

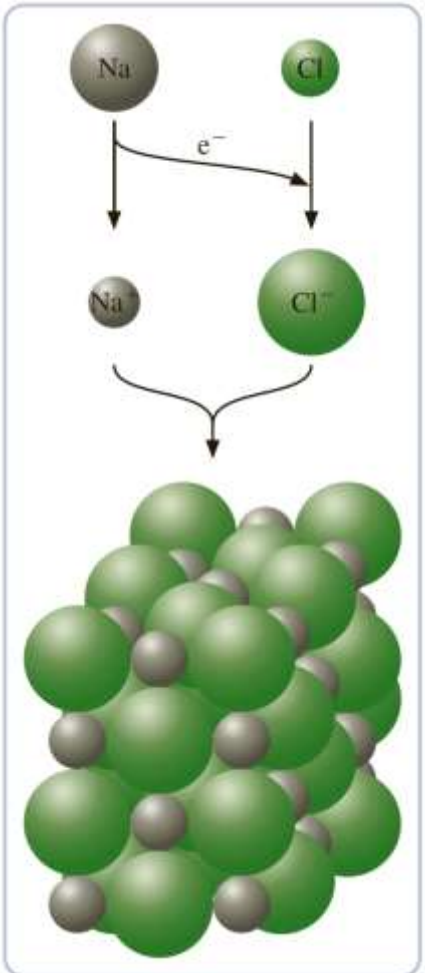
EBBING - GAMMON

General
Chemistry
ELEVENTH EDITION

Ionic and Covalent Bonding

➤ 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.



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

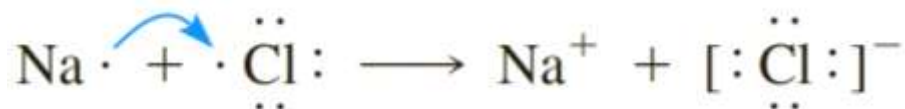
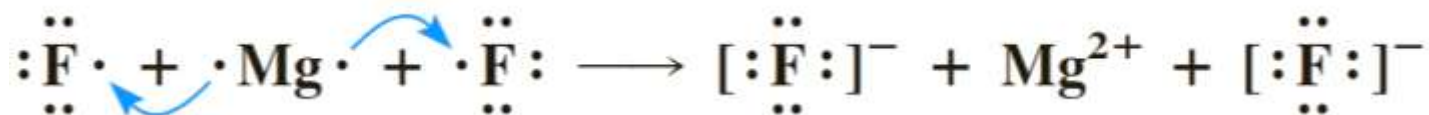


Table 9.1 Lewis Electron-Dot Symbols for Atoms of the Second and Third Periods

	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



➤ Energy Involved in Ionic Bonding

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



✓ The overall energy is $(496 - 349) = + 147 \text{ kJ/mol}$

→ 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.

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

Coulomb's law
$$E = \frac{kQ_1Q_2}{r}$$

Coulomb's law states that *the potential energy obtained in bringing two charges Q_1 and Q_2 , 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.*

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

$$k = 8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$$

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

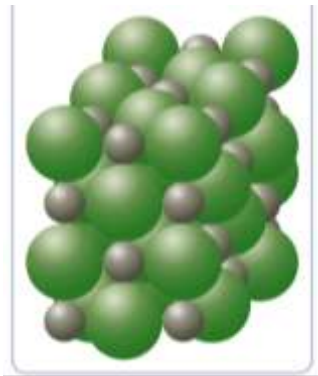
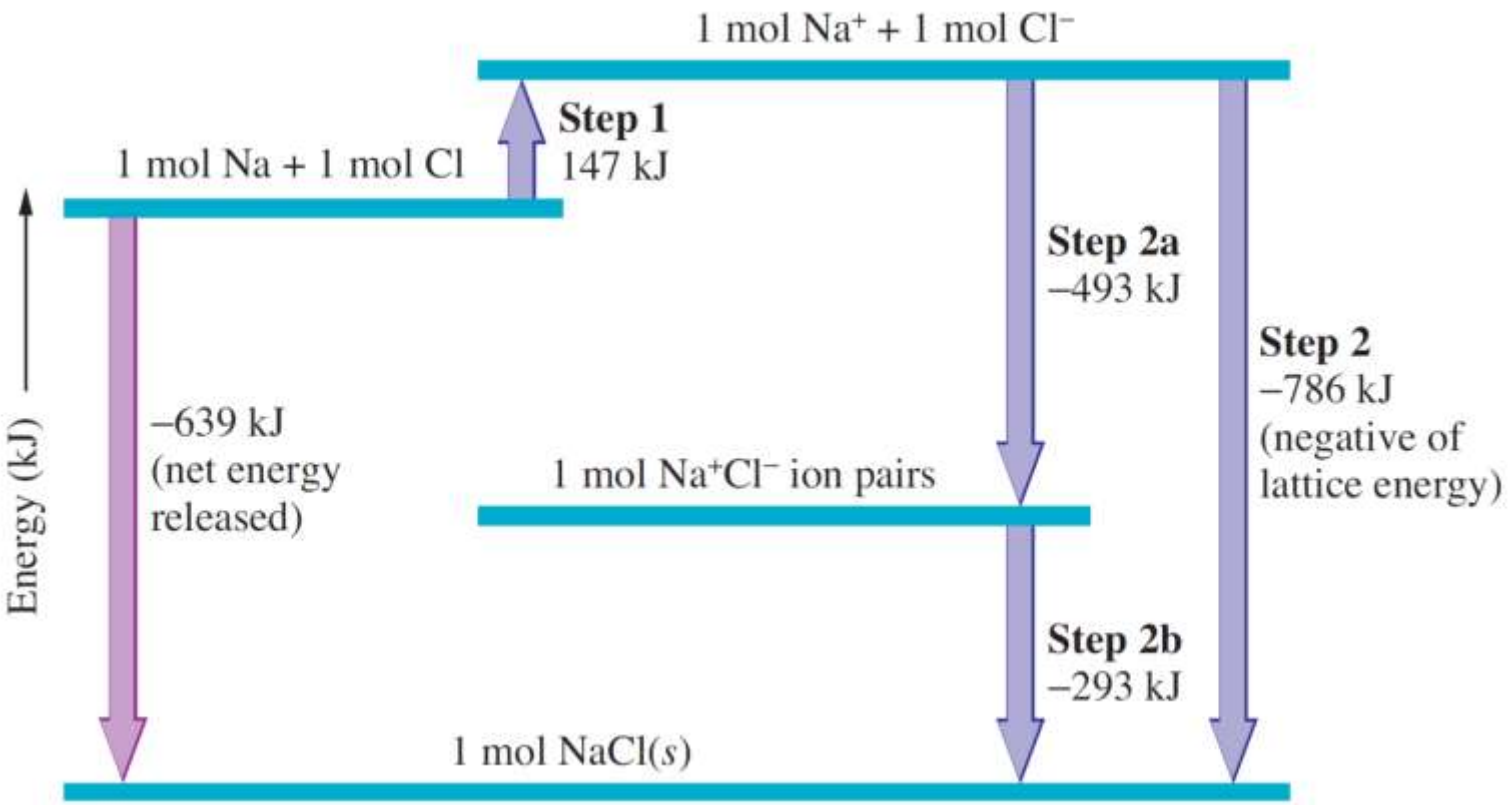
$$e = 1.602 \times 10^{-19} \text{ C}$$

