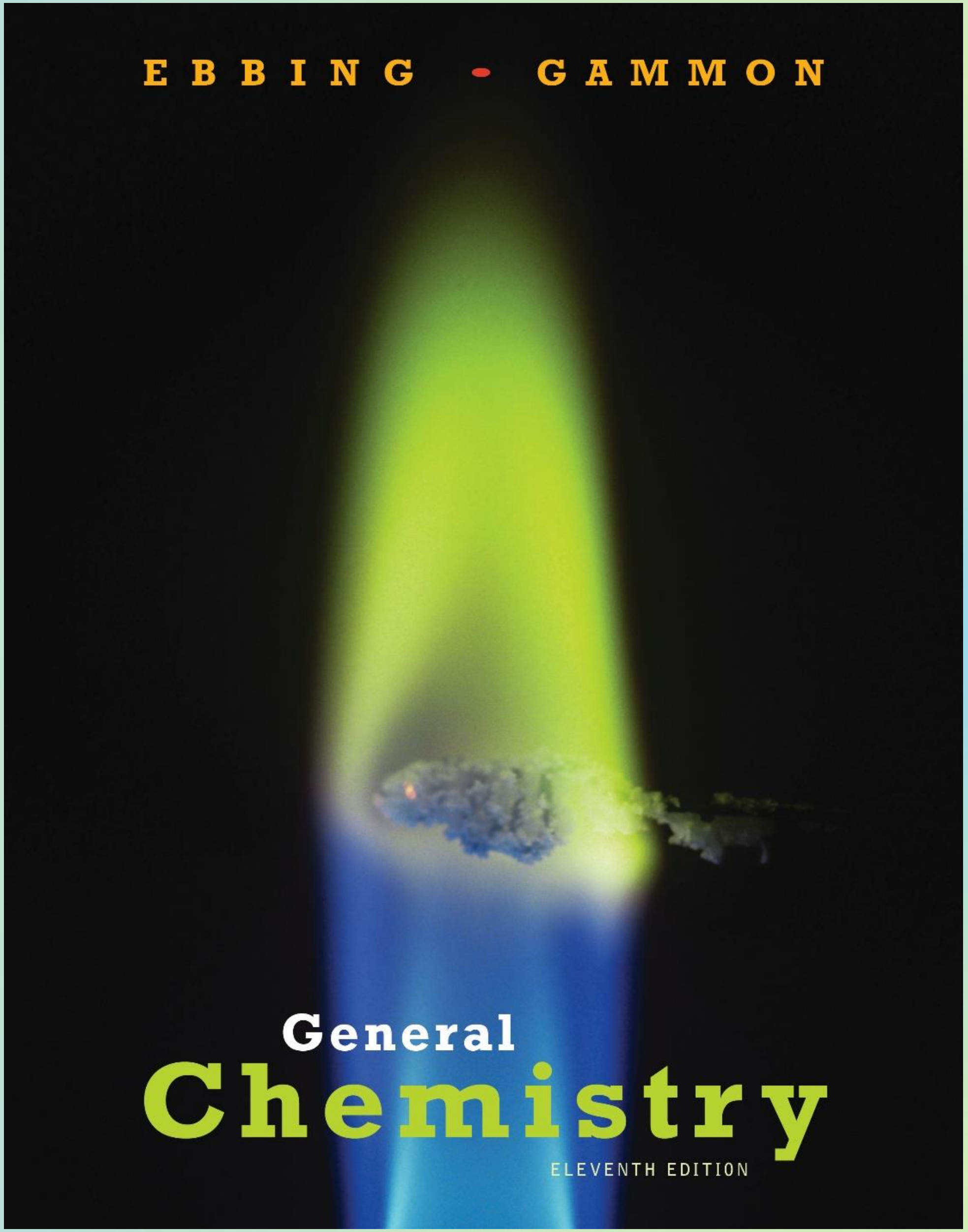
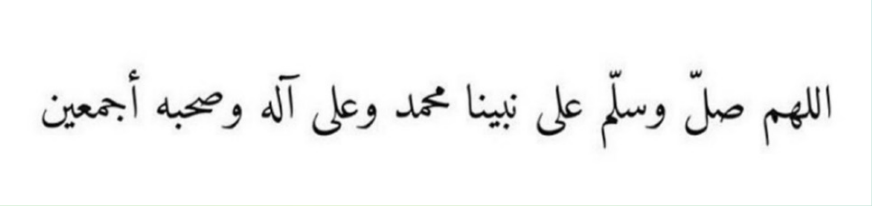
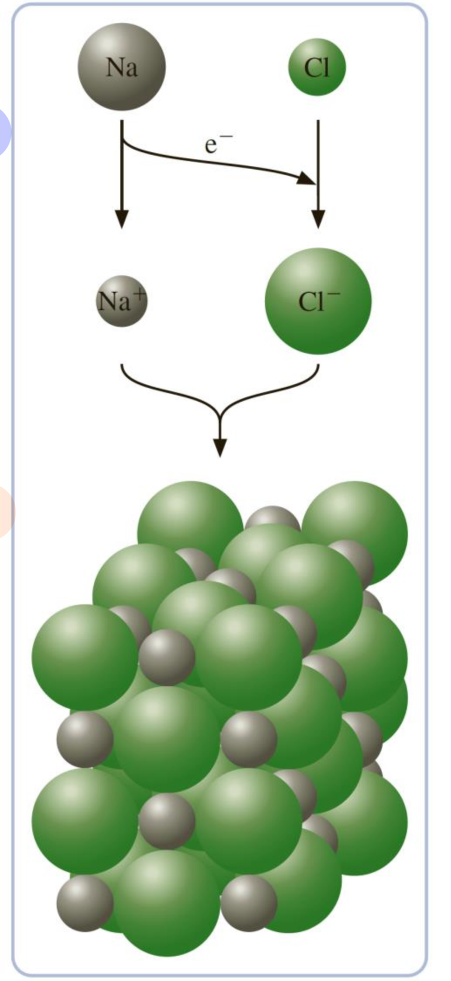




Ionic and Covalent Bonding

- 9.1 Describing Ionic Bonds
- 9.2 Electron Configurations of Ions
- 9.3 Ionic Radii
- 9.4 Describing Covalent Bonds
- 9.5 Polar Covalent Bonds and Electronegativity
- 9.6 Writing Lewis Electron-Dot Formulas
- 9.7 Delocalized Bonding: Resonance
- 9.8 Exceptions to the Octet Rule
- 9.9 Formal Charge and Lewis Formulas
- 9.10 Bond Length and Bond Order
- 9.11 Bond Enthalpy

➢ Ionic Bonds 9.1 Describing Ionic Bonds



- ✓ An **ionic bond** is *a chemical bond formed by the electrostatic attraction between positive and negative ions.*
- ✓ The bond forms between two atoms when one or more electrons are transferred from the valence shell of one atom to the valence shell of the other.
- ✓ The atom that loses electrons becomes a *cation* (positive ion), and the atom that gains electrons becomes an *anion* (negative ion).
- ✓ As a result of the electron transfer, ions are formed, each of which has a noble-gas configuration.

$$\text{Na}([\text{Ne}]3s^1) + \text{Cl}([\text{Ne}]3s^23p^5) \longrightarrow \text{Na}^+([\text{Ne}]) + \text{Cl}^-([\text{Ne}]3s^23p^6)$$

Low ionization E

High electron affinity

➢ Lewis Electron-Dot Symbols

✓ is a symbol in which the electrons in the valence shell of an atom or ion are represented by dots placed around the letter symbol of the element

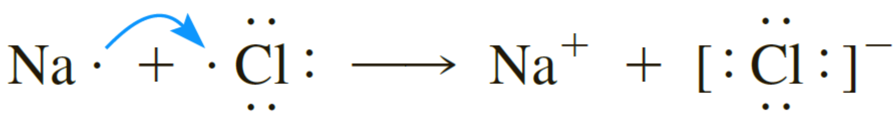
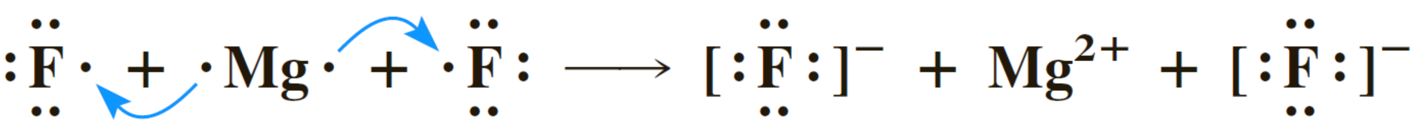


Table 9.1 Lewis Electron-Dot Symbols for Atoms of the Second and Third Periods

Period	1A ns^1	2A ns^2	3A ns^2np^1	4A ns^2np^2	5A ns^2np^3	6A ns^2np^4	7A ns^2np^5	8A ns^2np^6
Second	Li·	·Be·	·B·	·C·	:N·	:O·	:F·	:Ne:
Third	Na·	·Mg·	·Al·	·Si·	:P·	:S·	:Cl·	:Ar:

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

Example 9.1



➢ Energy Involved in Ionic Bonding

✓ Formation of an ionic bond between a sodium atom and a chlorine atom:

(1) $Na_{(g)} \rightarrow Na^{+}_{(g)} + e^{-}$ ΔH i.e = 496 kJ/mol Ionization energy

(2) $Cl_{(g)} + e^{-} \rightarrow Cl^{-}_{(g)}$ ΔH E.A = −349 kJ/mol Electron affinity

✓ The overall energy is (496 − 349) = 147 kJ/mol Endothermic

→ the process requires more energy to remove an electron from the sodium atom than is gained when the electron is added to the chlorine atom.

→ formation of ions from the atoms is not in itself energetically favorable.

Exothermic

BUT When positive and negative ions bond → energy is released to make the overall process favorable.

→ $\Delta H = (-)$

Coulomb's law

$$E = \frac{kQ_1Q_2}{r}$$

Coulomb's law states that *the potential energy obtained in bringing two charges* Q1 *and* Q2, *initially far apart, up to a distance* r *apart is directly proportional to the product of the charges and inversely proportional to the distance between them.*

$$E = \frac{kQ_1Q_2}{r}$$

→ Forming ione pair

Used to calculate electrostatic attraction

$k = 8.99 \times 10^9$ J.m/C^2 Constant

The charge on Na^+ is $+e$ and that on Cl^- is $-e$.

$e = 1.602 \times 10^{-19}$ C

r = distance between Na^+ and Cl^- = 282 pm ($\times 10^{-12}$), or 2.82×10^{-10} m.

