
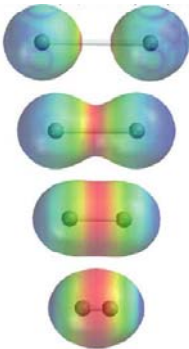
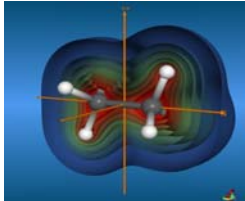



Chapter 8

Chemical Bonding I: Basic Concepts






Dr. A. Al-Saadi



Chapter 8

Preview



- Ionic Bonding vs. covalent bonding.
- Electronegativity and dipole moment.
- Bond polarity.
- Lewis structure:
 - How to draw a Lewis structure (octet rule).
 - Formal charge.
 - Resonance.
 - Exceptions to the octet rule.
- Bond enthalpy

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Lewis Dot Symbols

- Lewis proposed that atoms combine in order to achieve a more stable configuration (*isoelectronic with a noble gas*).
- **Lewis dot symbol** shows only the **valence electrons**.
- Write Lewis dot symbols for the following:
 - ◆ A boron atom
 - ◆ A nitrogen atom

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Lewis Dot Symbols

- **Lewis dot symbol** shows only the **valence electrons**.

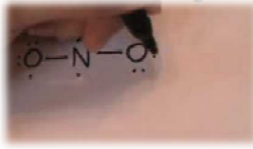
1A 1	2A 2											3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
·H																	He:
·Li	·Be·											·B·	·C·	·N·	·O·	·F·	·Ne:
·Na	·Mg·	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	9	10	1B 11	2B 12	·Al·	·Si·	·P·	·S·	·Cl·	·Ar:
·K	·Ca·											·Ga·	·Ge·	·As·	·Se·	·Br·	·Kr:
·Rb	·Sr·											·In·	·Sn·	·Sb·	·Te·	·I·	·Xe:
·Cs	·Ba·											·Tl·	·Pb·	·Bi·	·Po·	·At·	·Rn:
·Fr	·Ra·																

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Chapter 8 Section 1

Lewis Dot Symbols



- From the Lewis dot symbol, which of the following species are isoelectronic with a noble gas?
 - ◆ Si
 - ◆ Br
 - ◆ O^{2-}
 - ◆ Ca^{2+}

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Chapter 8 Section 1

Ionic Bonds vs. Covalent Bonds

Ionic Bonds	Covalent Bonds
<ul style="list-style-type: none"> ○ Electrostatic (Coulombic) attraction between oppositely charged ions. ○ Normally formed between a metal and a nonmetal. ○ Involve total transfer of electron(s) from one atom to another. 	<ul style="list-style-type: none"> ○ Normally formed between nonmetals. ○ No electron transfer. ○ Electrons are being shared between the atoms.

Can you think of examples from each type?

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Chapter 8 Section 1

Lewis Dot Symbols of Covalent and Ionic Compounds

- Atoms combine in order to achieve a more stable configuration (*isoelectronic with a noble gas*).
- Reaction of two non-metals.
 - $$\text{H} \cdot \quad \cdot \ddot{\text{Cl}} : \quad \longrightarrow$$

$$1s^1 \quad [\text{Ne}]3s^23p^5$$
- Reaction of a nonmetal and a metal.
 - $$\longrightarrow$$

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Chapter 8 Section 2

Ionic Bonding

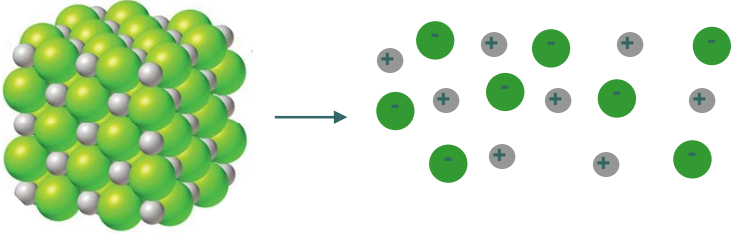
- Ionic bonding:** electrostatic attraction holding two oppositely charged ions together in an ionic compound.
- Table salt is potassium iodide. Can you show the Lewis dot symbol of a molecular unit of the ionic compound KI?
- The formation of KI or any ionic compound is *very highly exothermic*.

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Chapter 8 Section 2

Lattice Energy

- **Lattice Energy** : the energy required to completely separate one mole of a solid ionic compound into its gaseous ions.



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Chapter 8 Section 2

Lattice Energy

- **Lattice Energy** : the energy required to completely separate one mole of a solid ionic compound into its gaseous ions.

$$\text{MX}(s) \rightarrow \text{M}^+(g) + \text{X}^-(g)$$

- Example:

$$\text{KI}(s) \rightarrow \text{K}^+(g) + \text{I}^-(g) \quad \Delta H = 632 \text{ kJ/mol}$$
 - Generally the greater the lattice energy, the more stable the compound.
 - Lattice energy depends on the magnitude of the charge as well as the distance between them.

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Lattice Energy

- The greater the lattice energy, the more stable the compound.

TABLE 8.1 Lattice Energies of Selected Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Melting Point (°C)
LiF	1017	845
LiCl	828	610
LiBr	787	550
LiI	732	450
NaCl	788	801
NaBr	736	750
NaI	686	662
KCl	699	772
KBr	689	735
KI	632	680
MgCl ₂	2527	714
Na ₂ O	2570	Sub*
MgO	3890	2800

*Na₂O sublimes at 1275°C.