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

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

-
- ✓ The minus sign means energy is **released**
 - ✓ This energy is for the formation of **one ion pair**
 - ✓ Multiplying by Avogadro's number, $6.02 \times 10^{23} \rightarrow -493 \text{ kJ/mol}$

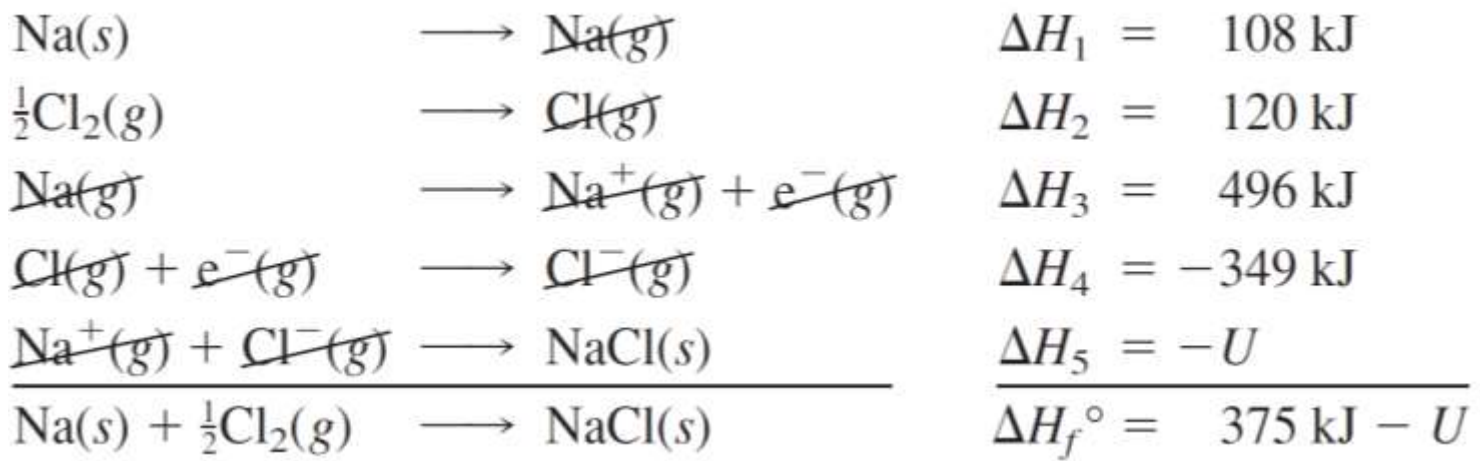
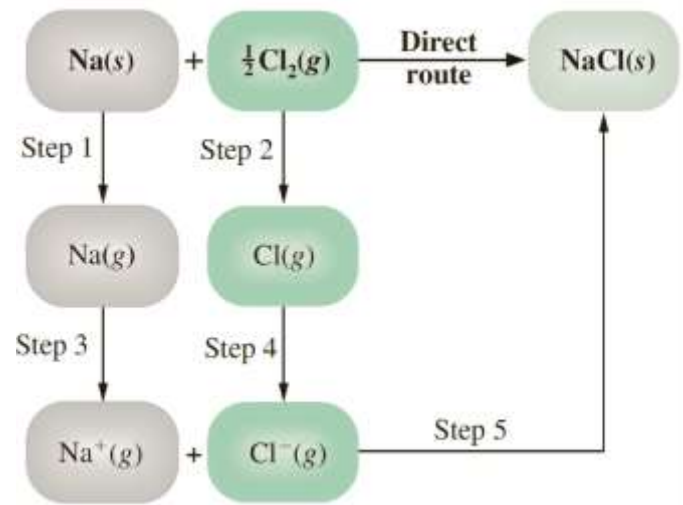
- ✓ The **lattice energy** is *the change in energy that occurs (required) when an ionic solid is separated into isolated ions in the gas phase.*
- ✓ For sodium chloride, the process is: $\text{NaCl}(s) \longrightarrow \text{Na}^+(g) + \text{Cl}^-(g)$



