CHAPTER 9
IONIC AND COVALENT BONDING

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9. Ionic and Covalent Bonding

- Chemical bond: a strong attractive force that exists between certain atoms in a substance

  Ionic bonds: *e.g.*, NaCl

  Covalent bonds: *e.g.*, Cl_2

  Metallic bonding: *e.g.*, Na

9.1 Describing Ionic Bonds

- Ionic bond: a chemical bond formed by the electrostatic attraction between positive and negative ions

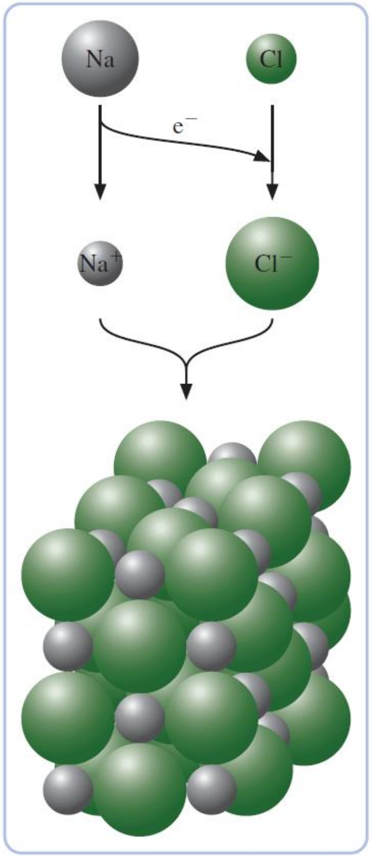
Cation (positive ion): loses electron

Anion (negative ion): gains electron

9.1 Describing Ionic Bonds

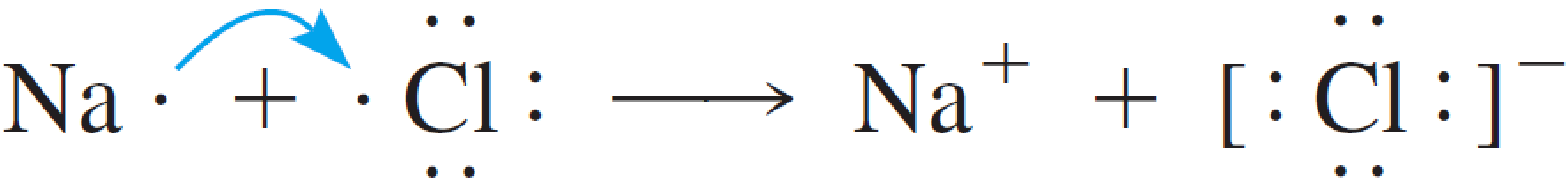
- Why ionic bonding occurs

$$\mathrm{Na([Ne]3}s^{1}) + \mathrm{Cl([Ne]3}s^{2}3p^{5}) \longrightarrow \mathrm{Na^{+}([Ne])} + \mathrm{Cl^{-}([Ne]3}s^{2}3p^{6})$$



9.1 Describing Ionic Bonds

- Lewis Electron-Dot Symbols



Period	1A ns^1	2A ns^2	3A ns^2np^1	4A ns^2np^2
Second	$\mathrm{Li}\cdot$	$\cdot\mathrm{Be}\cdot$	$\cdot\dot{\mathrm{B}}\cdot$	$\cdot\underset{\cdot}{\dot{\mathrm{C}}}\cdot$
Third	$\mathrm{Na}\cdot$	$\cdot\mathrm{Mg}\cdot$	$\cdot\dot{\mathrm{Al}}\cdot$	$\cdot\underset{\cdot}{\dot{\mathrm{Si}}}\cdot$

9.1 Describing Ionic Bonds

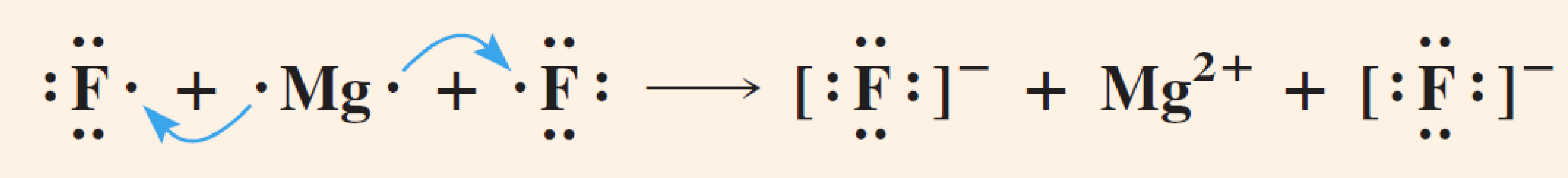
- Lewis Electron-Dot Symbols

$$\mathrm{Na}\cdot \; + \; \cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow \mathrm{Na}^{+} \; + \; [:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:]^{-}$$

5A ns^2np^3	**6A** ns^2np^4	**7A** ns^2np^5	**8A** ns^2np^6
$:\dot{\underset{\cdot}{\mathrm{N}}}\cdot$	$:\dot{\underset{\cdot\cdot}{\mathrm{O}}}\cdot$	$:\ddot{\underset{\cdot\cdot}{\mathrm{F}}}\cdot$	$:\ddot{\underset{\cdot\cdot}{\mathrm{Ne}}}:$
$:\dot{\underset{\cdot}{\mathrm{P}}}\cdot$	$:\dot{\underset{\cdot\cdot}{\mathrm{S}}}\cdot$	$:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot$	$:\ddot{\underset{\cdot\cdot}{\mathrm{Ar}}}:$

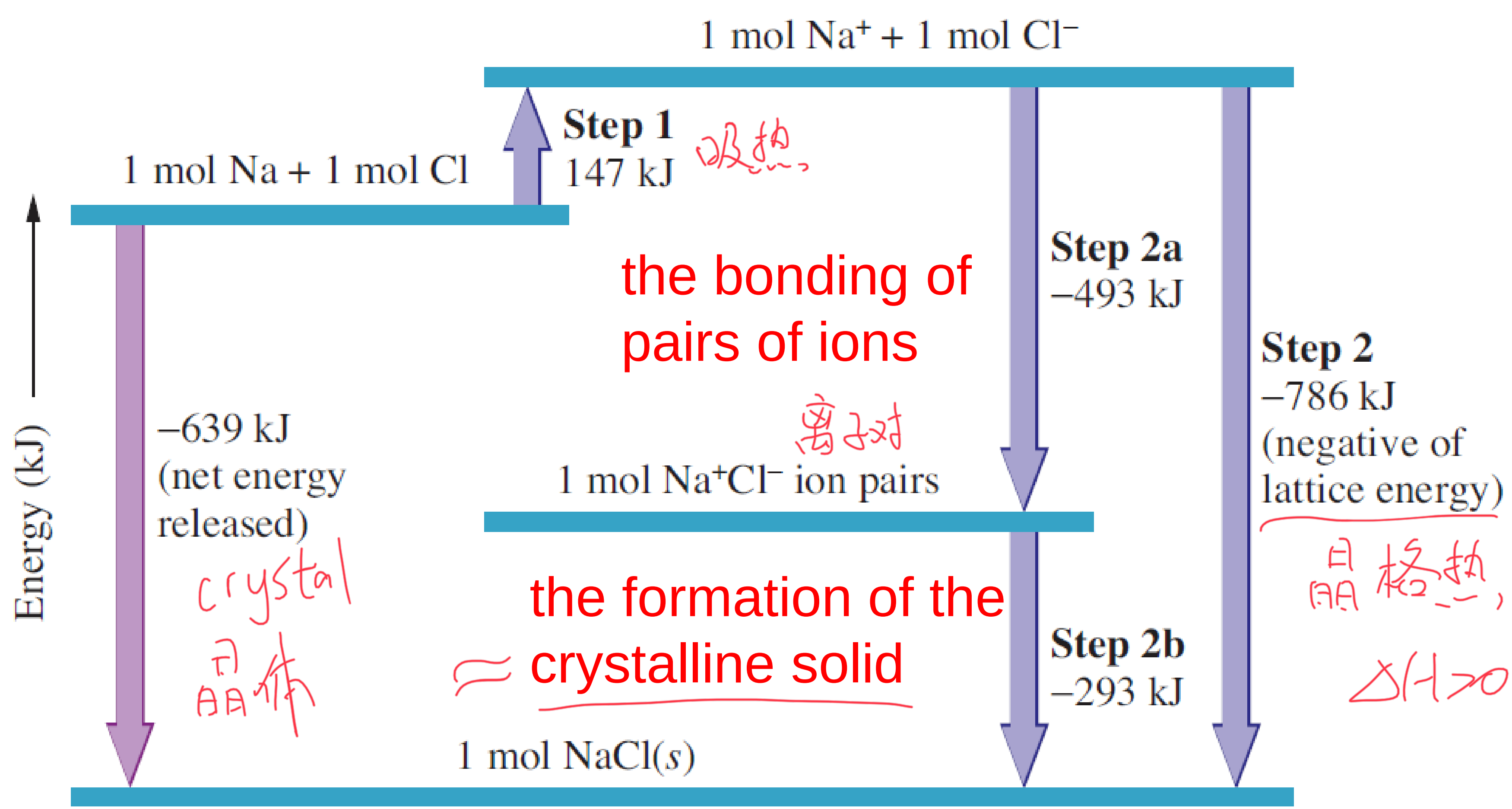
P331 Example 9.1

Use Lewis electron-dot symbols to represent the transfer of electrons from magnesium to fluorine atoms to form ions with noble-gas configurations.