Release = exothermic = stable

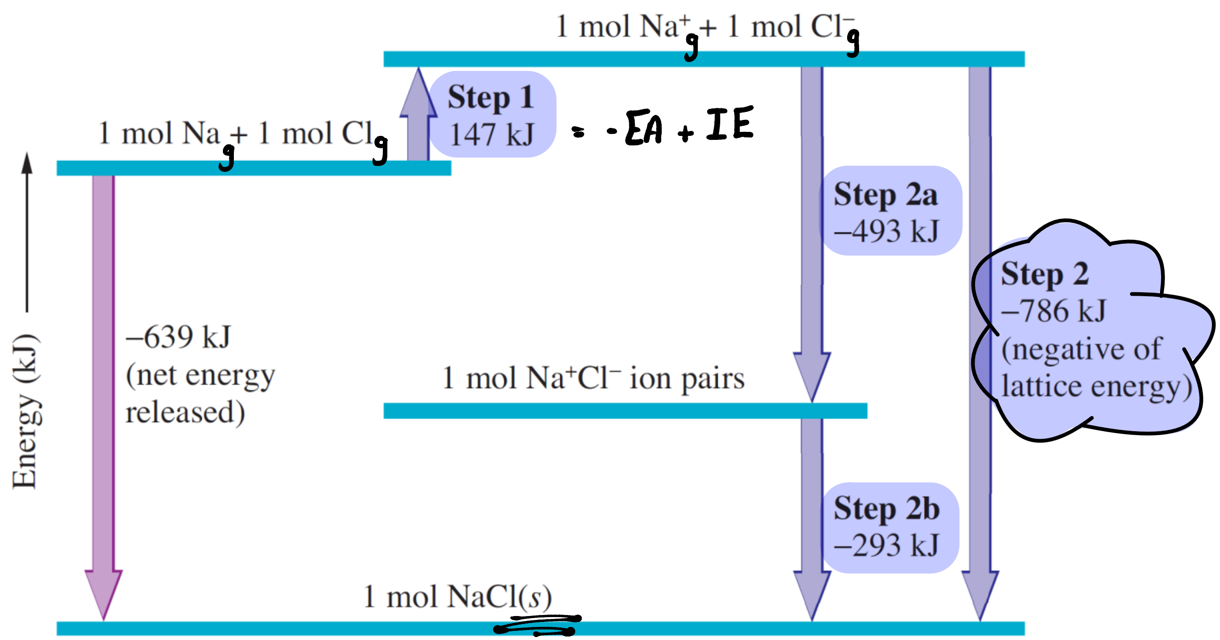
$$E = \frac{-(8.99 \times 10^9\ \mathrm{J \cdot m/C^2}) \times (1.602 \times 10^{-19}\ \mathrm{C})^2}{2.82 \times 10^{-10}\ \mathrm{m}} = -8.18 \times 10^{-19}\ \mathrm{J}$$

- ✓ The minus sign means energy is released Exothermic
- ✓ This energy is for the formation of one ion pair
- ✓ Multiplying by Avogadro's number, 6.02×10^{23} → −493 kJ/mol

For 1 mole

✓ The **lattice energy** is *the change in energy that occurs when an ionic solid is separated into isolated ions in the gas phase.* For sodium chloride, the process is

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

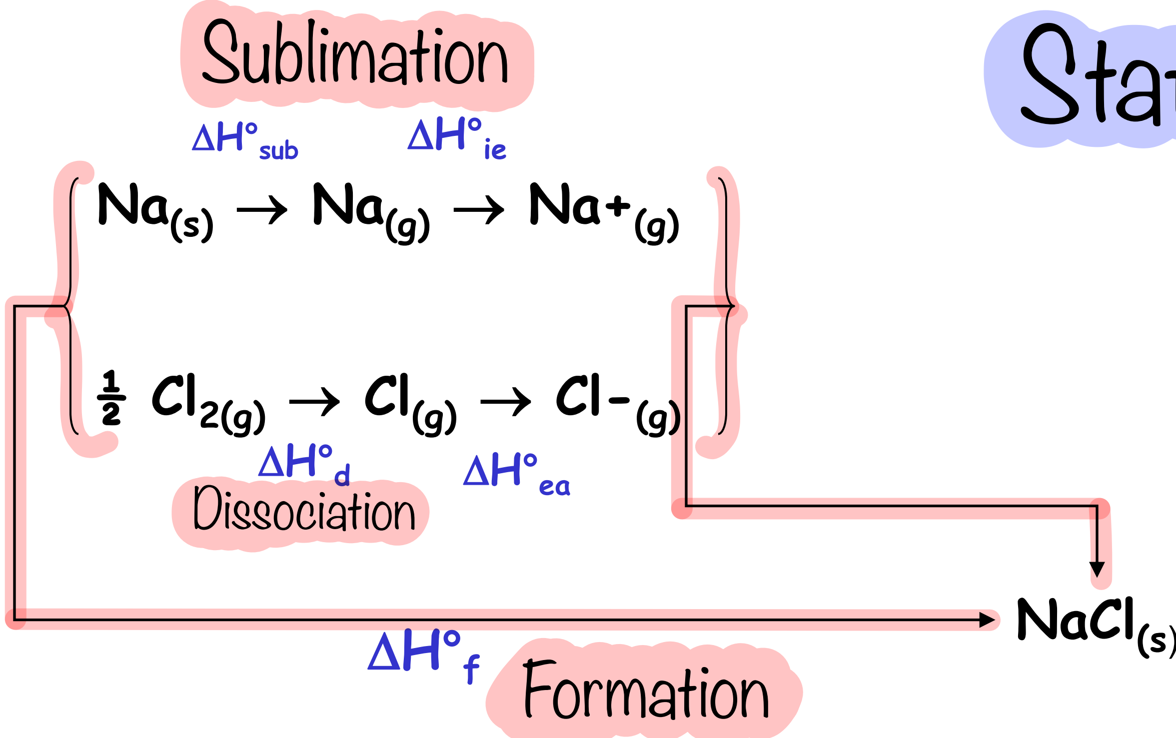


✓ The negative sign shows that there has been a net decrease in energy, which you expect when stable bonding has occurred.

✓ Ionic bond forms between elements if the ionization energy of one is sufficiently small and the electron affinity of the other is sufficiently large

The Born-Haber Cycle for NaCl (Energy diagram)

State function



$$\Delta H^\circ_f = \Delta H^\circ_{sub} + \Delta H^\circ_{ie} + 1/2\ \Delta H^\circ_d + \Delta H^\circ_{ea} + U_o$$

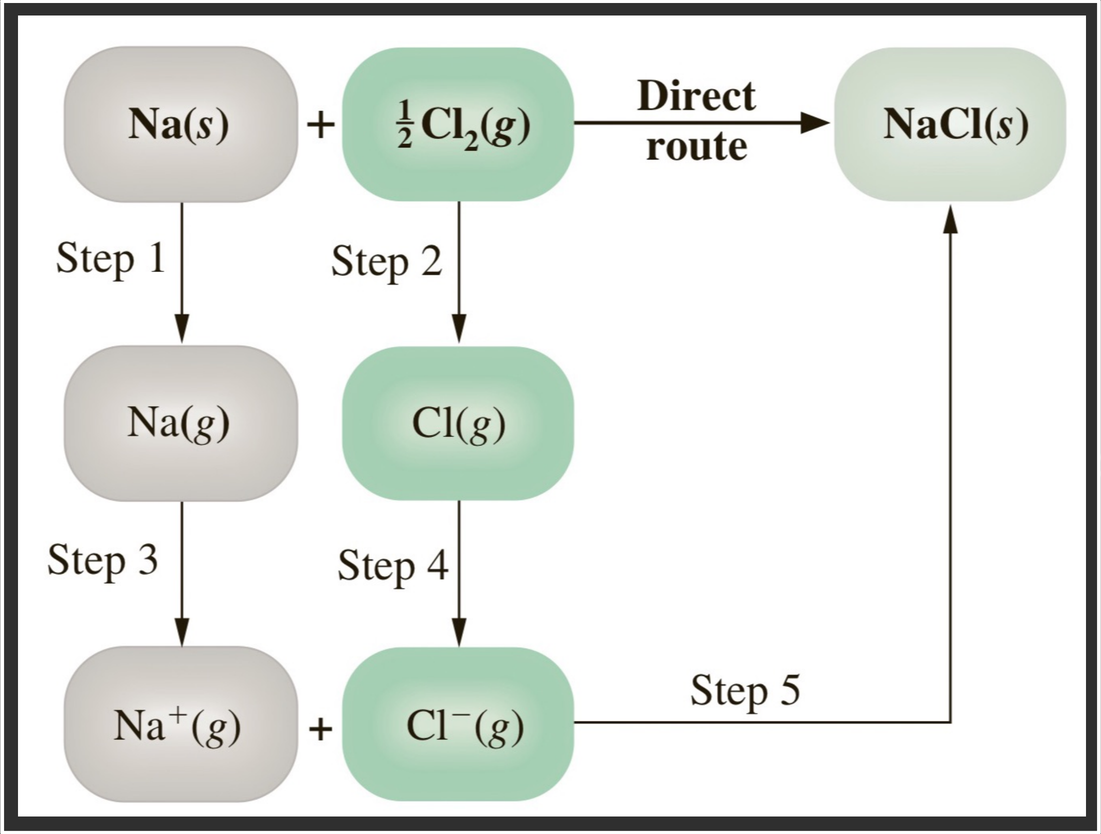
U_o = Lattice Energy

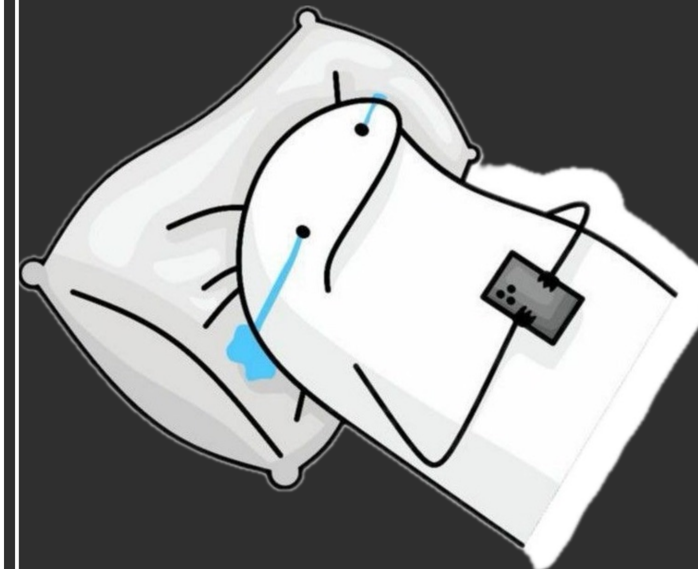
$$-411 = 109 + 496 + 1/2\ (242) + (-349) + U_o$$

$$U_o = -788 \text{ kJ/mol}$$

You must use the correct stoichiometry and signs to obtain the correct lattice energy.

Positive





Extra explanation

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

➢ Properties of Ionic Substances

✓ Strong ionic bonds (strong electrostatic interaction) → high-melting points of ionic solids.

m.p of MgO (2800 °C) > m.p NaCl (801 °C)

$$E = \frac{kQ_1Q_2}{r}$$

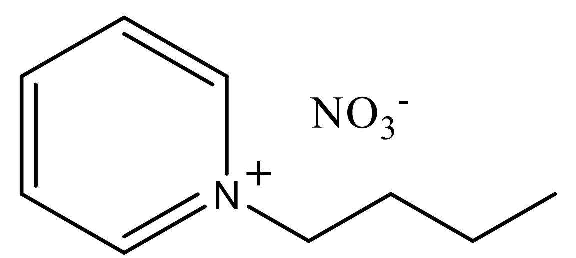
charges (Mg^{2+} and O^{2-}), 2:2

charges (Na^+ and Cl^-), 1:1

✓ The liquid melt from an ionic solid consists of ions, and so the liquid melts conducts an electric current.

✓ Ionic liquids have low m.p (RT) because of the cations are large and non-spherical.

melting point



9.2 Electron Configurations of Ions

➢ Ions of the Main-Group 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

Easy to remove

✓ Valence electrons are easily removed

✓ Much higher energy is needed to remove further electrons.

→ No compounds are found with ions having charges greater than the group number.

✓ Boron (Group 3A) doesn't form ionic compounds with B^{3+} ions, the bonding is normally covalent.

✓ The remaining elements of Group 3A do form compounds containing 3^+ ions because of decreasing ionization energy

✓ Thallium in 3A Period 6, has compounds with 1^+ ions and compounds with 3^+ ions

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

- ✓ The first three elements of Group 4A (C, Si, and Ge) are (metalloids) and usually form covalent rather than ionic bonds.
- ✓ Tin (Sn) and lead (Pb) (group 4A) commonly form ionic compounds with 2^+ ions.
- ✓ Tin forms tin(II) chloride, $SnCl_2$, which is an ionic compound and tin(IV) chloride $SnCl_4$ which is a covalent compound.
- ✓ Bi (group 5A) forms ionic Bi^{3+} cpds and covalent Bi^{5+} cpds.
- ✓ Anions of Groups 5A to 7A gain electrons (large EA) to form noble-gas or pseudo-noble-gas configurations.
- ✓ Hydrogen forms compounds of the 1^- ion, H^- (hydride ion).
- ✓ Although the electron affinity of nitrogen ($2s^22p^3$) = 0
- ✓ N^{3-} ion ($2s^22p^6$) is stable in the presence of Li^+ (Li_3N) and other alkaline earth elements ions (Mg_3N_2).

