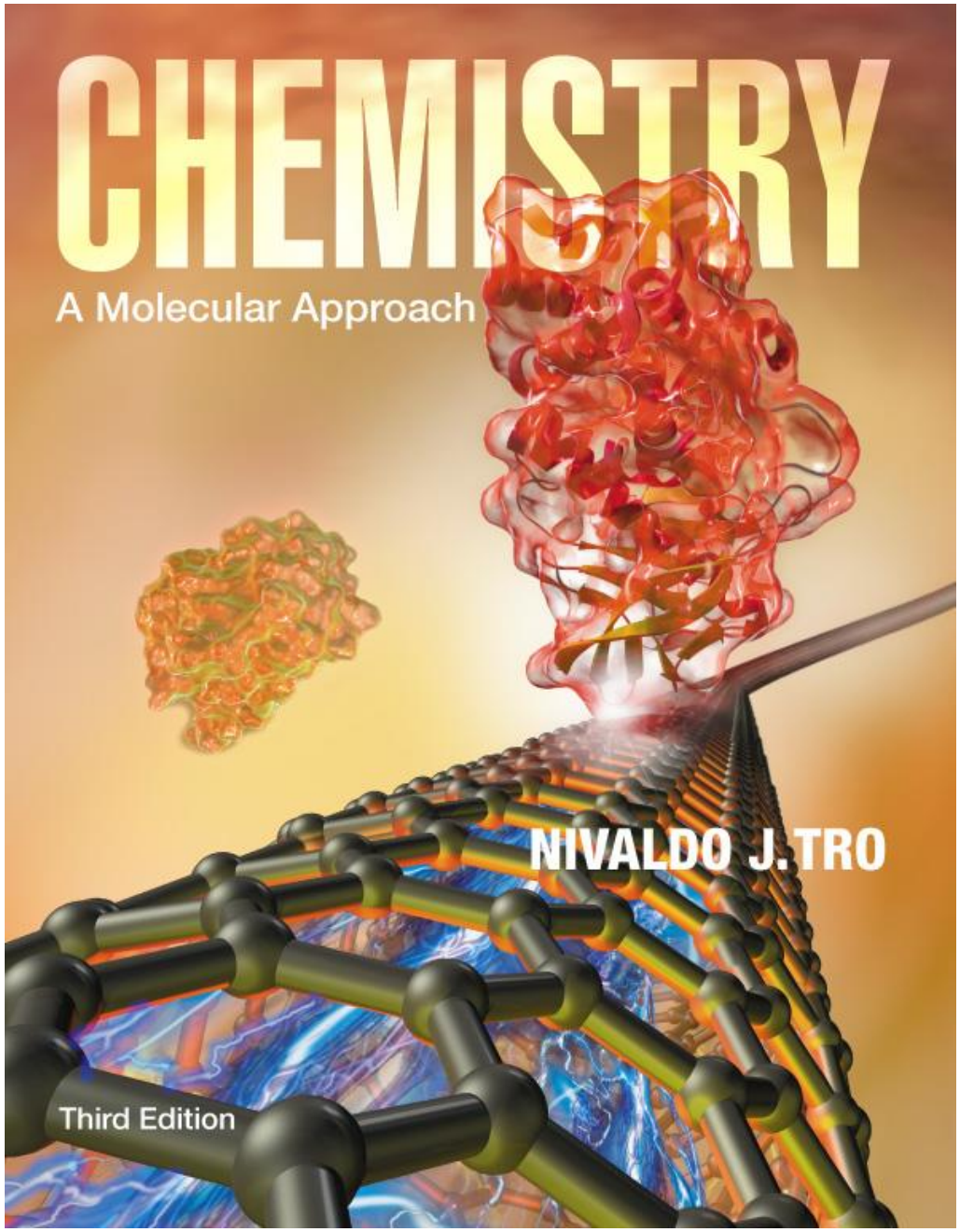

Lecture Presentation

Chapter 9

Chemical Bonding I: The Lewis Model

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Key Equations and Relationships

Dipole Moment (μ): Separation of Two Particles of Equal but Opposite Charges of Magnitude q by a Distance r (9.6)

$$\mu = qr$$

Percent Ionic Character (9.6)

$$\text{Percent ionic character} = \frac{\text{measured dipole moment of bond}}{\text{dipole moment if electron were completely transferred}} \times 100\%$$

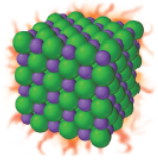
Formal Charge (9.8)

$$\text{Formal charge} = \text{number of valence electrons} - (\text{number of nonbonding electrons} + {}^{1}/_{2}\,\text{number of shared electrons})$$