- ✓ 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)

- 1- Sublimation of sodium
2. Dissociation of chlorine
3. Ionization of sodium
4. Formation of chloride ion (E.A.)
5. Formation of NaCl(s) from ions



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

enthalpy of formation determined calorimetrically $\rightarrow -411 \text{ kJ}$

$$375 \text{ kJ} - U = -411 \text{ kJ} \quad \rightarrow \quad U = (375 + 411) \text{ kJ} =$$

➤ Properties of Ionic Substances

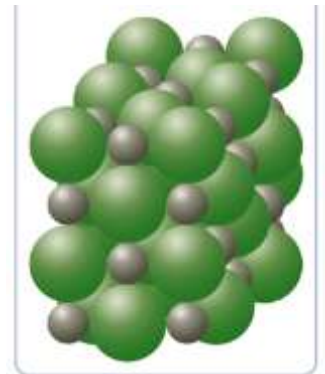
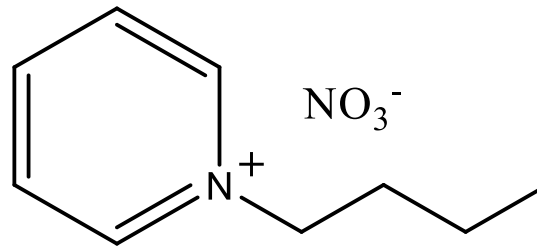
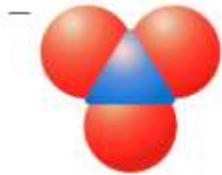
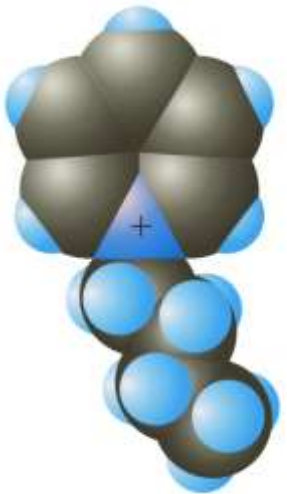
- ✓ Strong ionic bonds (strong electrostatic interaction)
→ high-melting points of ionic solids.

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

charges (Mg²⁺ and O²⁻), charges (Na⁺ and Cl⁻),

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

- ✓ 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 the cations are large and non-spherical → weak ionic bonding



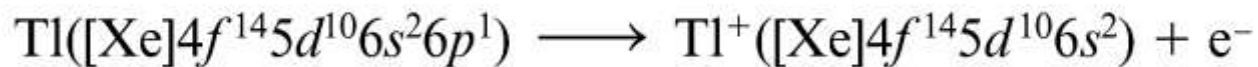
9.2 Electron Configurations of Ions

➤ Ions of the Main-Group Elements

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

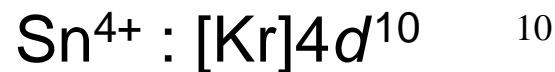
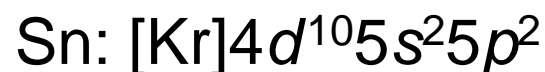
Element	Successive Ionization Energies			
	First	Second	Third	Fourth
Na	496	4,562	6,910	9,543
Mg	738	1,451	7,733	10,542
Al	578	1,817	2,745	11,577

- ✓ 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. **e.g : Na²⁺, Mg³⁺, Al⁴⁺ (Doesn't exist)**
- ✓ Boron (Group 3A) doesn't form ionic compounds with B³⁺ 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



- ✓ 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 ($2s^2 2p^3$) = 0 N^{3-} ion ($2s^2 2p^6$) is stable in the presence of Li^+ (Li_3N) and other alkaline earth elements ions (Mg_3N_2).

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



➤ Transition-Metal Ions

✓ M^{2+} is a common oxidation state as two electrons are removed from the outer **ns** shell. Fe: [Ar] 4s² 3d⁶

Fe²⁺ : [Ar] 3d⁶ loses 4s electrons first

Fe³⁺ : [Ar] 3d⁵ then loses 3d electrons

(Q) What are the correct electron configurations for Cu & Cu²⁺ ?

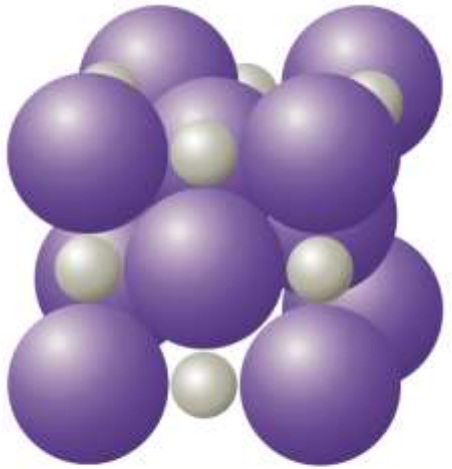
- A. [Ar] 4s²3d⁹, [Ar] 3d⁹
- B. [Ar] 3d¹⁰4s¹, [Ar] 4s¹3d⁸
- C. [Ar] 3d¹⁰4s¹, [Ar] 3d⁹
- D. [Ar] 4s²3d⁹, [Ar] 3d¹⁰4s¹
- E. [K] 4s²3d⁹, [Ar] 3d⁹

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

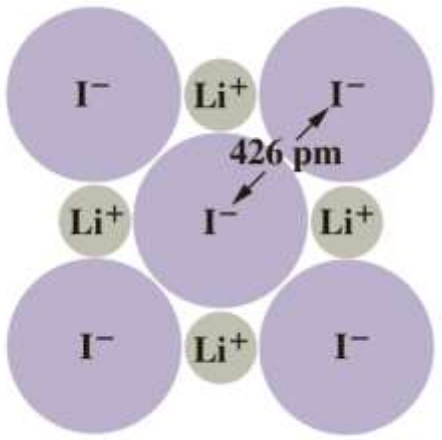
- A. [Kr] 5d² [Kr] 4d¹
- B. [Ar] 4d² [Ar] 5s²
- C. [Kr] 5s²4d² [Kr]
- D. [Kr] 5s² 4d⁶ [Kr] 4d⁶
- E. [Kr] 4d² [Kr]

➤ 9.3 Ionic Radii

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



a A three-dimensional view of the crystal.