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Predicting Lattice Energy

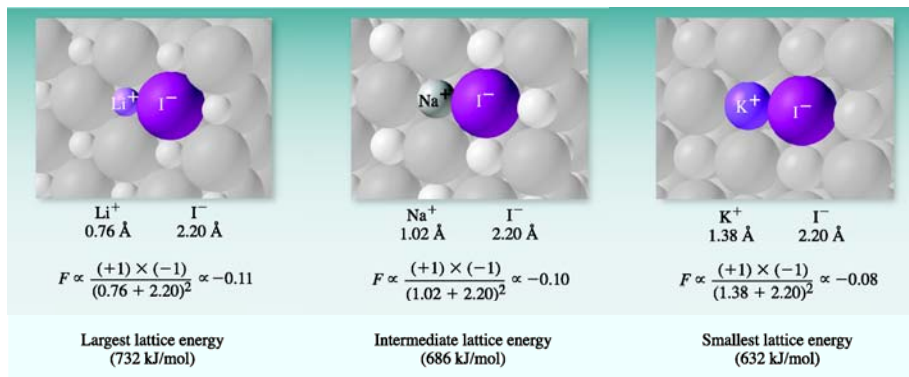
- Coulomb's law can be used to estimate the lattice energies for ionic compounds.
- Lattice Energy = $\left| k \left(\frac{Q_1 Q_2}{d^2} \right) \right|$
 - The attraction force has a “-ve” sign (exothermic process).
 - The process is more exothermic as the charge magnitudes increase and as the distance between the ions decreases.
 - The lattice energy is the energy required to separate between the opposite charges, so it is a “+ve” quantity.

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Predicting Lattice Energy

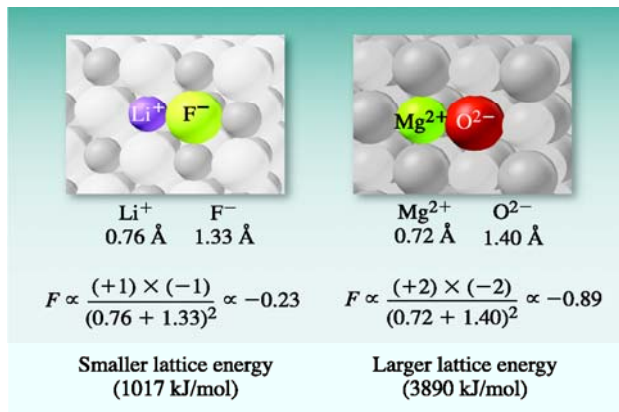
- Lattice energy depends on the magnitude of the two charges and the the distance between them.



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Predicting Lattice Energy



- Compare the *lattice energies* for LiF and MgO solids using the above equation.

$$\frac{E_{\text{MgO}}^{\text{lattice}}}{E_{\text{LiF}}^{\text{lattice}}} = \frac{(+2)(-2)}{(+1)(-1)} = 4$$

← MgO
← LiF

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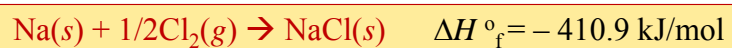
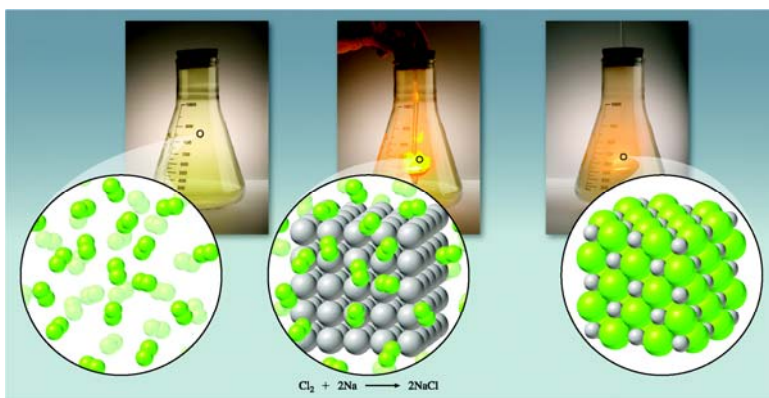
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Calculation of Lattice Energy

- Although lattice energy is a useful quantity, there is no way to determine it experimentally.
- Therefore, we use Hess's law to calculate lattice energy from available thermodynamic quantities.
 - Energy of sublimation,
 - Electron affinity,
 - Ionization energy,
 - Bond energy and
 - Enthalpy of formation .

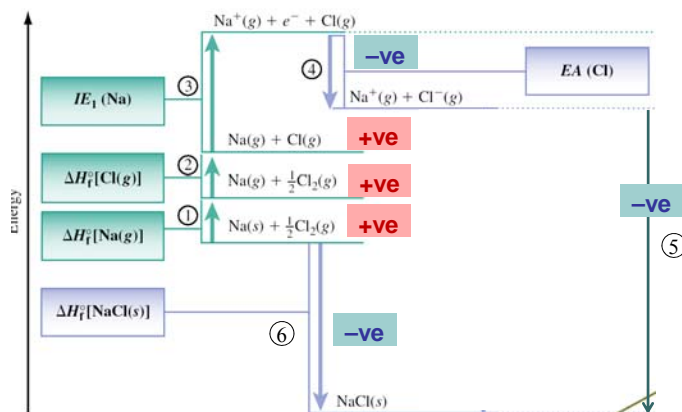
The Born-Haber cycle

Calculation of Lattice Energy



Chapter 8 Section 2

The Born-Haber Cycle to Calculate the Lattice Energy of NaCl(s)



From Hess's
Law:

$$1 + 2 + 3 + 4 + 5 = 6$$

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Chapter 8 Section 2

The Born-Haber Cycle to Calculate the Lattice Energy of NaCl(s)

TABLE 8.2

Theoretical Series of Steps in the Formation of NaCl from its Constituent Elements

Step	Chemical Equation	Energy Change (kJ/mol)
1. Atomization of Na(s)*	$\text{Na}(s) \longrightarrow \text{Na}(g)$	107.7
2. Dissociation of Cl ₂ (g) [†]	$\frac{1}{2}\text{Cl}_2(g) \longrightarrow \text{Cl}(g)$	121.4
3. Ionization of Na(g) [‡]	$\text{Na}(g) \longrightarrow \text{Na}^+(g) + e^-$	495.9
4. Electron affinity of Cl [§]	$\text{Cl}(g) + e^- \longrightarrow \text{Cl}^-(g)$	-349

