CHEMICAL BONDING

• Chemical bonds are strong attractive force that exist between the atoms of a substance. Chemical bonds are commonly classified into 3 types:

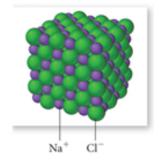
> Lowest potential energy (most stable)

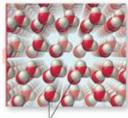
Ionic Bonding

- Ionic bonds form between metals and nonmetals.
- Ionic bonds form by transfer of electrons (metals have low IEs and nonmetals have negative EAs).
- Ionic bonds are formed by the electrostatic attraction of cation and anion, lowering their overall potential energy (Coulomb's law).

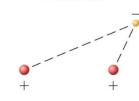
Covalent Bonding

- Covalent bonds form between two nonmetals.
- Covalent bonds form by sharing of electrons (nonmetals have high IEs).
- The shared electrons interact with nuclei of both of the bonding atoms, lower their potential energy (Coulomb's law).



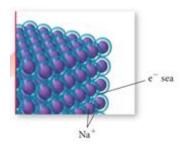


H2O molecules



Metallic Bonding

- Metallic bonds form between metallic ions
- Bonds are formed through "non-localized" pooling of electrons commonly referred to as "sea of electrons".



LEWIS STRUCTURES

- The valence electrons in an atom are the electrons in the outer most principal shell. Since these are the most important electrons in bonding, they are most focused upon.
- *Lewis structures* use Lewis symbols to show *valence electrons* of main-group elements as dots surrounding the symbol of the atom.
- For example, the electron configuration and Lewis structure of oxygen are shown below:



• The Lewis structures for all main-group elements in the first 3 periods are shown below:

1A							8A
H·	2A	3A	4A	5A	6A	7A	He
Li	∙Be∙	۰ġ۰	۰Ċ٠	٠ÿ٠	:ö∙	÷Ë·	:Ņe:
Na·	·Mg·	·Àl·	·Śi∙	.ÿ.	÷ÿ∙	∶Ċŀ	:Är:

Lewis symbols for the first 3 periods of Main-Group Elements

- Lewis symbols provide a simple way to visualize the number of valence electrons in a maingroup element. Note that the elements with eight valence electrons are particularly stable because they have a full outer shell.
- The tendency of atoms in bonding to gain eight electrons in their outer shell and become stable is called the *octet rule*. Helium is an exception to this rule, since it only has two electrons in its outer level (*duet*).

LEWIS STRUCTURES FOR IONIC COMPOUNDS

- *Ionic bonds* are formed by transfer of electrons from a metal to a non-metal. Therefore, the Lewis structure for these compounds is drawn by moving the electrons from metal to non-metal.
- For example, the Lewis structure for potassium chloride is written as shown below:

$$K \cdot : \dot{C} : \longrightarrow K^+ : \dot{C} : \longrightarrow K^+$$

Note that:

The transfer of electron gives chlorine an octet and leaves potassium with an octet from the previous principal shell, which is now the valence shell.

K
$$1s^22s^22p^63s^23p^64s^1$$

K⁺ $1s^22s^22p^63s^23p^64s^0$
Octet in previous level

- Potassium becomes positively charged because it loses an electron and chlorine becomes negatively charged because it gains an electron.
- The Lewis structure of the anion is usually written within brackets with the charge written outside the brackets. The positive and negative charges attract one another, forming the ionic bond in KCl.
- Lewis structures can be used to predict the correct formula for ionic compounds. Examples below show how these formulas can be predicted.