Example 9:2

(Q) Write the electron configuration and the Lewis symbol for N^{3-}.

N: [He]$2s^22p^3$

N^{3-}: [He]$2s^22p^6$

$[:\ddot{\underset{..}{N}}:]^{3-}$

Sn: [Kr]$4d^{10}5s^25p^2$

Sn^{2+} : [Kr]$4d^{10}5s^2$ ← Very Stable

Sn^{4+} : [Kr]$4d^{10}$ ← Covalent

Exercise 9.1 Represent the transfer of electrons from magnesium to oxygen atoms to assume noble-gas configurations. Use Lewis electron-dot symbols.

See Problems 9.37 and 9.38.

$\cdot Mg \cdot + :\dot{O}: \rightarrow (Mg)^{+2} + (:\ddot{O}:)^{-2}$

Lewis Symbol

Exercise 9.2 Write the electron configuration and the Lewis symbol for Ca^{2+} and for S^{2-}.

See Problems 9.39 and 9.40.

Exercise 9.3 Write the electron configurations of Pb and Pb^{2+}.

See Problems 9.41 and 9.42.

$_{20}Ca^{+2} = [Ar]\,4s^2 \rightarrow [Ar] \rightarrow (Ca)^{+2}$

$_{16}S^{-2} = [Ne]\,3s^2\,3p^4 \rightarrow [Ne]\,3s^2\,3p^6 \rightarrow (:\ddot{S}:)^{-2}$

$_{82}Pb = [Xe]\,4f^{14}\,5d^{10}\,6p^2\,6s^2$

$Pb^{+2} = [Xe]\,4f^{14}\,5d^{10}\,6s^2$

Exercise 9.4 Write the electron configuration of Mn^{2+}.

See Problems 9.43 and 9.44.

$_{25}Mn^{+2} = [Ar]\,4s^2\,3d^5$

$\rightarrow [Ar]\,3d^5$

➢ Transition-Metal Ions

Example 9:3

✓ M^{2+} is a common oxidation state as two electrons are removed from the outer ***ns*** shell.

Fe: [Ar] $4s^2 3d^6$

Fe^{2+} : [Ar] $3d^6$ loses 4*s* electrons first (less energy loss first)

Fe^{3+} : [Ar] $3d^5$ then loses 3*d* electrons

(Q) What are the correct electron configurations for Cu & Cu^{2+} ?

A. [Ar] $3d^9 4s^2$, [Ar] $3d^9$

B. [Ar] $3d^{10} 4s^1$, [Ar] $3d^8 4s^1$

C. [Ar] $3d^{10} 4s^1$, [Ar] $3d^9$

D. [Ar] $3d^9 4s^2$, [Ar] $3d^{10} 4s^1$

E. [K] $3d^9 4s^2$, [Ar] $3d^9$

(Q) What are the correct electron configurations for zirconium(II) and zirconium(IV) ions?

A. [Kr] $5d^2$ [Kr] $4d^1$

B. [Ar] $4d^2 5s^2$ [Ar] $5s^2$

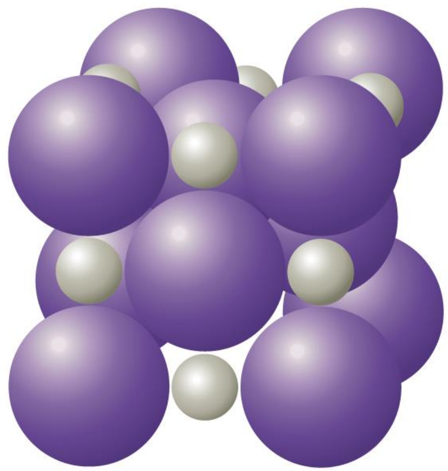
C. [Kr] $4d^2$ [Kr]

D. [Kr] $4d^6 5s^2$ [Kr] $4d^6$

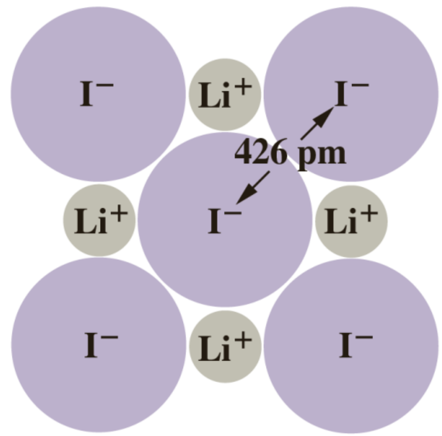
E. [Rb] $4d^2$ [Rb]

➢ 9.3 Ionic Radii : Half the distance between the center of two similar ions

Determining the iodide ion radius in the lithium iodide (LiI) crystal



a A three-dimensional view of the crystal.

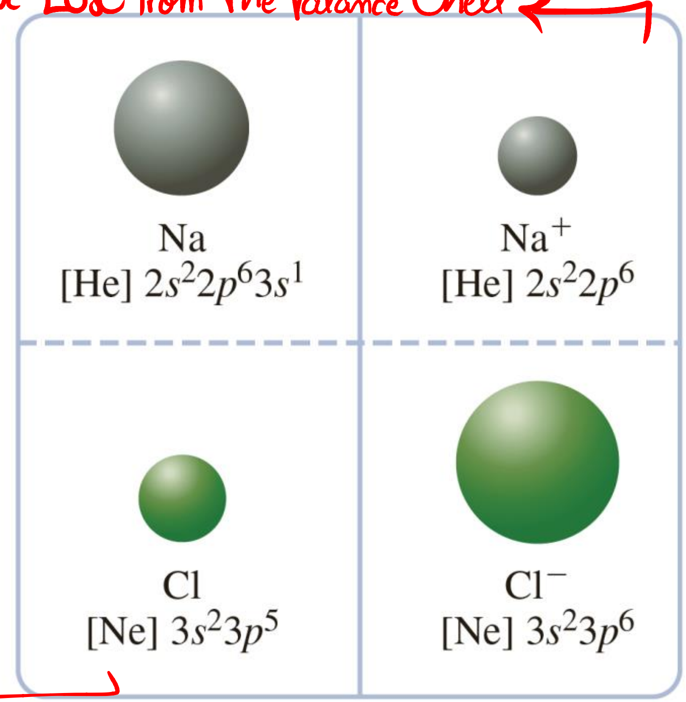


Ionic radius of I^-

= 426 / 2 = 213 pm

→ $\times 10^{-12}$

we Lose from the Valance Chell ←



Exercise 9.6

arrange the following ions in order of increasing ionic radius: Sr^{2+}, Mg^{2+}, Ca^{2+}.

→ $Mg^{2+} < Ca^{2+} < Sr^{2+}$

→ Mg < Ca < Sr

Increase in the repulsion يزيد التنافر ←

✓ 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		

Number of cells increase

Whenever the negative charge increase the size increase

Whenever the positive charge increase the size decrease

Exercise 9.5: Which has the larger radius, S or S^{-2} Explain?

S2−, because it has two additional electrons.

➢ Pattern across a period

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

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

✓ All of these cations have Ne configuration $1s^22s^22p^6$ but different nuclear charges (they are isoelectronic).

✓ **Isoelectronic** *refers to different species having the same number and configuration of electrons*

9.47 Arrange the following in order of increasing ionic radius:

As^{3-}, Se^{2-}, Br^-

33	34	35
As	**Se**	**Br**
$4s^24p^3$	$4s^24p^4$	$4s^24p^5$

Br^- < Se^{2-} < As^{3-}

✓ Within an isoelectronic series, the radius increases as the atomic number decreases

(Q) arrange the following ions in order of decreasing ionic radius:

F^-, Mg^{2+}, O^{2-} Example 9.4

isoelectronic series→ Mg^{2+} (Z=12) < F^- (Z=9) < O^{2-} (Z=8)

9.49 Arrange the following in order of increasing ionic radius: F^-, Na^+, and N^{3-}.

isoelectronic series→ Na^+ (Z=11) < F^- (Z=9) < N^{3-} (Z=7)

9.48 Which has the larger radius, N^{3-} or P^{3-}? **P^{3-}**

Exercise 9.7 Without looking at Table 9.3, arrange the following ions in order of increasing ionic radius: Cl^-, Ca^{2+}, P^{3-}. (You may use a periodic table.)

See Problems 9.49 and 9.50.

$Ca^{+2} < Cl^{-1} < P^{3-}$

➢ Covalent Bonds

✓ *a chemical bond formed by the sharing of a pair of electrons between atoms.*

9.4 Describing Covalent Bonds

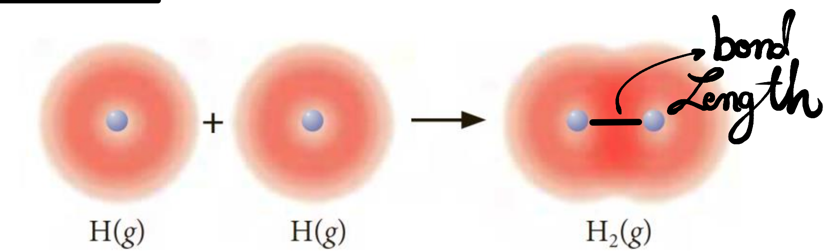


Figure 9.10

The electron probability distribution for the H_2 molecule The electron density (shown in red) occupies the space around both atoms.

✓ The distance between nuclei at minimum energy is called the *bond length* of H_2.

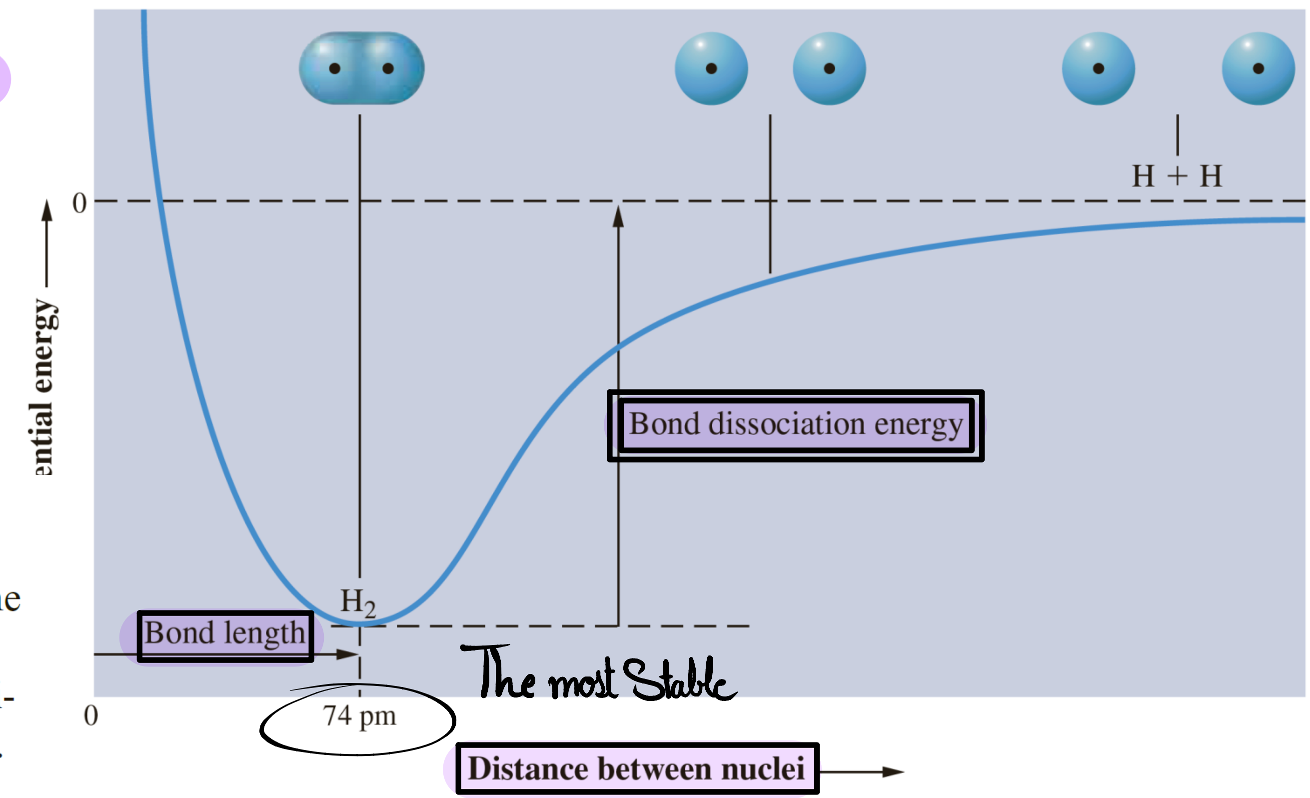


Figure 9.11

Potential-energy curve for H_2 The stable molecule occurs at the bond distance corresponding to the minimum in the potential-energy curve.

