

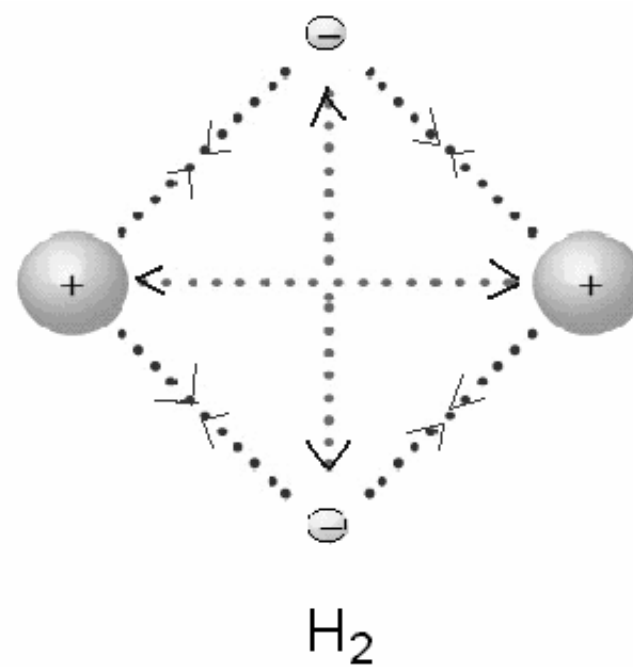
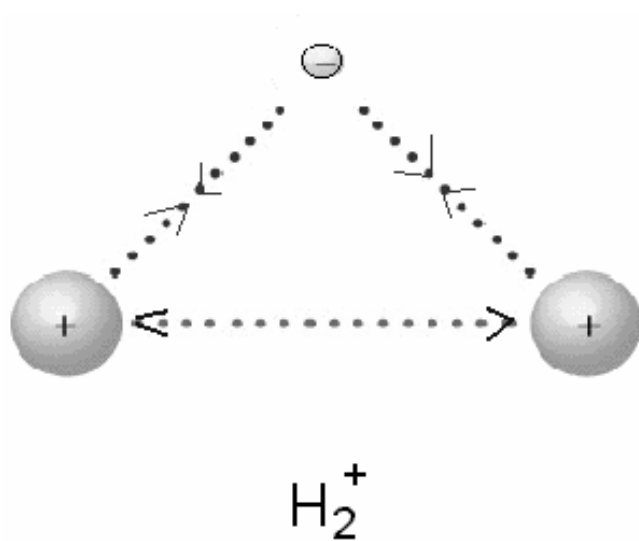
Chapter 13

Bonding: General Concepts

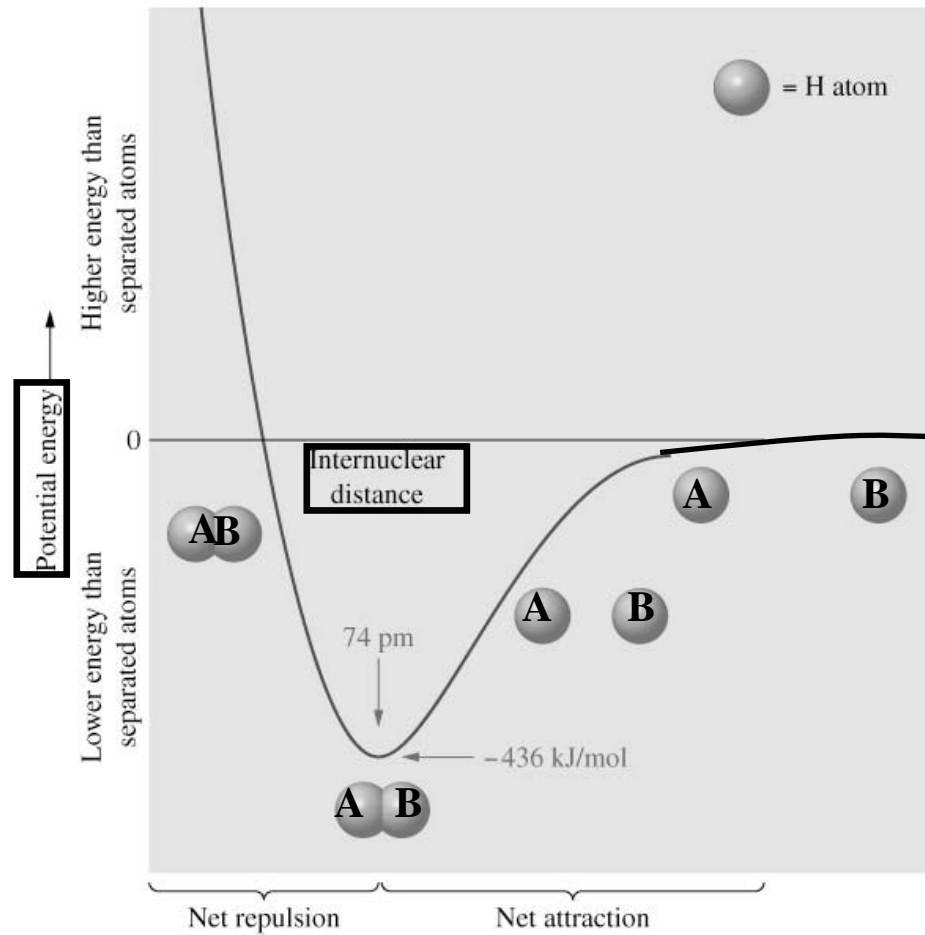
Chemical Bonds: A Preview

- Forces called **chemical bonds** hold atoms together in molecules and keep ions in place in solid ionic compounds.
- Chemical bonds are electrical forces; they reflect a balance in the forces of attraction and repulsion between electrically charged particles.
- Through appropriate measurements, scientists can determine the internuclear distances that correspond to the lowest energy states of molecules.
- Quantum mechanical calculations can then be used to develop a theoretical model that fits the experimental measurements.

Electrostatic Attractions and Repulsions



Energy of Interaction



Electronegativity

- **Electronegativity (EN, expressed as χ)**, is a measure of the ability of an atom to attract bonding electrons to itself when the atom is in a molecule.
- **Mulliken's EN**

$$\text{Absolute EN, } \chi = (\text{IE} + \text{EA})/2$$

- **Pauling's EN**

$$\text{define } \chi_{\text{H}} = 2.2$$

$$\Delta \chi = \chi_{\text{A}} - \chi_{\text{B}} = [\Delta_{\text{AB}}(\text{kJ})/96.49]^{1/2} = [\Delta_{\text{AB}}(\text{kcal})/23.06]^{1/2}$$

$$\Delta_{\text{AB}} = D(\text{A-B}) - 1/2 [D(\text{A-A}) + D(\text{B-B})]$$


 Bond dissociation energy of A-B

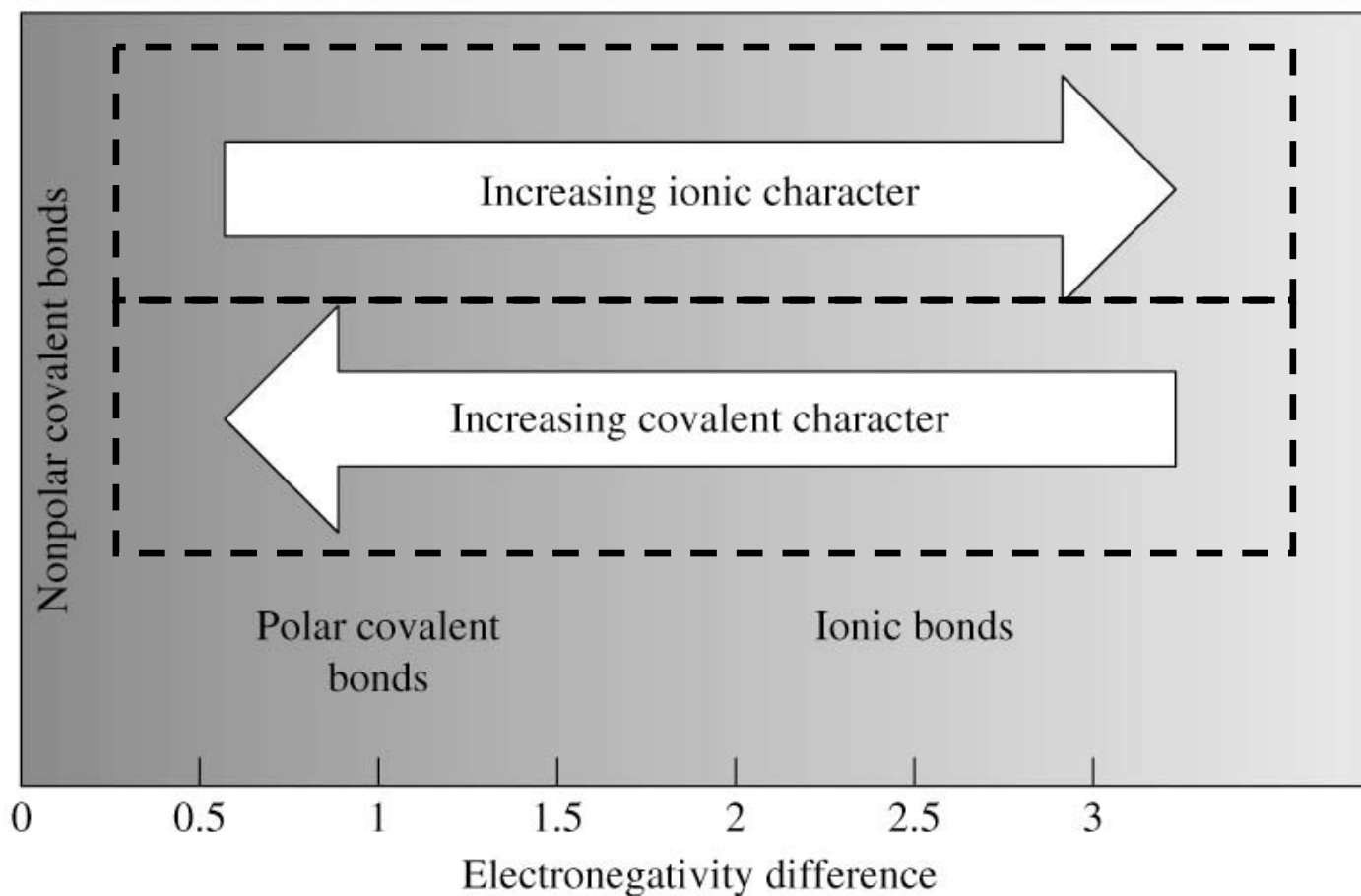
Pauling's Electronegativities

		<div><div><div>Below 1.0</div><div>1.0–1.4</div><div>1.5–1.9</div></div><div><div>2.0–2.4</div><div>2.5–2.9</div><div>3.0–4.0</div></div></div>															
	1A	2A										3A	4A	5A	6A	7A	
1	H 2.2											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
2	Li 1.0	Be 1.5									Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0		
3	Na 0.9	Mg 1.2	3B	4B	5B	6B	7B	8B			1B	2B	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
4	K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.7	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
5	Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
6	Cs 0.7	Ba 0.9	La* 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
7	Fr 0.7	Ra 0.9	Ac† 1.1	*Lanthanides: 1.1–1.3 †Actinides: 1.3–1.5													

Electronegativity Difference and Bond Type

- Two identical atoms have the same electronegativity and share a bonding electron pair equally. This is called a **non-polar covalent bond**. (For $\chi_A \sim \chi_B$, or $|\chi_A - \chi_B| < 0.3$)
- In covalent bonds between atoms with somewhat larger electronegativity differences ($0.3 < |\chi_A - \chi_B| < 1.8$) , electron pairs are shared unequally. The electrons are drawn closer to the atom of higher electronegativity, and the bond is called a **polar covalent bond**.
- With still larger differences in electronegativity ($|\chi_A - \chi_B| > 1.8$) , electrons may be completely transferred from metal to nonmetal atoms to form **ionic bonds**.

