, -101; F, -220; Li, 179; Mg, 651; Ne, -249; N, -210; O, -218; P, 590; Si, 1410; Na, 98; S, 119.

**Ans:**

**(M)** The following data are plotted at right below. Melting point clearly is a periodic property for these two periods. It rises to a maximum and then falls off in each case.

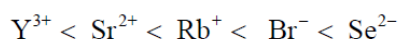
Element	Atomic Number Z	Melting Point °C
Li	3	179
Be	4	1278
B	5	2300
C	6	3350
N	7	-210
O	8	-218
F	9	-220
Ne	10	-249
Na	11	98
Mg	12	651
Al	13	660
Si	14	1410
P	15	590
S	16	119
Cl	17	-101
Ar	18	-189



18. The following species are isoelectronic with the noble gas krypton. Arrange them in order of increasing radius and comment on the principles involved in doing so:  $\text{Rb}^+$ ,  $\text{Y}^{3+}$ ,  $\text{Br}^-$ ,  $\text{Sr}^{2+}$ ,  $\text{Se}^{2-}$ .

**Ans:**

**(E)** In an isoelectronic series, all of the species have the same number and types of electrons. The size is determined by the nuclear charge. Those species with the largest (positive) nuclear charge are the smallest. Those with smaller nuclear charges are larger in size. Thus, the more positively charged an ion is in an isoelectronic series, the smaller it will be.

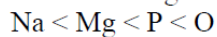


32. Compare the elements Na, Mg, O, and P.  
 (a) Place the elements in order of increasing ionization energy.  
 (b) Place the elements in order of increasing electron affinity.

**Ans:**

**(M)**

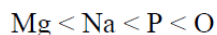
- (a) Ionization energy in the periodic table decreases from top to bottom in a group, and increases from left to right across a period, as summarized in Figure 9-10. Therefore, the elements listed in order of increasing ionization energy are:



- (b) If an atom has a high affinity for an electron, the electron affinity tends to be a large negative value. Non-metals have a greater affinity to gain electrons compared with metals. Metals prefer to lose electrons to form cations.

Oxygen has the greatest affinity since it would only have to add two electrons to reach a noble gas configuration, as compared with phosphorus. Sodium has more affinity for an electron than magnesium because sodium's 3s orbital would be full upon addition of an electron. Magnesium is less likely to add an electron because its electron would populate the higher energy 3p orbital.

Therefore, the elements listed in order of increasing electron affinity are:



36. Write electron configurations consistent with the following data on numbers of unpaired electrons:  
 $\text{Ni}^{2+}$ , 2;  $\text{Cu}^{2+}$ , 1;  $\text{Cr}^{3+}$ , 3.

**Ans:**

**(E)** First we write the electron configuration of the element, then that of the ion. In each case, the number of unpaired electrons written beside the configuration agrees with the data given in the statement of the problem.

- |        |                            |                   |                                   |                      |
|--------|----------------------------|-------------------|-----------------------------------|----------------------|
| (a) Ni | $[\text{Ar}] 3d^8 4s^2$    | $\longrightarrow$ | $\text{Ni}^{2+} [\text{Ar}] 3d^8$ | Two unpaired $e^-$   |
| (b) Cu | $[\text{Ar}] 3d^{10} 4s^1$ | $\longrightarrow$ | $\text{Cu}^{2+} [\text{Ar}] 3d^9$ | One unpaired $e^-$   |
| (c) Cr | $[\text{Ar}] 3d^5 4s^1$    | $\longrightarrow$ | $\text{Cr}^{3+} [\text{Ar}] 3d^3$ | Three unpaired $e^-$ |

46. Match each of the lettered items in the column on the left with the most appropriate numbered item(s) in the column on the right. Some of the numbered items may be used more than once and some not at all.