➢ Lewis Formulas

$$\mathrm{H}\cdot + \cdot\mathrm{H} \longrightarrow \mathrm{H}:\mathrm{H}$$

$$\mathrm{H}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow \mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:$$

$$\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:$$

lone pairs

bonding pair

$$3\mathrm{H}\cdot + \cdot\underset{\cdot}{\overset{\cdot}{\mathrm{N}}}: \longrightarrow \begin{array}{c} \mathrm{H} \\ \mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{N}}}: \\ \mathrm{H} \end{array}$$

➢ Coordinate Covalent Bonds

✓ *is a bond formed when both electrons of the bond are donated by one atom*

$$\mathrm{A}\cdot + \cdot\mathrm{B} \longrightarrow \mathrm{A}:\mathrm{B}$$

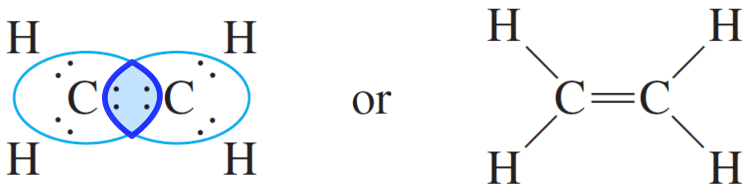
$$\mathrm{A} + :\mathrm{B} \longrightarrow \mathrm{A}:\mathrm{B}$$

$$\mathrm{H}^{+} + :\mathrm{NH_3} \longrightarrow \left[\begin{array}{c} \mathrm{H} \\ \mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{N}}}:\mathrm{H} \\ \mathrm{H} \end{array}\right]^{+}$$

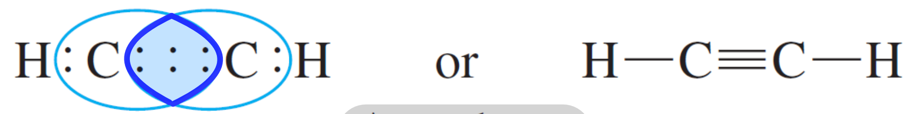
➢ Octet Rule → 8

✓ The tendency of atoms in molecules to have eight electrons in their valence shells (two for hydrogen atoms)

➢ Multiple Bonds



Ethylene



Acetylene

9.5 Polar Covalent Bonds (Polar Bonds)

✓ is a covalent bond in which the bonding electrons spend more time near one atom than the other.

H : H	δ^+ H : Cl δ^-	Na^+ :Cl:$^-$
Nonpolar covalent	Polar covalent	Ionic
There is no different in the electronegativity	Sharing	Tranlsferring

(Electronegativity)

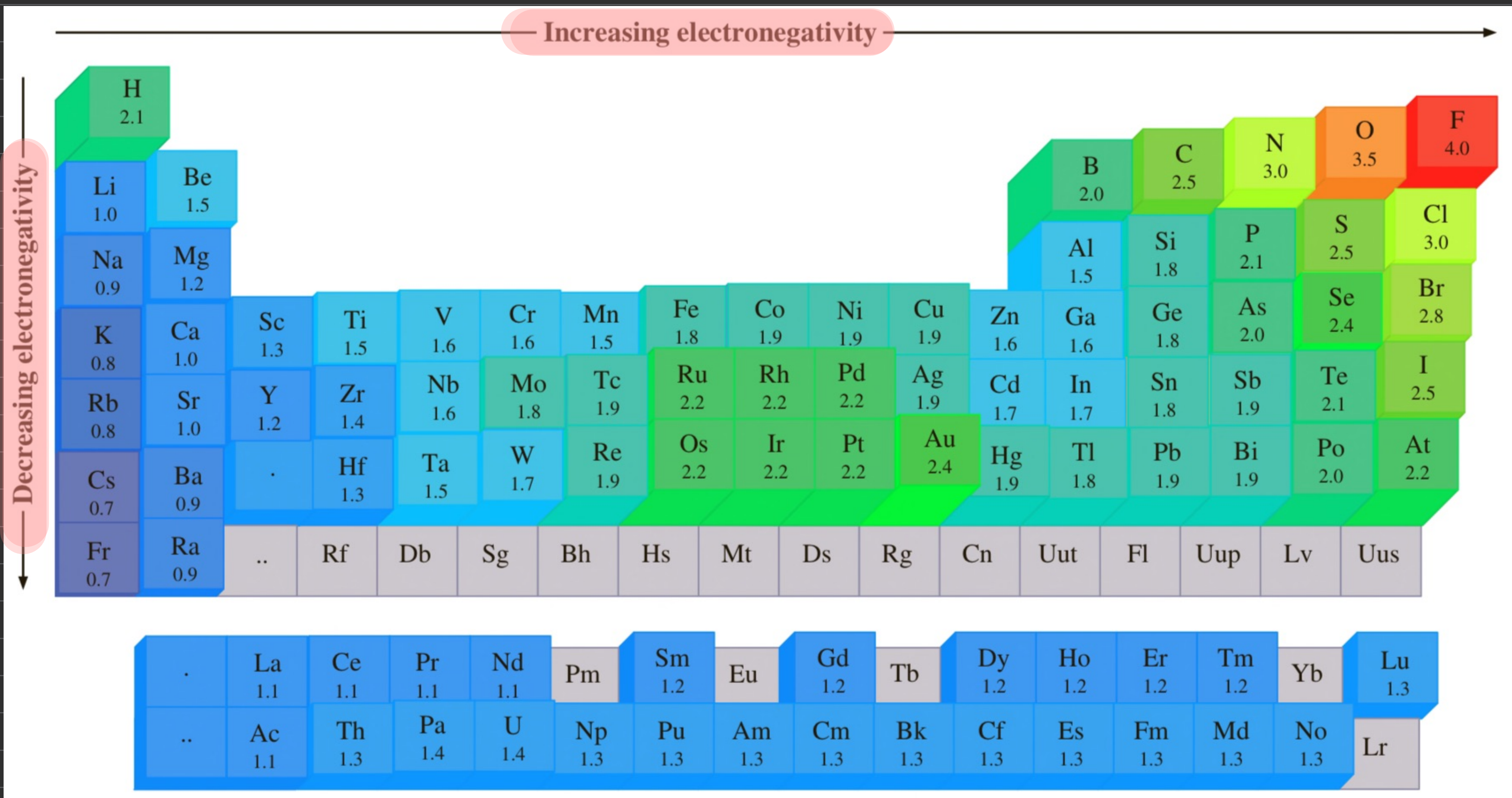


Figure 9.15

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

✓ Mulliken electronegativity (χ):

$$X = \frac{I.E. + E.A.}{2}$$

✓ F has large *E.A.* and large *I.E.* → large electronegativity #

✓ Li has small *E.A.* and small *I.E.* → small electronegativity

✓ Pauling's electronegativity (χ): depends on bond enthalpies

✓ *Electronegativity increases from left to right and decreases from top to bottom in the periodic table.* Without consider the Nobel gases

✓ Metals are the least electronegative elements (they are *electropositive*) and nonmetals the most electronegative.

✓ The absolute value of the difference in electronegativity of two bonded atoms gives a rough measure of the polarity of a bond

	H—H,	H—Cl, and	Na—Cl
$\Delta\chi$:	0.0	0.9	2.1
	Non-polar	Polar	Ionic pond

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

Polar molecule

Example 9.5 Using Electronegativities to Obtain Relative Bond Polarities

Gaining Mastery Toolbox

Critical Concept 9.5
The absolute value of the difference in electronegativity of two bonded atoms is a rough measure of the polarity of the bond. (A useful rule to remember is that electronegativity increases left to right and decreases top to bottom in the periodic table.)

Solution Essentials:
- Electronegativity

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

Problem Strategy Order the bonds by the increasing positive value of the difference of electronegativities of the atoms forming the bond. The bonds should then be roughly in order of increasing polarity.

Solution The absolute values of the electronegativity differences are P—H, 0.0; H—O, 1.4; C—Cl, 0.5. Hence, the order is **P—H, C—Cl, H—O.**

Answer Check Make sure you have the correct electronegativities and differences.

Exercise 9.8 Using electronegativities, decide which of the following bonds is most polar: C—O, C—S, H—Br.

See Problems 9.57 and 9.58.

C - O = (3.5 - 2.5) = 1
C - S = (2.5 - 2.5) = 0
H - Br = (3.8 - 2.1) = .7

From the Table OR Figure 9.15 → given in the Exam. :)

* So (C - O) is the most polar.

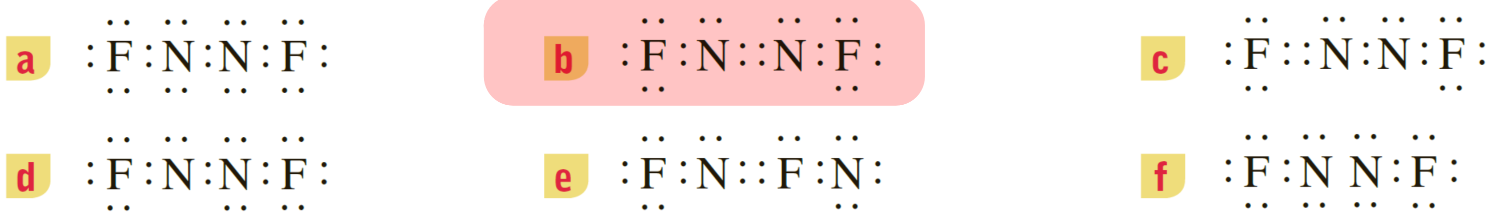
➢ Writing Lewis Electron-Dot Formulas 9.6

These will be done in class:

H_2O, NF_3, CCl_2F_2, CO_2, SCl_2, $POCl_3$, $COCl_2$, HSO_3Cl, CO_3^{2-}, NH_4^+, BF_4^-, H_3O^+, ClO_2^-.

CONCEPT CHECK 9.2

Each of the following may seem, at first glance, to be plausible electron-dot formulas for the molecule N_2F_2. Most, however, are incorrect for some reason. What concepts or rules apply to each, either to cast it aside or to keep it as the correct formula?



Rwitting Lewis structure rules :

1. Count the valance electrons (ve) for all atoms in the formula, add one For each negative charge, and subtract one For each positive charge ..

Ex.