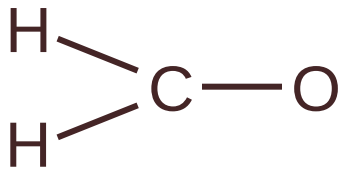
Enthalpy Change of a Reaction (ΔH_{rxn}): Relationship of Bond Energies (9.10)

$$\Delta H_{rxn} = \Sigma(\Delta H\text{'s bonds broken}) + \Sigma(\Delta H\text{'s bonds formed})$$

Key Learning Outcomes

Chapter Objectives	Assessment
Predicting Chemical Formulas of an Ionic Compound (9.4)	Example 9.1 For Practice 9.1 Exercises 41–42
Predicting Relative Lattice Energies (9.4) 	Example 9.2 For Practice 9.2 For More Practice 9.2 Exercise 46
Classifying Bonds: Pure Covalent, Polar Covalent, or Ionic (9.6)	Example 9.3 For Practice 9.3 Exercises 55–56
Writing Lewis Structures for Covalent Compounds (9.7)	Example 9.4–9.5 For Practice 9.4–9.5 Exercises 51–52
Writing Lewis Structures for Polyatomic Ions (9.7)	Example 9.6 For Practice 9.6 Exercises 59–64
Writing Resonance Lewis Structures (9.8) 	Example 9.7 For Practice 9.7 Exercises 63–64
Assigning Formal Charges to Assess Competing Resonance Structures (9.8)	Example 9.8 For Practice 9.8 For More Practice 9.8 Exercises 65–66
Drawing Resonance Structures and Assigning Formal Charge for Organic Compounds (9.8)	Example 9.9 For Practice 9.9 Exercises 69–72
Writing Lewis Structures for Compounds Having Expanded Octets (9.9)	Example 9.9 For Practice 9.9 For More Practice 9.9 Exercises 77–78
Calculating ΔH_{rxn} from Bond Energies (9.10)	Example 9.10 For Practice 9.10 For More Practice 9.10 Exercises 81–83

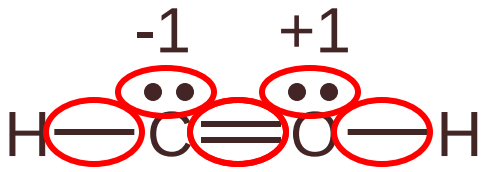
Two possible skeletal structures of formaldehyde (CH_2O)



An atom's ***formal charge*** is the difference between the number of valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.

$$\text{formal charge on an atom in a Lewis structure} = \text{total number of valence electrons in the free atom} - \text{total number of nonbonding electrons} - \frac{1}{2}\left(\text{total number of bonding electrons}\right)$$

The sum of the formal charges of the atoms in a molecule or ion must equal the charge on the molecule or ion.



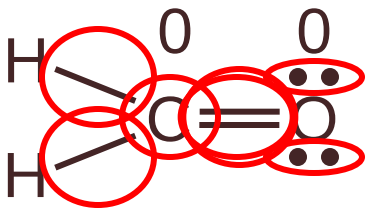
C – 4 e^-
O – 6 e^-
2H – 2x1 e^-
12 e^-

2 single bonds (2x2) = 4
1 double bond = 4
2 lone pairs (2x2) = 4
Total = 12

$$\text{formal charge on an atom in a Lewis structure} = \text{total number of valence electrons in the free atom} - \text{total number of nonbonding electrons} - \frac{1}{2}\left(\text{total number of bonding electrons}\right)$$

$$\text{formal charge on C} = 4 - 2 - \tfrac{1}{2} \times 6 = -1$$

$$\text{formal charge on O} = 6 - 2 - \tfrac{1}{2} \times 6 = +1$$



C – 4 e^-
O – 6 e^-
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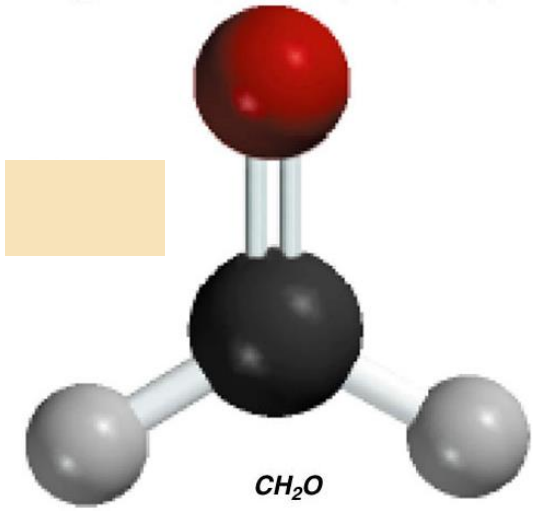
12 e^-