9.1 Describing Ionic Bonds

- Energy Involved in Ionic Bonding



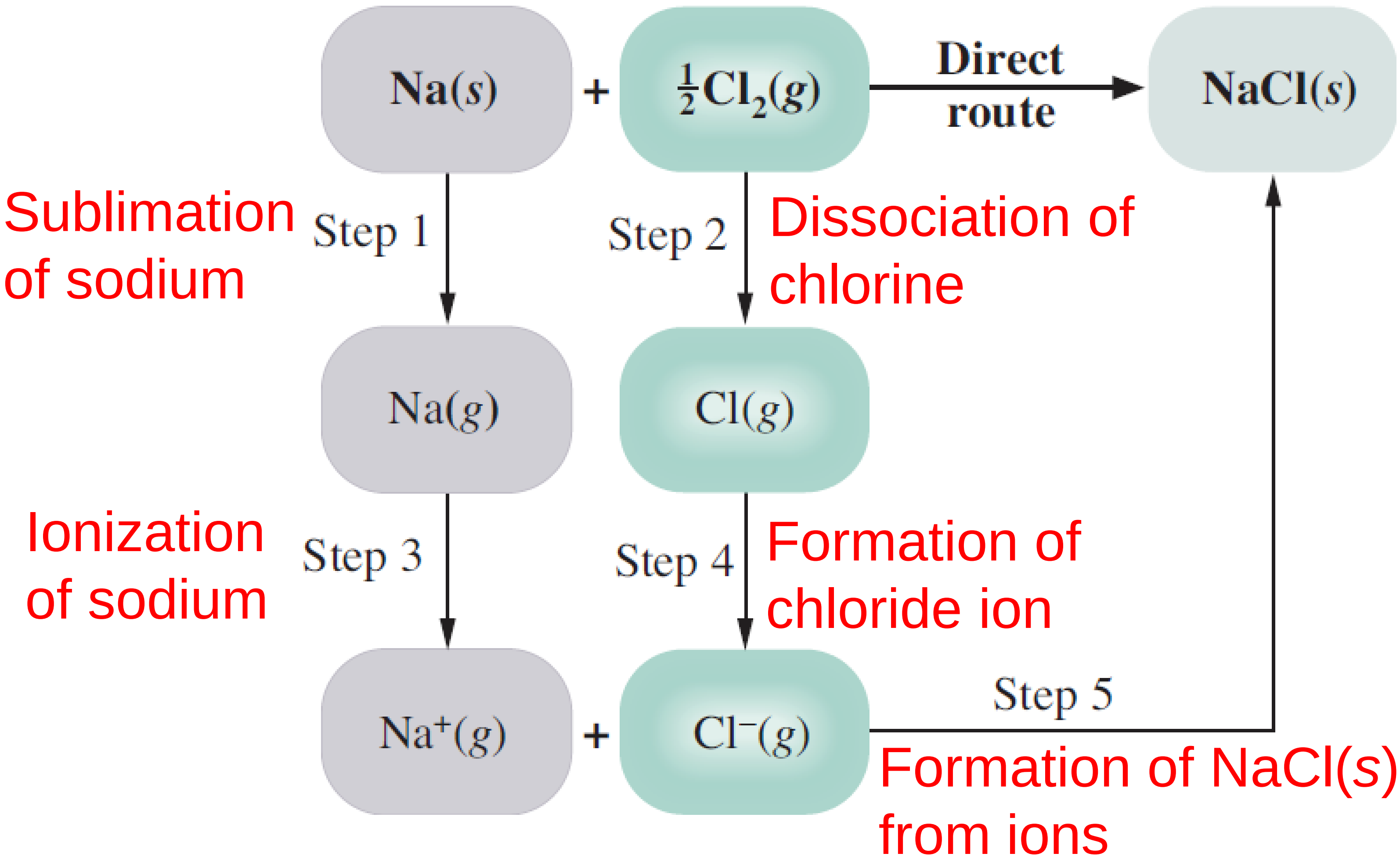
9.1 Describing Ionic Bonds

- Lattice energy: the change in energy that occurs when an ionic solid is separated into isolated ions in the gas phase

$$NaCl(s) \longrightarrow Na^{+}(g) + Cl^{-}(g)$$

9.1 Describing Ionic Bonds

- Lattice Energies from the Born–Haber Cycle



9.1 Describing Ionic Bonds

- Lattice Energies from the Born–Haber Cycle

Following Hess's law

$$
\begin{array}{llll}
Na(s) & \longrightarrow \cancel{Na(g)} & \Delta H_1 = & 108\text{ kJ} \\
\frac{1}{2}Cl_2(g) & \longrightarrow \cancel{Cl(g)} & \Delta H_2 = & 120\text{ kJ} \\
\cancel{Na(g)} & \longrightarrow \cancel{Na^+(g)} + \cancel{e^-(g)} & \Delta H_3 = & 496\text{ kJ} \\
\cancel{Cl(g)} + \cancel{e^-(g)} & \longrightarrow \cancel{Cl^-(g)} & \Delta H_4 = & -349\text{ kJ} \\
\cancel{Na^+(g)} + \cancel{Cl^-(g)} & \longrightarrow NaCl(s) & \Delta H_5 = & -\ U \\
\hline
Na(s) + \frac{1}{2}Cl_2(g) & \longrightarrow NaCl(s) & \Delta H_f^\circ = & 375\text{ kJ} - U
\end{array}
$$

$$375\text{ kJ} - U = -411\text{ kJ} \qquad U = (375 + 411)\text{ kJ} = 786\text{ kJ}$$

9.1 Describing Ionic Bonds

- Properties of Ionic Substances:

  High Melting Points

  NaCl, 800 °C

  MgO, 2800 °C

- depends on the strength of the interaction between the atoms or ions

9.2 Electron Configurations of Ions

- Ions of the Main-Group Elements
- Most of the cations are obtained by removing all the valence electrons from the atoms of metallic elements

Table 9.2 Ionization Energies of Na, Mg, and Al (in kJ/mol)*

Element	Successive Ionization Energies			
	First	Second	Third	Fourth
Na	496	4,562	6,910	9,543
Mg	738	1,451	7,733	10,542
Al	578	1,817	2,745	11,577

*Energies for the ionization of valence electrons lie to the left of the colored line.

9.2 Electron Configurations of Ions

- Ions of the Main-Group Elements

1. Cations of Groups IA to IIIA having noble-gas or pseudo-noble-gas configurations. The ion charges equal the group numbers.

9.2 Electron Configurations of Ions

- Ions of the Main-Group Elements

2. Cations of Groups IIIA to VA having ns^2 electron configurations. The ion charges equal the group numbers minus two. Examples are Tl^+, Sn^{2+}, Pb^{2+}, and Bi^{3+}.

$$\mathrm{Tl}([\mathrm{Xe}]4f^{14}5d^{10}6s^2 6p^1) \longrightarrow \mathrm{Tl}^+([\mathrm{Xe}]4f^{14}5d^{10}6s^2) + \mathrm{e}^-$$

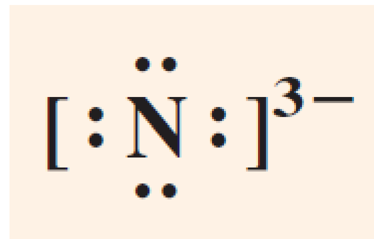
9.2 Electron Configurations of Ions

- Ions of the Main-Group Elements

3. Anions of Groups VA to VIIA having noble-gas or pseudo-noble-gas configurations. The ion charges equal the group numbers minus eight.

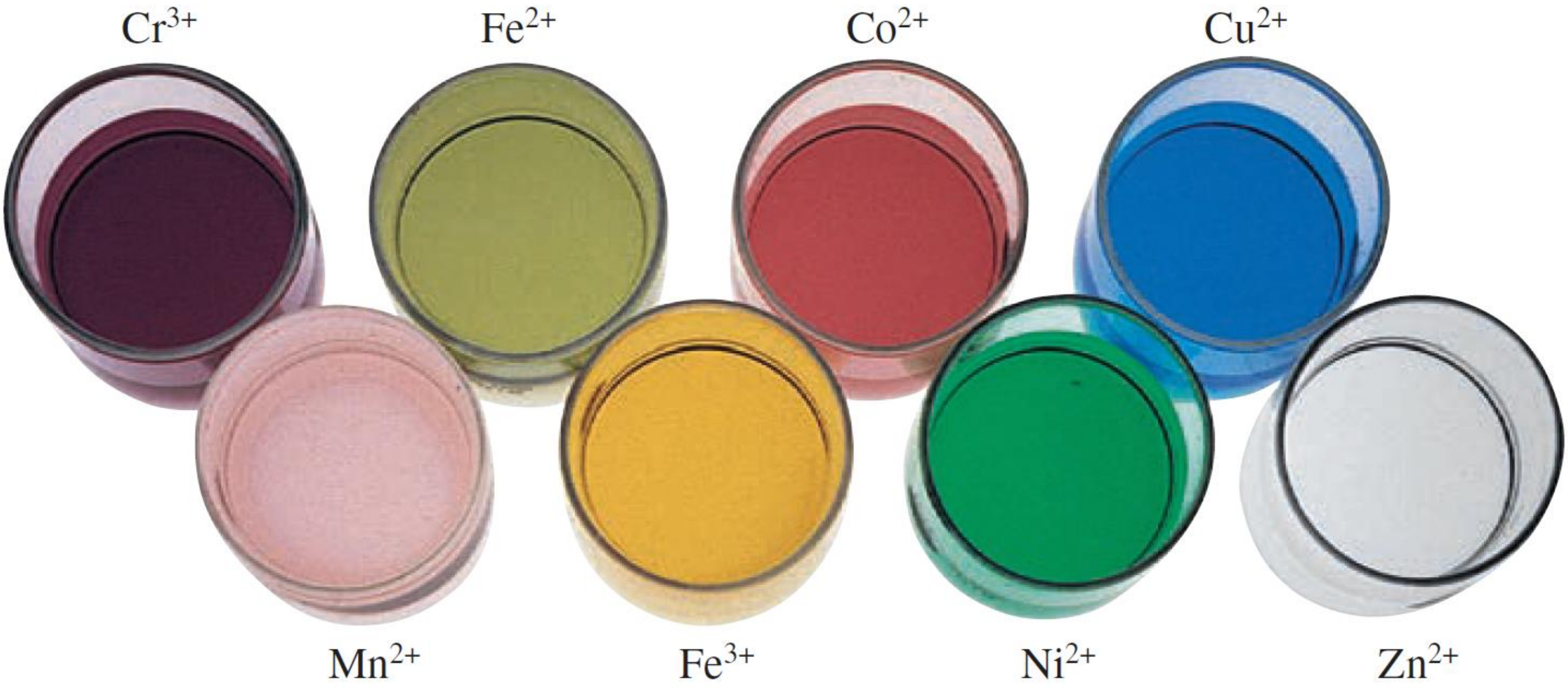
P337 Example 9.2

Write the electron configuration and the Lewis symbol for N_3^-.