Examples:

Use Lewis symbols to predict the formula for the compound that forms between each pair of elements:

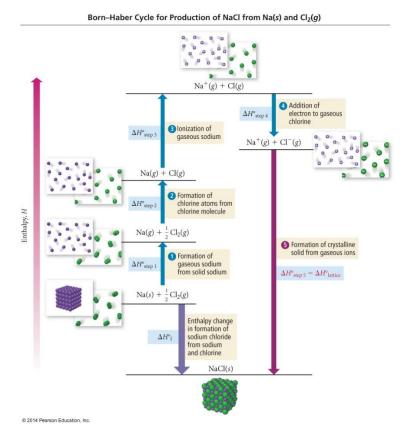
- 1. Calcium and chlorine
- 2. Aluminum and oxygen

LATTICE ENERGY

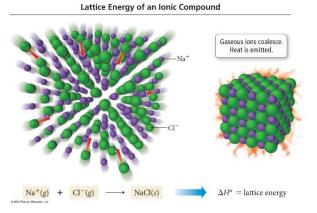
• The formation of an ionic compound from its constituent elements is usually very exothermic. For example, formation of NaCl from sodium and chlorine is shown below:

Na (s) + $\frac{1}{2}$ Cl₂ (g) \rightarrow NaCl (s)

- Where does this energy come from? The transfer of electron from sodium to chlorine absorbs energy. Recall that the IE₁ for Na is +496 kJ/mol and the EA for Cl is only -349 kJ/mol. Based on these energies, the reaction should be endothermic.
- The answer lies in *lattice energy*—the energy associated with formation of a crystalline lattice from the gaseous ions.
- To better understand the energetics of ionic bond formation, a hypothetical series of steps is created to represent the formation of an ionic compound from its constituent elements (the *Born-Haber cycle*). This cycle for the formation of NaCl is shown below:



 $\Delta H_{\rm f}^{\circ} = -411 \text{ kJ/mol}$



LATTICE ENERGY

• Using the Born-Haber cycle for NaCl, the lattice energy for the formation of NaCl crystals can be summarized as:

 $\Delta H_{f}^{\circ} = \Delta H^{\circ}_{step 1} + \Delta H^{\circ}_{step 2} + \Delta H^{\circ}_{step 3} + \Delta H^{\circ}_{step 4} + \Delta H^{\circ}_{step 5}$ lattice energy

Therefore,

 $\Delta H^{\circ}_{lattice} = -788 \text{ kJ}$

• The value of lattice energy is a large negative number, which more than compensates for the endothermic nature of electron transfer we discussed earlier.

Trends in Lattice Energy:

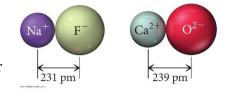
- The lattice energy of crystals are affected by two factors: ion size and ion charge.
- The lattice energy of several alkali metals chlorides are listed below:

Metal Chloride	Lattice Energy kJ/mol
LiCl	-834
NaCl	-788
KCI	-701
CsCl	-657
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- As can be seen, the lattice energy decreases as one moves down a group. This is due to the fact that ionic radius increases as one moves down a group, and as a result the distance between ions (bond length) increases.
- Also consider the lattice energy of the following two compounds:

Compound	Lattice Energy (kJ/mol)
NaF	-910
CaO	-3414

• Note that the lattice energy of CaO is much greater than the lattice energy of NaF. Comparing the bond length of each (239 pm vs. 231 pm), it is clear that the slightly longer bond length in CaO is not the cause of the large difference in their lattice energies.



>241 pm

>276 pm

→ 314 pm

→ 348 pm

Cl

Cl

Cl

• The difference in the lattice energies between CaO and NaF can be attributed to the larger ion charges in Ca²⁺ and O²⁻ compared to Na⁺ and F⁻.

LATTICE ENERGY

- The trends in lattice energy can be summarized as follows:
 - Lattice energies become less exothermic (less negative) with increasing ionic radius.
 - Lattice energies become more exothermic (more negative) with increasing ionic charge.

Examples:

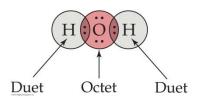
1. Arrange the following ionic compounds in order of increasing magnitude of lattice energy: CaO, KBr, KCl, SrO

2. Arrange the following in order of increasing magnitude of lattice energy: LiBr, KI, CaO

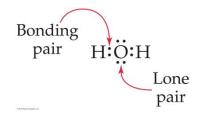
3. Lattice energy of CsF is -744 kJ/mol, whereas that of BaO is -3029 kJ/mol. Explain this large difference.