2 single bonds (2x2) = 4
1 double bond = 4
2 lone pairs (2x2) = 4
Total = 12

$$\text{formal charge on an atom in a Lewis structure} = \text{total number of valence electrons in the free atom} - \text{total number of nonbonding electrons} - \frac{1}{2}\left(\text{total number of bonding electrons}\right)$$

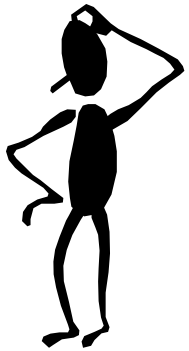
formal charge on C $= 4 - 0 - \frac{1}{2} \times 8 = 0$

formal charge on O $= 6 - 4 - \frac{1}{2} \times 4 = 0$

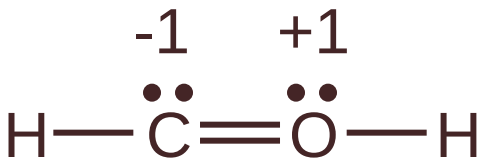


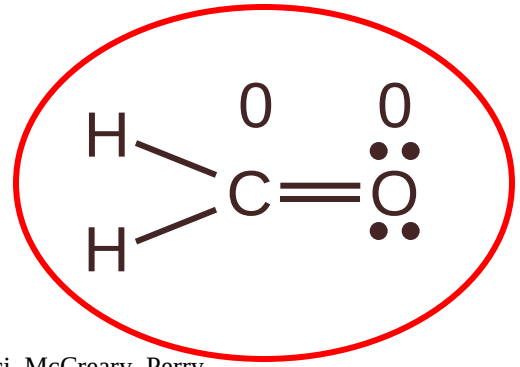
Formal Charge and Lewis Structures

1. For neutral molecules, a Lewis structure in which there are no formal charges is preferable to one in which formal charges are present.
2. Lewis structures with large formal charges are less plausible than those with small formal charges.
3. Among Lewis structures having similar distributions of formal charges, the most plausible structure is the one in which negative formal charges are placed on the more electronegative atoms.

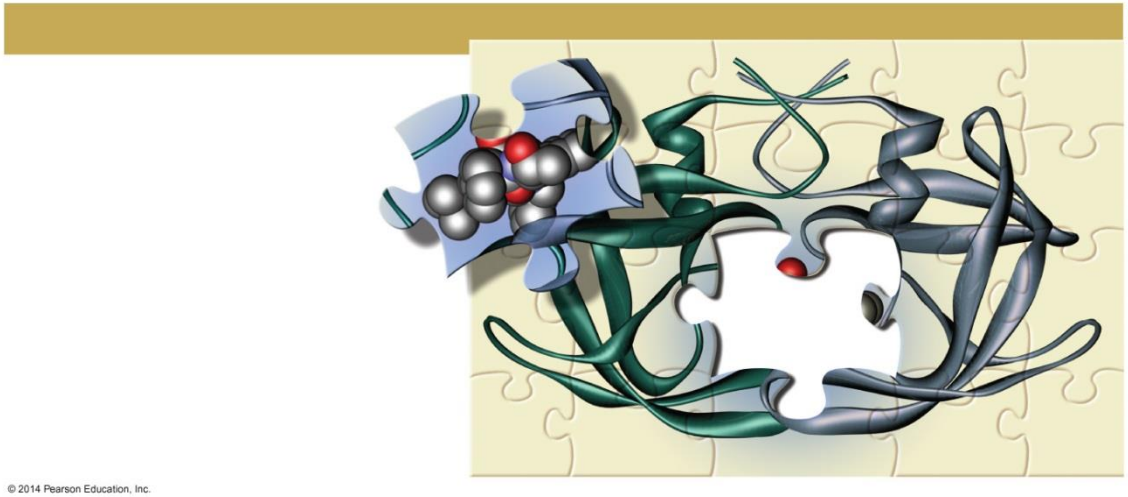


Which is the most likely Lewis structure for CH_2O?





9.1 **Bonding Models and AIDS Drugs**



- HIV-protease is a protein synthesized by the human immunodeficiency virus (HIV).
- This particular protein is crucial to the virus's ability to multiply and cause AIDS.
- Pharmaceutical companies designed molecules that would disable HIV-protease by sticking to the molecule's active site—***protease inhibitors***.
- To design such a molecule, researchers used ***bonding theories*** *to simulate* the shape of potential drug molecules and how they would interact with the protease molecule.