$H_2O = Ve \rightarrow \overset{H}{(1 \times 2)} + \overset{O}{(6 \times 1)} = 8e^-$

$CCl_4 = Ve \rightarrow \overset{C}{(4 \times 1)} + \overset{Cl}{(7 \times 4)} = 32e^-$

$NO_3^{-1} = Ve \rightarrow \overset{N}{(5 \times 1)} + \overset{O}{(6 \times 3)} + 1 = 24e^-$

$CO_3^{-2} = Ve \rightarrow \overset{C}{(4 \times 1)} + \overset{O}{(6 \times 3)} + 2 = 24e^-$

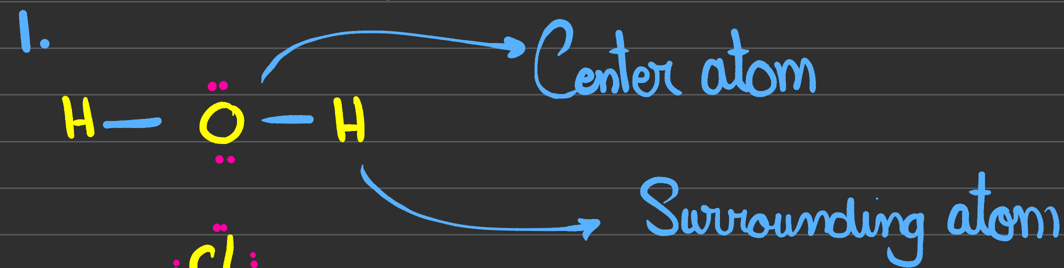
$NH_4^{+1} = Ve \rightarrow (5 \times 1) + (1 \times 4) - 1 = 8e^-$

N: Group (5) → group Number; 1 atom → Number of Atoms

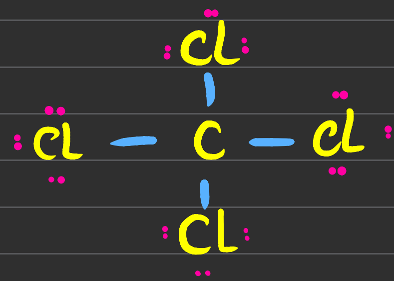
H: Group (1); 4 atom

2. Draw skeletal For the structure, put the least electro negativity atom in the center (with exception For H) ...

Ex: * H_2O 8e- =



* CCl_4 32e- =



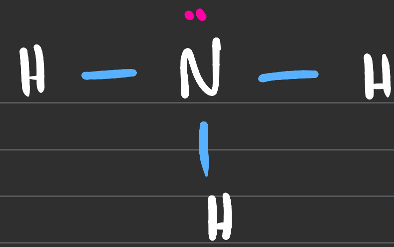
3. Draw single bond between the center and the surrounding Atoms...

4. Complete octet for each atom (exept H=2) from surrounding atoms...

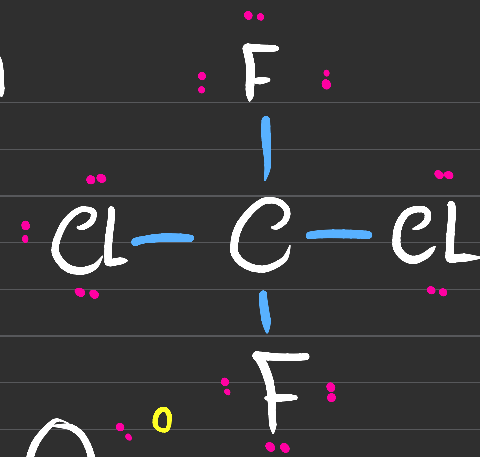
5. Draw double or triple bond if needed ...

Ex: N_2 = $V_e \rightarrow (5 \times 2) = 10e^-$ $:N \equiv N:$

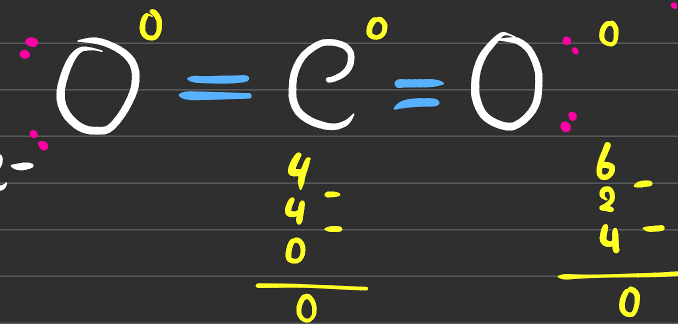
2. $NH_3 : (5 \times 1) + (1 \times 3) = 8e^-$



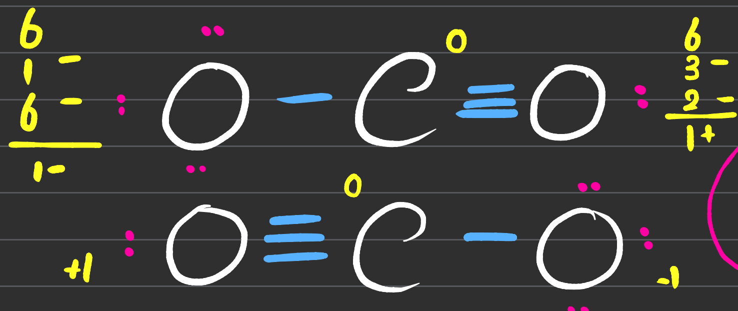
3. $CCl_2F_2 : (4 \times 1) + (7 \times 2) \times (7 \times 2) = 32e^-$



more Stable →



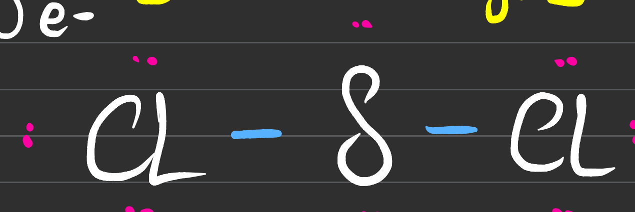
4. $CO_2 : (4 \times 1) + (6 \times 2) = 16e^-$



Resonance : Different Structure for the Same Formula...

we have to determine which one is the most Stable ←

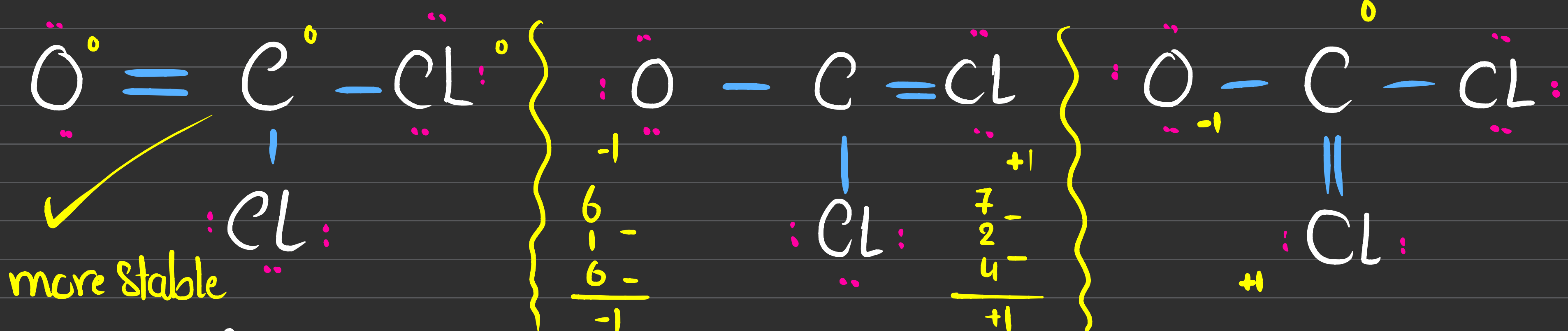
5. $SCl_2 : (6 \times 1) + (7 \times 2) = 20e^-$ [Formal charge]



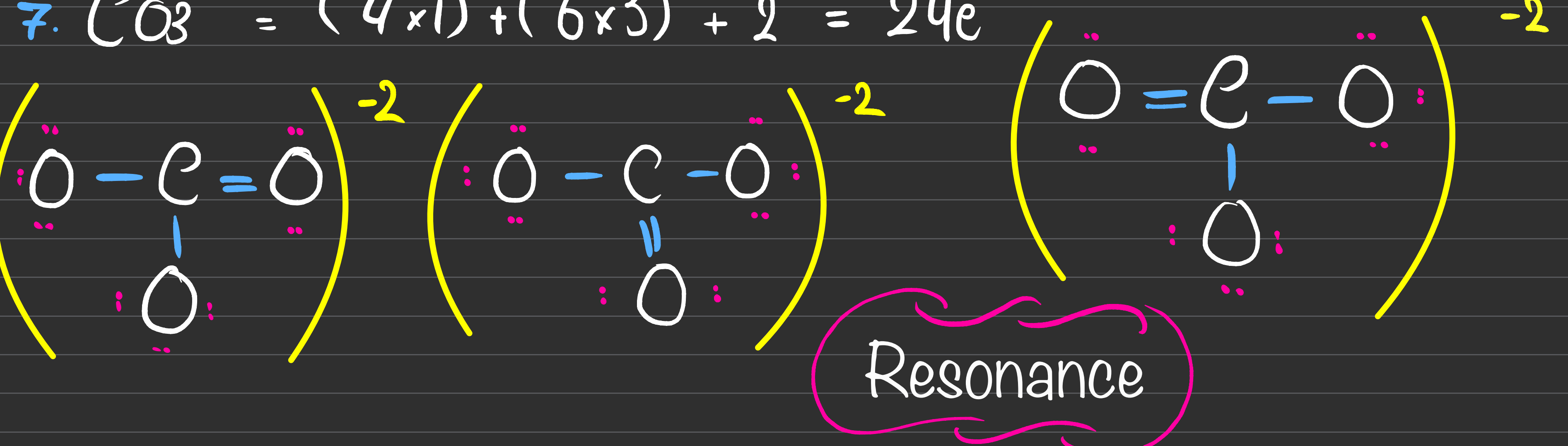
* How we can Calculate the Formula charge for the atom?

* Formula charge = Ve − ($\frac{1}{2}$ × bonding e⁻) − (non bonding e⁻)

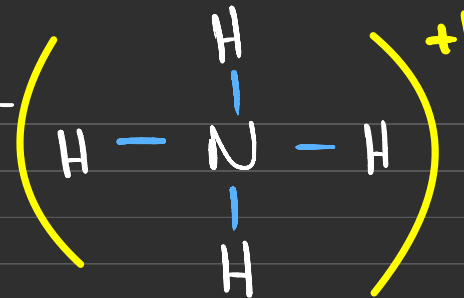
6. $COCl_2$ = (4×1) + (6×1) + (7×2) = 24e⁻



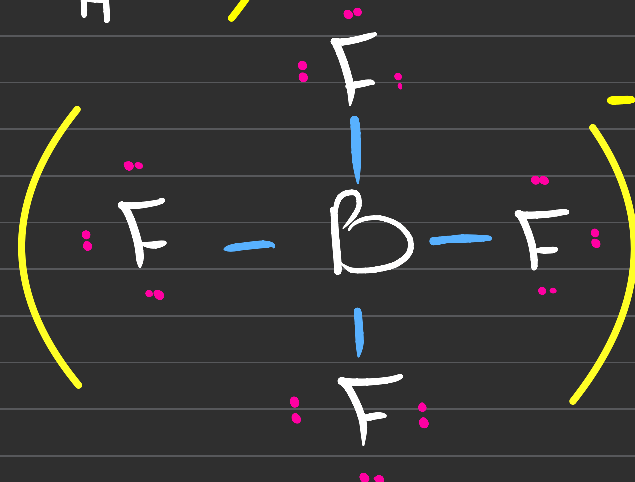
7. CO_3^{-2} = (4×1) + (6×3) + 2 = 24e⁻



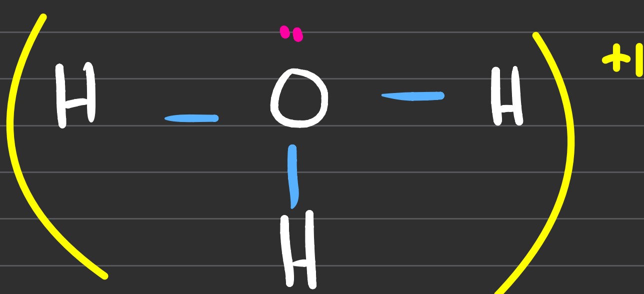
8. $NH_4^{+} = (5\times1)+(1\times4)-1 = 8e^-$