- |                       |   |
|-----------------------|---|
| (a) Tl                | 1. an alkaline earth metal                      |
| (b) $Z = 70$          | 2. element in period 5 and group 15             |
| (c) Ni                | 3. largest atomic radius of all the elements    |
| (d) $[\text{Ar}]4s^2$ | 4. an element in period 4 and group 16          |
| (e) a metalloid       | 5. $3d^8$                                       |
| (f) a nonmetal        | 6. one $p$ electron in the shell of highest $n$ |
|                       | 7. lowest ionization energy of all the elements |
|                       | 8. an $f$ -block element                        |

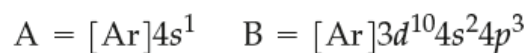
**Ans:**

(E)

- (a) 6. Tl's electron configuration  $[\text{Xe}] 4f^{14}5d^{10}6s^26p^1$  has one  $p$  electron in its outermost shell.
- (b) 8.  $Z = 70$  identifies the element as Yb, an  $f$ -block of the periodic table, or an inner transition element.
- (c) 5. Ni has the electron configuration  $[\text{Ar}] 4s^23d^8$ . It also is a  $d$ -block element.
- (d) 1. An  $s^2$  outer electron configuration, with the underlying configuration of a noble gas, is characteristic of elements of group 2(2A), the alkaline earth elements. Since the noble gas core is  $[\text{Ar}]$ , the element must be Ca.
- (e) 2. The element in the fifth period and Group 15 is Sb, a metalloid.
- (f) 4 and 6. The element in the fourth period and Group 16 is Se, a nonmetal. (Note, B is a nonmetal with electron configuration  $1s^22s^22p^1$  (having one  $p$  electron in the shell of highest  $n$ ). 6 is also a possible answer.



60. Two elements, A and B, have the electron configurations shown.



- (a) Which element is a metal?
- (b) Which element has the greater ionization energy?
- (c) Which element has the larger atomic radius?
- (d) Which element has the greater electron affinity?

**Ans:**

(E)

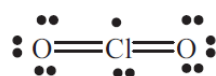
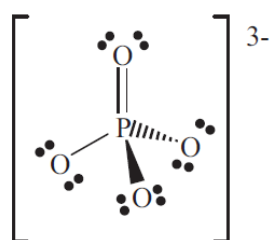
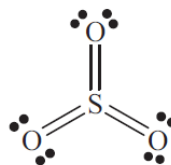
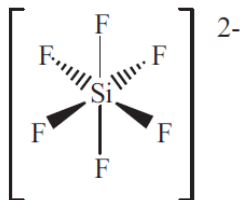
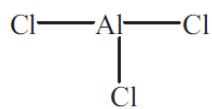
- (a) A; Element "A" (K) has an electron configuration consistent with group 1A, which is the alkali metals.
- (b) B; Element "B" (As) is a non-metal. It is easier for As to gain an electron to form  $\text{As}^-$  than for K to form  $\text{K}^+$ .
- (c) A; Element "A" (K) has the larger atomic radius. In general, size decreases going across a period.
- (d) B; Element "B" (As) has the greatest electron affinity. Non-metals have a greater tendency to add electrons compared with metals.

## Ch.10:

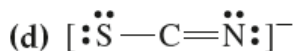
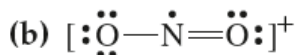
6. Which of the following have Lewis structures that *do not* obey the octet rule:  $\text{NF}_3$ ,  $\text{AlCl}_3$ ,  $\text{SiF}_6^{2-}$ ,  $\text{SO}_3$ ,  $\text{PH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{ClO}_2$ ?

**Ans:**

**(M)**  $\text{AlCl}_3$ ,  $\text{SiF}_6^{2-}$ ,  $\text{SO}_3$ ,  $\text{PO}_4^{3-}$ , and  $\text{ClO}_2$  do not follow the octet rule. For simplicity, where possible, the 3 lone pairs on halogens are not shown in the structures below.



12. Indicate what is wrong with each of the following Lewis structures. Replace each one with a more acceptable structure.



**Ans:**

(M)

(a)  $\text{Mg} - \ddot{\text{O}} :$  is incorrectly written as a covalent structure. One expects an ionic Lewis structure, namely  $[\text{Mg}]^{2+} [ : \ddot{\text{O}} : ]^{2-}$

(b)  $[: \ddot{\text{O}} - \dot{\text{N}} = \ddot{\text{O}} :]^+$  has too many valence electrons—8.5 electron pairs or 17 valence electrons—it should have  $(2 \times 6) + 5 - 1 = 16$  valence electrons or 8 electron pairs. A plausible Lewis structure is  $[\ddot{\text{O}} = \text{N} = \ddot{\text{O}}]^{2+}$ , which has 1+ formal charge on N and 0 formal charge of zero on each oxygen.