LEWIS STRUCTURES FOR COVALENT COMPOUNDS

- Lewis model provides a simple and useful model for covalent bonding. Molecular compounds are represented with Lewis structures, where neighboring atoms share some (or all) of their valence electrons to attain the octets (or duets for H).
- For example, the Lewis structure for water (H₂O) is shown below:



• The electrons that are shared between the atoms are called *bonding pair* electrons, while those that are only on one atom are called *lone pair* electrons.



• The bonding pair electrons can often represented as dash lines, to emphasize that they are chemical bonds, but the lone pair electrons are always displayed as dots. For example, the Lewis structure of water can also be represented as shown below:

• The Lewis model also explains why halogens are diatomic. Since each Cl atom has only one unpaired electron, 2 chlorine atoms can share the unpaired electron to complete their octet, as shown below:

• The Lewis model also allows atoms to share more than one pair of electrons to achieve octet. For example, when 2 oxygen atoms share only one pair of electrons, they do not achieve octet (diagram on left). However, sharing of 2 pair of electrons (one lone pair and one bonding pair) does achieve octet (diagams on right).

ELECTRONEGATIVITY & BOND POLARITY

- Lewis structures, although useful, have limitations in representing bonding in covalent molecules. One limitation is that representing electrons as dots and bonds as two dots shared between atoms, make them appear as being shared equally.
- For example, the two shared electrons in HF molecule are not shared equally and laboratory observations have shown that the H side of molecule possesses a slightly positive charge while the F side of the molecule possesses a slightly negative charge. This partial separation of the charges in H–F molecule can be shown as:

$$\stackrel{+\longrightarrow}{H-F}$$
 or $\stackrel{\delta^+}{H-F}$

- Note that the charges depicted on H and F are partial (represented by δ) and therefore the bond is not ionic. However, due to the charge separation, the bond is said to be polar and is classified as *polar covalent bond*.
- The ability of an element to attract electrons to itself in a chemical bond (which results in polar and ionic bonds) is called electronegativity.
- Electronegativity was quantified by Linus Pauling by comparing the bond energies of a heteronuclear diatomic molecule (such as HF) with bond energies of its homonuclear counterparts (such as H₂ and F₂). Through such comparisons, electronegativity values were assigned to elements as shown in table below:

Н 2.20																	He n.a.
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	0 3.44	F 3.98	Ne
Na	Mg											Al	Si	P	S	C1	n.a. Ar
0.93	1.31											1.61	1.90	2.19	2.58	3.16	n.a.
к	Ca	Sc	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.82	1.00	1.36	1.54	1.63	1.66	1.55	1.83	1.88	1.91	1.90	1.65	1.81	2.01	2.18	2.55	2.96	3.00
Rb	Sr	Y	Zr	Nb	Mo	Τc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Хе
0.82	0.95	1.22	1.33	1.60	2.16	1.90	2.20	2.28	2.20	1.93	1.69	1.78	1.96	2.05	2.10	2.66	2.60
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.79	0.89	1.10	1.30	1.50	2.36	1.90	2.20	2.20	2.28	2.54	2.00	1.62	2.33	2.02	2.00	2.20	n.a.
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	_	Uuq	_	_	_	_
0.70	0.89	1.10	n.a.		n.a.												

ELECTRONEGATIVITY & BOND POLARITY

- The following trends can be summarized for electronegativities of main-group elements:
 - > Electronegativity generally increases across a period in the periodic table.
 - > Electronegativity generally decreases down a group in the periodic table.
 - > Fluorine is the most electronegative element.
 - Francium is the least electronegative element (sometimes called most electropositive)
- The periodic trends in electronegativity are consistent with other periodic trends studied earlier. In general, electronegativity is inversely proportional to atomic size-the larger the atom, the less ability it has to attract electrons to itself in a chemical bond.
- The degree of polarity in a chemical bond depends on the electronegativity difference (Δ EN) between the two bonding atoms. The polarity of a bond is quantified by the size of *its dipole moment* (μ).
- Dipole moment occurs when there is a separation of positive and negative charge in a bond. The greater the electronegativity difference between the atoms forming the bond (Δ EN), the greater the dipole moment. For example:

TABLE 9.2 Dipole Moments of Several Molecules in the Gas Phase				
Molecule	ΔEN	Dipole Moment (D)		
Cl ₂	0	0		
CIF	1.0	0.88		
HF	1.9	1.82		
LiF	3.0	6.33		

• This relationship between electronegativity of atoms and polarity of bonds between them can be summarized as shown below:

The greater the ΔEN for the elements forming the bond



The larger the dipole moment

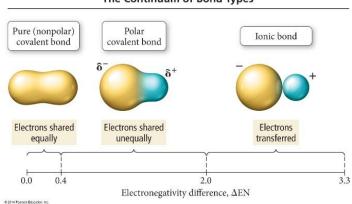


The more polar the bond formed

ELECTRONEGATIVITY AND BOND POLARITY

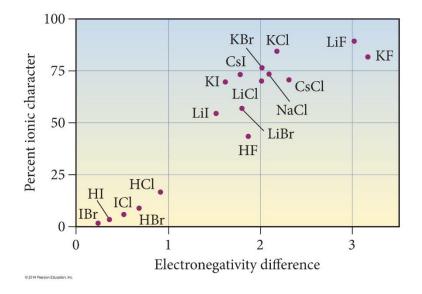
• The bond forming between two atoms can be classified based on the magnitude of the ΔEN . The table below lists the parameters of this classification:

TABLE 9.1 The Effect of Electronegativity Difference on Bond Type				
Electronegativity Difference (Δ EN)	Bond Type	Example		
Small (0-0.4)	Covalent	Cl ₂		
Intermediate (0.4–2.0)	Polar covalent	HCI		
Large (2.0+)	Ionic	NaCl		



The Continuum of Bond Types

- The diagram below shows the percent ionic character of several diatomic gas-phase molecules. As can be expected, as the electronegativity difference between the bonding atoms increases, percent ionic character generally increases.
- Also, as can be seen, no bond is 100% ionic. In general, bonds with more than 50% ionic character are classified as ionic.



Examples:

1) Determine whether each bond listed below is non-polar covalent, polar covalent or ionic.

Sr–F N–Cl N–O

2) Draw Lewis structure for BrF with an arrow representing the dipole moment.

WRITING LEWIS STRUCTURES FOR MOLECULAR COMPOUNDS & POLYATOMIC IONS

- Lewis structures for molecular compounds and polyatomic ions can be drawn according to the following steps:
 - 1. Count the total number of valence electrons to be used in the structure. For ions, add one electron for each negative charge, and subtract one electron for each positive charge.
 - 2. Write a skeleton structure, arranging the atoms in the most symmetrical pattern. Remember the number of bonds commonly formed by atoms.
 - 3. Connect each atom by a dashed line representing 2 electrons each.
 - 4. Determine the number of electrons left by subtracting number of electrons used from the total determined in step 1.
 - 5. Distribute the remaining electrons around the atoms in pairs in order to achieve eight electrons around each (*octet rule*). Hydrogen is an exception (doublet).
 - 6. If there are not enough electrons to achieve octet rule for each atom, form double or triple bonds by sharing more than one pair of electrons.

Examples:

Draw Lewis structure for each molecule or ion, using the step-wise procedure outlined above:

1) H ₂ CO	Total number of electrons:
2) ClO ⁻	Total number of electrons:
3) N ₂ H ₄	Total number of electrons:

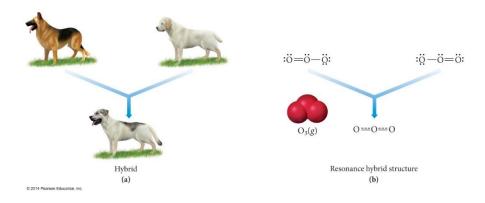
RESONANCE STRUCTURES

• When writing Lewis structures, it might be possible to write more than one good (valid) structure for some molecules. For example, when writing Lewis structure for O₃, we can draw two correct structures, with the double bond on alternate sides:

- In cases such as this–where more there are more than one valid Lewis structures for the same molecule–we find that in nature, the molecule exists an average of the two structures. Both structures above predict the molecule to possess one double bond and one single bond. However, experimental results indicate that the bonds in O₃ are equivalent and each is intermediate in strength and length between a double bond and a single bond.
- Therefore, we represent the molecule with both structures, *called resonance structures*, with a double-headed arrow between them.

$$\ddot{\mathbf{0}} = \ddot{\mathbf{0}} - \ddot{\mathbf{0}} : \longleftrightarrow : \ddot{\mathbf{0}} - \ddot{\mathbf{0}} = \ddot{\mathbf{0}}$$

• A resonance structure is one of two or more structures that have the same skeletal formula, but different electron arrangements. The actual structure of the molecule is intermediate between the two or more resonance structures and is called a *resonance hybrid*.



- In Lewis model, the electrons are represented as *localized* either on one atom (lone pair) or between atoms (bonding pair). However, in nature, electrons are in molecules are often *delocalized* over seveal atoms or bonds. The delocalization of electrons lowers their potential energy and stabilizes them.
- Resonance structures attempt to more accurately reflect the delocalization of electrons in a molecule. The resulting stabilization of the electrons through delocalization is called *resonance stabilization*, and makes an important contribution to the stability of many molecules.

RESONANCE STRUCTURES

- When writing resonance structures, it is important to note that the positions of the bonding and non-bonding electrons change, but the arrangement of the atoms remains the same.
- For example, the resonance structures in ozone are formed by moving the electrons, as indicated by the red arrows.



• The resonance hybrid that actually exists is written as follows, indicating that the dotted electrons are delocalized and exist on all three oxygen atoms.



Examples:

1) Draw the three resonance structures possible for the nitronium ion (NO_2^+) .

2) Identify which of the following structures are resonance structures:

(a)
$$\overline{O} = N = \overline{N}$$
 (c) $\overline{N} = N \equiv O$

(b) $\overline{N} = 0 = \overline{N} (d) \overline{0} - N \equiv N$

FORMAL CHARGES

- When the resonance structures for a molecule are equivalent (equally valid), the true structure (resonance hybrid) is an equally weighted average of these structures.
- In many cases, resonance structures can be written that are not equivalent. For reasons that will be discussed shortly (formal charges), one possible structure may be better than another. In these cases, the resonance hybrid is still the average of the possible structures, but the better resonance structure contributes more to the true structure.
- *Formal charge* is a fictitious charge assigned to each atom in a Lewis structure that helps to distinguish among competing Lewis structures. The formal charge of an atom in a Lewis structure is the charge it would have if all the bonding electrons were shared equally between the bonded atoms.
- For example, for HF, even though we know that that F is more electronegative than H, and therefore has a partial negative charge, the formal charges are assigned by ignoring the difference in electronegativity of H and F.

H:
$$\dot{F}$$
:
Formal charge = 0 Formal charge = 0

• Formal charge on an atom can be calculated as shown below:

Formal charge = number of valence electrons -

(number of nonbonding electrons + $\frac{1}{2}$ number of bonding electrons)

• Formal charge for H and F can be calculated as shown below:

Formal charge =
$$1 - [0 + \frac{1}{2}(2)] = 0$$

Number of valence
electrons for H
Number of electrons that H
"owns" in the Lewis structure
Formal charge = $7 - [6 + \frac{1}{2}(2)] = 0$
Number of valence electrons for F
Number of electrons that F
"owns" in the Lewis structure

FORMAL CHARGES

- The concept of formal charges can be used to distinguish between competing skeletal structures or competing resonance structures. In general, the following four rules apply to assigning formal charges:
 - 1) The sum of all formal charges in a neutral molecule must be zero.
 - 2) The sum of all formal charges in an ion must equal the charge of the ion.
 - 3) Small (or zero) formal charges on individual atoms are better than large ones.
 - 4) When formal charge cannot be avoided, negative formal charges must reside on the most electronegative atom.
- The table below shows how formal charges can be used to determine which skeletal structure for HCN is best (most stable). Note that both skeletal structures satisfy the octed rule equally.