*Standard heat of formation (ΔH_f°) of Na(g) from Appendix 2. (Some time called heat of sublimation)[†]Standard heat of formation (ΔH_f°) of Cl(g) from Appendix 2. (Some time called bond enthalpy)

6. Heat of formation NaCl(s) - 410.9

From Hess's
Law:

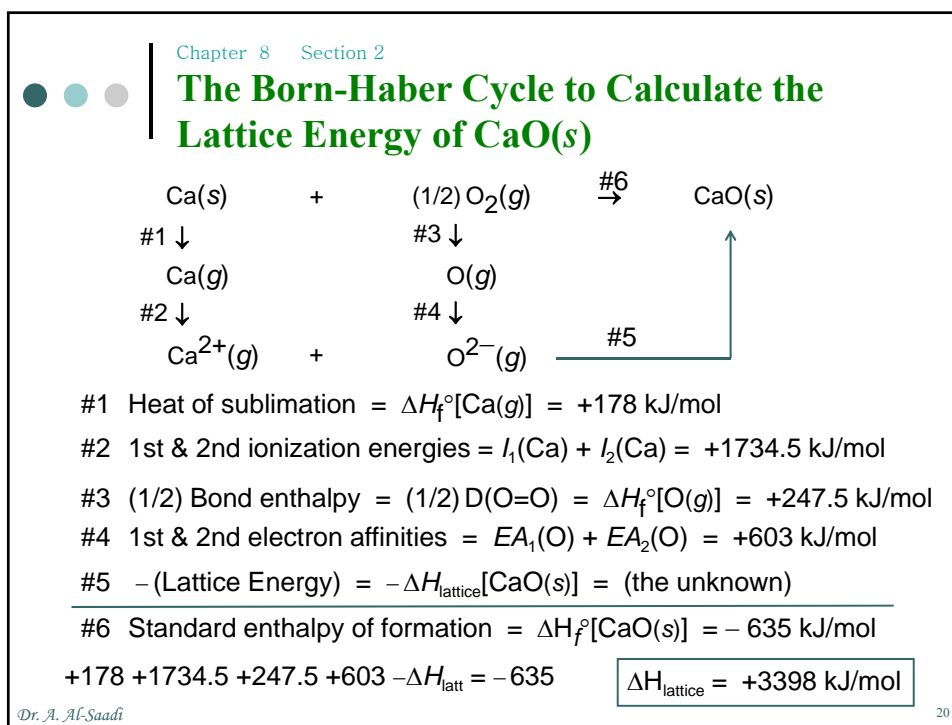
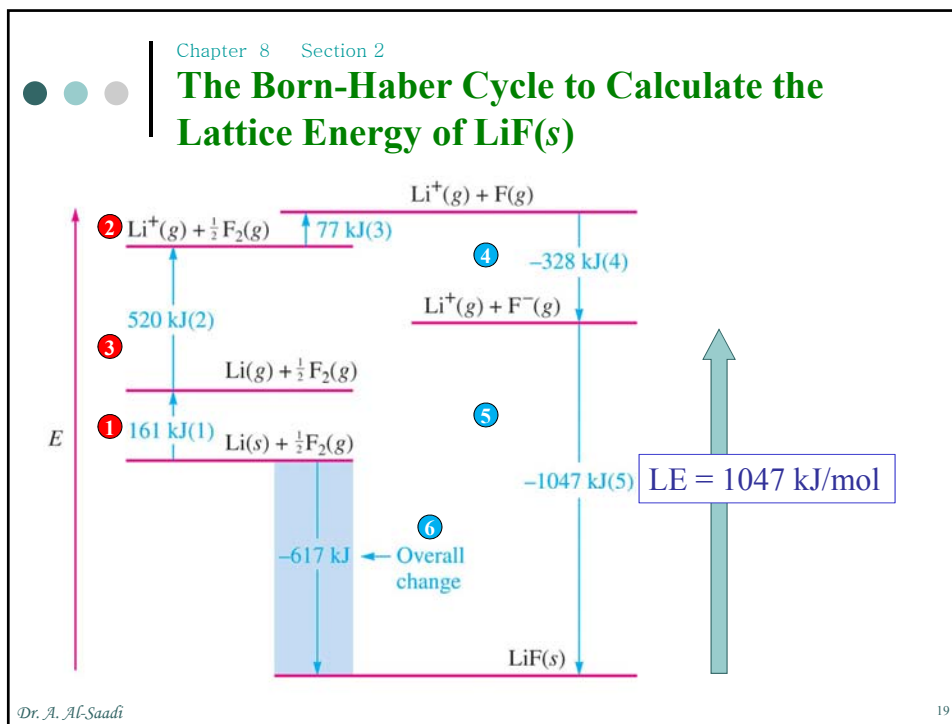
$$1 + 2 + 3 + 4 + 5 = 6$$

$$5 = 6 - (1 + 2 + 3 + 4) = -786 \text{ kJ/mol}$$

$$\text{Thus, } LE = 786 \text{ kJ/mol}$$

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Chapter 8 Section 3

Covalent Bonding

Ionic Bonds

- Electrostatic (Coulombic) attraction between oppositely charged ions.
- Normally formed between a metal and a nonmetal.
- Involve total transfer of electron(s) from one atom to another.
- Generally strong, high melting point.

Covalent Bonds

- Normally formed between nonmetals.
- No electron transfer.
- Electrons are being shared between the atoms as *electron pairs*.
- Weaker than ionic bonds.

Important reading materials:
Comparison between Ionic and Covalent Compounds, pp. 286.

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Chapter 8 Section 3

Covalent Bonding

Atoms combine in order to achieve a more stable configuration (*isoelectronic with a noble gas*).