Lewis Bonding Theory

- One of the simplest bonding theories is called **Lewis theory**.

- Lewis theory emphasizes valence electrons to explain bonding.
- Using Lewis theory, we can draw models, called **Lewis structures**.
  - Also known as electron dot structures
- Lewis structures allow us to predict many properties of molecules.
  - Such as molecular stability, shape, size, and polarity

Bonding Theories

- Explain how and why atoms attach together to form molecules
- Explain why some combinations of atoms are stable and others are not
  - Why is water H_2O, not HO or H_3O?
- Can be used to predict the shapes of molecules
- Can be used to predict the chemical and physical properties of compounds

Why Do Atoms Bond?

- Chemical bonds form because they lower the potential energy between the charged particles that compose atoms.

- A chemical bond forms when the potential energy of the bonded atoms is less than the potential energy of the separate atoms.

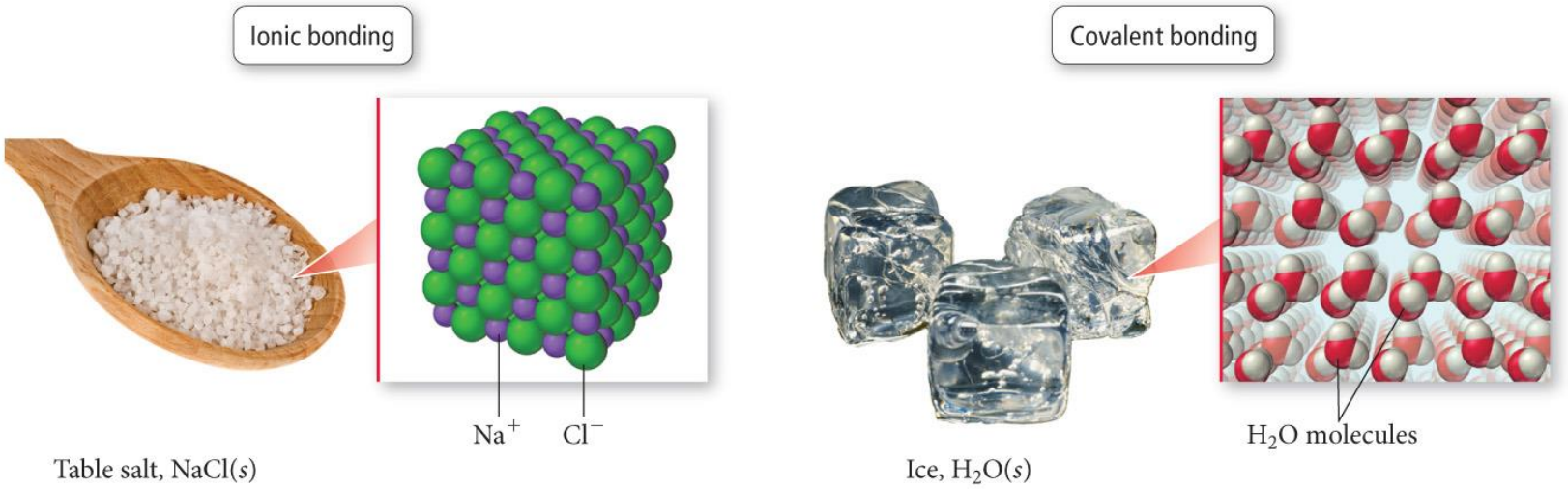
- To calculate this potential energy, you need to consider the following interactions:
  - Nucleus-to-nucleus repulsions
  - Electron-to-electron repulsions
  - Nucleus-to-electron attractions

9.2 Types of Bonds

- We can classify bonds based on the kinds of atoms that are bonded together.

Types of Atoms	Type of Bond	Characteristic of Bond
Metal and nonmetal	Ionic	Electrons transferred
Nonmetal and nonmetal	Covalent	Electrons shared
Metal and metal	Metallic	Electrons pooled

Types of Bonding



Ionic Bonds

- When a metal atom loses electrons it becomes a **cation**.
  - Metals have low ionization energy, making it *relatively* easy to remove electrons from them.

- When a nonmetal atom gains electrons it becomes an **anion**.
  - Nonmetals have high electron affinities, making it advantageous to add electrons to these atoms.