9.2 Electron Configurations of Ions

- Transition-Metal Ions: involve *d* electrons



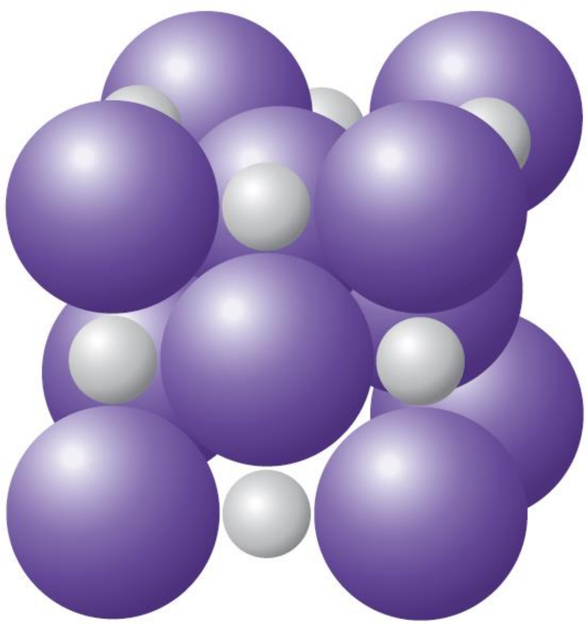
P338 Example 9.3

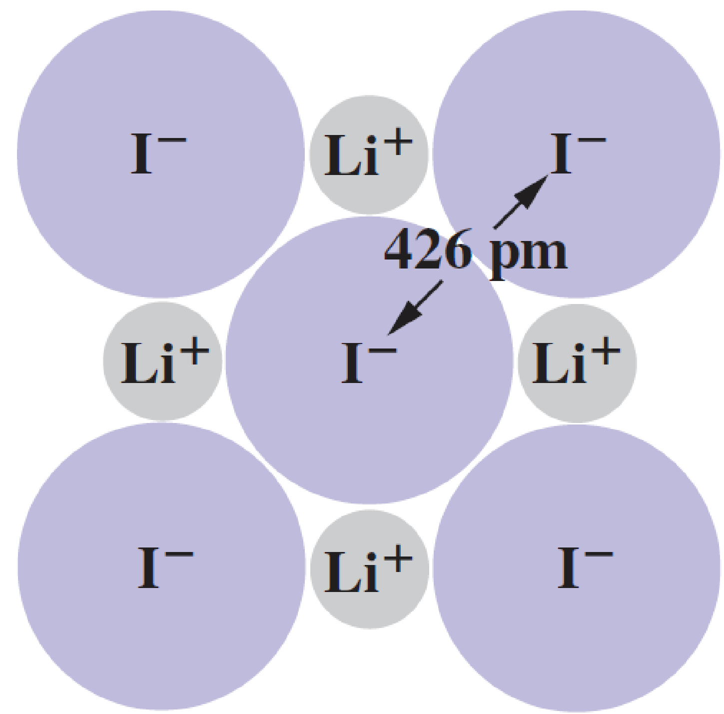
Write the electron configurations of Fe^{2+} and Fe^{3+}

$[Ar]3d^6$ $[Ar]3d^5$

9.3 Ionic Radii

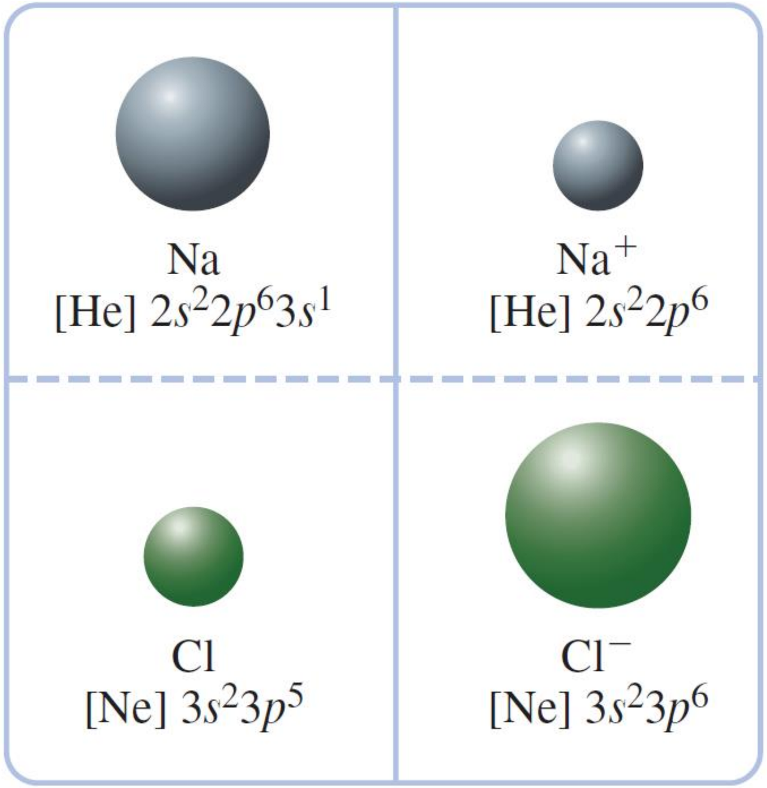
- Ionic radius: a measure of the size of the spherical region around the nucleus of an ion within which the electrons are most likely to be found





9.3 Ionic Radii

- a cation is smaller than the corresponding atom
- an anion is larger than the corresponding atom



9.3 Ionic Radii

Ionic radii increase down any column because of the addition of electron shells.

Table 9.3 Ionic Radii (in pm) of Some Main-Group Elements

Period	1A	2A	3A	6A	7A
2	Li^+	Be^{2+}		O^{2-}	F^-
	60	31		140	136
3	Na^+	Mg^{2+}	Al^{3+}	S^{2-}	Cl^-
	95	65	50	184	181
4	K^+	Ca^{2+}	Ga^{3+}	Se^{2-}	Br^-
	133	99	62	198	195
5	Rb^+	Sr^{2+}	In^{3+}	Te^{2-}	I^-
	148	113	81	221	216
6	Cs^+	Ba^{2+}	Tl^{3+}		
	169	135	95		

9.3 Ionic Radii

Cation	Na^+	Mg^{2+}	Al^{3+}
Radius (pm)	95	65	50

$1s^2 2s^2 2p^6$ isoelectronic

the ionic radius decreases with increasing atomic number

9.3 Ionic Radii

Anion	S^{2-}	Cl^-
Radius (pm)	184	181

the ionic radius decreases with atomic number

P341 Example 9.4

Arrange the following ions in order of decreasing ionic radius: F^-, Mg^{2+}, O^{2-}.

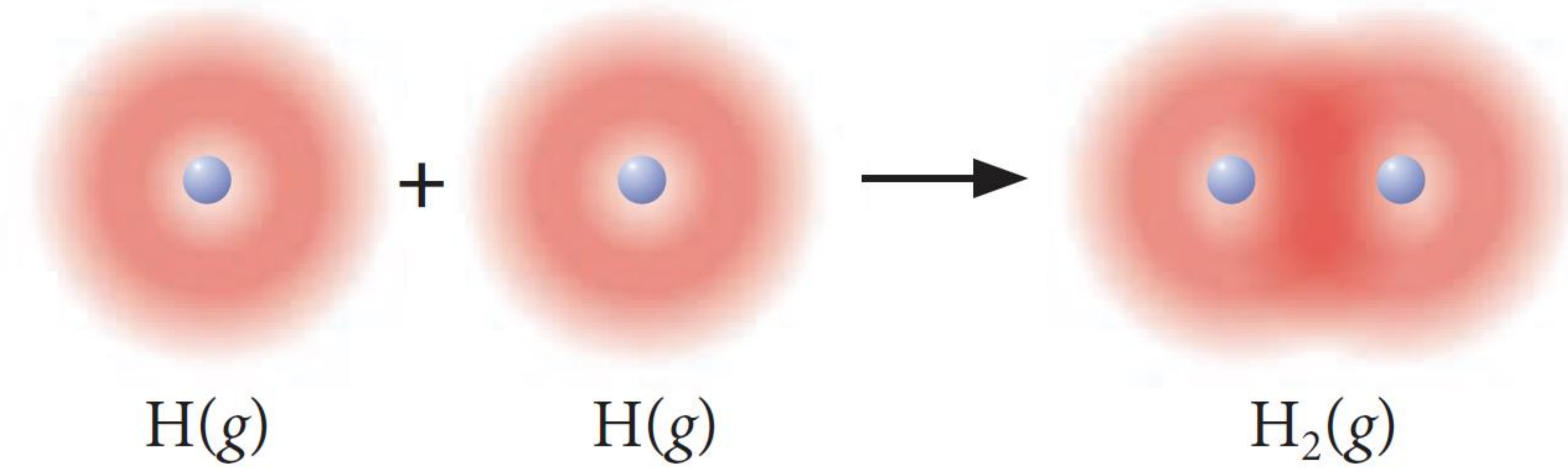
O^{2-}, F^-, Mg^{2+}

9.4 Describing Covalent Bonds

- covalent bond: a chemical bond formed by the sharing of a pair of electrons between atoms
- Molecule: a group of atoms, frequently nonmetal atoms, strongly linked by chemical bonds