Electronegativity and Bond Type



Ionic Bonds and Ionic Crystals

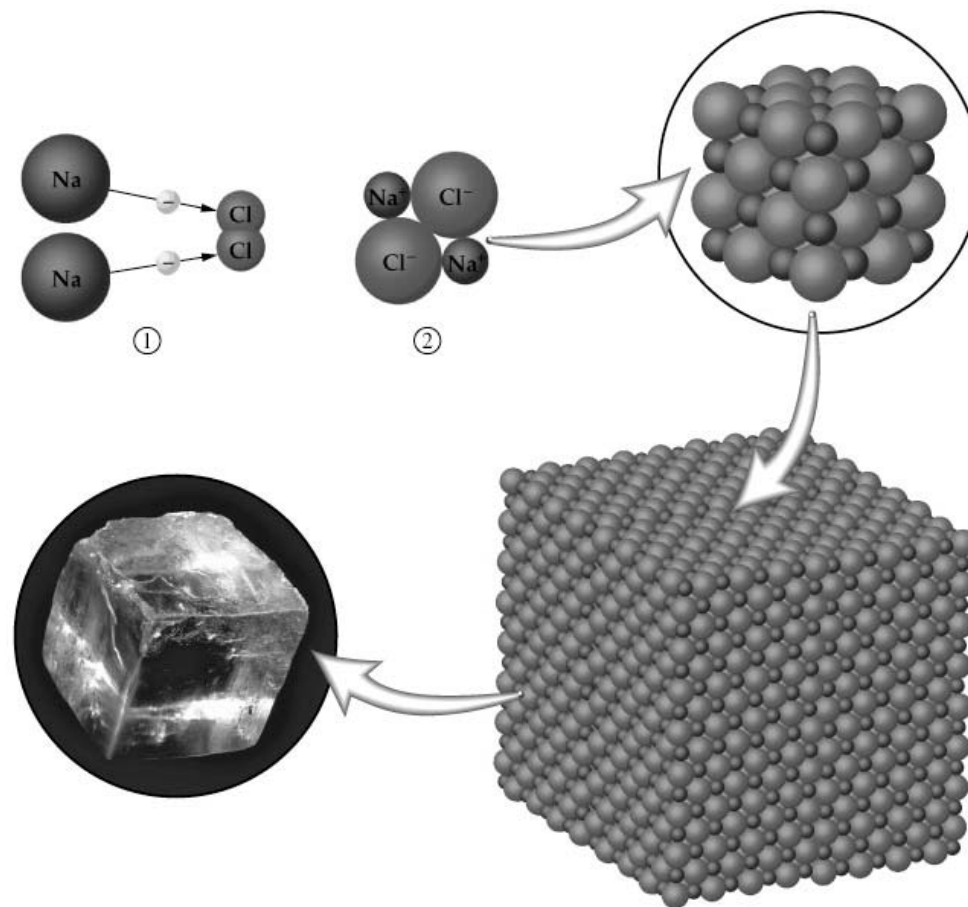
- When atoms lose or gain electrons, they acquire a noble gas configuration, but do not *become* noble gases.
- Because the two ions formed in a reaction between a metal and a non-metal have opposite charges, they are strongly attracted to one another and form an *ion pair*.
- The net attractive electrostatic forces that hold the cations and anions together are **ionic bonds**.
- The highly ordered solid collection of ions is called an **ionic crystal**.