9. $BF_4^{-1} = (3\times1)+(7\times4)+1 = 32e^-$



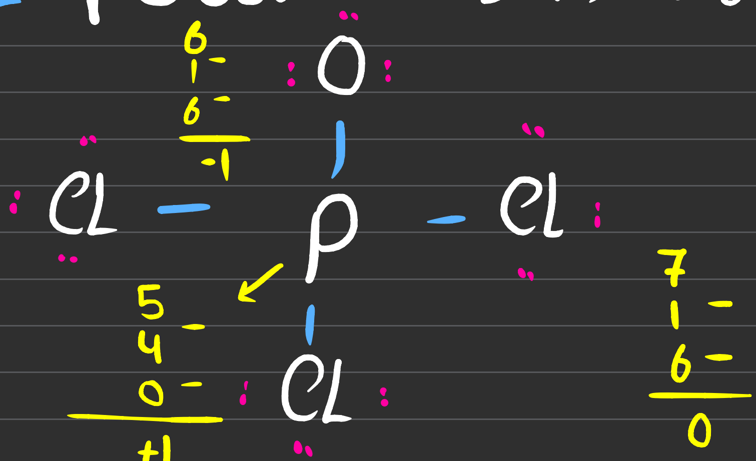
10. $H_3O^{+1} = (1\times3)+(6\times1)-1 = 8e$

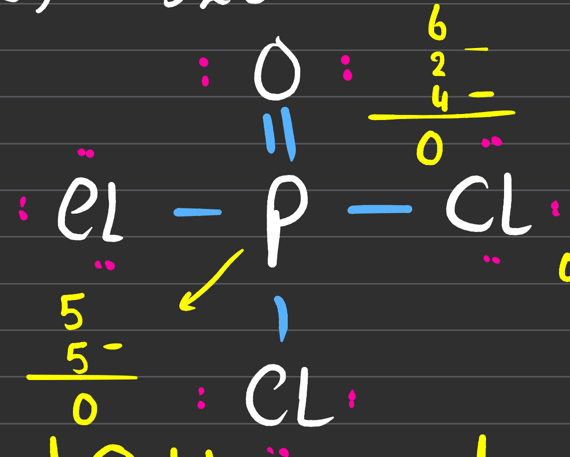


11. $ClO_2^{-} = (7\times1)+(6\times2)+1 = 20e^-$

Exceptions

12. $POCl_3 = (5\times1)+(6\times1)+(7\times3) = 32e^-$

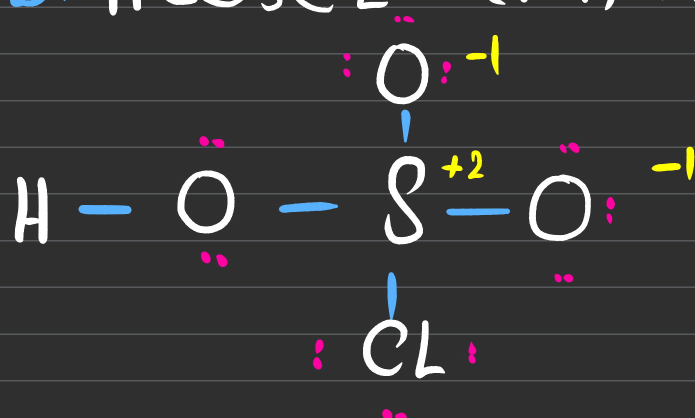


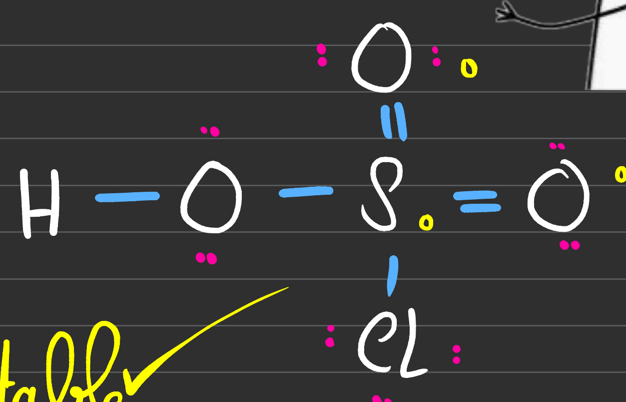


Expand Octet = More Stable

→ The Center atom have more the $8e^-$

13. $HSO_3Cl = (1\times1)+(6\times1)+(6\times3)+(7\times1) = 32e^-$

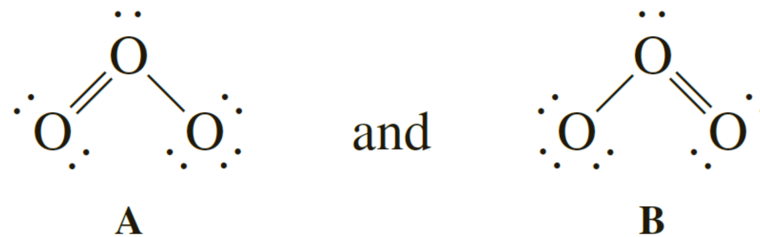


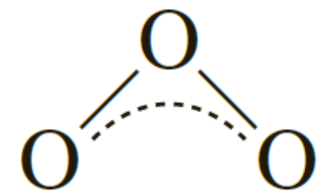


more Stable ✓

9.7 Delocalized Bonding: Resonance

Ozone (O_3)

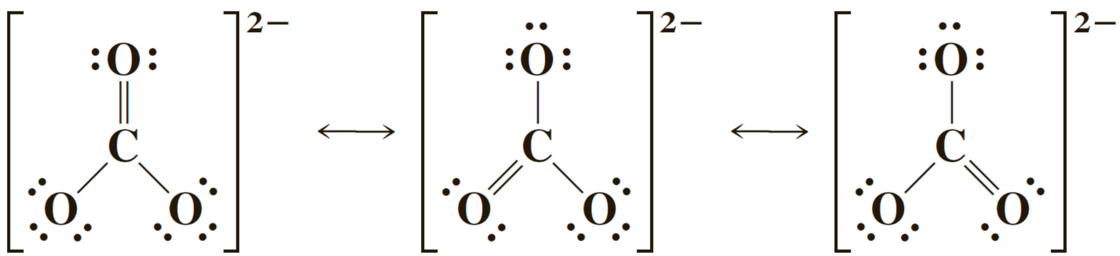




✓ The lengths of the two oxygen–oxygen bonds (that is, the distances between the atomic nuclei) are both 128 pm.

✓ **delocalized bonding** Example 9.9

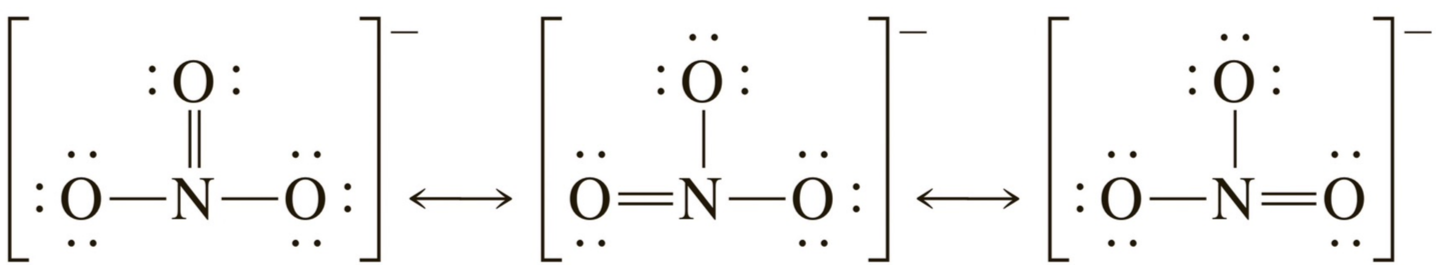
CO_3^{2-}



How many resonance ? 3

Exercise 9.12

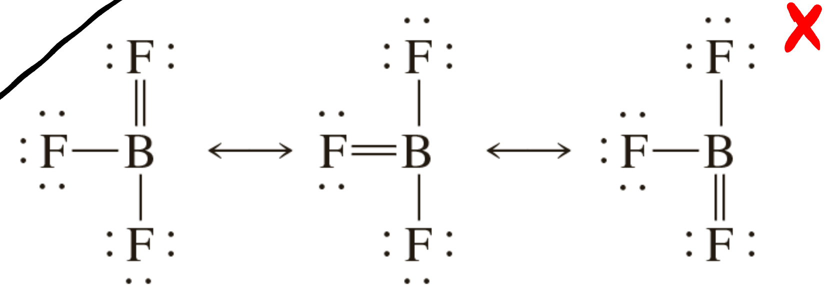
NO_3^-



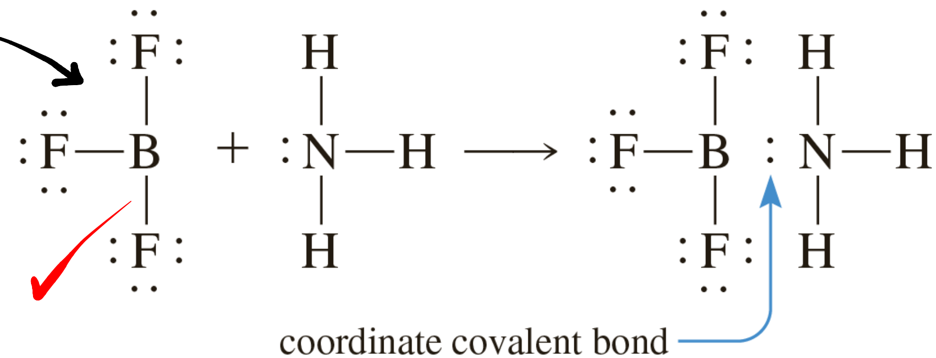
9.8 Exceptions to the Octet Rule

These will be done in class:
PF_5, SF_6, XeF_4, SF_4
BF_3, $BeCl_2$,

Expand Octet



InComplete Octet



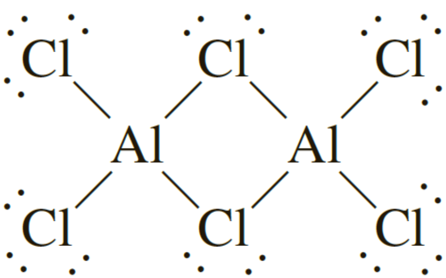
* NO = 5 + 6 = 11e-

·N̈ = Ö

Odd (e-) Number

*من برّا الكتاب...