Ionic radius of I^-
 $= 426 / 2 = 213 \text{ pm}$

Exercise 9.6

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

$$Mg^{2+} < Ca^{2+} < Sr^{2+}$$

 Na [He] $2s^2 2p^6 3s^1$	 Na^+ [He] $2s^2 2p^6$
 Cl [Ne] $3s^2 3p^5$	 Cl^- [Ne] $3s^2 3p^6$

✓ 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		

1 IA																				18 VIIIA
1 H Hydrogen 1.008	2 IIA																	2 He Helium 4.002602		
3 Li Lithium 6.94	4 Be Beryllium 9.0121831											5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998403163	10 Ne Neon 20.1797			
11 Na Sodium 22.98976928	12 Mg Magnesium 24.305	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 Al Aluminium 26.9815385	14 Si Silicon 28.0855	15 P Phosphorus 30.973761998	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948			
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955908	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938044	26 Fe Iron 55.845	27 Co Cobalt 58.933194	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.921595	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798			
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90584	40 Zr Zirconium 91.224	41 Nb Niobium 92.90637	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293			

➤ Pattern across a period

Cation	Na ⁺	Mg ²⁺	Al ³⁺	Anion	S ²⁻	Cl ⁻
Radius (pm)	95	> 65	> 50	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

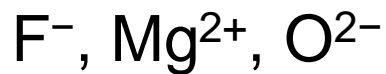
9.47 Arrange the following in order of increasing ionic radius:



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

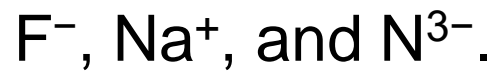
1A										18									
H										He									
Hydrogen										Helium									
1.008										4.002602									
2		3		4		5		6		7		8		9		10			
IIA		IIIB		IVB		VB		VIB		VIIB		VIII		IIB		IIIA			
Li		Be		B		C		N		O		F		Ne					
Lithium		Beryllium		Boron		Carbon		Nitrogen		Oxygen		Fluorine		Neon					
6.94		9.0121831		10.81		12.011		14.007		15.999		18.998403163		20.1797					
11		12		13		14		15		16		17		18					
Na		Mg		Al		Si		P		S		Cl		Ar					
Sodium		Magnesium		Aluminium		Silicon		Phosphorus		Sulfur		Chlorine		Argon					
22.98976928		24.305		26.9815385		28.085		30.973761998		32.06		35.45		39.948					
19		20		21		22		23		24		25		26		27			
K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co			
Potassium		Calcium		Scandium		Titanium		Vanadium		Chromium		Manganese		Iron		Cobalt			
39.0983		40.078		44.955908		47.867		50.9415		51.9961		54.938044		55.845		58.933194			
37		38		39		40		41		42		43		44		45			
Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh			
Rubidium		Strontium		Yttrium		Zirconium		Niobium		Molybdenum		Technetium		Ruthenium		Rhodium			
85.4678		87.62		88.90584		91.224		92.90637		95.95		(98)		101.07		102.90550			
46		47		48		49		50		51		52		53		54			
Pd		Ag		Cd		In		Sn		Sb		Te		I ¹⁴		Xe			
Palladium		Silver		Cadmium		Indium		Tin		Antimony		Tellurium		Iodine		Xenon			
106.42		107.8682		112.414		114.818		118.710		121.760		127.60		126.90447		131.293			

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



isoelectronic series $\rightarrow Mg^{2+}$ ($Z=12$) $\leftarrow F^-$ ($Z=9$) $\leftarrow O^{2-}$ ($Z=8$)

9.49 Arrange the following in order of increasing ionic radius:



isoelectronic series $\rightarrow Na^+$ ($Z=11$) $\leftarrow F^-$ ($Z=9$) $\leftarrow N^{3-}$ ($Z=7$)

9.48 Which has the larger radius, N^{3-} or P^{3-} ? **P^{3-}**
 NOT isoelectronic

1 IA												18 VIIIA					
1 H Hydrogen 1.008											2 He Helium 4.002602						
3 Li Lithium 6.94	4 Be Beryllium 9.0121831											5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998403163	10 Ne Neon 20.1797
11 Na Sodium 22.98976928	12 Mg Magnesium 24.305											13 Al Aluminium 26.9815385	14 Si Silicon 28.085	15 P Phosphorus 30.973761998	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955908	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938044	26 Fe Iron 55.845	27 Co Cobalt 58.933194	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.921595	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90584	40 Zr Zirconium 91.224	41 Nb Niobium 92.90637	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293

➤ Covalent Bonds

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

9.4 Describing Covalent Bonds

✓ The distance between nuclei at minimum energy is called the *bond length* of H₂.

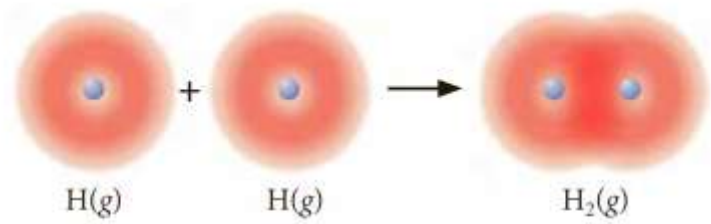


Figure 9.10 ▲
The electron probability distribution for the H₂ molecule
The electron density (shown in red) occupies the space around both atoms.