Interionic Forces of Attraction - Coulombic Force

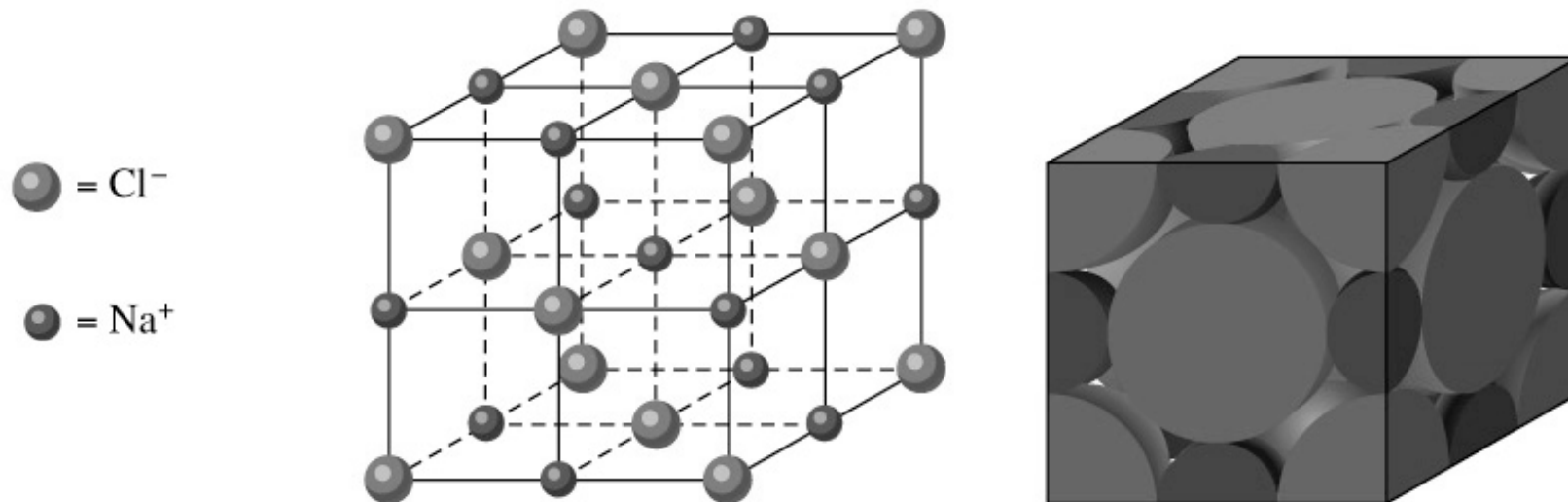


$$E = (Z^+Z^-)/4\pi\epsilon r$$

Formation of a Crystal of Sodium Chloride



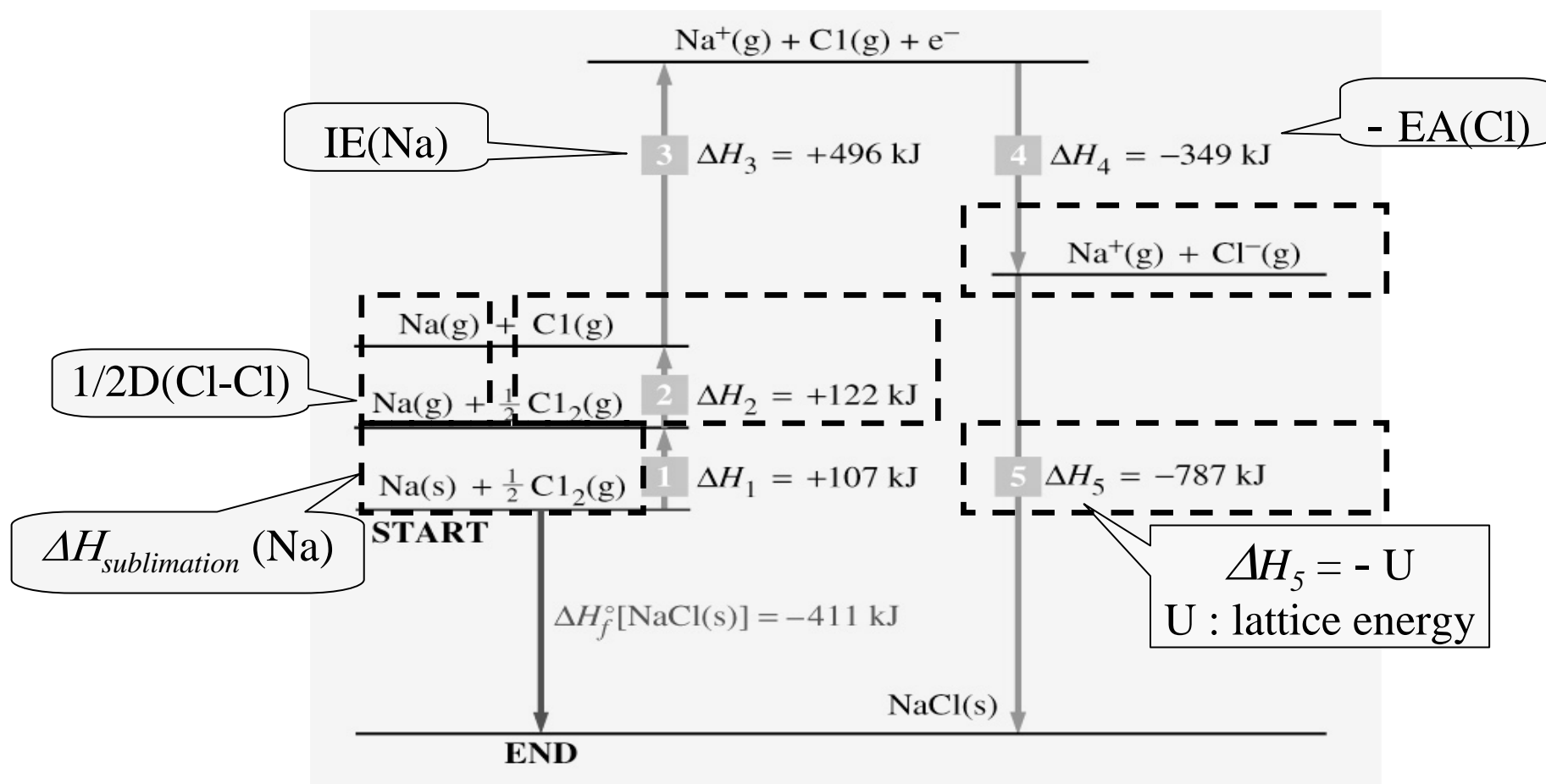
Unit Cell of Sodium Chloride



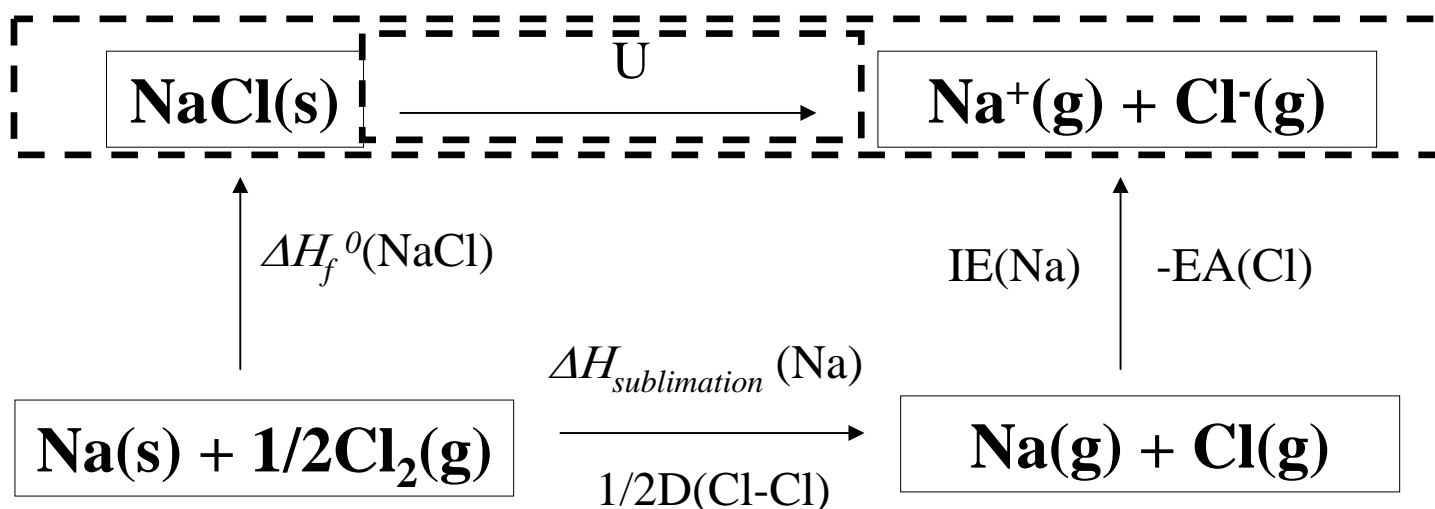
Energy Changes in Ionic Compound Formation

- The enthalpy of formation of the ionic compound is more important than first ionization energy and electron affinity.
- The overall enthalpy change can be calculated using a step-wise procedure called the **Born-Haber cycle**.
- The sum of the enthalpy change values for the individual steps is in accordance with Hess's Law.
- The large negative value of the lattice energy is the major factor that makes ionic compound formation an energetically favorable process.

A Born-Haber Cycle Example



A Born-Haber Cycle Example



lattice energy $U = -\Delta H_f^0(\text{NaCl}) + \Delta H_{\text{sublimation}}(\text{Na}) + 1/2D(\text{Cl-Cl}) + \text{IE}(\text{Na}) - \text{EA}(\text{Cl})$

$= (+411 + 107 + 122 + 496 - 349) \text{ kJ/mol}$

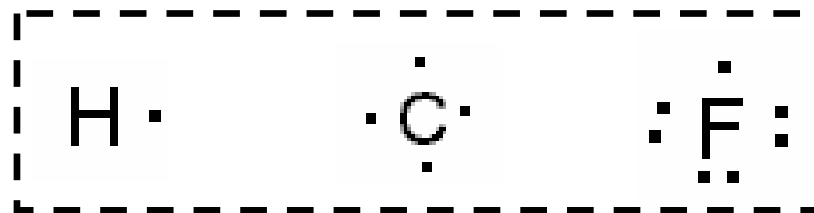
$= +787 \text{ kJ/mol}$

The Lewis Theory of Chemical Bonding

- Electrons, particularly valence electrons, play a fundamental role in chemical bonding.
- When metals and non-metals combine, valence electrons usually are transferred from the metal to the non-metal atoms giving rise to **ionic bonds**.
- In combinations involving only non-metals, one or more *pairs* of valence electrons are *shared* between the bonded atoms producing **covalent bonds**.
- In losing, gaining, or sharing electrons to form chemical bonds, atoms tend to acquire the electron configurations of noble gases.

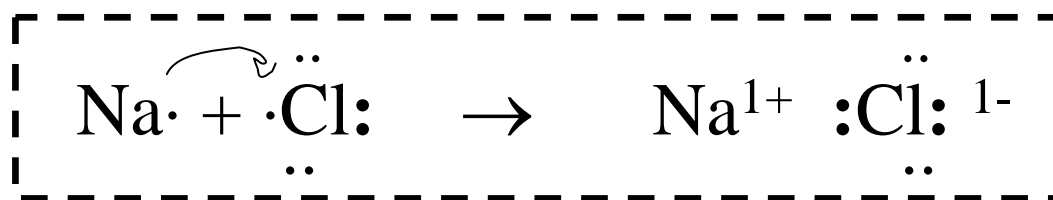
Lewis Symbols

- In a **Lewis symbol**, the chemical symbol for the element represents the nucleus and core electrons of the atom, and dots around the symbol represent the *valence* electrons.



Using Lewis Symbols to Represent Ionic Bonding

- Instead of using complete electron configurations to represent the loss and gain of electrons, Lewis symbols can be used for ionic bond.

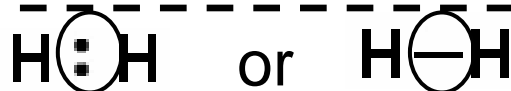


Lewis Structures Of Simple Molecules

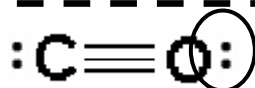
- A **Lewis structure** is a combination of Lewis symbols that represents the formation of covalent bonds between atoms.
- In most cases, a Lewis structure shows the bonded atoms with the electron configuration of a noble gas; that is, the atoms obey the **octet rule**. (H obeys the *duet rule*.)

Lewis Structures (continued)

- The shared pairs of electrons in a molecule are called **bonding pairs**.
- In common practice, the bonding pair is represented by a dash (-).

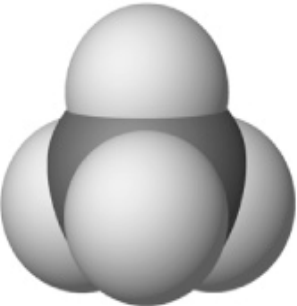
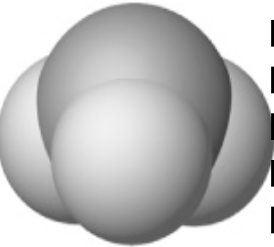
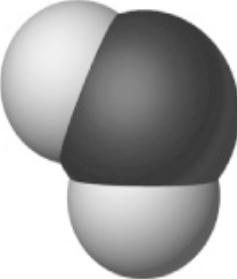
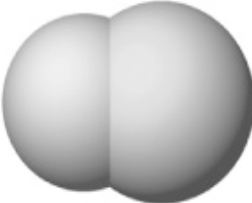


- The other electron pairs, which are not shared, are called *non-bonding pairs*, or **lone pairs**.



2nd period elements follow **octet rule**

The non-metals of the second period (except boron?) tend to form a number of covalent bonds equal to *eight minus the group number*.

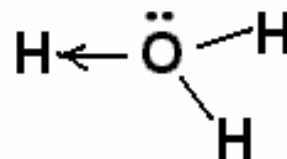
Group:	4A	5A	6A	7A
Lewis symbol:	$\cdot\ddot{\text{C}}\cdot$	$\cdot\ddot{\text{N}}\cdot$	$\cdot\ddot{\text{O}}\cdot$	$\cdot\ddot{\text{F}}\cdot$
Name and formula:	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$ Methane, CH ₄	$\begin{array}{c} \text{H} \\ \\ \text{H}-\ddot{\text{N}}-\text{H} \\ \\ \text{H} \end{array}$ Ammonia, NH ₃	$\begin{array}{c} \text{H} \\ \\ \text{H}-\ddot{\text{O}}: \\ \\ \text{H} \end{array}$ Water, H ₂ O	$\text{H}-\ddot{\text{F}}:$ Hydrogen fluoride, HF
Geometric shape:				

Coordinate Covalent Bonds

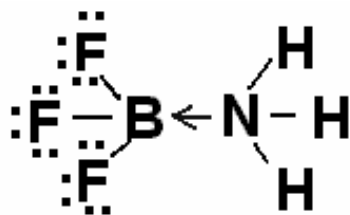
In some cases, one atom provides both electrons of the shared pair to form a bond called a **coordinate covalent bond (or dative bond)**.

For example:

- *hydronium ions*
 H_3O^+



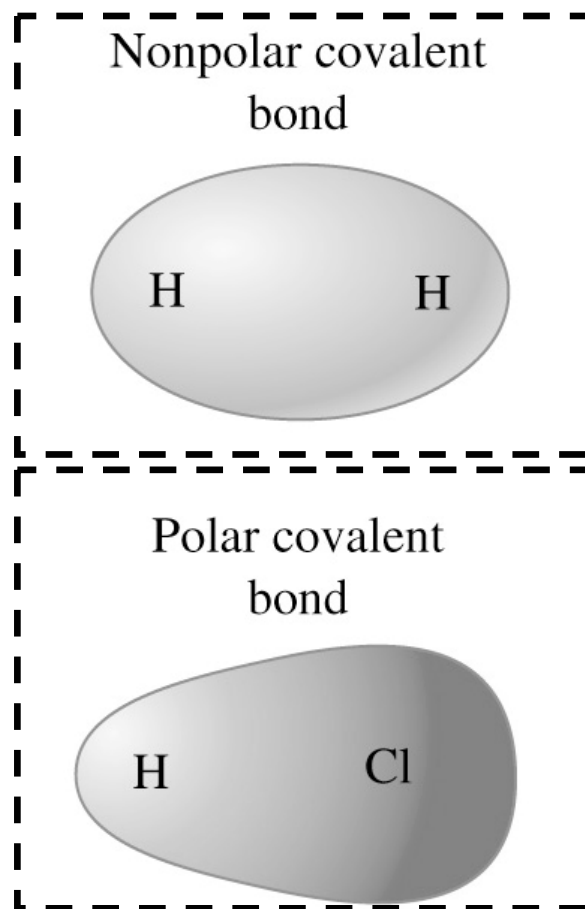
- $\text{F}_3\text{B}-\text{NH}_3$



Multiple Covalent Bonds

- The covalent bond in which one pair of electrons is shared is called a **single bond**.
- Multiple bonds can also form:
 - **Double bonds** have two shared pairs of electrons.
 - **Triple bonds** have three shared pairs of electrons.
- A double bond is represented by two dashes (=).
- A triple bond is represented by three dashes (≡).