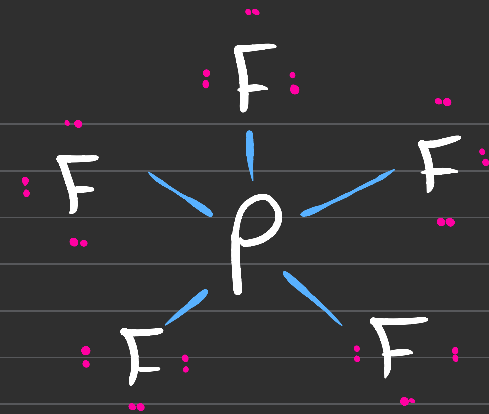
$AlCl_3$ @ RT & at melting point (very low 192°C)



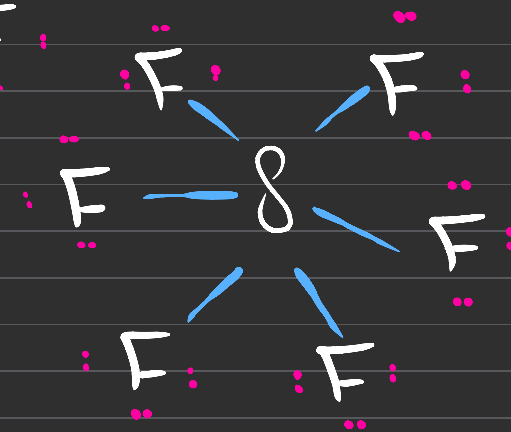
two of the Cl atoms are in ***bridge* positions**

Exceptions

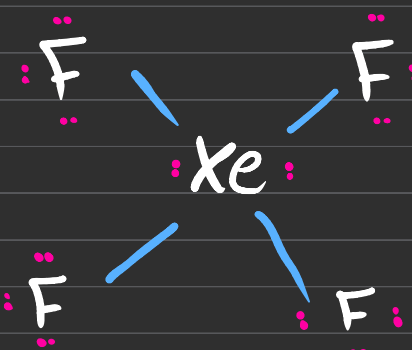
* PF_5 = 5 + 35 = 40e-



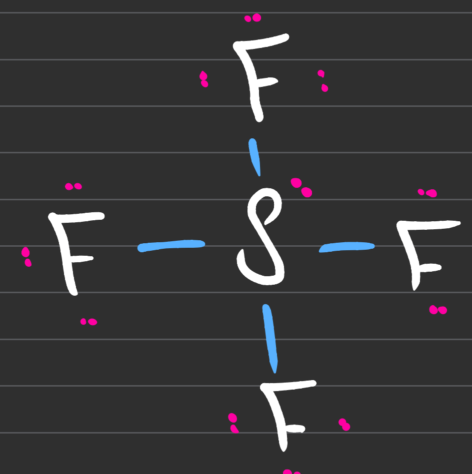
* SF_6 = 6 + 42 = 48 e-



* XeF_4 = 8 + 28 = 36e-



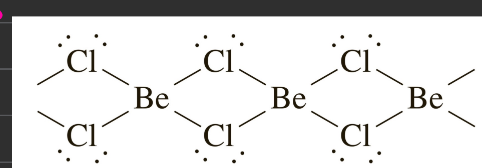
* SF_4 = 6 + 28 = 34e-



* $BeCl_2$ = 2 + 14 = 16 e-

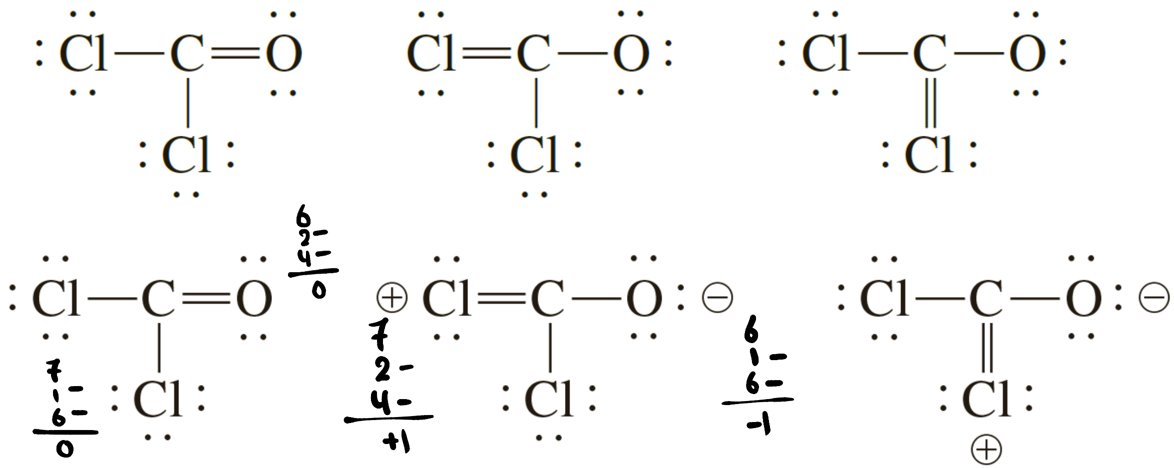
BF_3

BCl_3



9.9 Formal Charge and Lewis Formulas

$COCl_2$



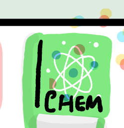
الصيغة الصح
الأكثر استقرارًا
هي الأقل شحنات أو
بدون شحنات ...

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.

RULE C When possible, choose Lewis formulas that do not have like charges on adjacent atoms.

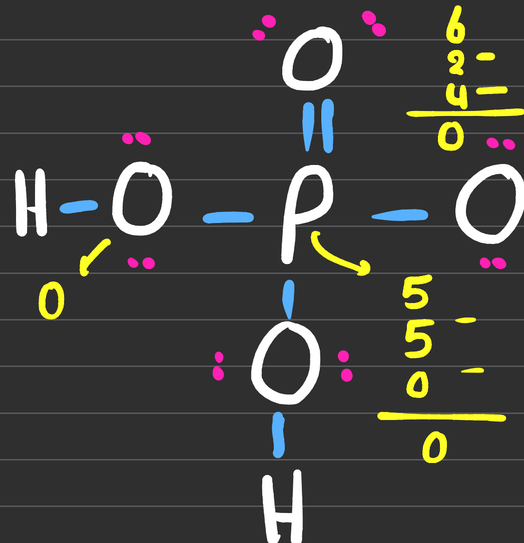
Example 9.11 _ exercise 9.15



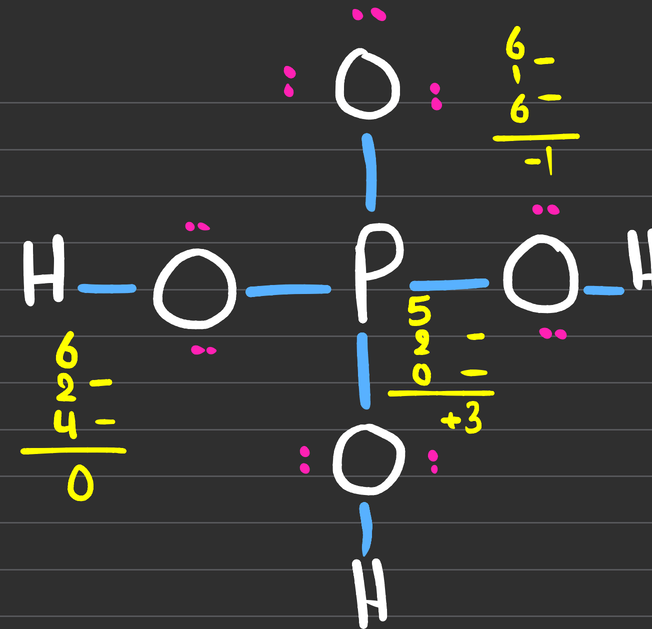
(Q) Write the Lewis formula that best describes the charge distribution in the sulfuric acid molecule, H_2SO_4, according to the rules of formal charge. (HNO_3, H_3PO_4, HCN)

* H_3PO_4 =

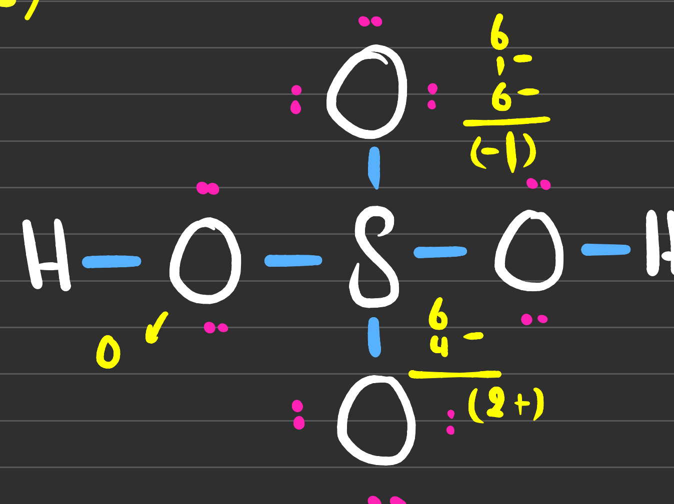
$V_e = 3 + 5 + 24 = 32e^-$

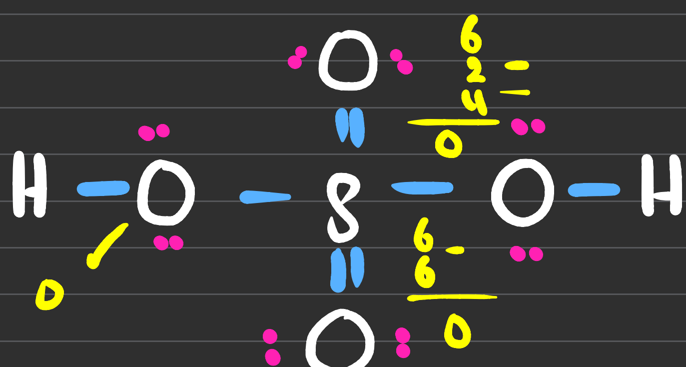


(more stable)



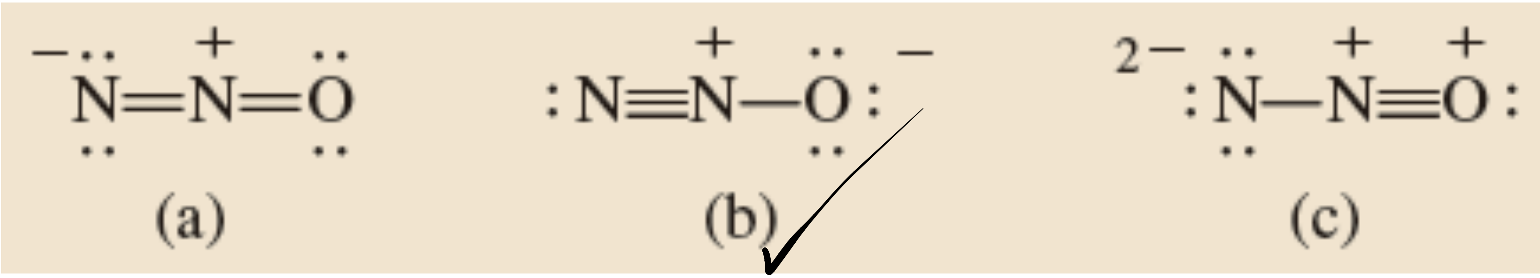
* $H_2SO_4 = 2 + 24 + 6 = 32e^-$





(more stable)

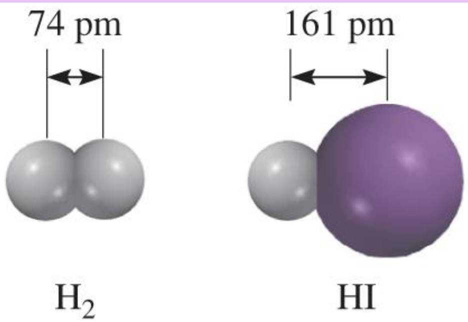
(Q) Draw three resonance structures for the molecule nitrous oxide, N_2O (the atomic arrangement is NNO)



Structure (b) is the most important one because the negative charge is on the more electronegative oxygen atom.

Structure (c) is the least important one because it has a larger separation of formal charges. Also, the positive charge is on the more electronegative oxygen atom.

➢ 9.10 Bond Length and Bond Order



Single Bond ⇐ لازم لما نقيس نستخدم نفس الذرتين H_2 - I_2 - Cl_2

covalent radius: Similar to the ionic length 9.3

Covalent radius of an atom X = half of the covalent bond length of a homonuclear X-X single bond.

If covalent radius of (C = 76 pm) & (Cl = 102 pm) → bond length of C-Cl = (76 + 102) = 178 pm

chloromethane, CH_3Cl, 178.4 pm;

tetrachloromethane, CCl_4, 176.6 pm;

Average Bond Lengths of Some Common Single, Double, and Triple Bonds

Bond Type	Bond Length (pm)
C—H	107
C—O	143
C=O	121
C—C	154
C=C	133
C≡C	120
C—N	143
C=N	138
C≡N	116
N—O	136
N=O	122
O—H	96

Bond lengths:

Triple bond < Double Bond < Single Bond

3 Strongest 2 1 Weakest

➢ Trends for atomic radii

Decrease →

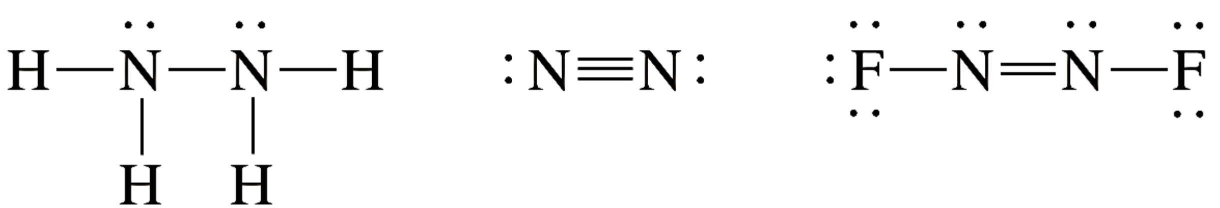
1. Within a period, the covalent radius tends to decrease with increasing atomic number.
2. Within a group, the covalent radius tends to increase with period number.