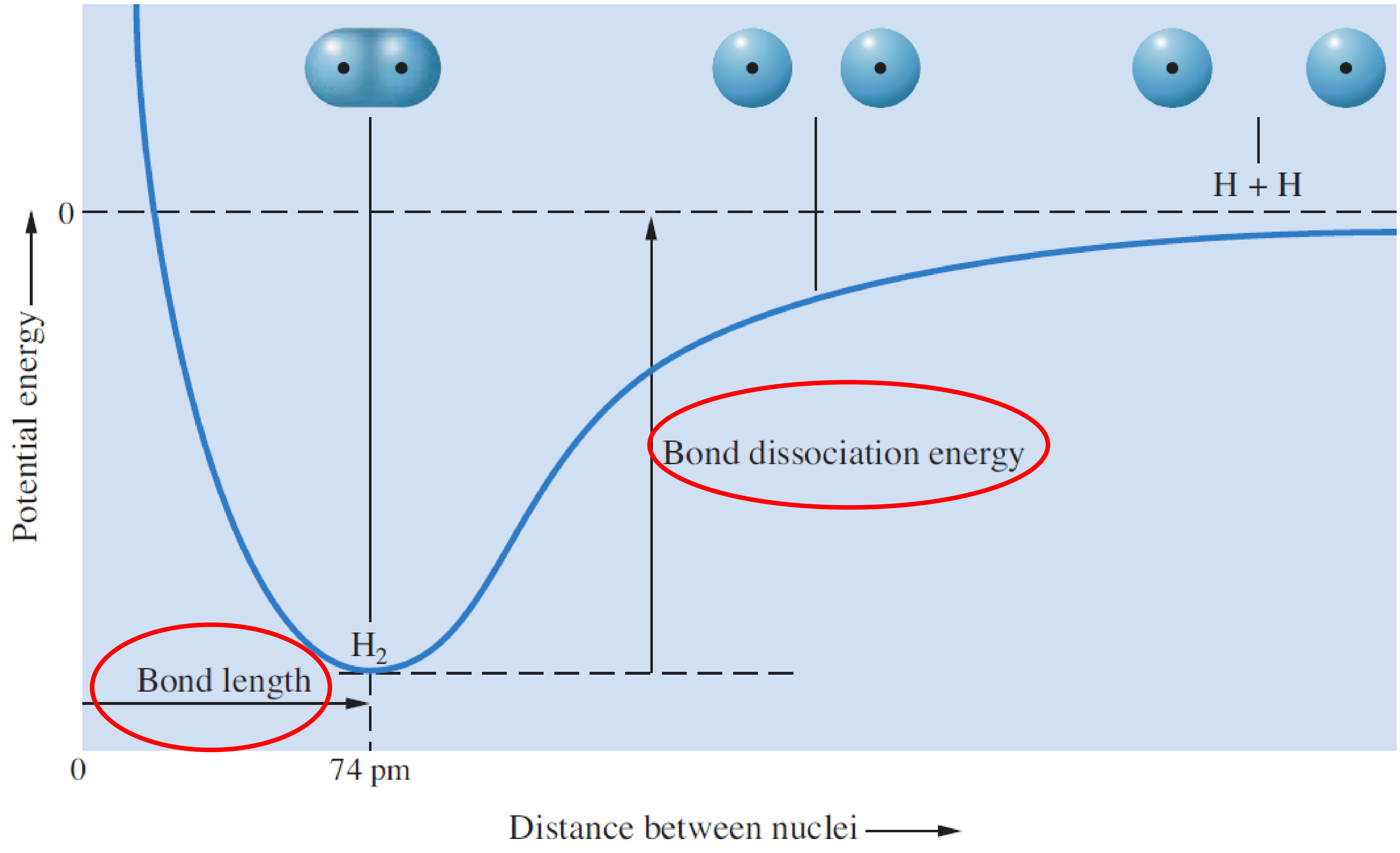
9.4 Describing Covalent Bonds

- the two electrons can be shared by the atoms



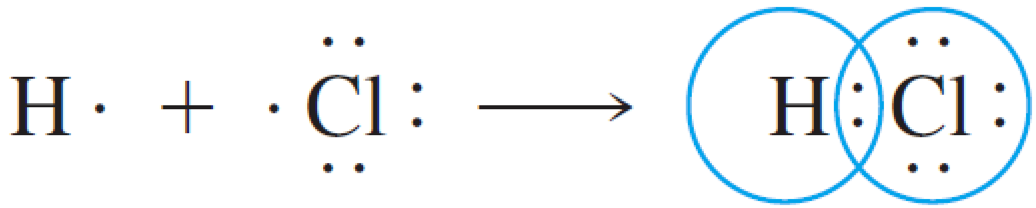
9.4 Describing Covalent Bonds

Potential-energy curve for H_2

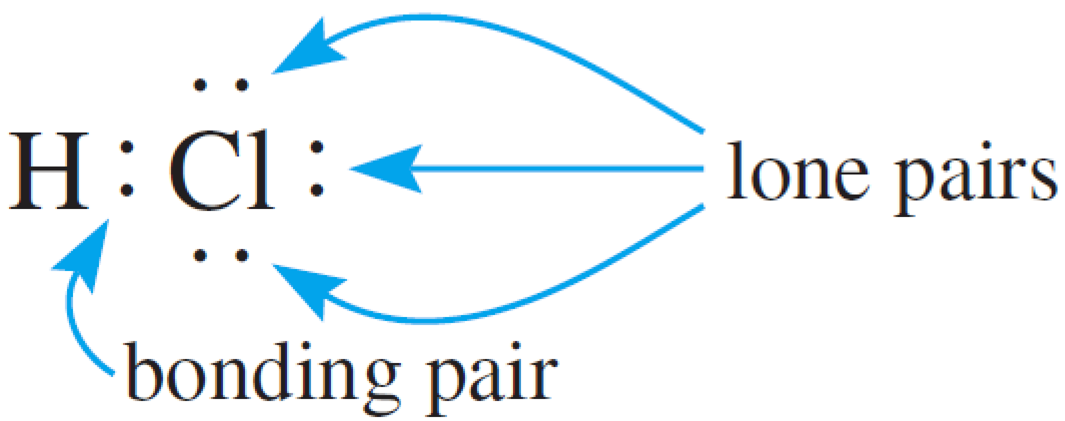


9.4 Describing Covalent Bonds

- Lewis Formulas



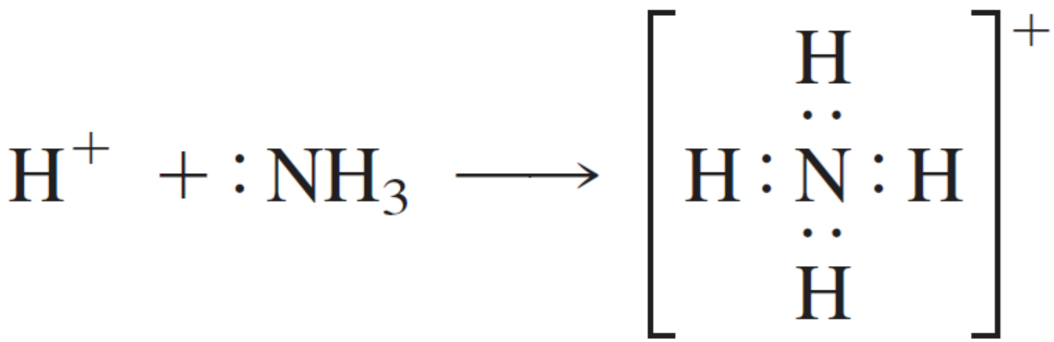
Lewis electron-dot formula



9.4 Describing Covalent Bonds

- Coordinate Covalent Bonds: a bond formed when both electrons of the bond are donated by one atom.