(c)  $[\ddot{\text{Cl}} :]^+ [ : \ddot{\text{O}} : ]^{2-} [ \ddot{\text{Cl}} : ]^+$  is written as an ionic structure, even though we expect a covalent structure between nonmetallic atoms. A more plausible structure is  $:\ddot{\text{Cl}} - \ddot{\text{O}} - \ddot{\text{Cl}}:$

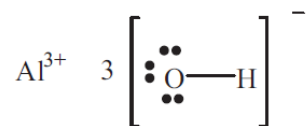
(d) In the structure  $[: \ddot{\text{S}} - \text{C} = \ddot{\text{N}} :]^-$  neither S nor C possesses an octet of electrons. In addition, there are only 7 pairs of valence electrons in this structure or 14 valence electrons. There should be  $6 + 4 + 5 + 1 = 16$  valence electrons, or 8 electron pairs. Two structures are possible.  $\ddot{\text{S}} = \text{C} = \ddot{\text{N}}$  has a formal charge of 1- on N and is preferred over  $:\ddot{\text{S}} - \text{C} \equiv \text{N}:$ , with its formal charge of 1- on S, which is less electronegative than N.

16. Each of the following ionic compounds consists of a combination of monatomic and polyatomic ions. Represent these compounds with Lewis structures.  
 (a)  $\text{Al}(\text{OH})_3$ ; (b)  $\text{Ca}(\text{CN})_2$ ; (c)  $\text{NH}_4\text{F}$ ; (d)  $\text{KClO}_3$ ;  
 (e)  $\text{Ba}_3(\text{PO}_4)_2$ .

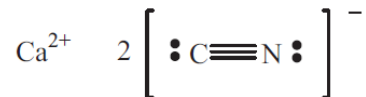
Ans:

(M)

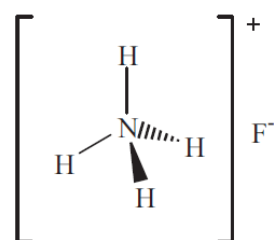
(a)



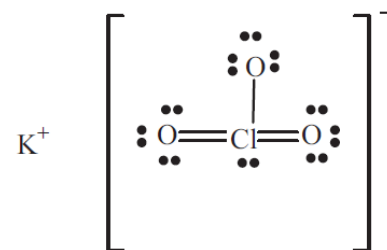
(b)



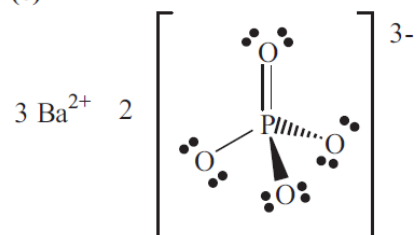
(c)



(d)



(e)



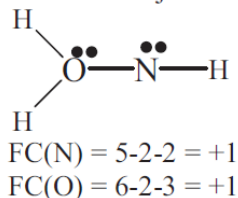
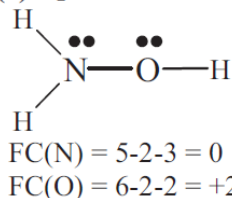
22. Assign formal charges to the atoms in the following species, and then select the more likely skeletal structure.

- (a)  $\text{H}_2\text{NOH}$  or  $\text{H}_2\text{ONH}$   
 (b)  $\text{SCS}$  or  $\text{CSS}$   
 (c)  $\text{NFO}$  or  $\text{FNO}$   
 (d)  $\text{SOCl}_2$  or  $\text{OSCl}_2$  or  $\text{OCl}_2\text{S}$   
 (e)  $\text{F}_3\text{SN}$  and  $\text{F}_3\text{NS}$

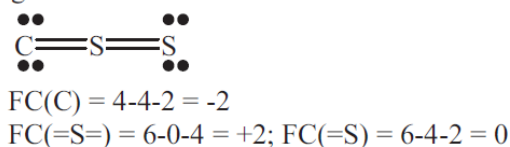
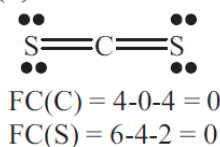
Ans:

(M)

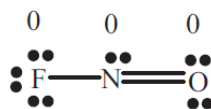
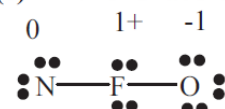
(a)  $\text{H}_2\text{NOH}$  is favored because same charges don't reside adjacent to each other.



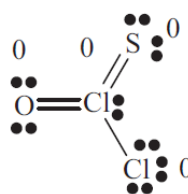
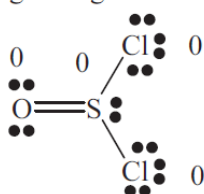
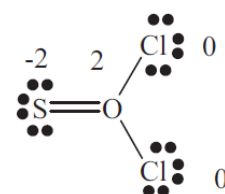
(b)  $\text{S}=\text{C}=\text{S}$  is favored, because FC on everything is zero.