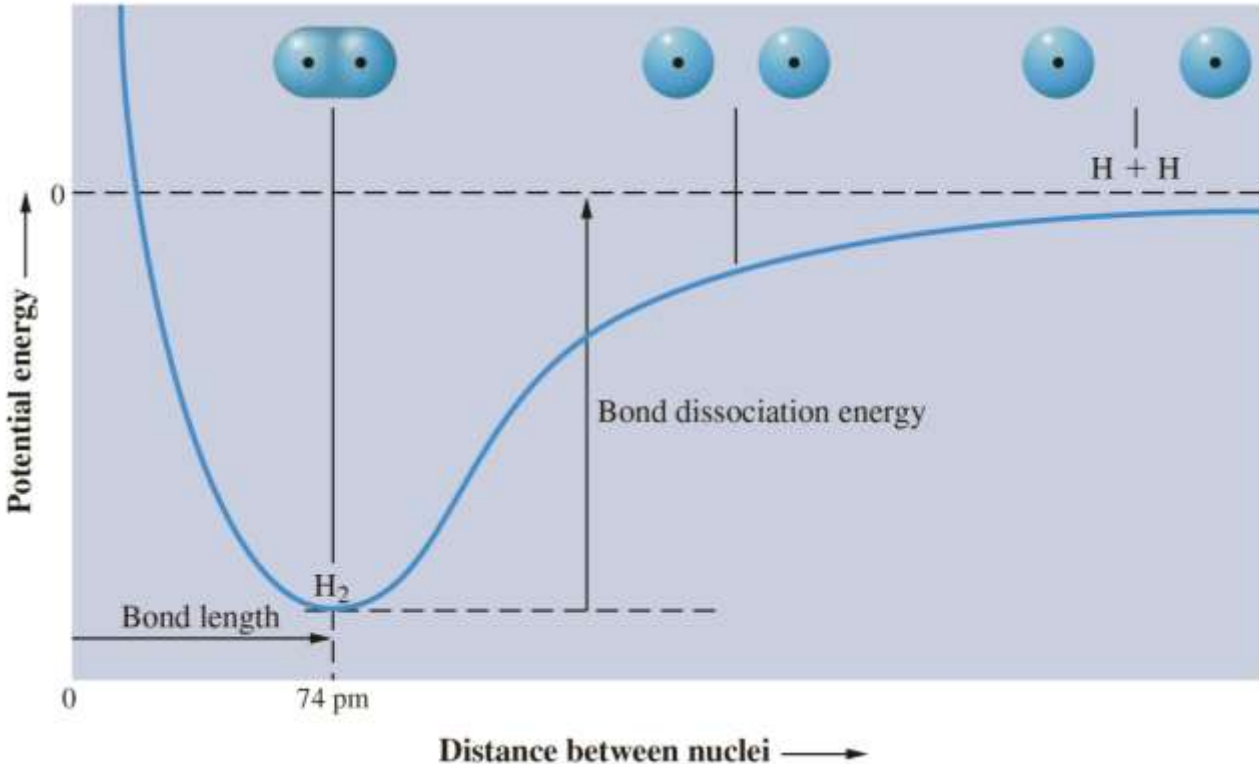
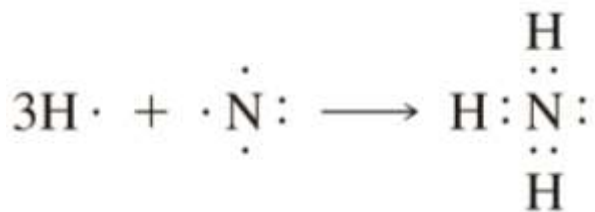
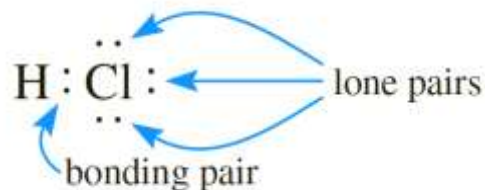
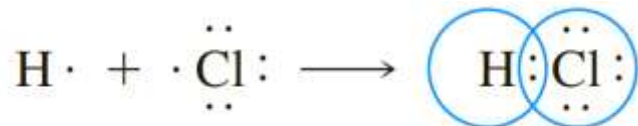
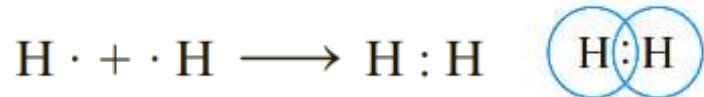


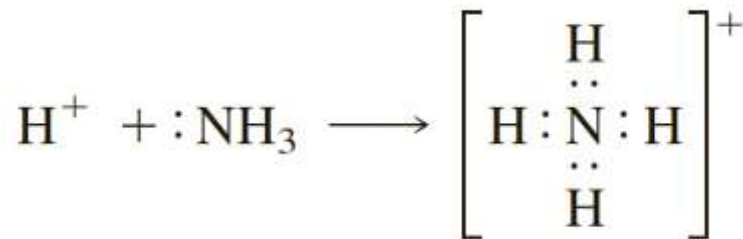
Figure 9.11 ◀
Potential-energy curve for H₂ The stable molecule occurs at the bond distance corresponding to the minimum in the potential-energy curve.