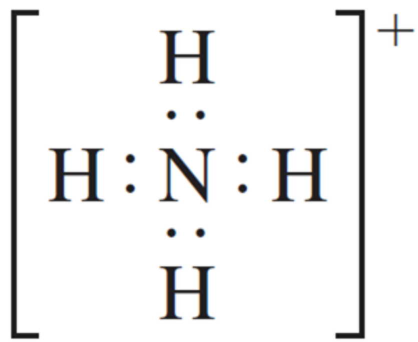
$$A + :B \longrightarrow A:B$$



- is not essentially different from other covalent bonds

9.4 Describing Covalent Bonds

- Octet Rule: the tendency of atoms in molecules to have eight electrons in their valence shells (two for hydrogen atoms)

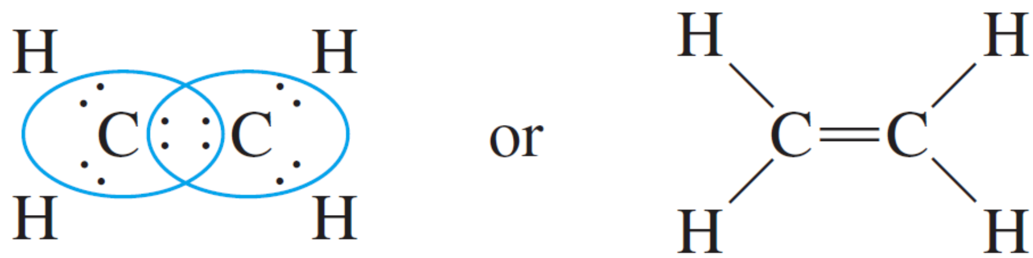


9.4 Describing Covalent Bonds

- Multiple Bonds

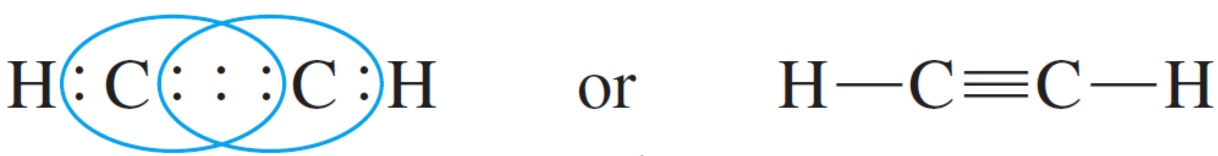
single bond

double bond



Ethylene

triple bond



Acetylene

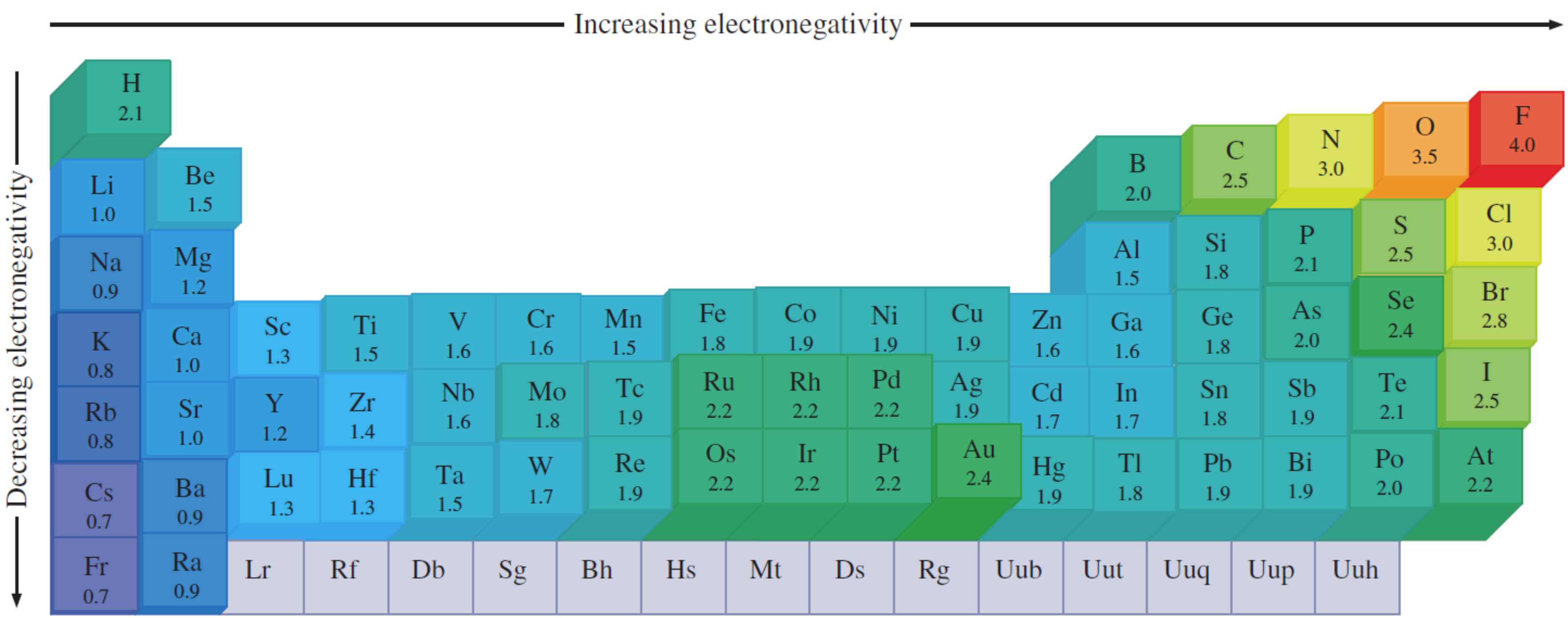
9.5 Polar Covalent Bonds; Electronegativity

- Polar covalent bond: a covalent bond in which the bonding electrons spend more time near one atom than the other
- Intermediate between a nonpolar covalent bond, and an ionic bond

Nonpolar covalent   Polar covalent   Ionic

9.5 Polar Covalent Bonds; Electronegativity

- Electronegativity: a measure of the ability of an atom in a molecule to draw bonding electrons to itself



9.5 Polar Covalent Bonds; Electronegativity

- Ionic bonds usually form between a metal atom and a nonmetal atom, because the electronegativity differences are largest between these elements

$$\overset{\delta+}{\mathrm{H}}\text{—}\overset{\delta-}{\mathrm{Cl}}$$

- Covalent bonds form primarily between two nonmetals because the electronegativity differences are small

P347 Example 9.5

Use electronegativity values (Figure 9.15) to arrange the following bonds in order of increasing polarity: P—H, H—O, C—Cl.

P—H, C—Cl, H—O,

5 1 4 7 1 6

4.2 5.5 6.6

9.6 Writing Lewis Electron-Dot Formulas

- skeleton structure: tells which atoms are bonded to one another

Central atom

- Lewis formula

Step 1: Calculate the total number of valence electrons for the molecule by summing the number of valence electrons (group number) for each atom.

主族数=价电子数

9.6 Writing Lewis Electron-Dot Formulas

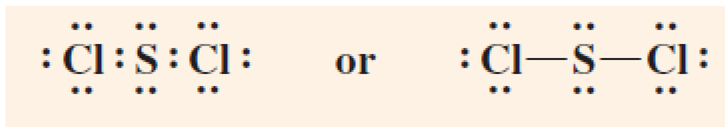
- **Step 2**: Write the skeleton structure of the molecule or ion H_2O

  $H:\ddot{\underset{..}{O}}:H$

- **Step 3**: Distribute electrons to the atoms surrounding the central atom (or atoms) to satisfy the octet rule for these surrounding atoms.
- **Step 4**: Distribute the remaining electrons as pairs to the central atom (or atoms)

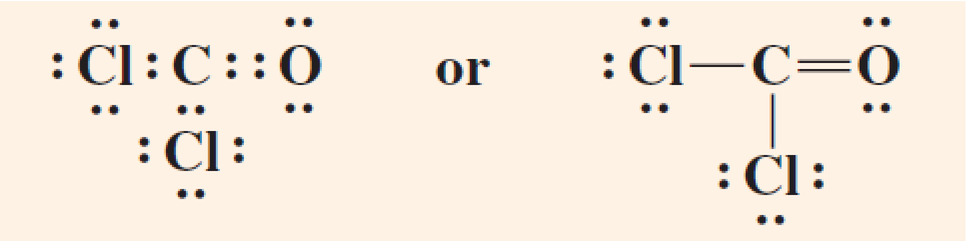
P348 Example 9.6

Sulfur dichloride, SCl_2, is a red, fuming liquid used in the manufacture of insecticides. Write the Lewis formula for the molecule.



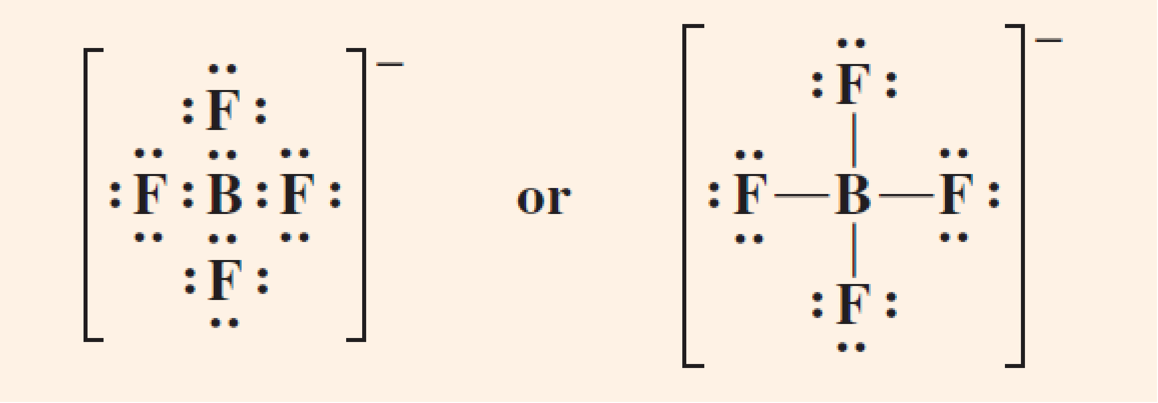
P348 Example 9.7

Carbonyl chloride, or phosgene, $COCl_2$, is a highly toxic gas used as a starting material for the preparation of polyurethane plastics. What is the electron-dot formula of $COCl_2$?



P348 Example 9.8

Obtain the electron-dot formula (Lewis formula) of the BF_4^- ion.