Polar and Non-polar Covalent Bonds



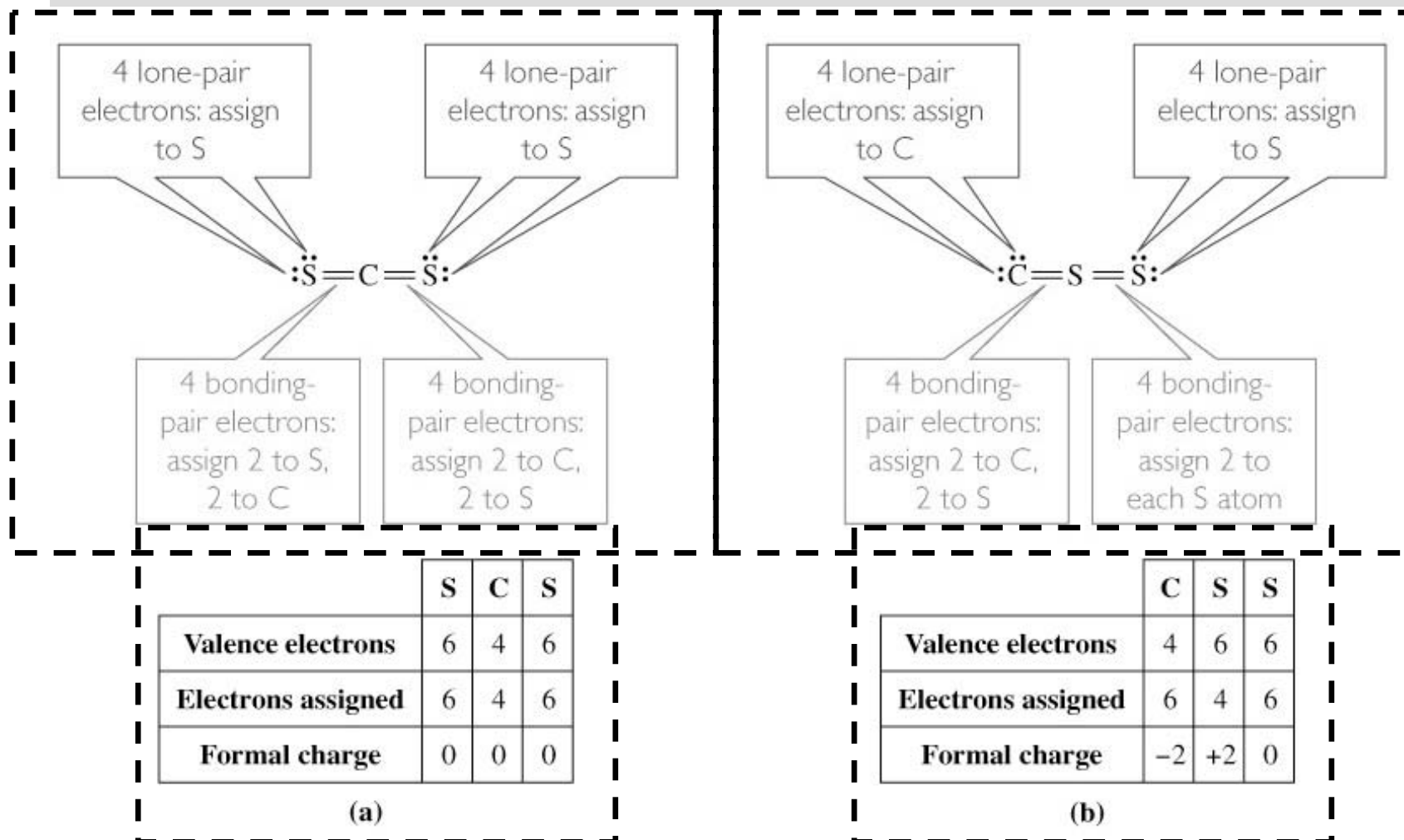
Formal Charge

Formal charge = # of valence electrons

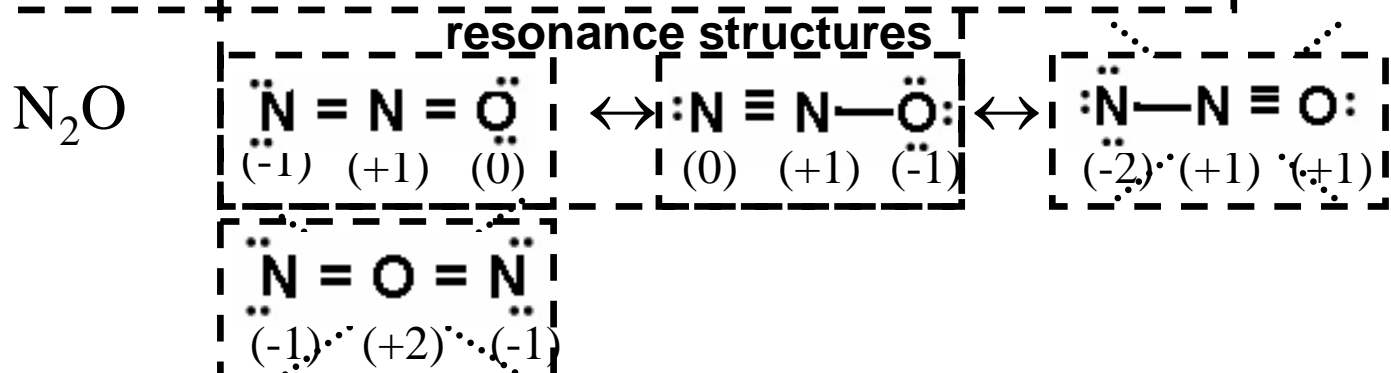
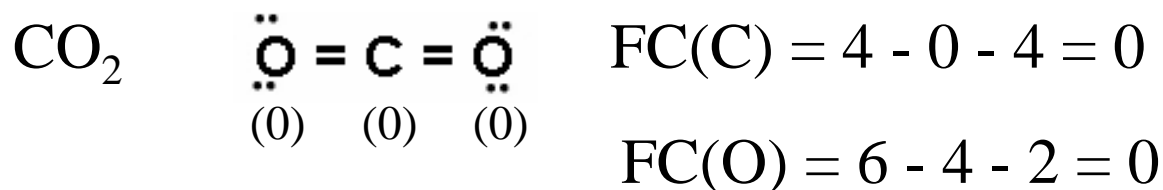
- [# of lone pair electrons + $\frac{1}{2}$ (bonding electrons)]

- Usually, the most plausible Lewis structure is one with no formal charges.
- When formal charges are required, they should be as small as possible.
- Negative formal charges should appear on the most electronegative atoms.
- Adjacent atoms in a structure should not carry formal charges of the same sign.

Formal Charge Illustrated

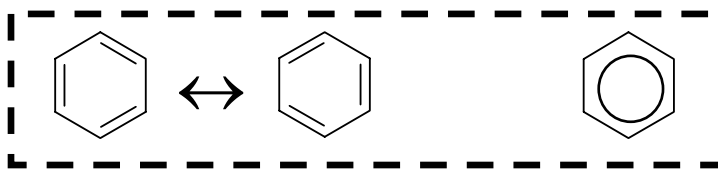


Lewis Structures & Formal Charge



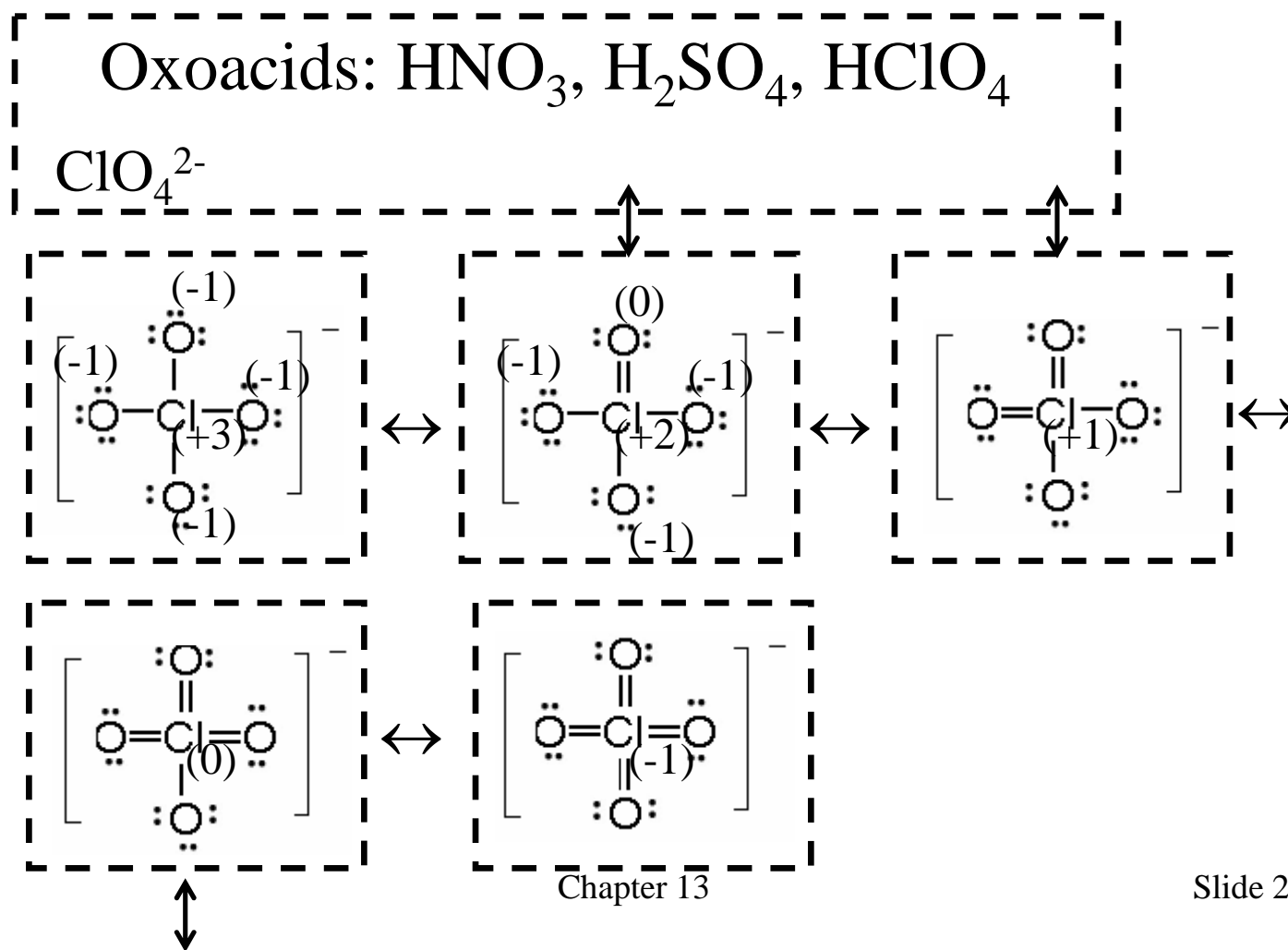
Resonance: Delocalized Bonding

- **Resonance theory** states that whenever a molecule or ion can be represented by two or more plausible Lewis structures that differ *only in the distribution of electrons*, the true structure is a composite, or hybrid, of them.
- The different plausible structures are called **resonance structures**.