	Structure A				Structure B					
	Н	—	С	=	N:	Н	_	Ν	=	C:
number of valence e	1		4		5	1		5		4
$-$ number of nonbonding e $^-$	-0		-0		-2	-0		-0		-2
-1/2 (number of bonding e ⁻)	$-1/_{2}(2)$		$-1/_{2}(8)$		$-1/_{2}(6)$	$-1/_{2}(2)$		$-1/_{2}(8)$		$-1/_{2}(6)$
Formal charge	0		0		0	0		+1		-1

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Examples:

1. Assign formal charges to each atom in the resonance structures of the cyanate ion (OCN⁻) shown below. Which resonance structure is likely to contribute to the correct structure of the ion?

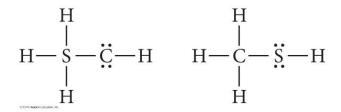
A B C
$$[:\ddot{\mathbf{0}} - \mathbf{c} = \mathbf{N}:]^{-}$$
 $[:\ddot{\mathbf{0}} = \mathbf{c} = \ddot{\mathbf{N}}:]^{-}$ $[:\mathbf{0} = \mathbf{c} - \ddot{\mathbf{N}}:]^{-}$

FORMAL CHARGES

Examples (cont'd):

- 2. Draw the Lewis structure (including resonance structures) for nitromethane (CH₃NO₂), and assign formal charges to each atom that has a formal charge. Which structure is favored? (The skeleton structure for nitromethane is shown below).
 - H O H C N O H

3. Use formal charges to determine which structure shown below is better.

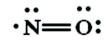


EXCEPTIONS TO THE OCTED RULE

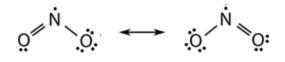
• The octet rule in the Lewis model has some exceptions. These exceptions are discussed below.

Odd-Electron Species:

• Molecules and ions with odd number of electrons in their Lewis structures are called *free radicals*. For example, nitrogen monoxide– a pollutant formed in auto exhaust–has 11 electrons in its Lewis structure. The Lewis structure for this molecule, therefore, has an odd electron and cannot achieve octet for both atoms.



• Free radicals tend to be unstable and reactive. For example, NO reacts with oxygen to form NO₂ (also an odd-electron molecule), with resonance structure shown below:

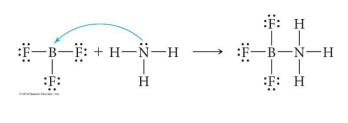


Incomplete Octet:

• Another exception to the octet rule involves elements that tend to form incomplete octets. The most important of these is boron, which fomrs compounds with only six electrons around B. For example BF₃ and BH₃ lack an octet for B.



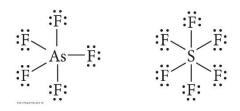
• As can be seen above, BF₃ molecule does not form a double bond between B and F due to the positive formal charge resulting on F (the more electronegative element). Boron, however, can complete an octet by reacting with another molecule (such as NH₃), as shown below:



EXCEPTIONS TO THE OCTED RULE

Expanded Octets:

• Elements in the 3rd period of the periodic table and beyond often exhibit expanded octets of up to 12 (and occasionally 14) electrons. For examples, consider the Lewis structures for AsF₅ and SF₆, shown below:



- Both As and S have expanded octets (10 and 12 electrons, respectively) and are stable. Elements in 3rd period and beyond have expanded octets because the d orbitals in these elements are energetically accessible to accommodate the extra electrons. By contrast, elements in the 2nd period never form expanded octets.
- In some Lewis structures, an expanded octet might be favorable due to formal charges. For example, consider the Lewis structure for sulfuric acid shown below. Note that this structure has acceptable formal charges (relatively small and negative charge residing on the more electronegative O).