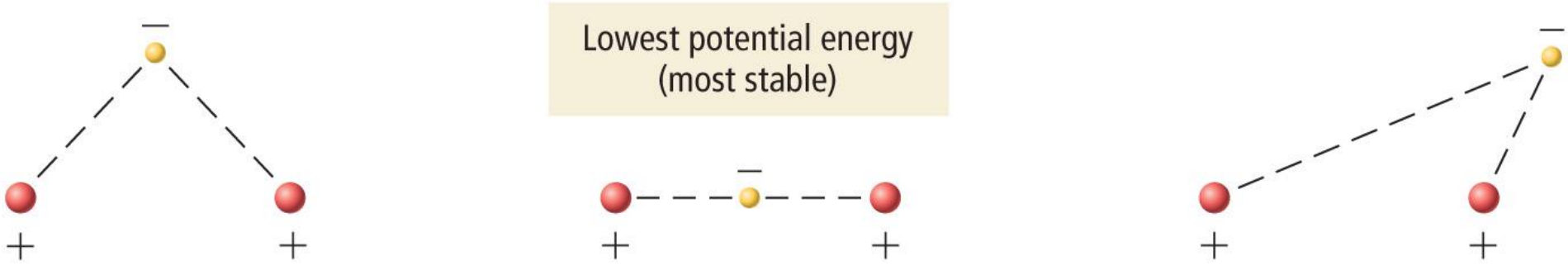
- The oppositely charged ions are then attracted to each other, resulting in an **ionic bond**.

Covalent Bonds

- Nonmetal atoms have relatively high ionization energies, so it is difficult to remove electrons from them.

- When nonmetals bond together, it is better in terms of potential energy for the atoms to share valence electrons.
  - Potential energy is lowest when the electrons are between the nuclei.

- Shared electrons hold the atoms together by attracting nuclei of both atoms.