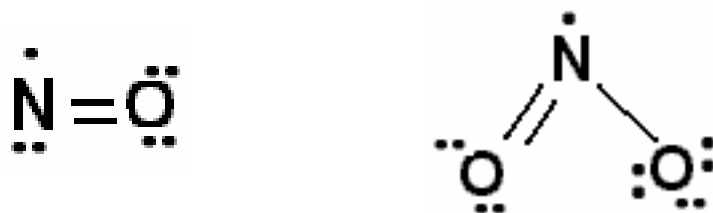
- The actual molecule or ion that is a hybrid of the resonance structures is called a **resonance hybrid**.
- Electrons that are part of the resonance hybrid are spread out over several atoms and are referred to as being **delocalized**.

Resonance

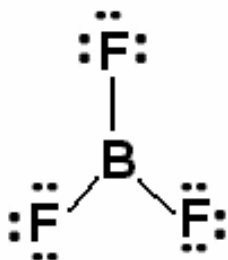


Molecules that Don't Follow the Octet Rule

- Molecules with an odd number of valence electrons have at least one of them unpaired and are called **free radicals**.

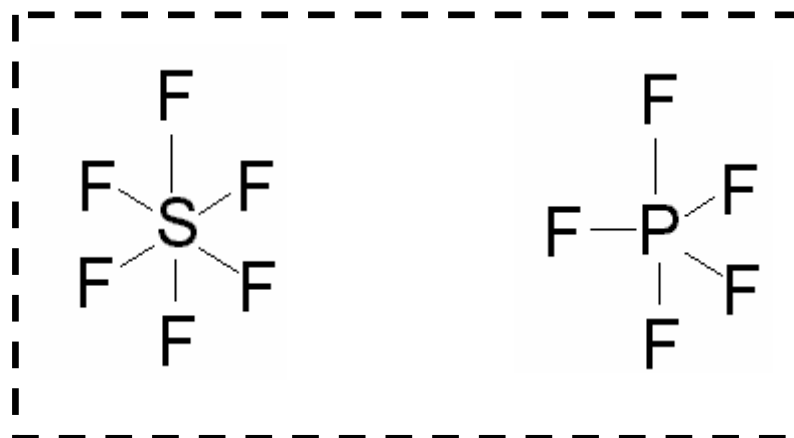


- Some molecules have incomplete octets. These are usually compounds of Be, B, and Al, generally have some unusual bonding characteristics, and are often quite reactive.



Molecules that Don't Follow the Octet Rule (continued)

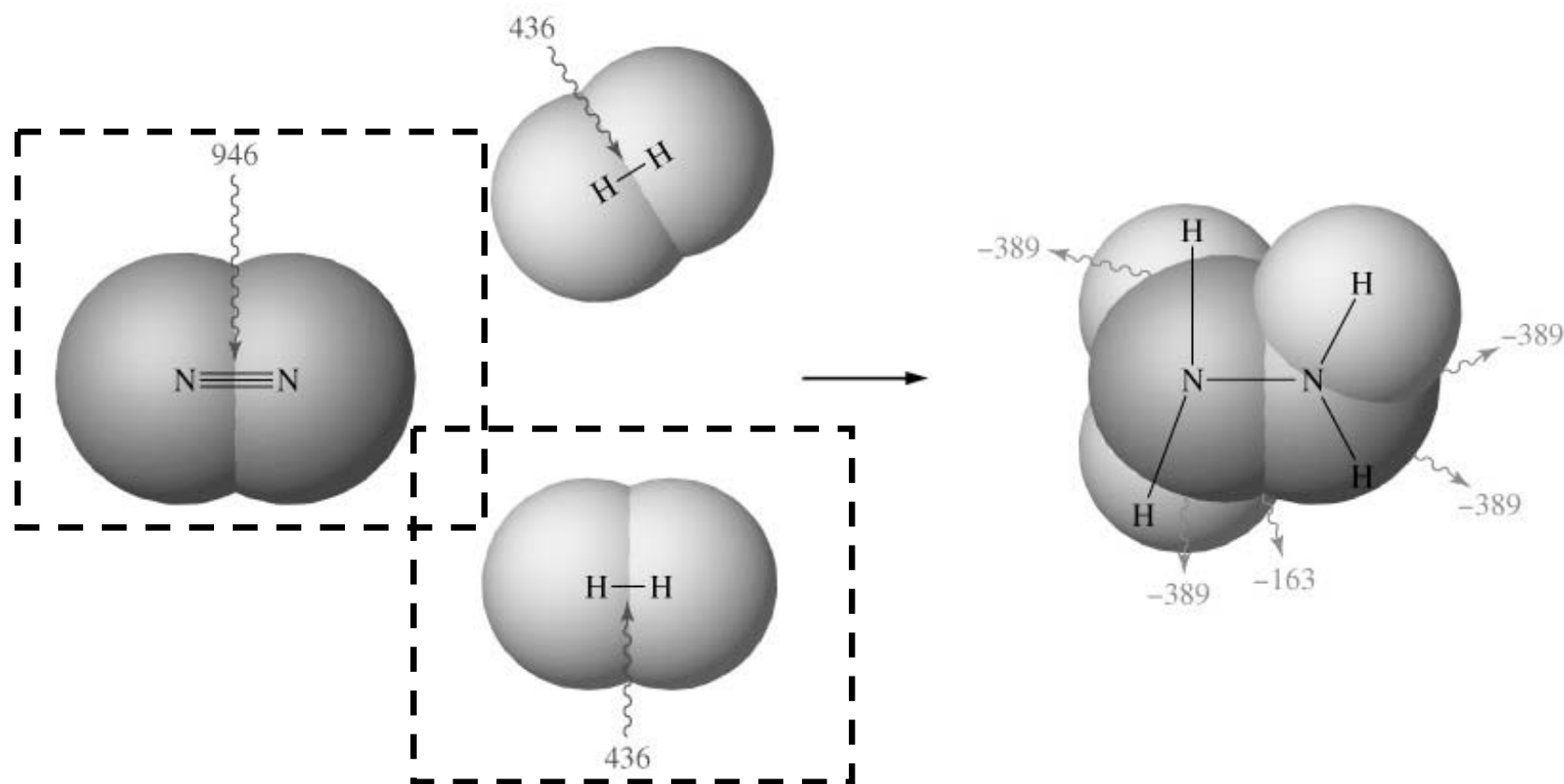
- Some compounds have expanded valence shells, which means that the central atom has more than eight electrons around it.
e.g. SF_6 , PCl_5



Bond Lengths

- The term **bond order** indicates whether a covalent bond is single (b.o. = 1), double (b.o. = 2), or triple (b.o. = 3).
- **Bond length** is the distance between the nuclei of two atoms joined by a covalent bond.
- Bond length depends on the particular atoms in the bond and on the bond order.
- The length of the covalent bond joining unlike atoms is the sum of the covalent radii of the two atoms.
- Bond lengths are usually measured in picometers (10^{-12} meter).

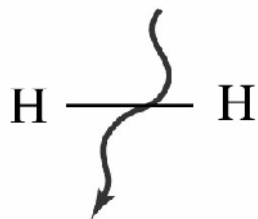
A Visualization of Bond Dissociation Energy



Bond Energies

- Bond-dissociation energy (D)** is the quantity of energy required to break one mole of covalent bonds between atoms in a molecule in the *gas* phase.

436 kJ/mol

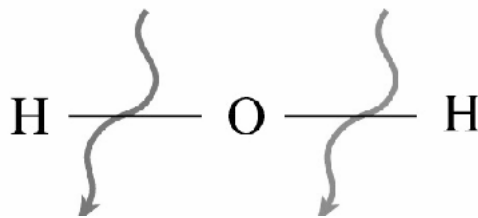


bond-dissociation energy of H-H
= 436 kJ/mol

- An **average bond energy** is the average of the bond-dissociation energies for a number of different molecules containing the particular bond.

499 kJ/mol

428 kJ/mol



average bond energy of O-H
= (499 + 428)/2 = 464 J/mol

Bond Energies

<i>Process</i>	<i>Energy Required (kJ/mol)</i>
$\text{CH}_4(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{g})$	435
$\text{CH}_3(\text{g}) \rightarrow \text{CH}_2(\text{g}) + \text{H}(\text{g})$	453
$\text{CH}_2(\text{g}) \rightarrow \text{CH}(\text{g}) + \text{H}(\text{g})$	425
$\text{CH}(\text{g}) \rightarrow \text{C}(\text{g}) + \text{H}(\text{g})$	339
	<u>Total = 1652</u>

Molecule	Measured C—H Bond Energy (kJ/mol)
----------	-----------------------------------

HBr ₃	380
HCl ₃	380
HF ₃	430
C ₂ H ₆	410

$$\text{Average} = \frac{1652}{4} = 413$$

Representative Bond Lengths & Average Bond Energies

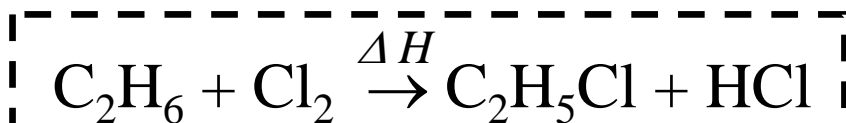
TABLE 9.1 Some Representative Bond Lengths and Bond Energies

Bond	Bond Length, pm	Bond Energy, kJ/mol	Bond	Bond Length, pm	Bond Energy, kJ/mol
H—H	74	436	C—O	143	360
H—C	110	414	C=O	120	736 ^a
H—N	100	389	C—Cl	178	339
H—O	97	464	N—N	145	163?
H—S	132	368	N=N	123	418
H—F	92	565	N≡N	110	946
H—Cl	127	431	N—O	136	222
H—Br	141	364	N=O	120	590
H—I	161	297	O—O	145	142?
C—C	154	347	O=O	121	498
C=C	134	611	F—F	143	159?
C≡C	120	837	Cl—Cl	199	243
C—N	147	305	Br—Br	228	193
C=N	128	615	I—I	266	151
C≡N	116	891			

^aThe value for the C—O bond in CO₂ is considerably different: 799 kJ/mol.