9.7 Delocalized Bonding: Resonance

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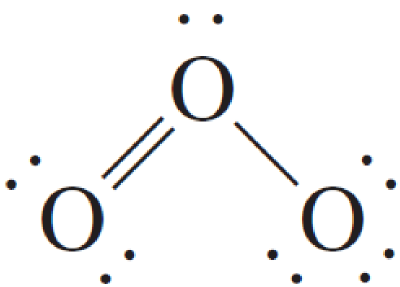
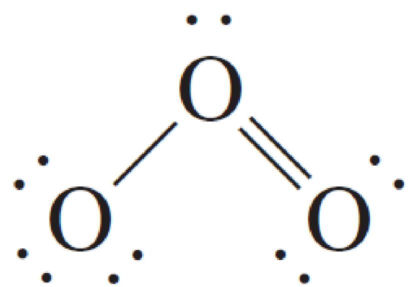
- Delocalized bonding: a type of bonding in which a bonding pair of electrons is spread over a number of atoms rather than localized between two

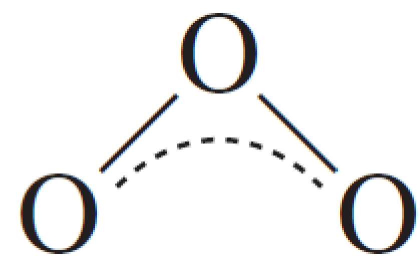


A

and

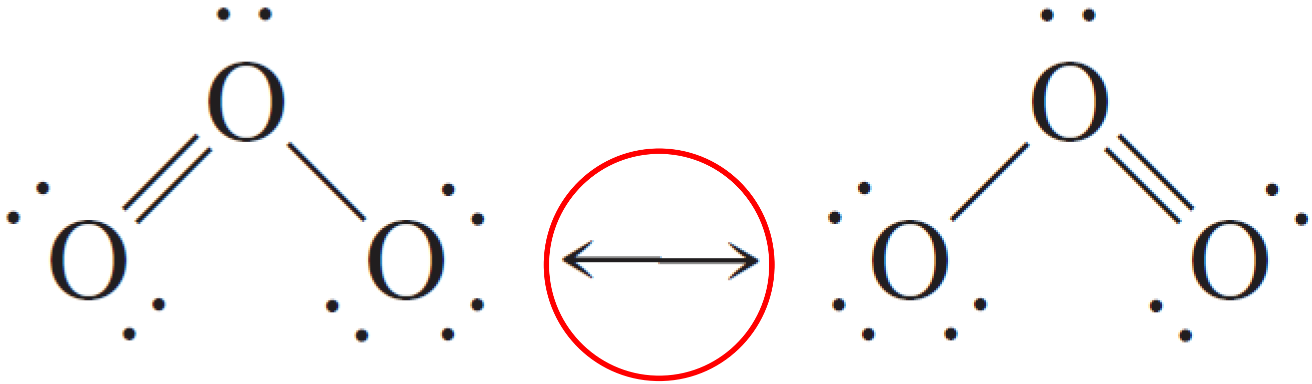


B



9.7 Delocalized Bonding: Resonance

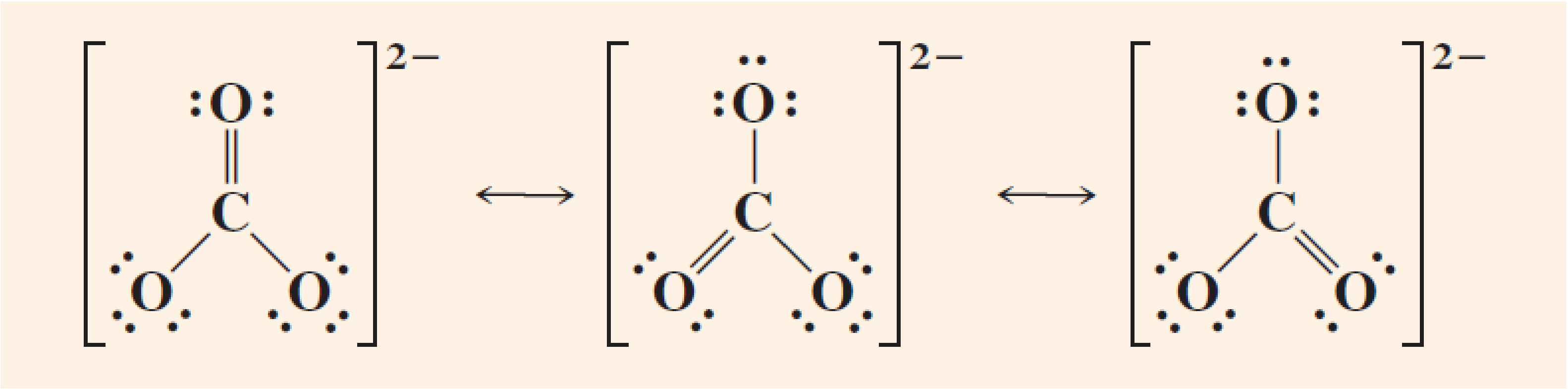
- Resonance formulas



A B

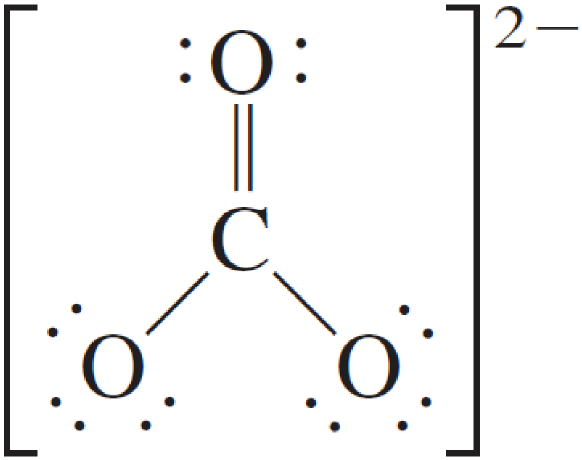
P351 Example 9.9

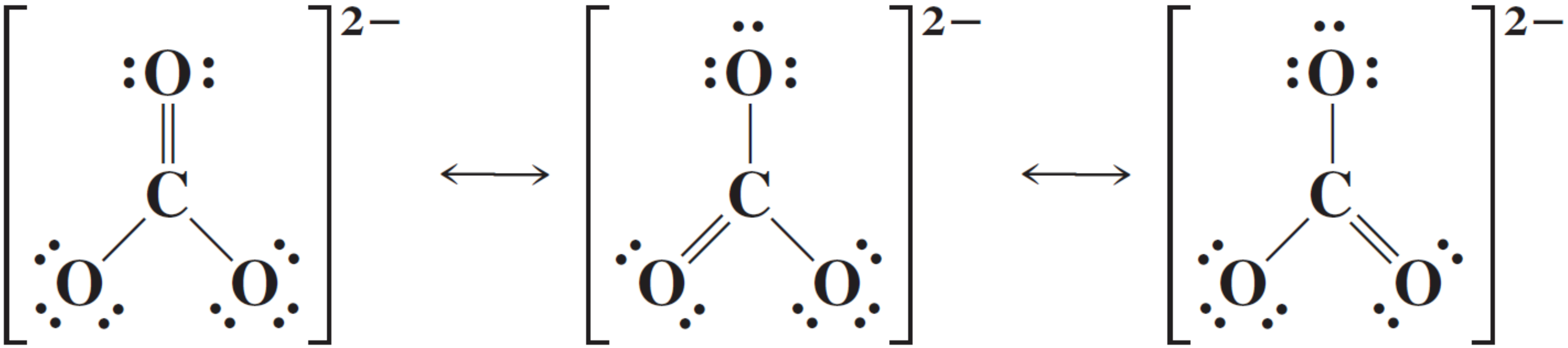
Describe the electron structure of the carbonate ion, CO_3^{2-}, in terms of electron-dot formulas