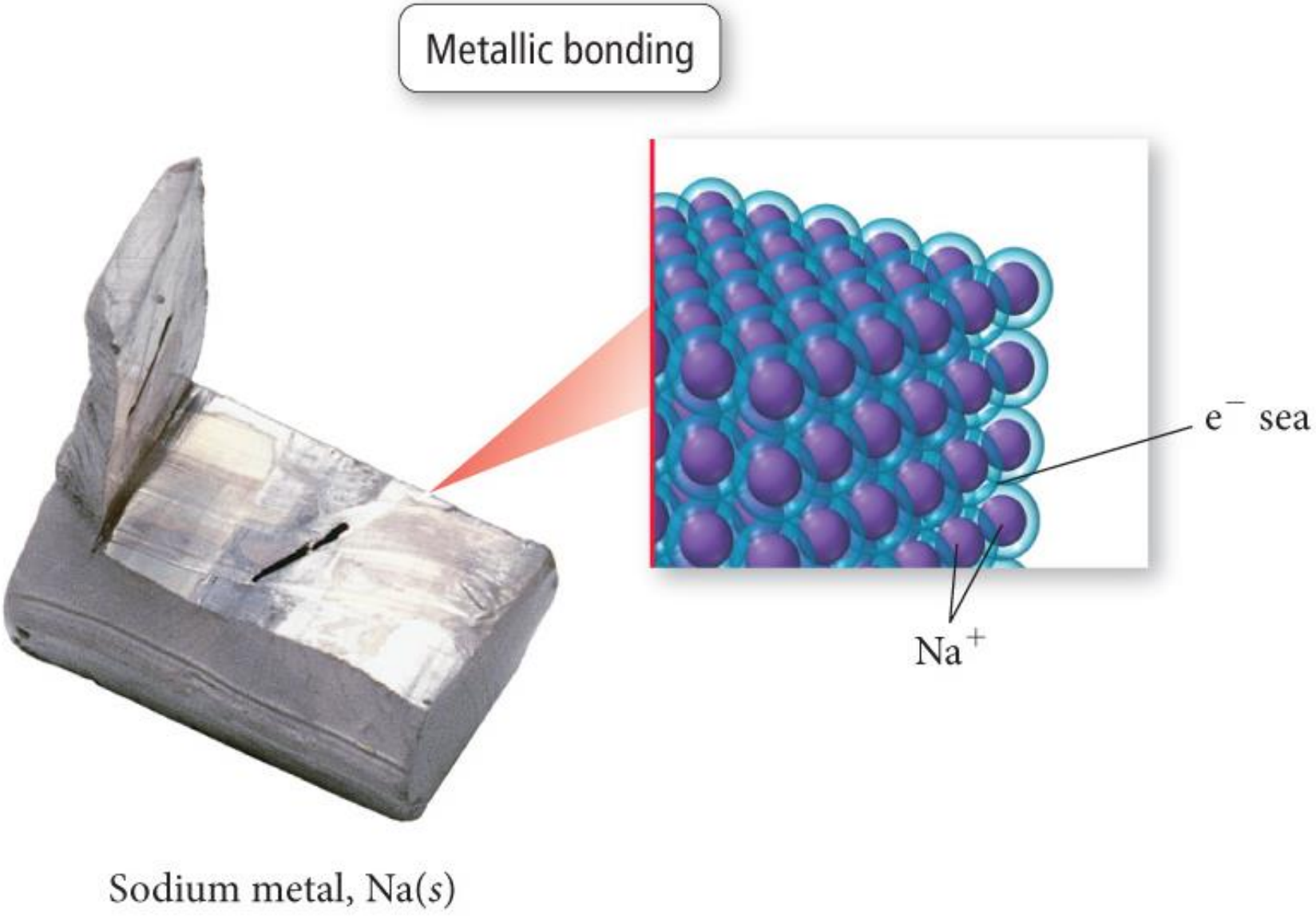
Metallic Bonds

- The *relatively* low ionization energy of metals allows them to lose electrons easily.

- The simplest theory of metallic bonding involves the metal atoms releasing their valence electrons to be shared as a pool by all the atoms/ions in the metal.
  - An organization of metal cation islands in a sea of electrons
  - Electrons delocalized throughout the metal structure

- Bonding results from attraction of cation for the delocalized electrons.

Metallic Bonding

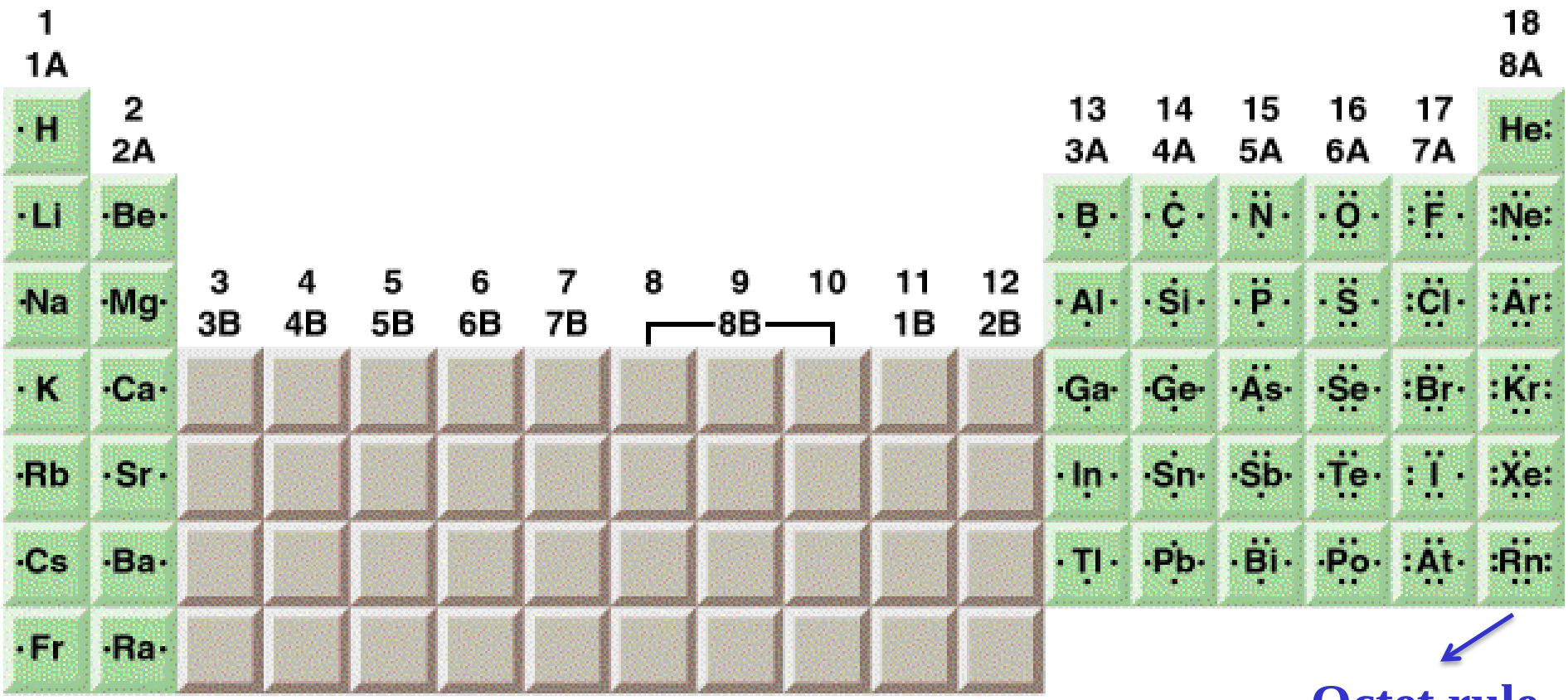


9.3 Representing Valence Electrons with Dots Valence Electrons and Bonding

Valence electrons are the outer shell electrons of an atom. The valence electrons are the electrons that particpate in chemical bonding.價電子是原子的外殼層電子。價電子是參與化學鍵結的電子。