➤ Lewis Formulas



➤ Coordinate Covalent Bonds

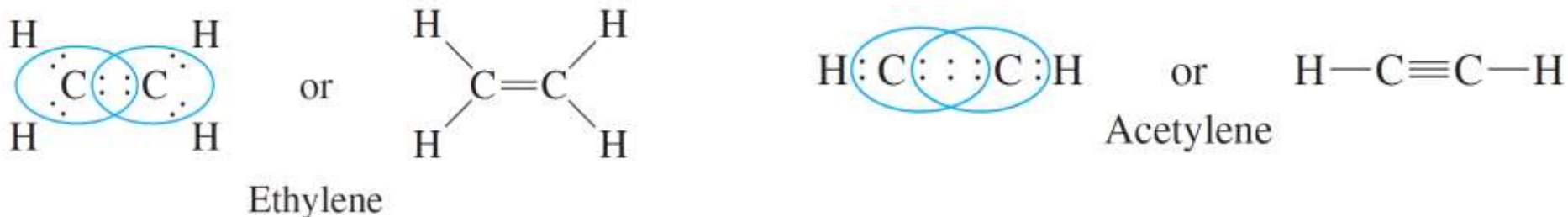
✓ is a bond formed when both electrons of the bond are donated by one atom



➤ Octet Rule

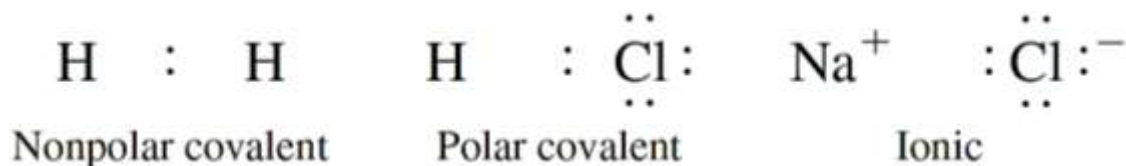
- ✓ *The tendency of atoms in molecules to have eight electrons in their valence shells (two for hydrogen atoms)*

➤ Multiple Bonds

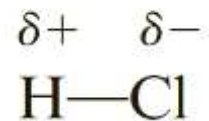
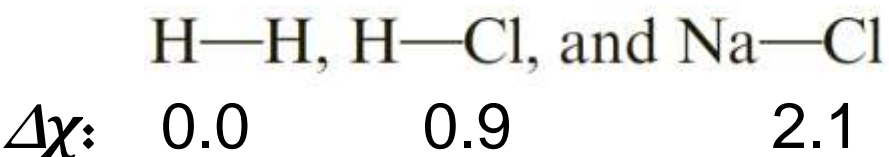


9.5 Polar Covalent Bonds (Polar Bonds)

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



- **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.*
- ✓ 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



Polar molecule

➤ Writing Lewis Electron-Dot Formulas

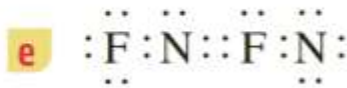
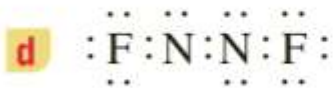
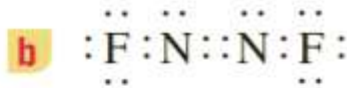
These will be done in class:

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^- .



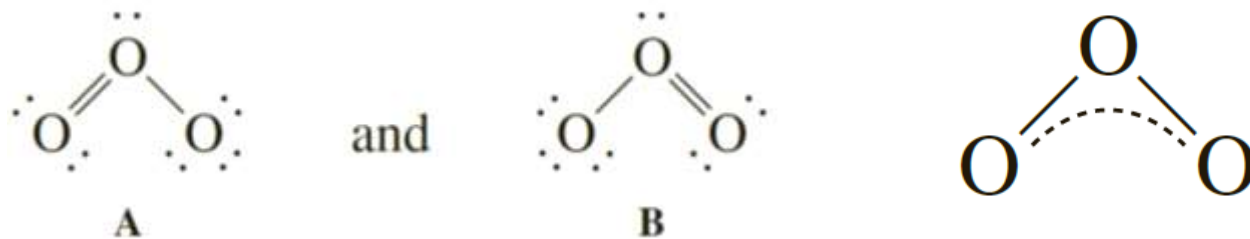
CONCEPT CHECK 9.2

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?