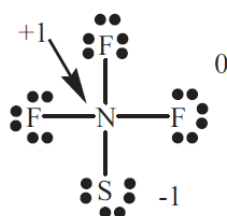
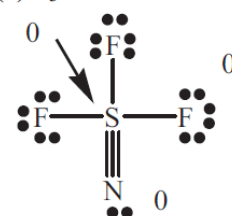
(c)  $\text{F}-\text{N}=\text{O}$  is favored.



(d)  $\text{OSCl}_2$  is favored. Even though the formal charges of all elements on both  $\text{OSCl}_2$  and  $\text{OCl}_2\text{S}$  are zero,  $\text{OSCl}_2$  represents a much more realistic structure because the O and Cl atoms are in their normal bonding configuration.



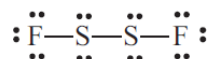
(e)  $\text{F}_3\text{SN}$  is favored.



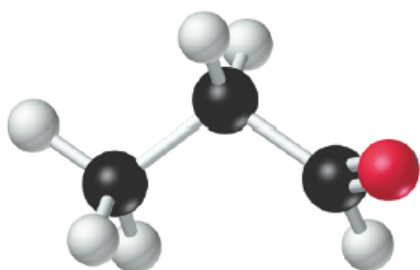
26. Two molecules that have the same formulas but different structures are said to be isomers. (In isomers, the same atoms are present but linked together in different ways.) Draw acceptable Lewis structures for *two* isomers of  $S_2F_2$ .

**Ans:**

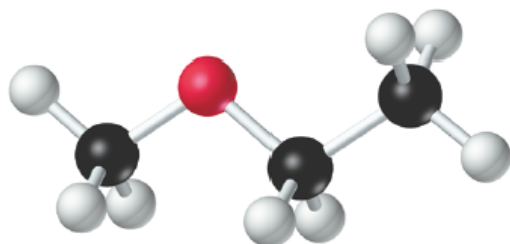
(E) The total number of valence electrons is  $(2 \times 7) + (2 \times 6) = 26$  valence electrons, or 13 pairs of valence electrons. It is unlikely to have F as a central atom; that would require an expanded octet on F. The most plausible structure is:



32. Write Lewis structures for the molecules represented by the following molecular models.

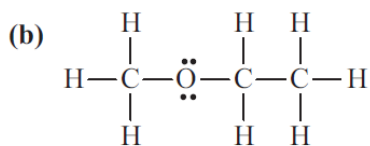
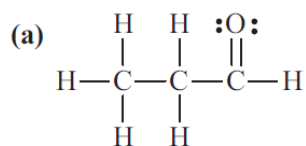


(a)



(b)

**Ans:**



38. Which of the following molecules would you expect to have a resultant dipole moment ( $\mu$ ); (a)  $F_2$ , (b)  $NO_2$ , (c)  $BF_3$ , (d)  $HBr$ , (e)  $H_2CCl_2$ , (f)  $SiF_4$ , (g)  $OCS$ ? Explain.

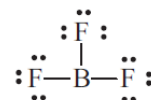
Ans:

(M)

(a)  $F_2$  cannot possess a dipole moment, since both of the atoms in the diatomic molecule are the same. This means that there is no electronegativity difference between atoms, and hence no polarity in the  $F-F$  bond.

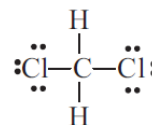
(b)  $\ddot{O}=\ddot{N}-\ddot{O}:$  Each nitrogen-to-oxygen bond in this molecule is polarized toward oxygen, the more electronegative element. The molecule is of the  $AX_2E$  category and hence is bent. Therefore the two bond dipoles do not cancel, and the molecule is polar.

(c) Although each  $B-F$  bond is polarized toward  $F$  in this trigonal planar  $AX_3$  molecule, these bond dipoles cancel. The molecule is nonpolar.

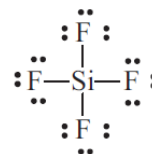


(d)  $H-\ddot{Br}:$  The  $H-Br$  bond is polar toward  $Br$ , and this molecule is polar as well.