Bond Dissociation Energies & $\Delta H_{\text{reaction}}$

- The sum of the enthalpy changes for breaking the old bonds and forming the new bonds is the enthalpy change for the reaction.



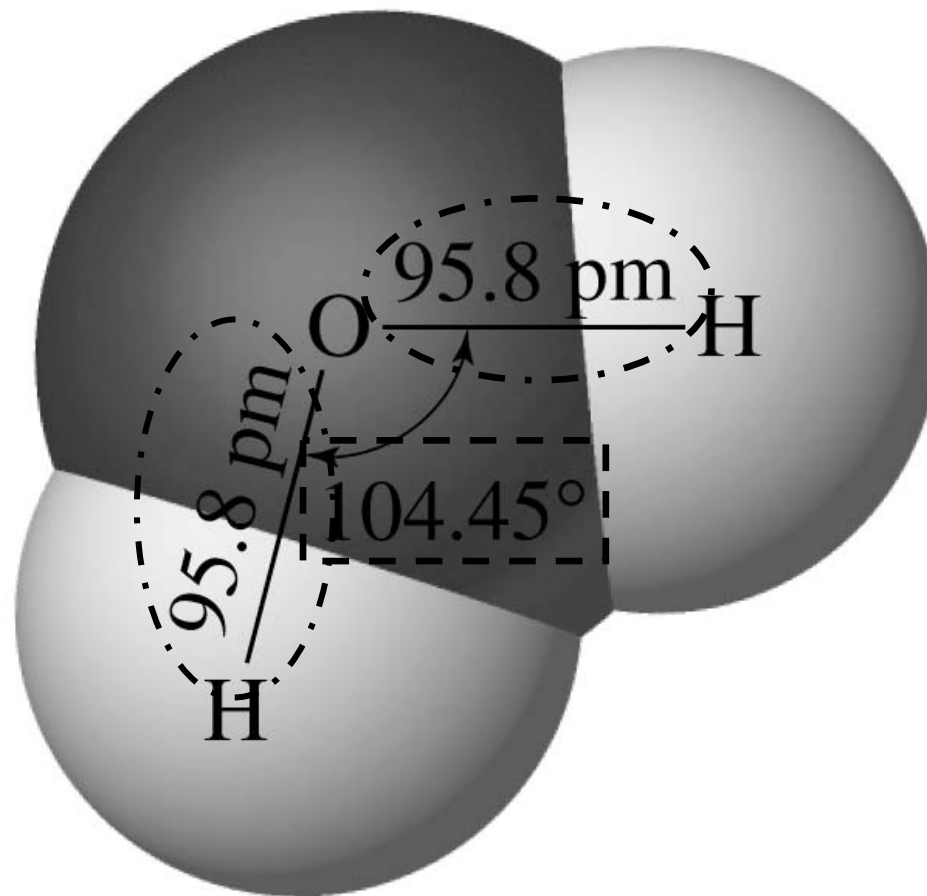
$$\begin{aligned}\Delta H_{\text{reaction}} &= \overset{\text{> 0}}{\Delta H_{\text{bond broken}}} + \overset{\text{< 0}}{\Delta H_{\text{bond formed}}} \\ &= \Sigma D(\text{bonds broken}) - \Sigma D(\text{bonds formed})\end{aligned}$$

$$\begin{aligned}\Delta H &= [D(\text{C-H}) + D(\text{Cl-Cl})] - [D(\text{C-Cl}) + D(\text{H-Cl})] \\ &= [414 + 243] - [339 + 431] = -113 \text{ kJ/mol}\end{aligned}$$

Molecular Geometry

- The **molecular geometry**, or the shape of a molecule is described by the geometric figure formed when the **atomic nuclei** are imagined to be joined by the appropriate straight lines.
- Determination of **molecular geometry**
 1. **Valence-Shell Electron-Pair Repulsion (VSEPR)**
 - Pairs of valence electrons in bonded atoms repel one another.
 - The mutual repulsions push electron pairs as far from one another as possible.
 2. **Ligand Field Stabilization Energy**
 - Mainly for compounds with the central atoms as transition metals

Molecular Geometry of Water



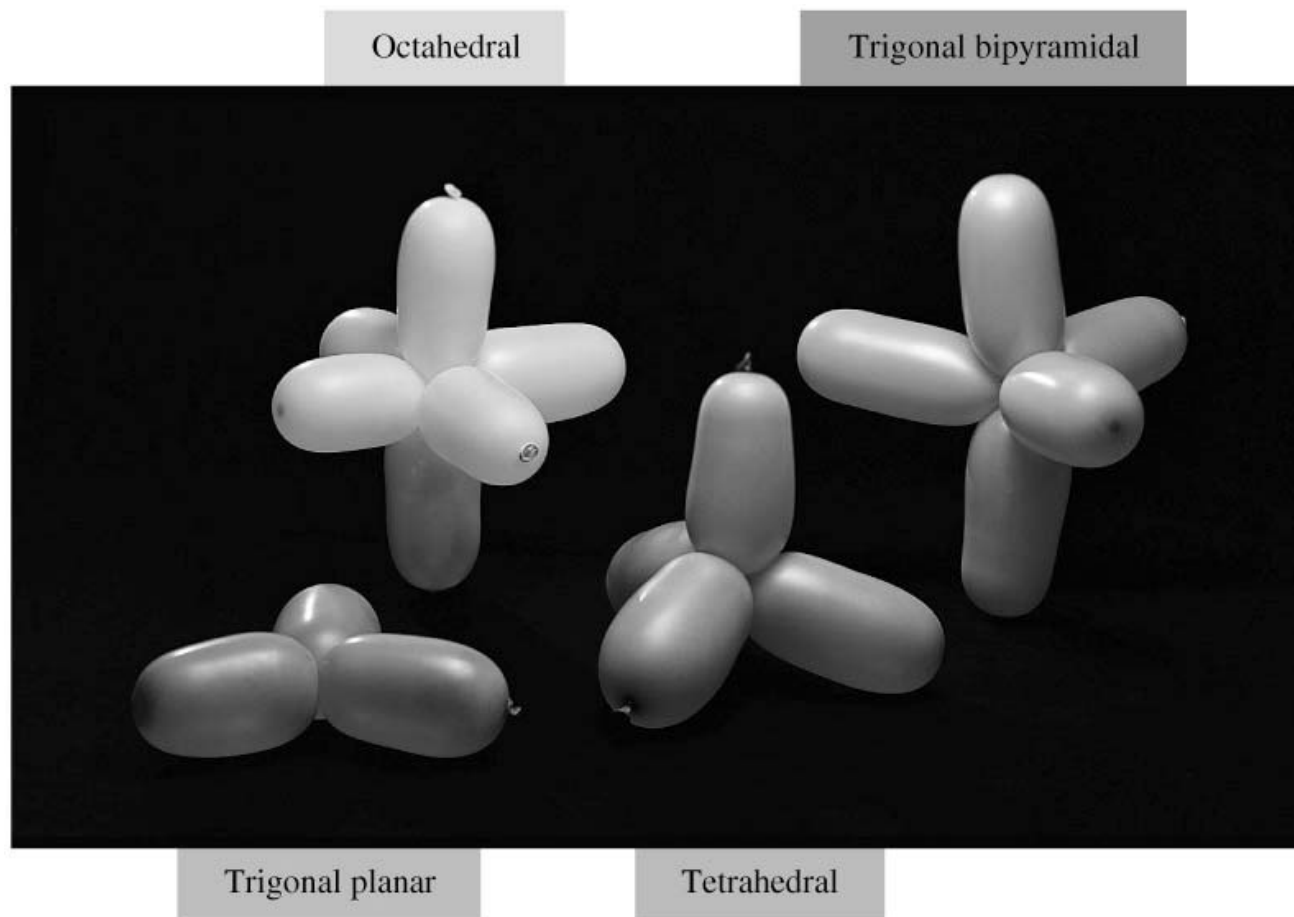
Electron-Group Geometries

- An **electron group** is any collection of valence electrons, localized in a region around a central atom, that repels other groups of valence electrons.
- The mutual repulsions among electron groups lead to an orientation of the groups that are called **electron-group geometry**.

Electron-Group Geometries

#. of Electron Pair	Electron-group Geometry
2	linear
3	trigonal planar
4	tetrahedral
5	Trigonal bipyramidal
6	octahedral

A Balloon Analogy



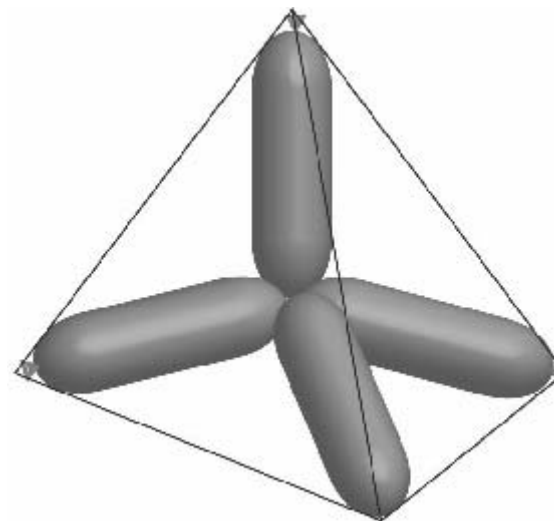
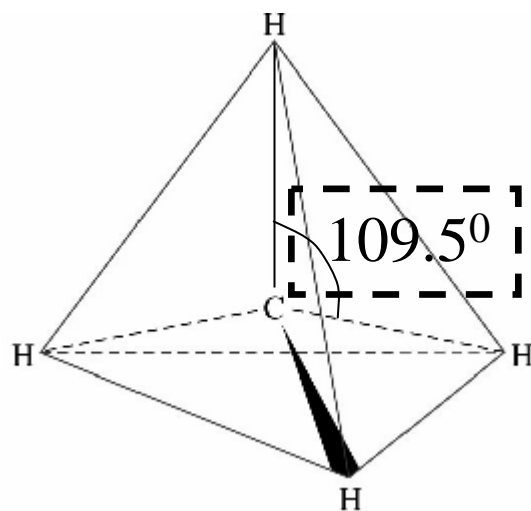
Geometries of Methane