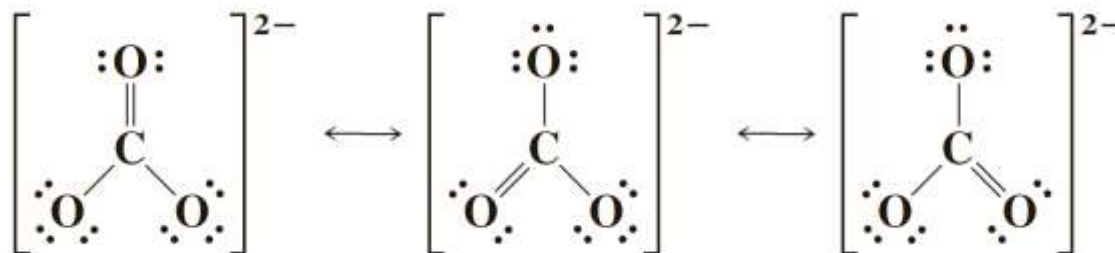
9.7 Delocalized Bonding: Resonance

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**

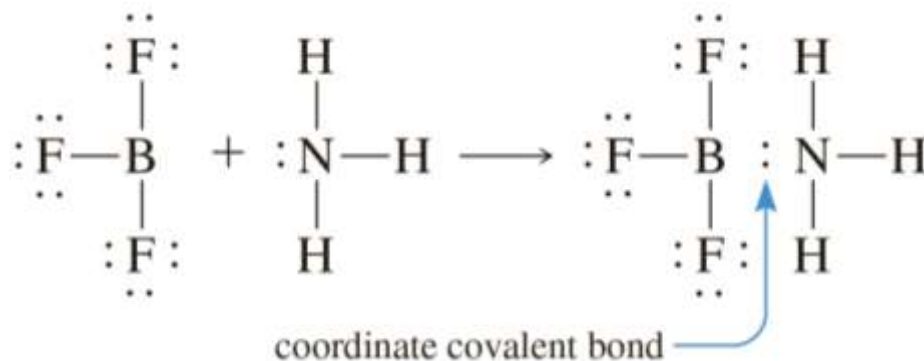
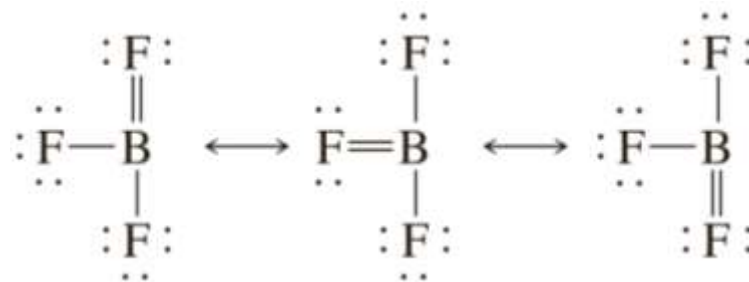
CO_3^{2-}



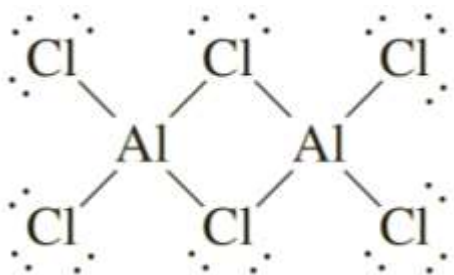
NO_3^-

9.8 Exceptions to the Octet Rule

These will be done in class:



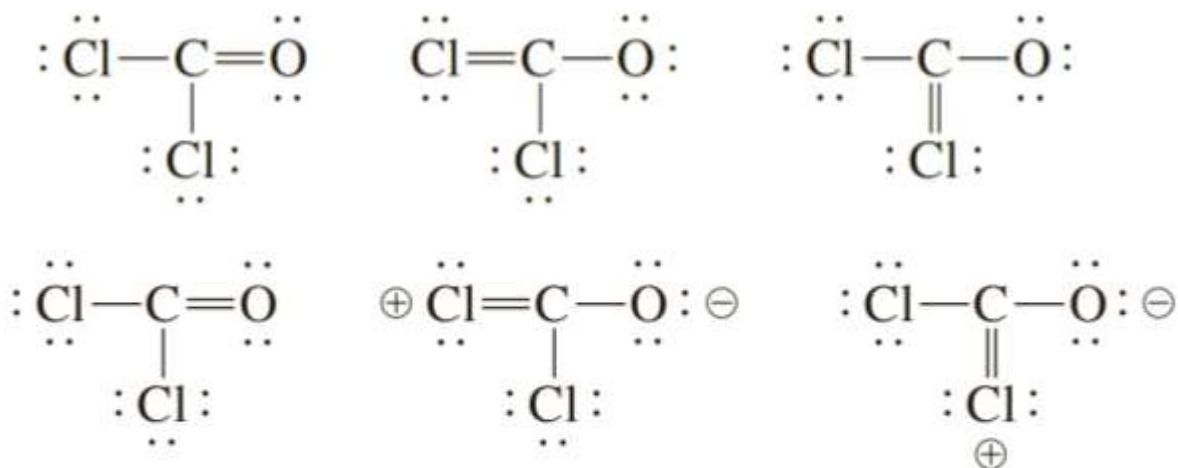
AlCl_3 @ RT & at melting point (very low 192°C)



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

9.9 Formal Charge and Lewis Formulas

COCl₂



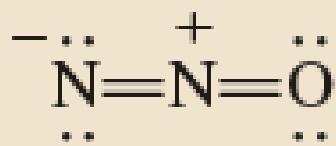
RULE A Whenever you can write several Lewis formulas for a molecule, choose the one having the lowest magnitudes of formal charges.

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.

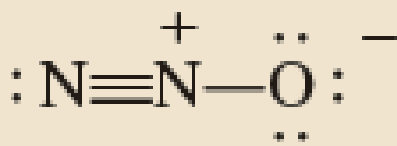
RULE C When possible, choose Lewis formulas that do not have like charges on adjacent atoms.

(Q) Write the Lewis formula that best describes the charge distribution in the sulfuric acid molecule, H₂SO₄, according to the rules of formal charge. (HNO₃, H₃PO₄, HCN)

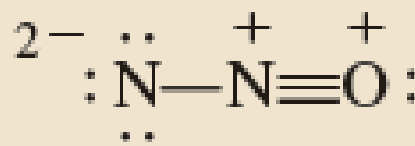
(Q) Draw three resonance structures for the molecule nitrous oxide, N_2O (the atomic arrangement is NNO)



(a)



(b)

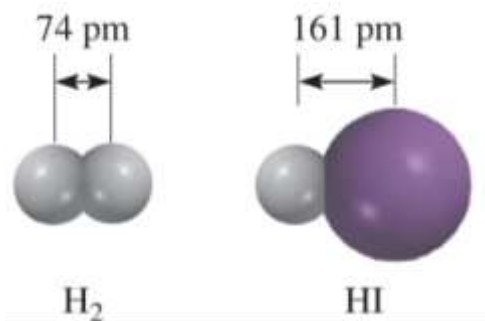


(c)

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



covalent radius:

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, CH₃Cl, 178.4 pm;

tetrachloromethane, CCl₄, 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

2

1

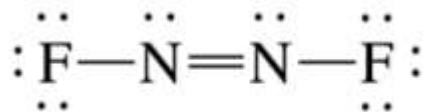
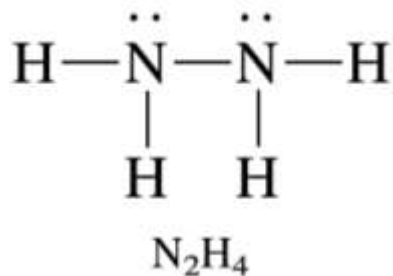
➤ Trends for atomic radii

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.