(e) The  $H-C$  bonds are not polar, but the  $C-Cl$  bonds are, toward  $Cl$ . The molecular shape is tetrahedral ( $AX_4$ ) and thus these two  $C-Cl$  dipoles do not cancel each other; the molecule is polar.

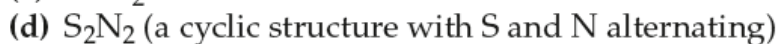
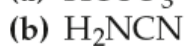
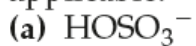


(f) Although each  $Si-F$  bond is polarized toward  $F$ , in this tetrahedral  $AX_4$  molecule these bond dipoles oppose and cancel each other. As a result, the molecule is nonpolar.



(g)  $\ddot{O}=\ddot{C}=\ddot{S}$  In this linear molecule, the two bonds from carbon both are polarized away from carbon. But the  $C=O$  bond is more polar than the  $C=S$  bond, and hence the molecule is polar.

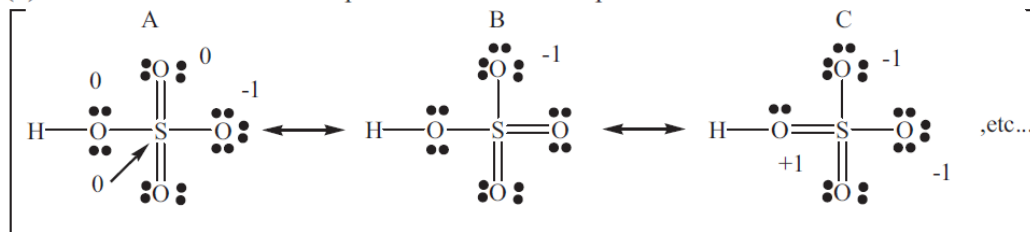
52. Draw Lewis structures for the following species, indicating formal charges and resonance where applicable:



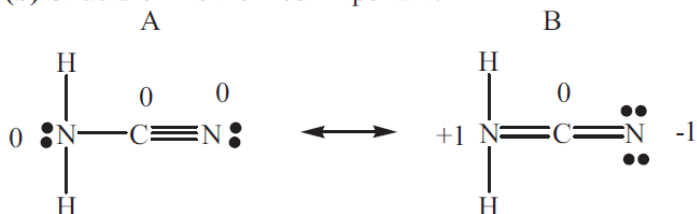
Ans:

(M)

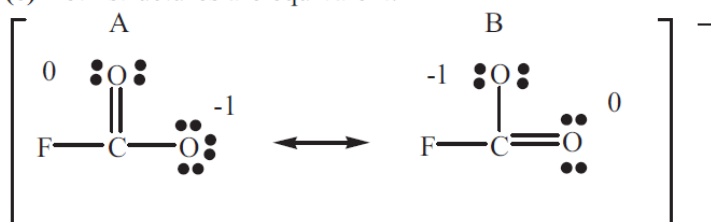
(a) Structures A and B are equivalent and most important.



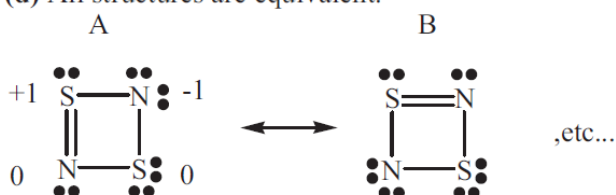
(b) Structure A is the most important.



(c) Both structures are equivalent.



(d) All structures are equivalent.







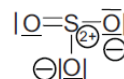
82. Which of the following molecules would you expect to be polar: (a) HCN; (b) SO<sub>3</sub>; (c) CS<sub>2</sub>; (d) OCS; (e) SOCl<sub>2</sub>; (f) SiF<sub>4</sub>; (g) POF<sub>3</sub>? Give reasons for your conclusions.

Ans:

(D)

(a) HCN is a linear molecule, which can be derived from its Lewis structure  $\text{H}-\text{C}\equiv\text{N}|$ . The  $\text{C}\equiv\text{N}$  bond is strongly polar toward N, while the  $\text{H}-\text{C}$  bond is generally considered to be nonpolar. Thus, the molecule has a dipole moment, pointed from C toward N.

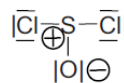
(b) SO<sub>3</sub> is a trigonal planar molecule, which can be derived from its Lewis structure. Each sulfur-oxygen bond is polar from S to O, but the three bonds are equally polar and are pointed in symmetrical opposition so that they cancel. The SO<sub>3</sub> molecule has a dipole moment of zero.