• The formal charge on the atoms in the structure of H₂SO₄ can be reduced by expanding the octet on sulfur (also shown above). Experiments show that the bond length of the sulfur–oxygen bonds in the two oxygens without the hydrogens are shorter than expected for the single sulfur–oxygen bonds, indicating the expanded octet Lewis structure plays an important role in describing the bonding in H₂SO₄.

EXCEPTIONS TO THE OCTED RULE

Examples:

- 1. Which molecule could have an expanded octet?
 - a) H₂CO₃
 - b) H₃PO₄
 - c) HNO₂
- 2. Write Lewis strtucture for XeF₂.

- 3. Write Lewis structure for each molecule shown below:
 - a) ClO₂

b) BeCl₂

BOND ENERGY

• The *bond energy* of a chemical bond is the energy required to break 1 mol of the bond in the gas phase. For example, the bond energy of the Cl–Cl bond in Cl₂ is 243 kJ/mol, and bond energy of HCl is 431 kJ/mol.

 $\begin{array}{ll} \mathrm{Cl}_2\left(\mathrm{g}\right) \ensuremath{\rightarrow}\ 2\ \mathrm{Cl}\left(\mathrm{g}\right) & \Delta\mathrm{H} = 243\ \mathrm{kJ} \\ \mathrm{HCl}\left(\mathrm{g}\right) \ensuremath{\rightarrow}\ \mathrm{H}\left(\mathrm{g}\right) \ensuremath{+}\ \mathrm{Cl}\left(\mathrm{g}\right) & \Delta\mathrm{H} = 431\ \mathrm{kJ} \end{array}$

- Bond energy is always positive, because it always takes energy to break a bond. HCl is said to be a *stronger* bond than Cl₂, because it requires more energy to break it. In general, compounds with stronger bond tend to be more stable and less reactive than compounds with weaker bonds.
- The triple bond of N_2 has a bond energy of 946 kJ/mol, which indicates that it is a very strong and stable bond. As a result, nitrogen is relatively inert.

 $N_2(g) \rightarrow 2 N(g) \qquad \Delta H = 946 \text{ kJ}$

• The bond energy of a particular bond in a polyatomic molecule can have different values in different molecules. For example, consider the C–H bond in the four molecules shown below:

$H_3C-H(g) \rightarrow H_3C(g) + H(g)$	$\Delta H = 438 \text{ kJ}$
$F_3C-H(g) \rightarrow F_3C(g) + H(g)$	$\Delta H = 446 \text{ kJ}$
$Br_3C-H(g) \rightarrow Br_3C(g) + H(g)$	$\Delta H = 402 \text{ kJ}$
$Cl_3C-H(g) \rightarrow Cl_3C(g) + H(g)$	$\Delta H = 401 \text{ kJ}$

- An *average bond energy* can be calculated for a chemical bond based on the average of bond energy values for that bond in a large number of compounds. Listed to the right is the average bond energy for a number of common chemical bonds.
- Note that in general, for a given pair of atoms, triple bonds are stronger than double bonds, which are in turn, stronger than single bonds.

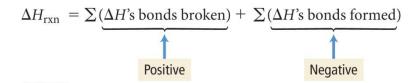
Bond	Bond Energy (kJ/mol)
н—н	436
н-с	414
H — N	389
н—о	464
H-S	368
H — F	565
H — CI	431
H — Br	364
н—і	297
c-c	347
c=c	611
C=C	837
C-N	305
C = N	615
C≡N	891
C-0	360
C=0	736*
C=0	1072
C — CI	339
*799 in CO ₂ .	