Shared electrons:

- Each H atom counts the two electrons as its own.
- Each H atom has the noble gas electron configuration of He.
- Shared electrons can be shown as a line.
- This is known as *Lewis structure*.

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

$$\text{H} - \text{H}$$

More examples:

- Fluorine molecule F_2

$\cdot\ddot{\text{F}}\cdot + \cdot\ddot{\text{F}}\cdot \longrightarrow \ddot{\text{F}}:\ddot{\text{F}}:$

Shared electrons

Each F atom has the noble gas electron configuration of Ne.
 This is known as the *Octet rule*.

Lone pairs

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Chapter 8 Section 3

Covalent Bonding and Octet Rule

- **Eight** is a “magic” number of electrons.
- **Octet Rule:** Atoms will gain, lose, or share electrons to acquire **eight** valence electrons.
- More examples:

$$\text{Na}\cdot + \cdot\ddot{\text{Cl}}\cdot \longrightarrow$$

$$\text{H}\cdot + \text{H}\cdot + \cdot\ddot{\text{O}}\cdot \longrightarrow$$

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Chapter 8 Section 4

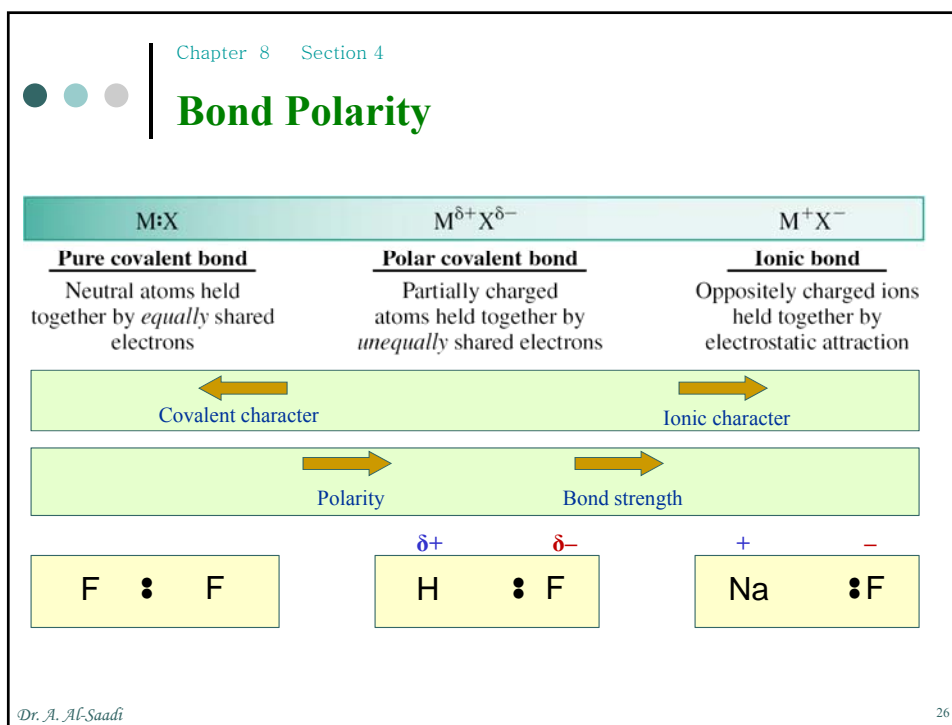
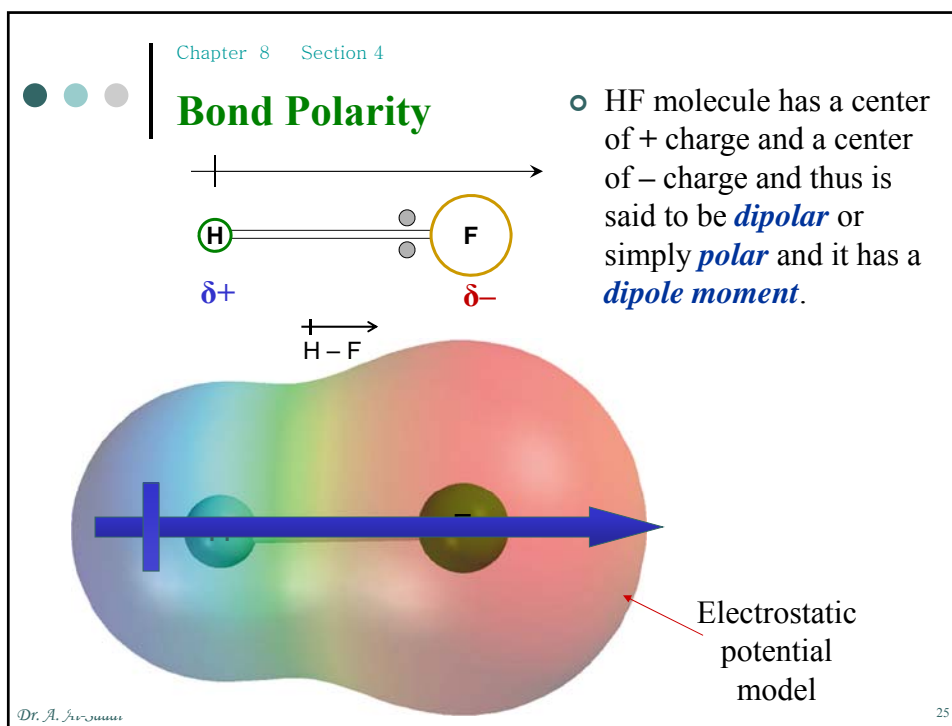
Bond Polarity

red ⇒ high electron density
green ⇒ intermed. electron density
blue ⇒ low electron density

- Let's inspect the *shared electrons* of the following compounds by drawing their Lewis structures:

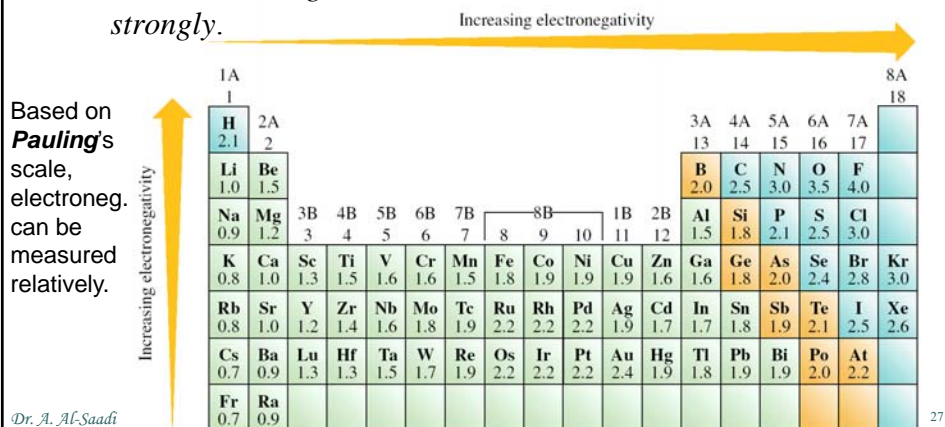
● F₂	F : F	Electrons are equally shared “ <i>pure covalent bond</i> ”	Electrostatic potential model
● HF	^{δ+} H : ^{δ-} F	Electrons are unequally shared “ <i>polar covalent bond</i> ”	
● NaF	⁺ Na : ⁻ F	Electrons are transferred to the nonmetal atom “ <i>ionic bond</i> ”	

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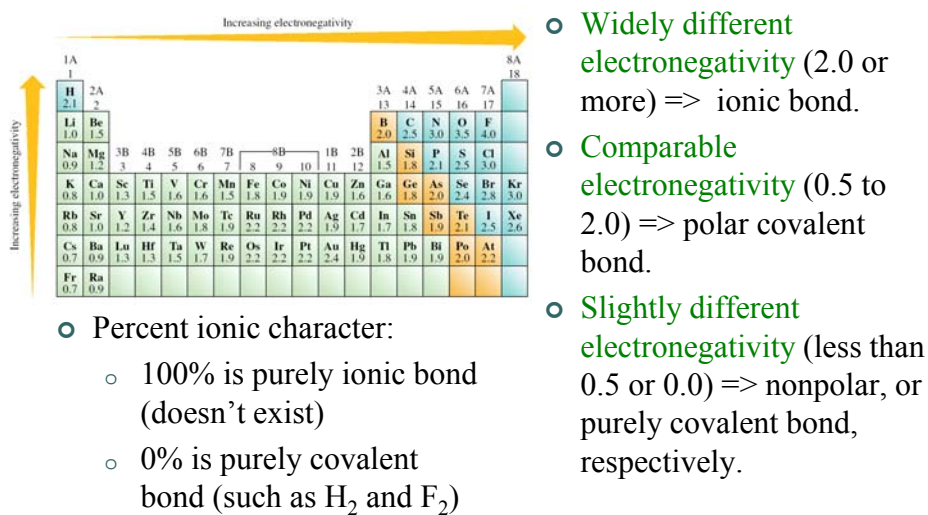


Electronegativity

- **Electronegativity:** ability of an atom to draw shared electrons to itself.
- *More electronegative* elements attract electrons *more strongly*.



Bond Polarity from Electronegativity



Chapter 8 Section 4

Bond Polarity from Electronegativity

TABLE 8.1 The Relationship Between Electronegativity and Bond Type

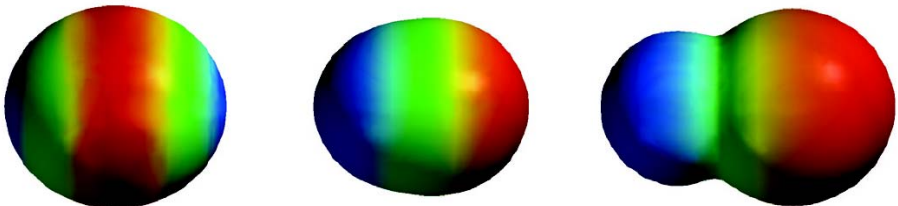
Electronegativity Difference in the Bonding Atoms	Bond Type
Zero	Covalent
Intermediate	Polar covalent
Large	Ionic

Covalent character ↑
Ionic character ↓

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Chapter 8 Section 4

Ionic, Polar and Nonpolar Bonds

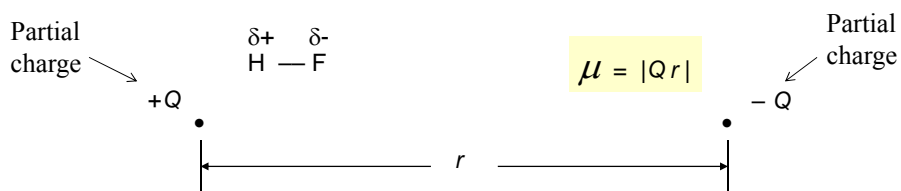


F_2	HF	NaF
$4.0 - 4.0 = 0.0$	$4.0 - 2.1 = 1.9$	$4.0 - 0.9 = 3.1$
Nonpolar, purely covalent bond	Polar covalent bond (in fact it is highly polar)	Ionic bond

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Dipole Moment and Partial Charge

- Dipole moment (μ)** : a quantitative measure of the polarity (a dipole) of the bond. (μ is always positive)



SI unit: coulomb•meter ($\text{C} \cdot \text{m}$)

common unit: debye (D)

$$1 \text{ D} = 3.34 \times 10^{-30} \text{ C} \cdot \text{m}$$

HF	1.82 D
HCl	1.08 D
HBr	0.82 D
HI	0.44 D

Dipole Moment and Partial Charge

HF	1.82 D
HCl	1.08 D
HBr	0.82 D
HI	0.44 D

TABLE 8.5 Bond Lengths and Dipole Moments of the Hydrogen Halides

Molecule	Bond Length (\AA)	Dipole Moment (D)
HF	0.92	1.82
HCl	1.27	1.08
HBr	1.41	0.82
HI	1.61	0.44

Lewis Structures

- **Lewis Structure** shows how *valence* electrons are arranged among the atoms to form a stable molecule.
- In order to have a stable form of a molecule, its atoms must achieve the *noble gas electron configurations*.