#. of electron group on C = $1/2 (4 + 4) = 4$

Electron group geometry: tetrahedral

VSEPR notation AX_4

Molecular geometry: tetrahedral



Molecular Geometry of Water

#. of electron group on O = $1/2 (6 + 2) = 4$

Electron group geometry: tetrahedral

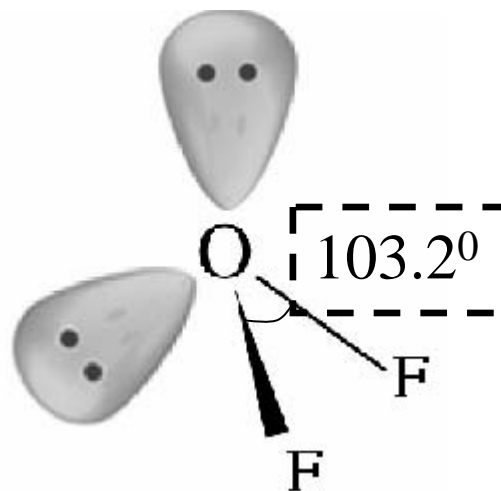
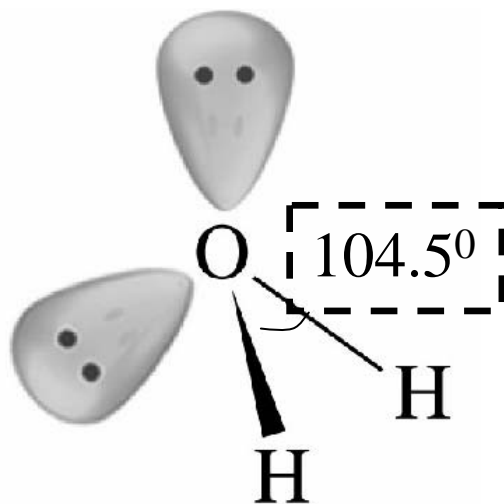
VSEPR notation AX_2E_2

Molecular geometry: bent

A: the central atom in a structure

X: terminal atoms

E: the lone pairs of electrons



Electron Repulsion

Electron Repulsion

- $\text{Lone-pair} - \text{Lone-pair} > \text{Lone-pair} - \text{Bonding-pair}$
 $> \text{Bonding-pair} - \text{Bonding-pair}$
- $\text{Triple bond} > \text{Double bond} > \text{Single bond}$

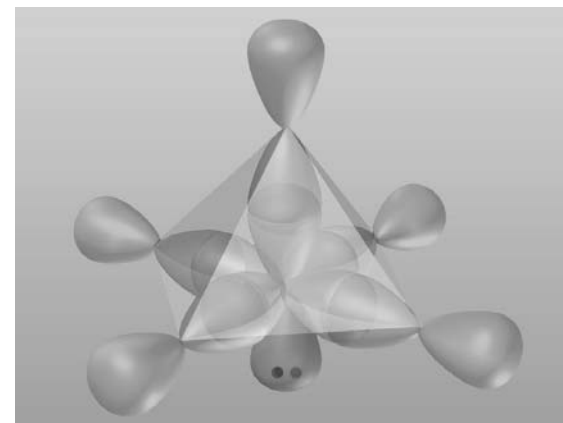
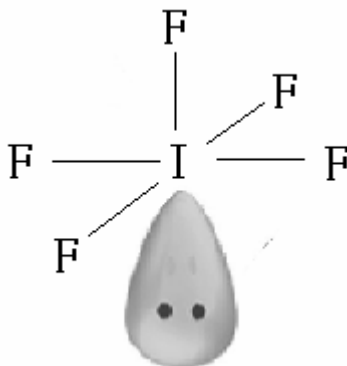
Molecular Geometry for Iodine Pentafluoride (IF₅)

#. of electron group on I = $1/2 (7 + 5) = 6$

Electron group geometry: octahedral

VSEPR notation AX₅E

Molecular geometry: Square pyramidal



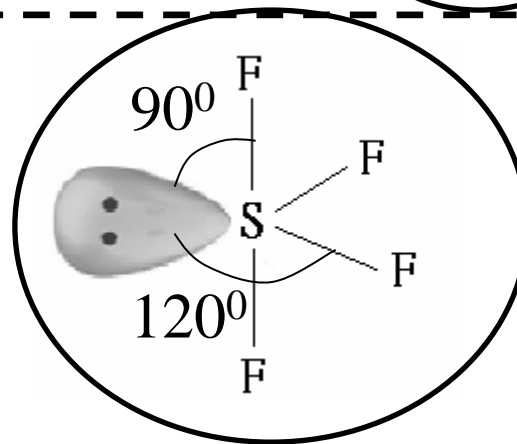
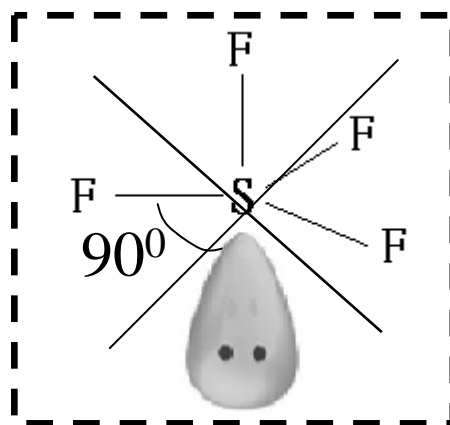
Molecular Geometry for Sulfur Tetrafluoride (SF₄)

#. of electron group on S = $1/2 (6 + 4) = 5$

Electron group geometry: trigonal bipyramidal

VSEPR notation AX₄E

Molecular geometry: ~~trigonal pyramidal~~ or Seesaw



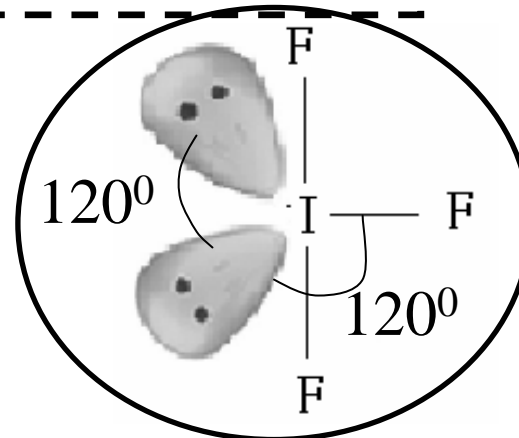
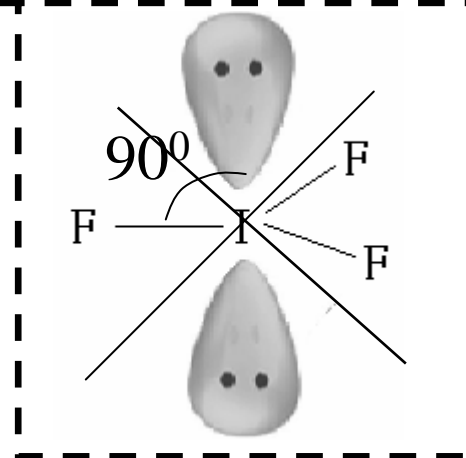
Molecular Geometry for Iodine Trifluoride (IF₃)

#. of electron group on I = $1/2 (7 + 3) = 5$

Electron group geometry: trigonal bipyramidal

VSEPR notation AX₃E₂

Molecular geometry: ~~triangular~~ or T-shaped



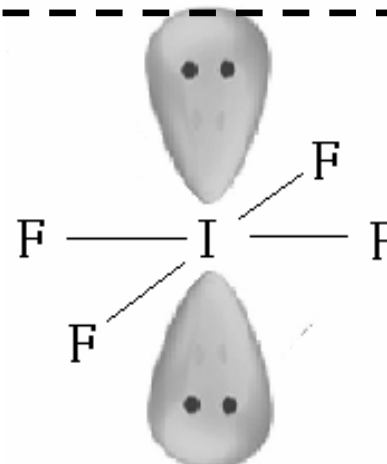
Molecular Geometry for Iodine Tetrafluoride Ion (IF_4^-)

#. of electron group on I = $1/2 (7 + 4 + 1) = 6$

Electron group geometry: octahedral

VSEPR notation AX_4E_2

Molecular geometry: Square planar



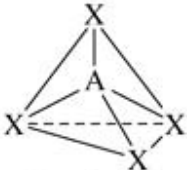
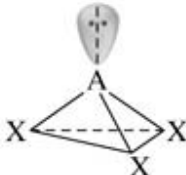

A VSEPR Summary

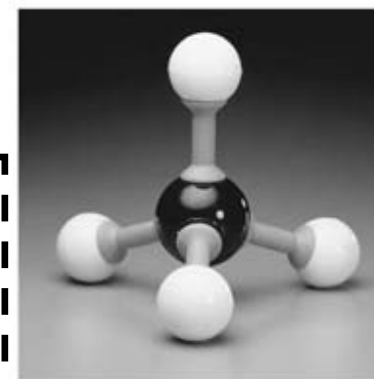
TABLE 10.1 VSEPR Notations, Electron-Group Geometry, and Molecular Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
2	Linear	0	AX ₂	$\text{X}-\text{A}-\text{X}$ Linear	180°	BeCl ₂ <div data-bbox="1563 580 1998 730" data-label="Chemical-Block"> </div> <div data-bbox="1720 751 1832 794" data-label="Caption"> <p>(BeCl₂)</p> </div>
3	Trigonal planar	0	AX ₃	$\begin{array}{c} \text{X} \\ \diagup \\ \text{X}-\text{A} \\ \diagdown \\ \text{X} \end{array}$ Trigonal planar	120°	BF ₃ <div data-bbox="1568 842 2002 1037" data-label="Chemical-Block"> </div> <div data-bbox="1742 1058 1823 1101" data-label="Caption"> <p>(BF₃)</p> </div>
3	Trigonal planar	1	AX ₂ E	$\begin{array}{c} \text{X} \\ \diagup \\ \text{X}-\text{A} \\ \diagdown \\ \text{X} \end{array}$ Angular	120°	SO ₂

A VSEPR Summary (continued)

TABLE 10.1 VSEPR Notations, Electron-Group Geometry, and Molecular Geometry (continued)

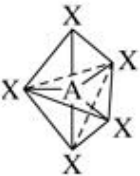
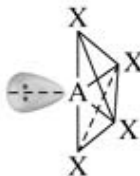
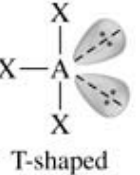
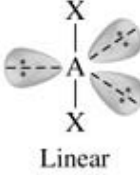
Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
4	Tetrahedral	0	AX ₄	 Tetrahedral	109.5°	CH ₄
4	Tetrahedral	1	AX ₃ E	 Trigonal pyramidal	109.5°	NH ₃
4	Tetrahedral	2	AX ₂ E ₂	 Angular	109.5°	OH ₂