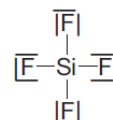
(c) CS<sub>2</sub> is a linear molecule, which can be derived from its Lewis structure  $\text{S}=\text{C}=\text{S}$ . Each carbon-sulfur bond is polar from C to S, but the two bonds are equally polar and are pointed in opposition to each other so that they cancel. The CS<sub>2</sub> molecule has a dipole moment of zero.

(d) OCS also is a linear molecule. Its Lewis structure is  $\text{O}=\text{C}=\text{S}$ . But the carbon-oxygen bond is more polar than the carbon-sulfur bond. Although both bond dipoles point from the central atom to the bonded atom, these two bond dipoles are unequal in strength. Thus, the molecule is polar in the direction from C to O.

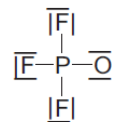
(e) SOCl<sub>2</sub> is a trigonal pyramidal molecule. Its Lewis structure is shown to the right. The lone pair is at one corner of the tetrahedron. Each bond in the molecule is polar, with the dipole moments pointing away from the central atom. The sulfur-chlorine bond is less polar than the sulfur-oxygen bond, and this makes the molecule polar. The dipole moment of the molecule points from the sulfur atom to the base of the trigonal pyramid, not toward the center of the base but slightly toward the O apex of that base.



(f) SiF<sub>4</sub> is a tetrahedral molecule, with the following Lewis structure. Each Si—F bond is polar, with its negative end away from the central atom toward F in each case. These four Si—F bond dipoles oppose each other and thus cancel. SiF<sub>4</sub>, as a result, has no dipole moment.



(g) POF<sub>3</sub> is a tetrahedral molecule. A valid Lewis structure is shown to the right. All four bonds are polar, with their dipole moments pointing away from the central atom. The P—F bond polarity is greater than that of the P—O bond. Thus, POF<sub>3</sub> is a polar molecule with its dipole moment pointing away from the P toward the center of the triangle formed by the three F atoms.



88. In which of the following molecules would you expect the oxygen-to-oxygen bond to be the *shortest*: (a)  $\text{H}_2\text{O}_2$ , (b)  $\text{O}_2$ , (c)  $\text{O}_3$ ? Explain.

**Ans:**

88. (M) First we need to draw the Lewis structure of each of the compounds cited, so that we can determine the order, and hence the relative length, of each O-to-O bond.

- (a) In  $\text{H}_2\text{O}_2$ , there are  $(2 \times 1) + (2 \times 6) = 14$  valence electrons or 7 electron pairs. A plausible Lewis structure is  $\text{H}-\overline{\text{O}}-\overline{\text{O}}-\text{H}$ .
- (b) In  $\text{O}_2$ , the total number of valence electrons is  $(2 \times 6 =) 12$  valence electrons, or 6 electron pairs. A plausible Lewis structure is  $\overline{\text{O}}=\overline{\text{O}}$ .
- (c) In  $\text{O}_3$ , the total number of valence electrons is  $(3 \times 6) = 18$  valence electrons, or 9 electron pairs. A plausible Lewis structure is  $\overline{\text{O}}=\overline{\text{O}}-\overline{\text{O}} \longleftrightarrow |\overline{\text{O}}-\overline{\text{O}}=\overline{\text{O}}$  (two most stable resonance contributors).

Thus,  $\text{O}_2$  should have the shortest O-to-O bond, because the O atoms are joined via a double bond. The single O—O bond in  $\text{H}_2\text{O}_2$  should be longest.

94. One of the chemical reactions that occurs in the formation of photochemical smog is  $\text{O}_3 + \text{NO} \longrightarrow \text{NO}_2 + \text{O}_2$ . Estimate the enthalpy change of this reaction by using appropriate Lewis structures and data from Table 10.3.

**Ans:**

(M) The reaction in terms of Lewis structures is  $\overline{\text{O}}=\overline{\text{O}}-\overline{\text{O}} + \overline{\text{O}}=\overline{\text{N}}\cdot \longrightarrow \overline{\text{O}}=\overline{\text{N}}-\overline{\text{O}}\cdot + \overline{\text{O}}=\overline{\text{O}}$

The net result is the breakage of an O—O bond (142 kJ/mol) and the formation of a N—O bond (222 kJ/mol).  $\Delta H = 142 \text{ kJ/mol} - 222 \text{ kJ/mol} = -80. \text{ kJ/mol}$