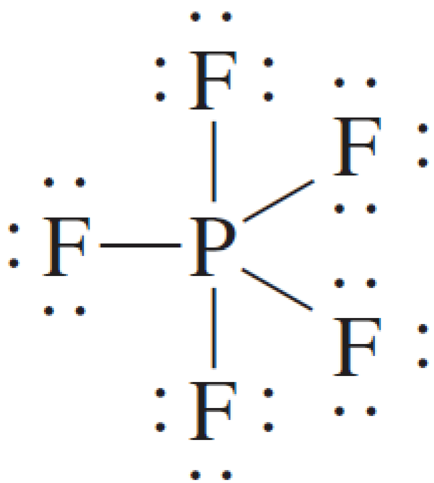
9.7 Delocalized Bonding: Resonance

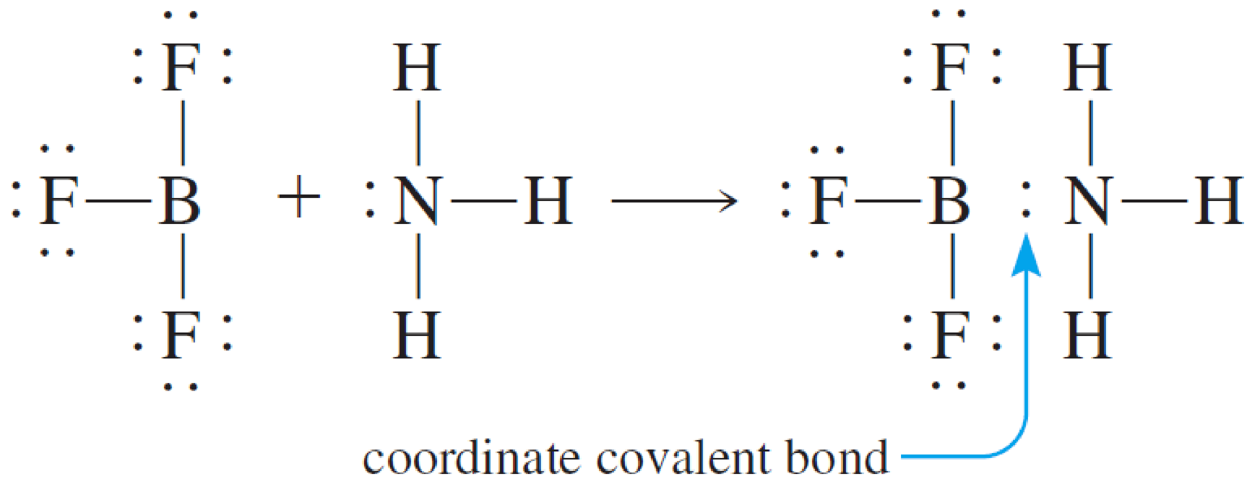
- Resonance formulas

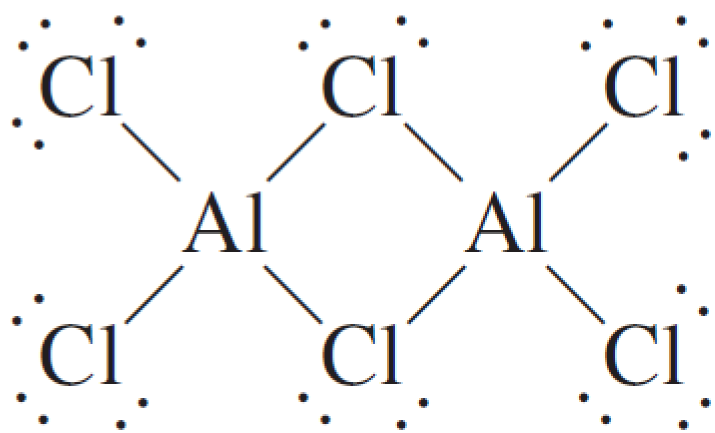




9.8 Exceptions to the Octet Rule







9.9 Formal Charge and Lewis Formulas

- formal charge: the hypothetical charge you obtain by assuming that bonding electrons are equally shared between bonded atoms and that the electrons of each lone pair belong completely to one atom.

9.9 Formal Charge and Lewis Formulas

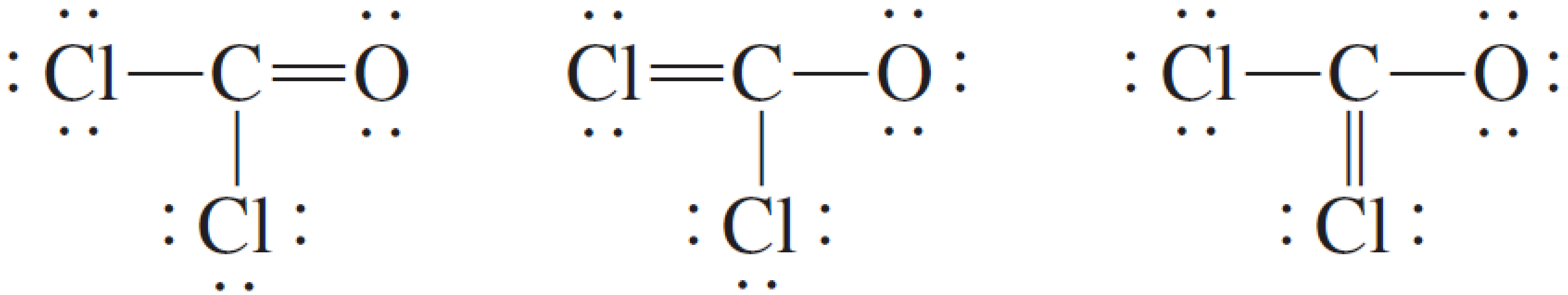
- rules for formal charge
- (1) Half of the electrons of a bond are assigned to each atom in the bond (counting each dash as two electrons).
- (2) Both electrons of a lone pair are assigned to the atom to which the lone pair belongs.

9.9 Formal Charge and Lewis Formulas

- rules for formal charge

Formal charge = valence electrons on free atom - 1/2 (number of electrons in a bond) - (number of lone-pair electrons)

Example:

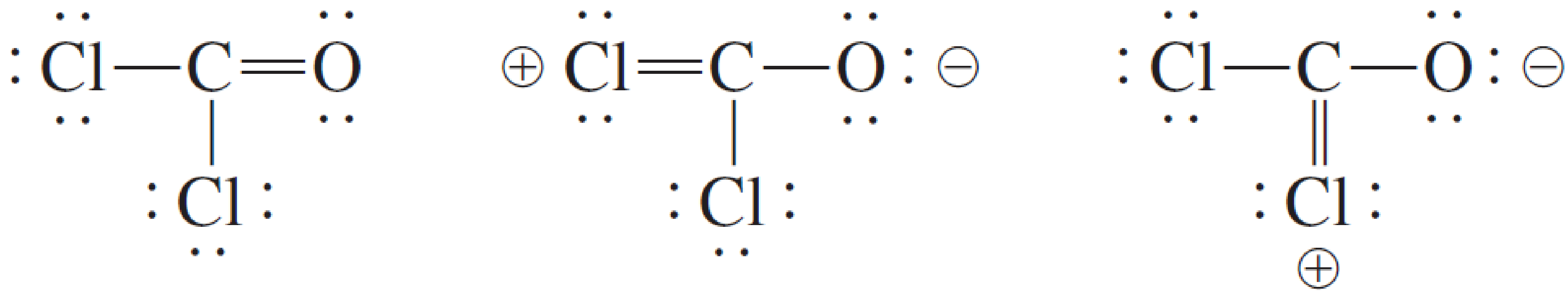


9.9 Formal Charge and Lewis Formulas

- rules for formal charge

Formal charge = valence electrons on free atom - 1/2 (number of electrons in a bond) - (number of lone-pair electrons)

Answer:

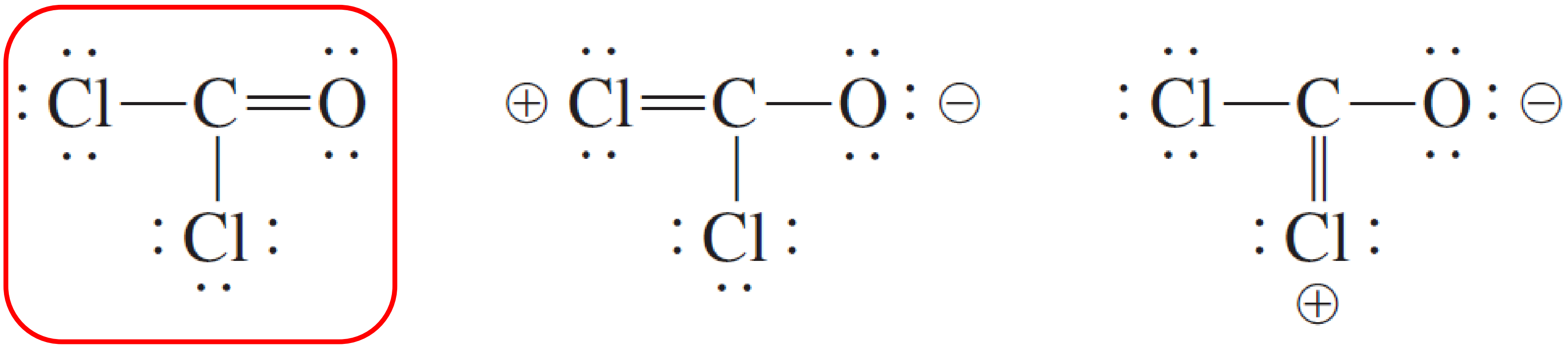


9.9 Formal Charge and Lewis Formulas

- rules in writing Lewis formulas
- **RULE A** Whenever you can write several Lewis formulas for a molecule, choose the one having the lowest magnitudes of formal charges.
- **RULE B** When two proposed Lewis formulas for a molecule have the same magnitudes of formal charges, choose the one having the negative formal charge on the more electronegative atom.

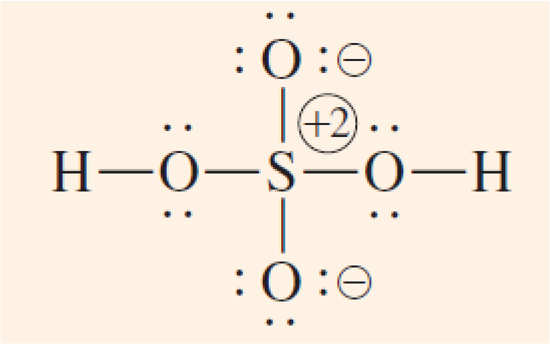
9.9 Formal Charge and Lewis Formulas

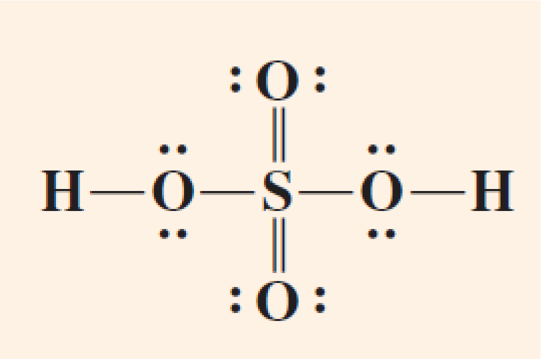
- rules in writing Lewis formulas
- **RULE C** When possible, choose Lewis formulas that do not have like charges on adjacent atoms.



P357 Example 9.11

Write the Lewis formula that best describes the charge distribution in the sulfuric acid molecule, H_2SO_4, according to the rules of formal charge.





9.10 Bond Length and Bond Order

- Bond length (or bond distance) is the distance between the nuclei in a bond.
- Covalent radii are values assigned to atoms in such a way that the sum of covalent radii of atoms A and B predicts an approximate A-B bond length.