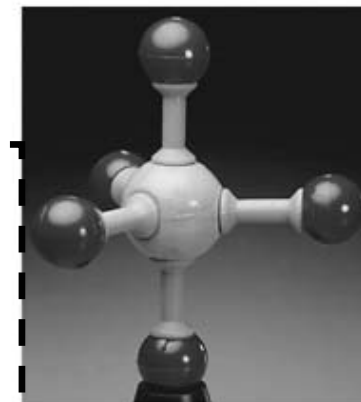


(CH₄)

A VSEPR Summary (continued)

TABLE 10.1 VSEPR Notations, Electron-Group Geometry, and Molecular Geometry (continued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
5	Trigonal bipyramidal	0	AX ₅	 Trigonal bipyramidal	90°, 120°, 180°	PCl ₅
5	Trigonal bipyramidal	1	AX ₄ E	 Seesaw	90°, 120°, 180°	SF ₄
5	Trigonal bipyramidal	2	AX ₃ E ₂	 T-shaped	90°, 180°	ClF ₃
5	Trigonal bipyramidal	3	AX ₂ E ₃	 Linear	180°	XeF ₂



(PCl₅)

A VSEPR Summary (continued)

TABLE 10.1 VSEPR Notations, Electron-Group Geometry, and Molecular Geometry (continued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
6	Octahedral	0	AX ₆	Octahedral	90°, 180°	SF ₆
6	Octahedral	1	AX ₅ E	Square pyramidal	90°	BrF ₅
6	Octahedral	2	AX ₄ E ₂	Square planar	90°	XeF ₄



(SF₆)

Polar Molecules and Dipole Moments

- A molecule with separate centers of positive and negative charge is called a **polar molecule**.
- The **dipole moment** (μ) of a molecule is the product of the magnitude of the charge (δ) and the distance (d) that separates the centers of positive and negative charge.

$$\mu = \delta d$$

Polar Molecules and Dipole Moments

- Dipole moments are generally expressed in a quantity called a *debye*.
- 1 **debye (D)** = $3.34 \times 10^{-30} \text{ C m} = 10^{-18} \text{ esu}$
- charge of electron = $1.602 \times 10^{-19} \text{ C} = 4.80 \times 10^{-10} \text{ esu}$

Polar Molecules and Dipole Moments

Calculation of percentage ionic character of HCl

$$\text{H-Cl}, \mu = 1.08 \text{ D}, r_{\text{H-Cl}} = 127 \text{ pm}$$

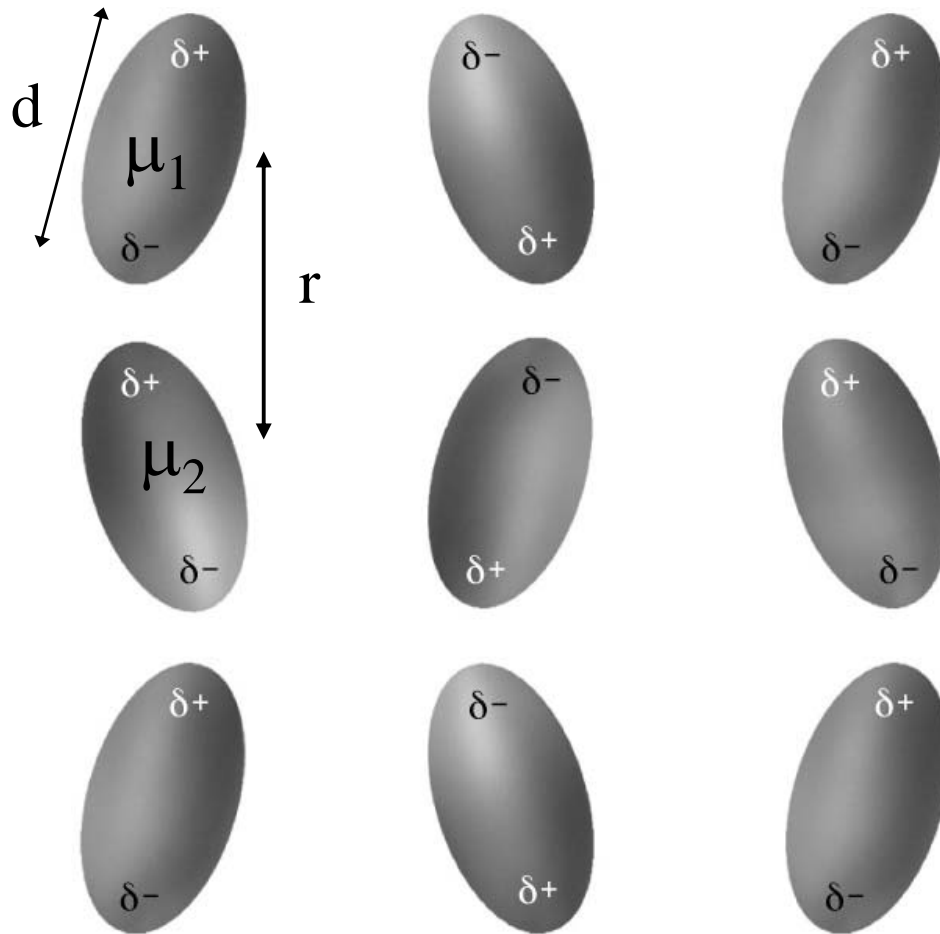
$$\delta = \mu / d = 1.08 \times 3.34 \times 10^{-30} / (127 \times 10^{-12})$$

$$= 2.84 \times 10^{-20} \text{ C}$$

$$\text{percentage ionic character} = [2.84 \times 10^{-20} / (1.602 \times 10^{-19})]$$

$$\times 100\% = 17.7\%$$

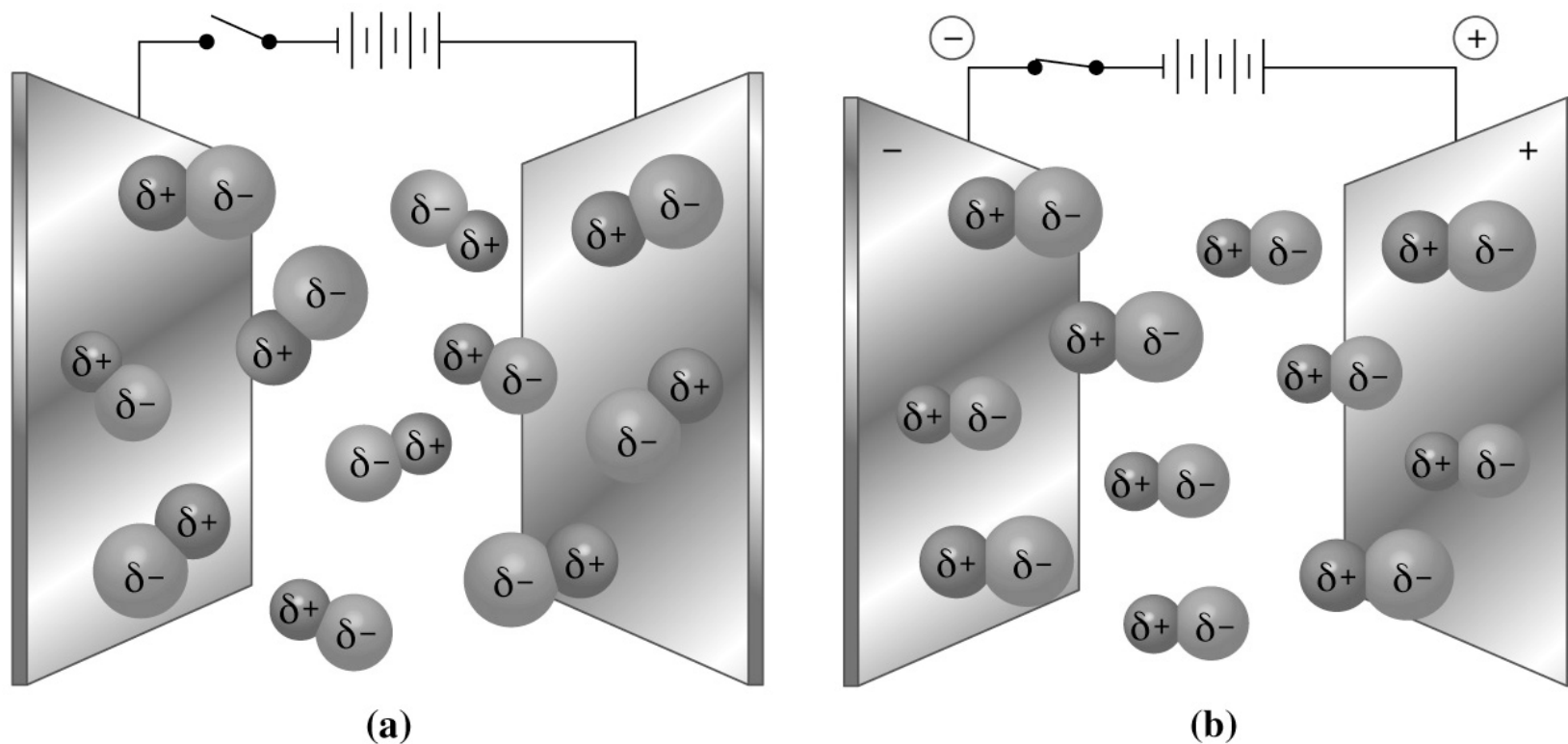
Dipole-Dipole Interactions



Dipole moment
 $\mu = \delta \cdot d$

$$E = - 2(\mu_1 \cdot \mu_2)/4\pi\epsilon r^3$$

How Polar Molecules Behave in an Electric Field



Bond Dipoles and Molecular Dipoles

- All polar covalent bonds have a **bond dipole**; a separation of positive and negative charge centers in an individual bond.
- Bond dipoles have both a magnitude and a direction.

• **molecular dipole = vector sum of bond dipoles**

CO₂, linear with no dipole moment ($\mu = 0$ D)

water is bent (bond angle = 104.5°) and $\mu = 1.84$ D.

Molecular Shapes and Dipole Moments

- Molecules can be predicted to be polar or non-polar based on the following three-step approach:
 - Use electronegativity values to predict bond dipoles.
 - Use the VSEPR method to predict the molecular shape.
 - From the molecular shape, **molecular dipole = vector sum of bond dipoles**
- Lone-pair electrons can also make a contribution to dipole moments.

e.g. NH_3 $\mu = 5.0 \times 10^{-30} \text{ C.m}$

NF_3 $\mu = 0.7 \times 10^{-30} \text{ C.m}$