Group	e^- configuration	# of valence e^-
1A	ns^1	1
2A	ns^2	2
3A	ns^2np^1	3
4A	ns^2np^2	4
5A	ns^2np^3	5
6A	ns^2np^4	6
7A	ns^2np^5	7

Lewis Dot Symbols



Octet rule

Octet Rule

- When atoms bond, they tend to gain, lose, or share electrons to result in eight valence electrons.
- ns^2np^6
  - Noble gas configuration
- Many exceptions
  - H, Li, Be, B attain an electron configuration like He.
    - He = two valence electrons, a **duet**.
    - Li loses its one valence electron.
    - H shares or gains one electron.
      - Though it commonly loses its one electron to become H^+
    - Be loses two electrons to become Be^{2+}.
      - Though it commonly shares its two electrons in covalent bonds, resulting in four valence electrons
    - B loses three electrons to become B^{3+}.
      - Though it commonly shares its three electrons in covalent bonds, resulting in six valence electrons
  - Expanded octets for elements in period 3 or below
    - Using empty valence *d* orbitals

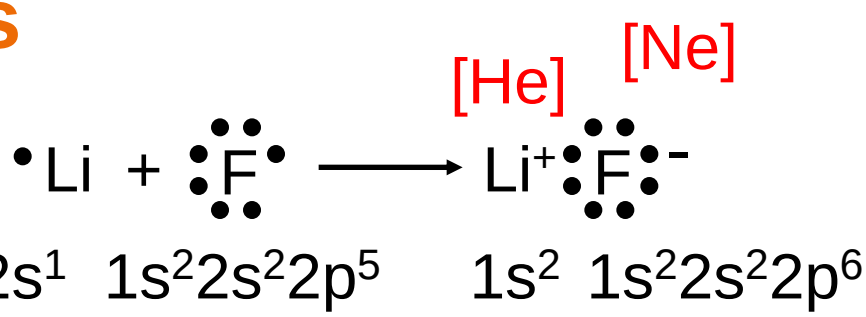
Q：The general electron configuration for noble gas atoms is:

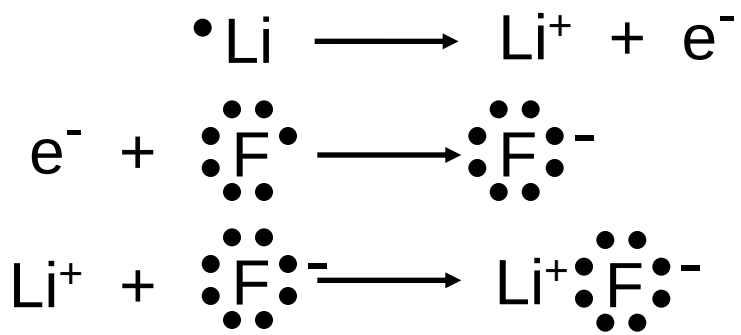
A. ns^2np^6
B. ns^2np^5
C. ns^2np^4
D. ns^2np^3
E. ns^2

Answer: A

9.4 Ionic Bonding: Lewis Symbols and Lattice Energies

The Ionic Bond離子鍵





K $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

K^+ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0$

Octet in previous level

Q：Which one of the following compounds is most likely to be an ionic ompound?