(Q) Consider the molecules N_2H_4 , N_2 , and N_2F_2 .

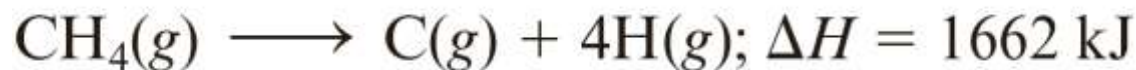
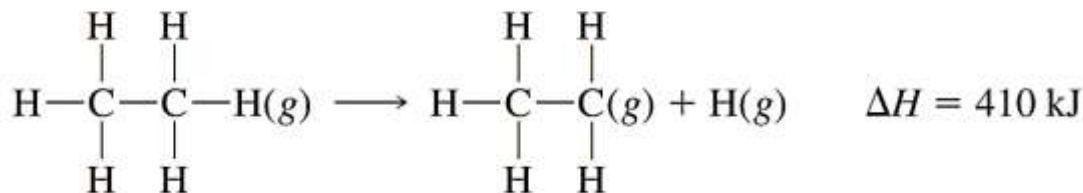
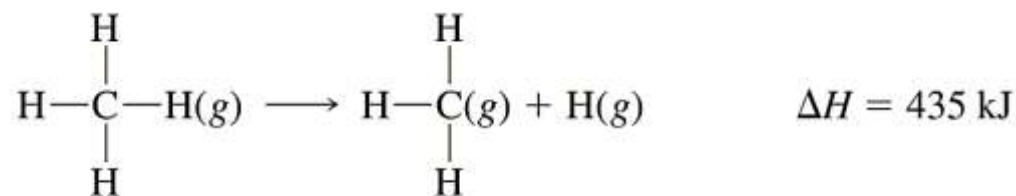
Which molecule has the shortest nitrogen–nitrogen bond?

Which has the longest nitrogen–nitrogen bond?



9.11 Bond Enthalpy (BE)

“bond enthalpy” and “bond energy” are often used interchangeably



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

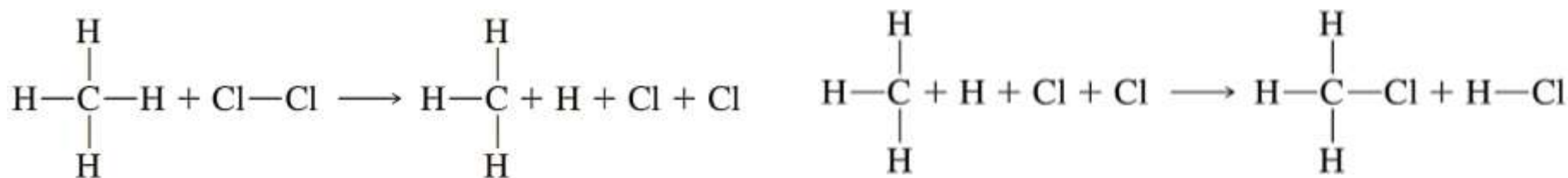
- ✓ Because it takes energy to break a bond, bond enthalpies are always positive numbers.
- ✓ Bond enthalpy is a measure of the strength of a bond: the larger the bond enthalpy, the stronger the chemical bond

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



Given that bond enthalpies (kJ/mol) for:

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



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$$\begin{aligned} \Delta H &\approx BE(\text{C}-\text{H}) + BE(\text{Cl}-\text{Cl}) - BE(\text{C}-\text{Cl}) - BE(\text{H}-\text{Cl}) \\ &= (413 + 242 - 328 - 431) \text{ kJ} \\ &= -104 \text{ kJ} \end{aligned}$$

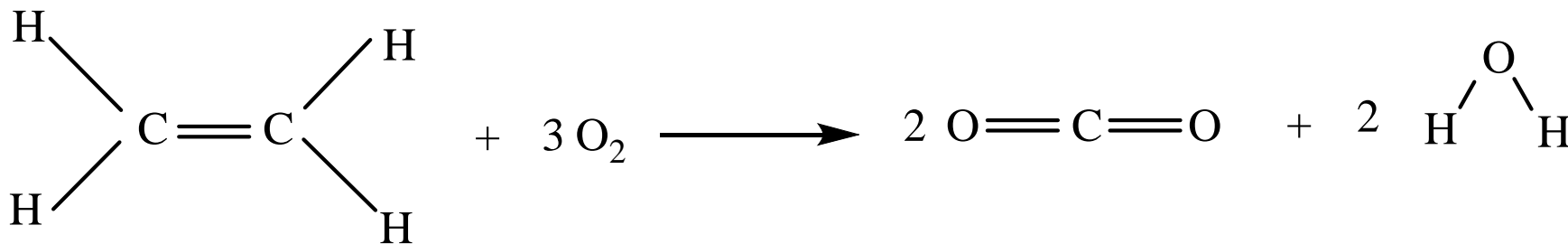
In general, the enthalpy of reaction is (approximately) equal to the sum of the bond enthalpies for bonds broken minus the sum of the bond enthalpies for bonds formed.

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



Given that bond enthalpies (kJ/mol) for:

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



$$\Delta H = \{[614 + (4 \times 413) + (3 \times 498)] - [(4 \times 804) + (4 \times 463)]\} \text{ kJ}$$
$$= -1308 \text{ kJ}$$