Octet rule $ns^2np^6 = 8$ valence electrons (*for all atoms*)

and

Duet rule $1s^2 = 2$ valence electrons (*only for hydrogen*)

Drawing Lewis Structures

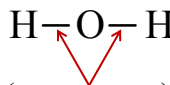
1. Sum valence electrons for the atoms forming a molecule.
2. Use a pair of electrons per bond. (**Bonding Pairs**)
3. Distribute the remaining atoms to achieve noble gas configurations for each atom (*duet rule* for H atoms and *octet rule* for the rest of atoms). (**Lone pairs**)

Example (1): H₂O molecule.

$$6e^- (\text{O}) + 2 \times 1e^- (\text{H}) = 8e^-$$

$$8e^- (\text{total no. of valence electrons}) - 4e^- (\text{bonding pairs}) = 4e^-$$

$4e^- = 2$ lone pairs go on the O atom.



Always do a reliability check

Drawing Lewis Structures

1. Sum valence electrons over all the atoms.
 - ⊙ The atom with the least electronegativity normally goes to the center (H is an exception).
2. Do "Bonding" Pairs.
3. Do "Lone" Pairs.
4. If needed, Make Use of "Double/Triple bonds".

Example (2): CO_2 .

Drawing Lewis Structures

1. Sum valence electrons over all the atoms.
 - ⊙ Each "-ve" charge on a molecule is added as one electron, and vice versa.
2. Do "Bonding" Pairs.
3. Do "Lone" Pairs.
4. If needed, Make Use of "Double/Triple bonds".

Example (3): CN^- .

Steps to Draw a Correct Lewis Structure

- 1) Sum the valence electrons. Add 1 electron for each negative charge and subtract 1 electron for each positive charge.
- 2) Draw skeletal structure with the central atom being the least electronegative element.
- 2) Subtract 2 electrons for each bond in the skeletal structure.
- 3) Complete electron octets for atoms bonded to the central atom except for hydrogen.
- 5) Place extra electrons on the central atom.
- 6) Add multiple bonds if atoms lack an octet.

Drawing Lewis Structures

- Some exercises:
 - CH₄
 - NH₃
 - NO⁺

Lewis Structures and Formal Charge

- Formal charge is useful to determine the most preferable Lewis structure for a compound when more than one possibility exists.

$$\text{Formal Charge} = \text{Total valence electrons} - \text{Total non-bonding electrons} - \frac{1}{2} \text{Total bonding electrons}$$

- What is the formal charges of H and O atoms in H_2O ?



$$\text{Formal Charge (O)} = 6 - 4 - \frac{1}{2} [4] = 0$$

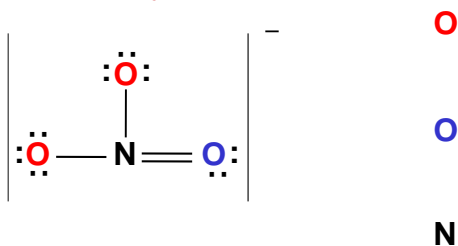
$$\text{Formal Charge (H)} = 1 - 0 - \frac{1}{2} [2] = 0$$

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Lewis Structures and Formal Charge

- What is the formal charges of N and O atoms in the nitrate ion (NO_3^-)?



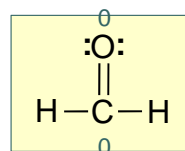
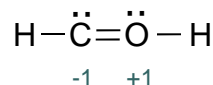
$$\text{The sum of formal charges} = (0) + (-1) \times 2 + (+1) = -1$$

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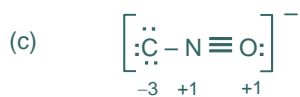
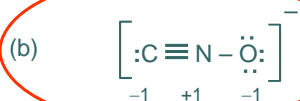
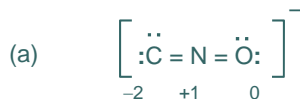
Formal Charge Guidelines

- A Lewis structure with *no* formal charges is generally better than one with formal charges.
 - Small formal charges are generally better than large formal charges.
 - Negative formal charges should be on the more electronegative atom(s)
- What is the best choice of Lewis structure of formaldehyde CH_2O ?



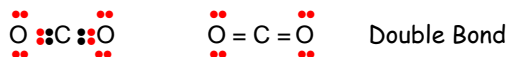
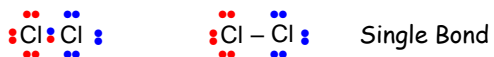
Another Example on Formal Charge

- Identify the best structure for the isocyanate ion (CNO^-).



Multiple Bonds

- **Single bond:** two atoms share **1 pair** of electrons.
- **Double bond:** two atoms share **2 pairs** of electrons.
- **Triple bond:** two atoms share **3 pairs** of electrons.



Multiple Bonds

- Bond lengths follow this order:
Triple bond < Double bond < Single bond

Average bond lengths of some common single, double and triple bonds

Bond Type	Bond Length (pm)		
		C–N	143
		C=N	138
C–H	107	C≡N	116
O–H	96	N–N	147
C–O	143	N=N	124
C=O	121	N≡N	110
C≡O	113	N–O	136
C–C	154	N=O	122
C=C	133	O–O	148
C≡C	120	O=O	121

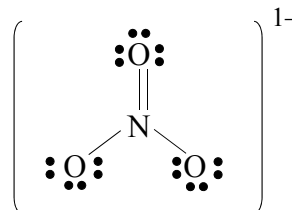
Resonance

$$(5+3 \times 6+1)e^- - 6e^- = 18e^-$$

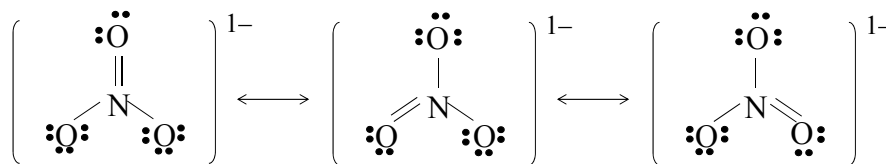
- NO_3^- ion.