USING BOND ENERGIES TO ESTIMATE ΔH_{rxn}

- Average bond energies can be used to estimate the enthalpy change for a reaction (ΔH_{rxn}).
- For example, consider the reaction between methane and chlorine:

$$H_3C-H(g) + Cl-Cl(g) \rightarrow H_3C-Cl(g) + H-Cl(g)$$

• We can imagine this reaction occurring by breaking 2 bonds (C–H and Cl–Cl) and forming 2 bonds (C–Cl and H–Cl). We know that when bonds break, process is endothermic (positive bond energy) and when bonds form, the process is exothermic (negative bond energy). The ΔH_{rxn} can then be calculated as shown below:



• For example, using table 9.3 in text, ΔH_{rxn} for the reaction above is calculated as follows:

$$\Delta H_{rxn} = \ (+414 \ kJ + 243 \ kJ) + (-339 \ kJ - 431 \ kJ) = +657 \ kJ - 770 \ kJ = -113 \ kJ$$

- Calculating ΔH_{rxn} from tabulated ΔH_f° values—as learned in Chapter 6–gives $\Delta H^\circ_{rxn} = -101$ kJ, which is fairly close to the value obtained from average bond energies.
- To summarize:
 - Breaking a chemical bond always requires energy, while forming a chemical bond always releases energy.
 - ▶ A reaction is exothermic when weak bonds break and strong bonds form.
 - ➤ A reaction is endothermic when strong bonds break and weak bonds form.

Examples:

1. Use average bond energy values from table 9.3 in textbook to calculate ΔH_{rxn} for the reaction shown below:

$$CH_4(g) + 2 H_2O(g) \rightarrow 4 H_2(g) + CO_2(g)$$

BOND LENGTHS

• The average bond length represents the length of a bond between two particular atoms in a large number of compunds. Listed below are the average bond lengths for some common bonds.

Bond	Bond Length (pm)	Bond	Bond Length (pm)	Bond	Bond Length (pm)
Н-Н	74	c-c	154	N — N	145
н-с	110	c=c	134	N=N	123
H — N	100	C=C	120	$N \equiv N$	110
н—о	97	C-N	147	N-0	136
H-S	132	C = N	128	N=0	120
H-F	92	C = N	116	0-0	145
H-CI	127	C-0	143	0=0	121

• Like bond energies, bond lengths depend not only on the kind of atoms involved in a bond, but also on the type of bond: single, double or triple. In general, for a particular pair of atoms, triple bonds are shorter than double bonds, which in turn are shorter than single bonds. For example, compare the bond lengths (and bond strengths) of the various C–C bonds:

Bond	Bond Length (pm)	Bond Strength (kJ/mol)
C≡C	120 pm	837 kJ/mol
c=c	134 pm	611 kJ/mol
cc	154 pm	347 kJ mol
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• Note that as the bond gets longer, it also gets weaker. The relationship between the length of the bond and the strength of the bond does not necessarily hold true for all bonds. Consider the series of nitrogen-halogen bonds shown below:

Bond	Bond Length (pm)	Bond Strength (kJ/mol)
N — F	139	272
N-CI	191	200
N — Br	214	243
N — I	222	159
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• Although the bonds generally get weaker as they get longer, the trend is not a smooth one.

BOND ORDER

- Bond order, defined in terms of the Lewis formula, is the number of pairs of electrons in a bond. Therefore, a single bond has a bond order of 1, a double bond has a bond order of 2 and a triple bond has a bond order of 3.
- Bond length depends on bond order. As the bond order increases, the bond strength increases and the nuclei are pulled inward, decreasing bond length. For example, the average C−C single bond has a bond length of 154 pm, whereas C = C is 134 pm long and C≡C is 120 pm long.
- When determining bond order in molecules that have resonance structures, the total pair of electrons is divided by the total number of bonds, commonly yielding fractional bond orders. For example, the bond order of O–O bonds in ozone (with 2 resonance structures) is calculated as shown below:

Bond order = $\frac{\text{total pair of electrons}}{\text{total number of bonds}} = \frac{3}{2} = 1.5$ $: \overrightarrow{0} = \overrightarrow{0} : \longleftrightarrow : \overrightarrow{0} = \overrightarrow{0} :$

Examples:

1. Consider the molecules N₂H₄, N₂ and N₂F₂. Which molecule has the shortest N–N bond length? Which molecule has the longest N–N bond length?

2. Oxalic acid $(H_2C_2O_4)$ has the structural arrangement shown below. Complete the Lewis structure for this molecule and compare the length and strength of the carbon-oxygen bonds.