↑ Decrease

Example 9.12

(Q) Consider the molecules N_2H_4, N_2, and N_2F_2 → Draw Lewis Structure

Which molecule has the shortest nitrogen–nitrogen bond? Which has the longest nitrogen–nitrogen bond?



N_2H_4	N_2	N_2F_2
Longest	Shortest	

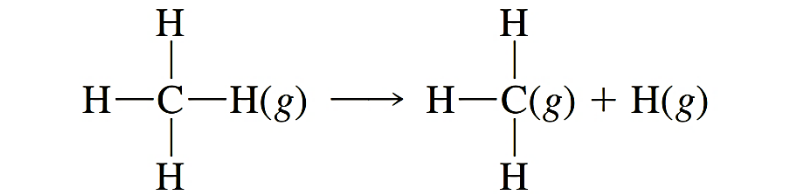
Exercise 9.16 Estimate the O—H bond length in H_2O from the covalent radii listed in Table 9.4.	See Problems 9.79, 9.80, 9.81, and 9.82.

H = 31 / O = 66 ⟶ H – O = 97

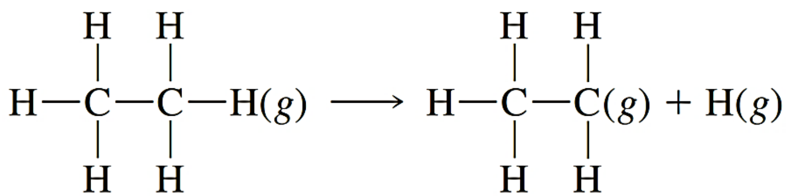
TABLE 9.4 (Text book) page 300

9.11 Bond Enthalpy (BE)

"bond enthalpy" and "bond energy" are often used interchangeably



$\Delta H = 435\ \text{kJ}$



$\Delta H = 410\ \text{kJ}$

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

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

✓ Because it takes energy to break a bond, bond enthalpies are always positive numbers.

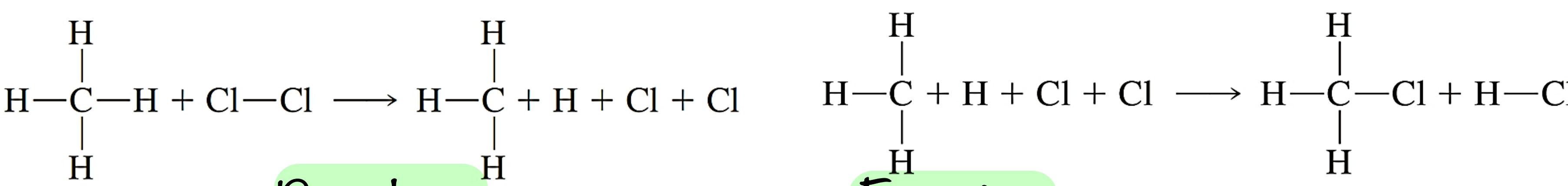
✓ Bond enthalpy is a measure of the strength of a bond: the larger the bond enthalpy, the stronger the chemical bond

(Q) Use bond enthalpies to estimate the enthalpy change for the following reaction:

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

Given that bond enthalpies (kJ/mol) for:

(C-H) = 413, (Cl-Cl) = 242, (C-Cl) = 328, (H-Cl) = 431,



Breaking Endothermic

Forming Exothermic

$$\Delta H \simeq BE(C{-}H) + BE(Cl{-}Cl) - BE(C{-}Cl) - BE(H{-}Cl)$$

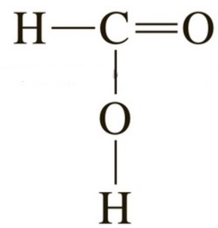
$$= (413 + 242 - 328 - 431)\ \text{kJ}$$

$$= -104\ \text{kJ}$$

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

Forming	= (−)
Breaking	= (+)

Exercise 9.17 Formic acid, isolated in 1670, is the irritant in ant bites. The structure of formic acid is



One of the carbon–oxygen bonds has a length of 136 pm; the other is 123 pm long. What is the length of the C=O bond in formic acid?

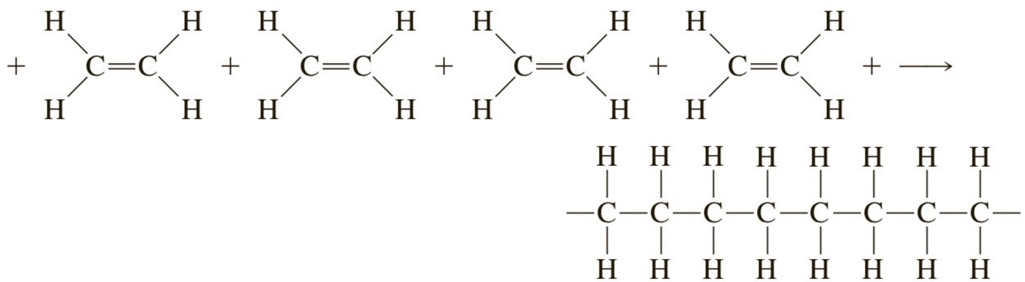
See Problems 9.83 and 9.84.

123 Pm →

The double bond is Shorter than the Single bond.

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 enthalpies.



Problem Strategy Break bonds in the reactants, and then form new bonds to give the products. The approximate enthalpy change equals the sum of the bond enthalpies for the bonds broken minus the sum of the bond enthalpies for the bonds formed.

Solution Imagine the reaction to involve the breaking of the carbon–carbon double bonds and the formation of carbon–carbon single bonds. For a very long chain, the net result is that for every C=C bond broken, two C—C bonds are formed.

$$\Delta H \simeq 614 - (2 \times 348) = \mathbf{-82\ kJ}$$

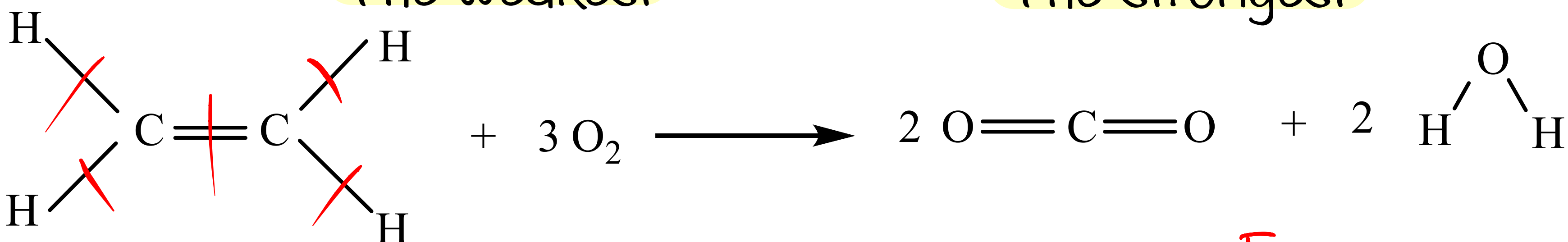
Exercise 9.18 Use bond enthalpies to estimate the enthalpy change for the combustion of ethylene, C_2H_4, according to the equation

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

Given that bond enthalpies (kJ/mol) for:

(C=C) = 614, (C-H) = 413, (O=O) =498, (C=O) = 804, (O-H) = 463

The weakest The strongest



Breaking Forming

ΔH = {[614 + (4 × 413) + (3 × 498)] − [(4 × 804) + (4 × 463)]} kJ
= −1308 kJ Endothermic

of several Lewis formulas gives the best description of a molecule or ion.

Bond lengths can be estimated from the *covalent radii* of atoms. Bond length depends on *bond order;* as the bond order increases, the bond length decreases. The A—B *bond enthalpy* is the average enthalpy change when an A—B bond is broken. You can use bond enthalpies to estimate ΔH for gas-phase reactions.

Learning Objectives	Important Terms
9.1 Describing Ionic Bonds	
▪ Define *ionic bond.* ▪ Explain the *Lewis electron-dot symbol* of an atom. ▪ Use Lewis symbols to represent ionic bond formation. **Example 9.1** ▪ Describe the energetics of ionic bonding. ▪ Define *lattice energy.* ▪ Describe the Born–Haber cycle to obtain a lattice energy from thermodynamic data. ▪ Describe some general properties of ionic substances.	**ionic bond** **Lewis electron-dot symbol** **Coulomb's law** **lattice energy**
9.2 Electron Configurations of Ions	
▪ State the three categories of monatomic ions of the main-group elements. ▪ Write the electron configuration and Lewis symbol for a main-group ion. **Example 9.2** ▪ Note the polyatomic ions given earlier in Table 2.5. ▪ Note the formation of 2+ and 3+ transition-metal ions. ▪ Write electron configurations of transition-metal ions. **Example 9.3**	
9.3 Ionic Radii	
▪ Define *ionic radius.* ▪ Define *isoelectronic ions.* ▪ Use periodic trends to obtain relative ionic radii. **Example 9.4**	**ionic radius** **isoelectronic**
9.4 Describing Covalent Bonds	
▪ Describe the formation of a covalent bond between two atoms. ▪ Define *Lewis electron-dot formula.* ▪ Define *bonding pair* and *lone (nonbonding) pair* of electrons. ▪ Define *coordinate covalent bond.* ▪ State the octet rule. ▪ Define *single bond, double bond,* and *triple bond.*	**covalent bond** **Lewis electron-dot formula** **bonding pair** **lone (nonbonding) pair** **coordinate covalent bond** **octet rule** **single bond** **double bond** **triple bond**
9.5 Polar Covalent Bonds; Electronegativity	
▪ Define *polar covalent bond.* ▪ Define *electronegativity.* ▪ State the general periodic trends in electronegativities. ▪ Use electronegativity to obtain relative bond polarity. **Example 9.5**	**polar covalent bond** **electronegativity**
9.6 Writing Lewis Electron-Dot Formulas	
▪ Write Lewis formulas with single bonds only. **Example 9.6** ▪ Write Lewis formulas having multiple bonds. **Example 9.7** ▪ Write Lewis formulas for ionic species. **Example 9.8**	

9.7 Delocalized Bonding; Resonance	
■ Define *delocalized bonding.* ■ Define *resonance description.* ■ Write resonance formulas. **Example 9.9**	**delocalized bonding** **resonance description**
9.8 Exceptions to the Octet Rule	
■ Write Lewis formulas (exceptions to the octet rule). **Example 9.10** ■ Note exceptions to the octet rule in Group 2A and Group 3A elements.	
9.9 Formal Charge and Lewis Formulas	
■ Define *formal charge.* ■ State the rules for obtaining formal charge. ■ State two rules useful in writing Lewis formulas. ■ Use formal charges to determine the best Lewis formula. **Example 9.11**	**formal charge**
9.10 Bond Length and Bond Order	
■ Define *bond length* (*bond distance*). ■ Define *covalent radii.* ■ Define *bond order*. ■ Explain how bond order and bond length are related. **Example 9.12**	**bond length (bond distance)** **covalent radii** **bond order**
9.11 Bond Enthalpy	
■ Define *bond enthalpy.* ■ Estimate ΔH from bond enthalpies. **Example 9.13**	**bond enthalpy**

Done by: Joud Jaber