☞ The nitrate ion structure is the average of all the three *equivalent* structures, not one of them.

☞ The three NO bonds are found from experiments to be identical.



Resonance structures:

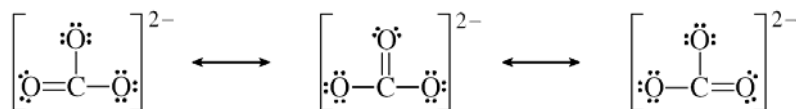


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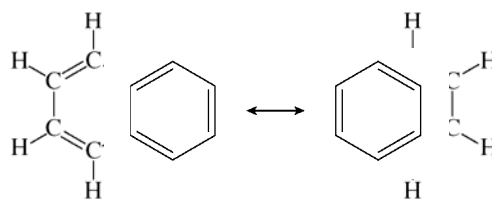
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More Examples on Resonance

- The carbonate ion (CO_3^{2-})



- Benzene molecule (C_6H_6)



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Exceptions to the Octet Rule

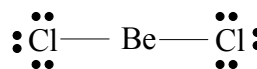
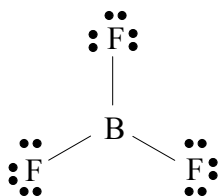
- Exceptions to the octet rule fall into three categories:
 - Molecules with an *incomplete octet*.
 - Molecules with an *odd number of electrons*.
 - Molecules with an *expanded octet*.

Molecules with an Incomplete Octet

- Some atoms are electron-deficient (can have less than 8 valence electrons).
 - Boron in BF_3

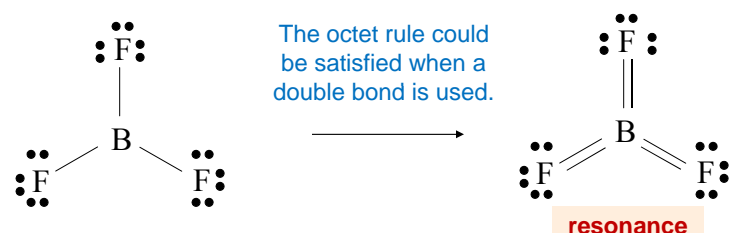
$$24e^- - 6e^- = 18e^-$$
 - Beryllium in BeCl_2

$$16e^- - 4e^- = 12e^-$$



Chapter 8 Section 8

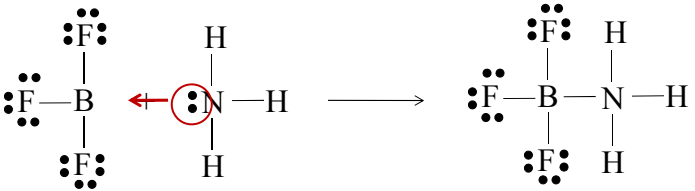
Exceptions to the Octet Rule



The octet rule could be satisfied when a double bond is used.

resonance

- BF₃ can also react with electron-rich molecules and form *coordinate covalent bonds*.



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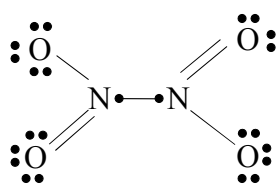
Chapter 8 Section 8

Molecules with an Odd Number of Electrons

- Some molecules contain an odd number of valence electrons and the octet rule can not be achieved.
- An example is nitrogen dioxide (NO₂).

$$17e^- - 4e^- = 13e^-$$

Molecules with an odd number of electrons are known as *free radicals*. Radicals are very reactive.



Now the octet rule is satisfied for the nitrogen atom

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Molecules with an Odd Number of Electrons

- Another example is nitric oxide (NO)

What possible Lewis structures one can draw?
How can you determine the best one?



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Chapter 8 Section 8

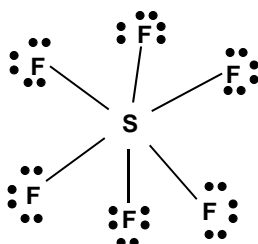


Molecules with Expanded Octets

- Some atoms with empty *d* orbitals, such as S or P, can exceed the octet rule.
- Sulfur hexachloride (SF₆)

$$(6+6 \times 7)e^- - 12e^- = 36e^-$$

$$36e^- - 36e^- = 0e^-$$



There are 12
electrons around
the S atom
"expanded octet"

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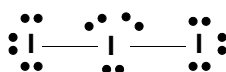
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Molecules with Expanded Octets

- (I_3^-)

$$(21+1)e^- - 4e^- = 18e^-$$

$$18e^- - 12e^- = 6e^-$$



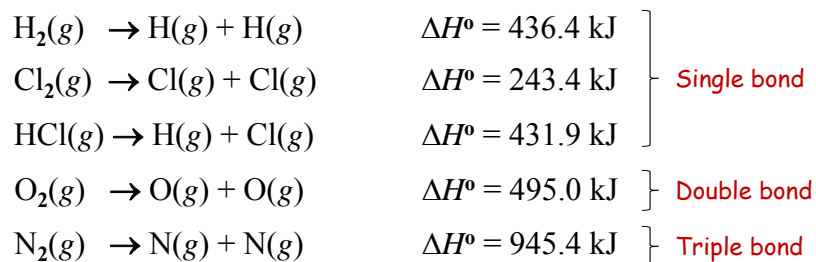
There are 10
electrons around
the I atom
"expanded octet"