9.10 Bond Length and Bond Order

Table 9.4 Single-Bond Covalent Radii

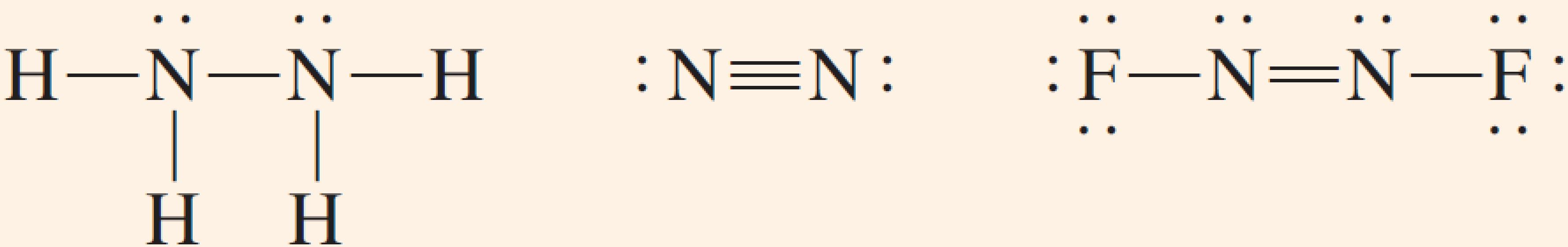
Atomic Number	Symbol	Name	Covalent Radius (pm)
1	H	Hydrogen	31
2	He	Helium	28
3	Li	Lithium	128
4	Be	Beryllium	96
5	B	Boron	84
6	C	Carbon	76
7	N	Nitrogen	71
8	O	Oxygen	66
9	F	Fluorine	57
10	Ne	Neon	58

9.10 Bond Length and Bond Order

- Bond order: the number of pairs of electrons in a bond.
- As the bond order increases, the bond strength increases and the nuclei are pulled inward, decreasing the bond length.

P359 Example 9.12

Consider the molecules N_2H_4, N_2, and N_2F_2. Which molecule has the shortest nitrogen–nitrogen bond? Which has the longest nitrogen–nitrogen bond?



N_2H_4 N_2 N_2F_2

9.11 Bond Energy

- A-B bond energy: the average enthalpy change for the breaking of an A-B bond in a molecule in the gas phase.

$$CH_4(g) \longrightarrow C(g) + 4H(g);\ \Delta H = 1662\ \text{kJ}$$

$$BE(\text{C—H}) = \frac{1}{4} \times 1662\ \text{kJ} = 416\ \text{kJ}$$

9.11 Bond Energy

- Bond energy is a measure of the strength of a bond: the larger the bond energy, the stronger the chemical bond.

9.11 Bond Energy

Table 9.5 Bond Enthalpies (in kJ/mol)*

Single Bonds									
	H	C	N	O	S	F	Cl	Br	I
H	436								
C	413	348							
N	391	393	163						
O	463	358	201	146					
S	339	259	—	—	266				
F	567	485	272	190	327	159			
Cl	431	328	200	203	253	253	242		
Br	366	276	243	—	218	237	218	193	
I	299	240	—	234	—	—	208	175	151

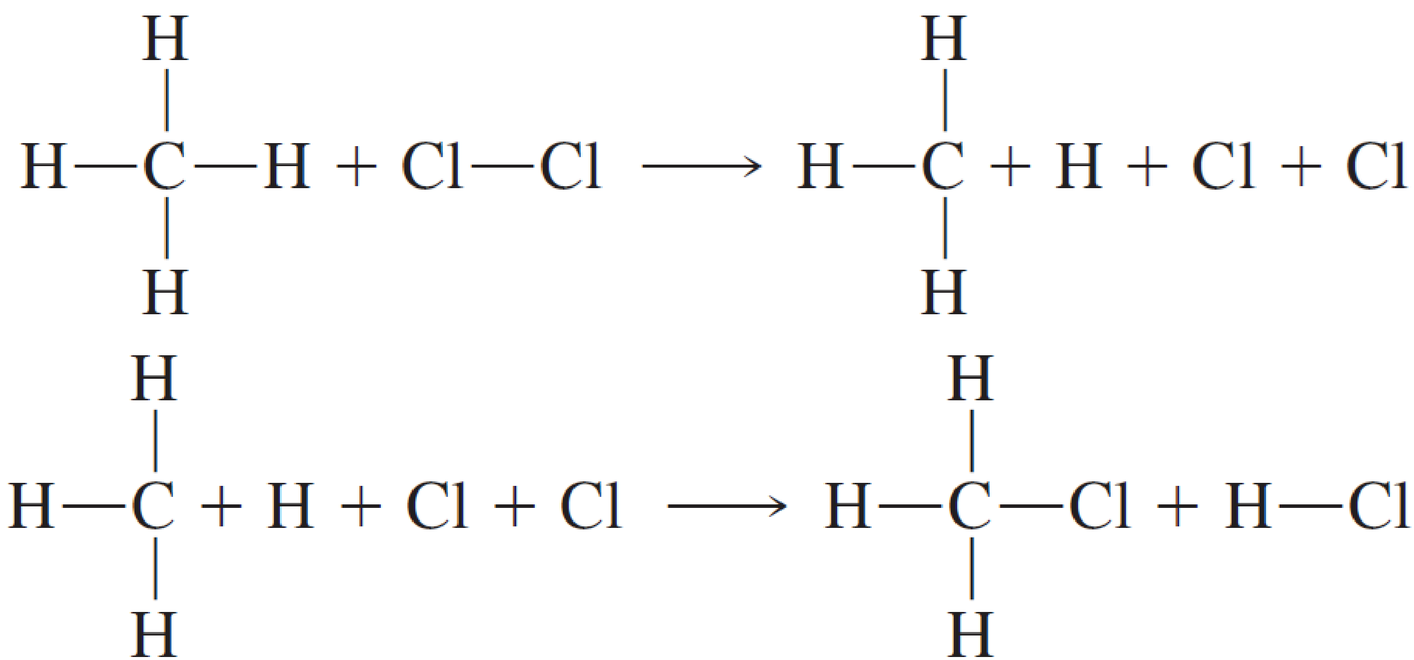
Multiple Bonds					
C=C	614	C=N	615	C=O	804 (in CO_2)
C≡C	839	C≡N	891	C≡O	1076
N=N	418	N=O	607	S=O	323
N≡N	945	O=O	498	S=S	418

*Data are taken from http://wiki.chemeddl.org/index.php/15.4_Bond_Enthalpies.

9.11 Bond Energy

- Use bond energies to estimate heats of reaction, or enthalpy changes, *H*, for gaseous reactions

$$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$$



9.11 Bond Energy

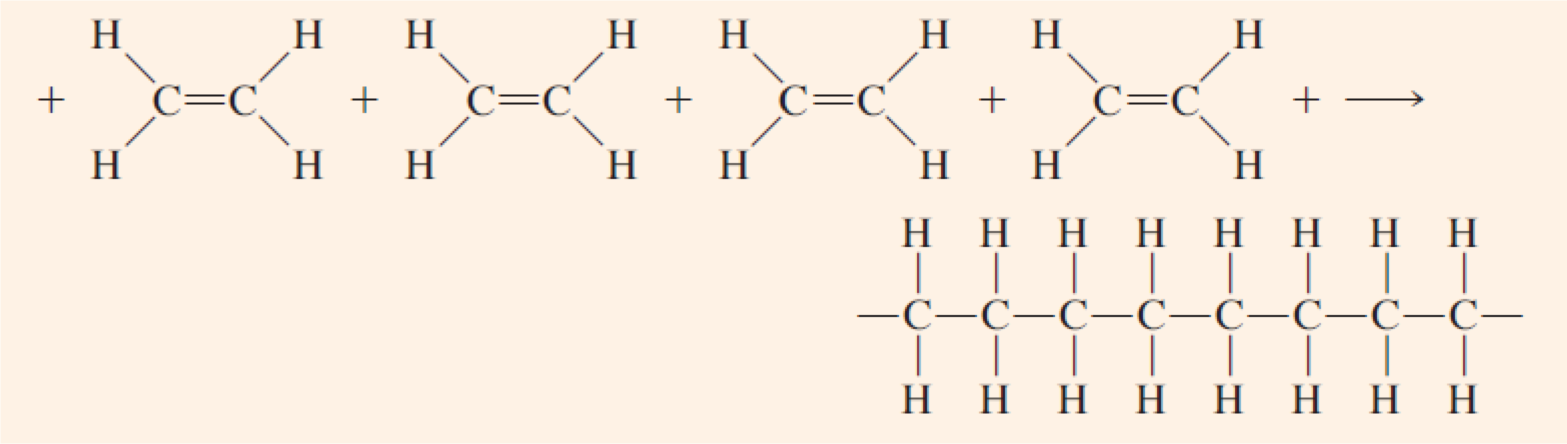
- In general, the enthalpy of reaction is (approximately) equal to the sum of the bond energies for bonds broken minus the sum of the bond energies for bonds formed.

Exothermic: weak bonds broke
strong bonds form

$$\Delta H \simeq BE(\mathrm{C{-}H}) + BE(\mathrm{Cl{-}Cl}) - BE(\mathrm{C{-}Cl}) - BE(\mathrm{H{-}Cl})$$
$$= (413 + 242 - 328 - 431)\ \mathrm{kJ}$$
$$= -104\ \mathrm{kJ}$$

P362 Example 9.13

Polyethylene is formed by linking many ethylene molecules into long chains. Estimate the enthalpy change per mole of ethylene for this reaction (shown below), using bond energies.



$$\Delta H = [602 - (2 \times 346)] \text{ kJ} = \mathbf{-90\ kJ}$$