Writing Lewis Structures (Octet Rule)

- Some more exercises:
 - CO_3^{2-} (Carbonate ion)
 - O_3 (Ozone)
 - SO_4^{2-} (Sulfate ion)
 - ClF_3
 - XeF_4

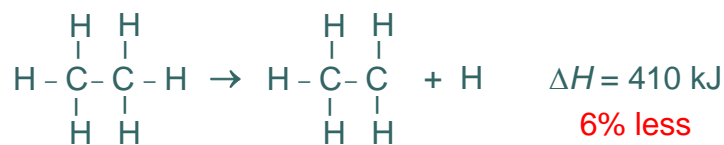
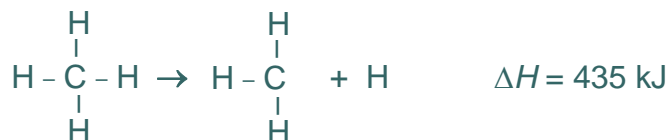
Bond Enthalpy

- **Bond enthalpy** (ΔH°) is the energy associated with breaking a particular bond in one mole of gaseous molecules.



Bond Enthalpy

- Bond enthalpies for polyatomic molecules depend upon the bond's environment.



Average Bond Enthalpy

- **Average** bond enthalpies are used for polyatomic molecules.
- Average bond enthalpies can be used to estimate the enthalpy of chemical reactions.

TABLE 8.6 Bond Enthalpies

Bond	Bond Enthalpy (kJ/mol)	Bond	Bond Enthalpy (kJ/mol)
H-H*	436.4	C-S	255
H-N	393	C=S	477
H-O	460	N-N	193
H-S	368	N=N	418
H-P	326	N≡N	941.4
H-F	568.2	N-O	176
H-Cl	431.9	N=O	607
H-Br	366.1	O-O	142
H-I	298.3	O=P	502
C-H	414	O=S	469
C-C	347	P-P	197
C=C	620	P=P	489
C≡C	812	S-S	268
C-N	276	S=S	352
C=N	615	F-F	156.9
C≡N	891	Cl-Cl	242.7
C-O	351	Cl-F	193
C=O [†]	745	Br-Br	192.5
C=O	1070	I-I	151.0
C-P	263		

*Bond enthalpies shown in red are for diatomic molecules.

[†]The C=O bond enthalpy in CO₂ is 799 kJ/mol.

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Average Bond Enthalpy

TABLE 8.5 Bond Lengths for Selected Bonds

Bond	Bond Type	Bond Length (pm)	Bond Energy (kJ/mol)
C-C	Single	154	347
C=C	Double	134	614
C≡C	Triple	120	839
C-O	Single	143	358
C=O	Double	123	745
C-N	Single	143	305
C=N	Double	138	615
C≡N	Triple	116	891

The more the number of shared electrons, the stronger the bond is and the shorter it becomes.

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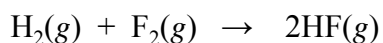
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Bond Energy and Enthalpy

ΔH_{rxn} = Energy required to break bonds
 – Energy released when new bonds formed

$$\Delta H_{\text{rxn}} = \sum \text{BE (bonds broken)} - \sum \text{BE (bonds formed)}$$

BE is the average bond energy per mole of bonds.



$$\begin{aligned} \Delta H_{\text{rxn}} &= \text{BE}_{\text{H-H}} + \text{BE}_{\text{F-F}} - 2 \text{BE}_{\text{H-F}} \\ &= 436 \text{ kJ/mol} + 157 \text{ kJ/mol} - 2 \text{ mol} (568 \text{ kJ/mol}) \\ &= -543 \text{ kJ} \end{aligned}$$

From
Chapter 5

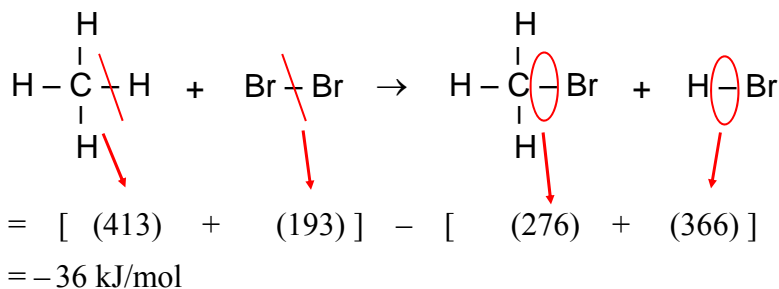
$$\begin{aligned} \Delta H^\circ &= 2 \times \Delta H_f^\circ(\text{HF}) \\ &= 2 \times -271 \text{ kJ/mol} = -542 \text{ kJ} \end{aligned}$$

Average Bond Enthalpy

Example: Calculate the enthalpy of reaction for



Solution: Consider ONLY bonds broken or formed.



Bond Energy and Enthalpy

TABLE 8.4 Average Bond Energies (kJ/mol)

Single Bonds				Multiple Bonds			
H—H	432	N—H	391	I—I	149	C=C	614
H—F	565	N—N	160	I—Cl	208	C≡C	839
H—Cl	427	N—F	272	I—Br	175	O=O	495
H—Br	363	N—Cl	200	S—H	347	C=O*	745
H—I	295	N—Br	243	S—F	327	C≡O	1072
		N—O	201	S—Cl	253	N=O	607
C—H	413	O—H	467	S—Br	218	N=N	418
C—C	347	O—O	146	S—S	266	N≡N	941
C—N	305	O—F	190			C≡N	891
C—O	358	O—Cl	203			C=N	615
C—F	485	O—I	234	Si—Si	340		
C—Cl	339			Si—H	393		
C—Br	276	F—F	154	Si—C	360		
C—I	240	F—Cl	253	Si—O	452		
C—S	259	F—Br	237				
		Cl—Cl	239				
		Cl—Br	218				
		Br—Br	193				

1(g)

-Cl

*C=O(CO₂) = 799