A. KF

B. CCl_4

C. CS_2

D. CO_2

E. ICl

Answer: A

Ion bond and Electrostatic (Lattice) Energy靜電(晶格)能

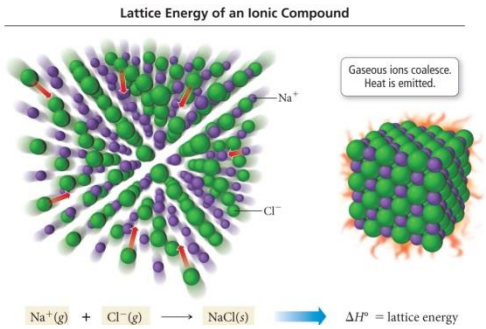
Lattice energy (E) is the energy required to completely separate one mole of a solid ionic compound into gaseous ions.晶格(*靜電*)能(E)是完全分離一莫耳的固態離子化合物轉為氣態離子所需的能量

$$E = k\frac{Q_+Q_-}{r}$$

Q_+ is the charge on the cation陽離子電荷

Q_- is the charge on the anion陰離子電荷

r is the distance between the ions 離子間的距離

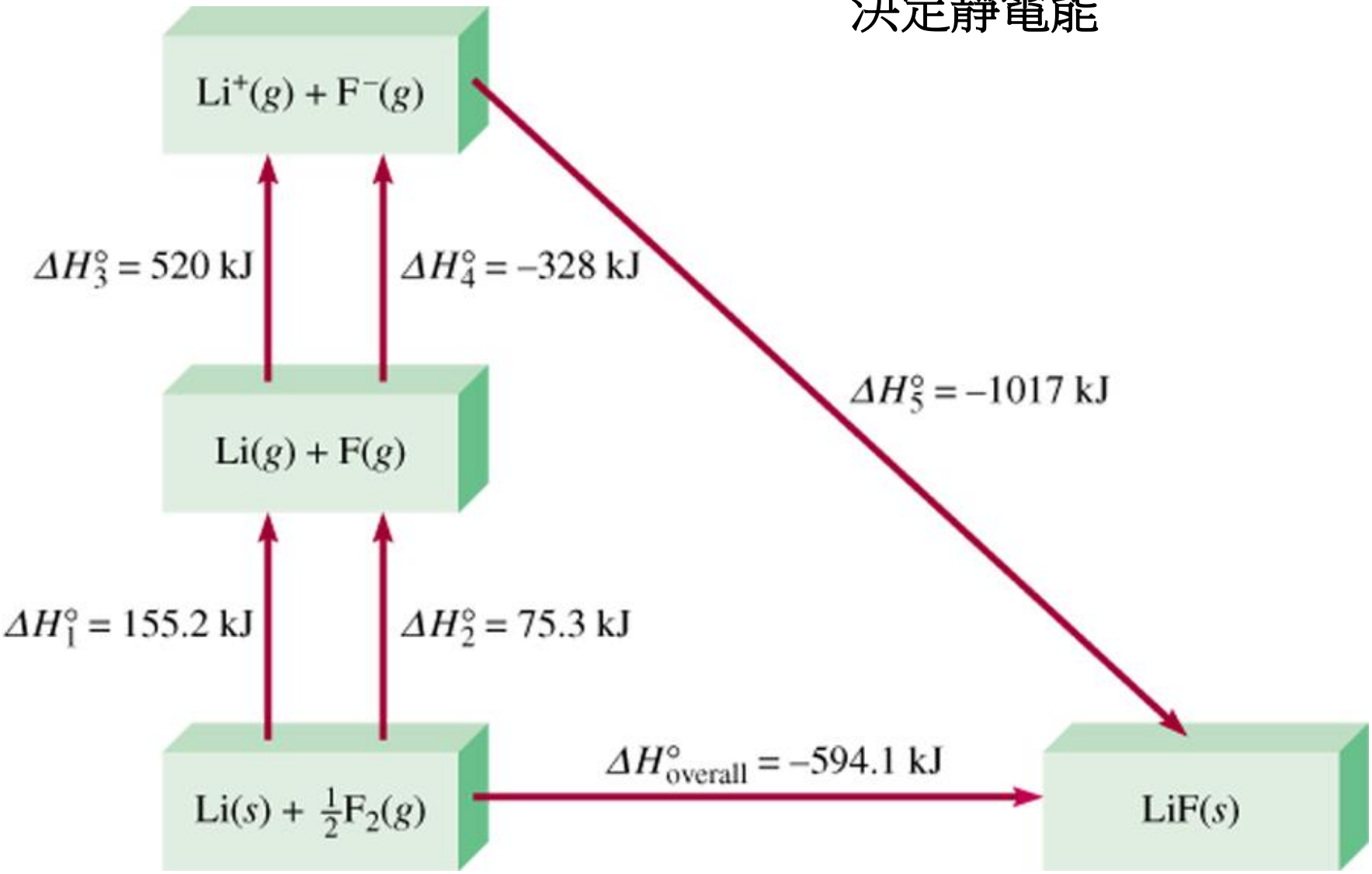


Lattice energy (E) increases as Q increases and/or as r decreases.當 **Q** 增加和 **/** 或 **r** 減少可以增加靜電能

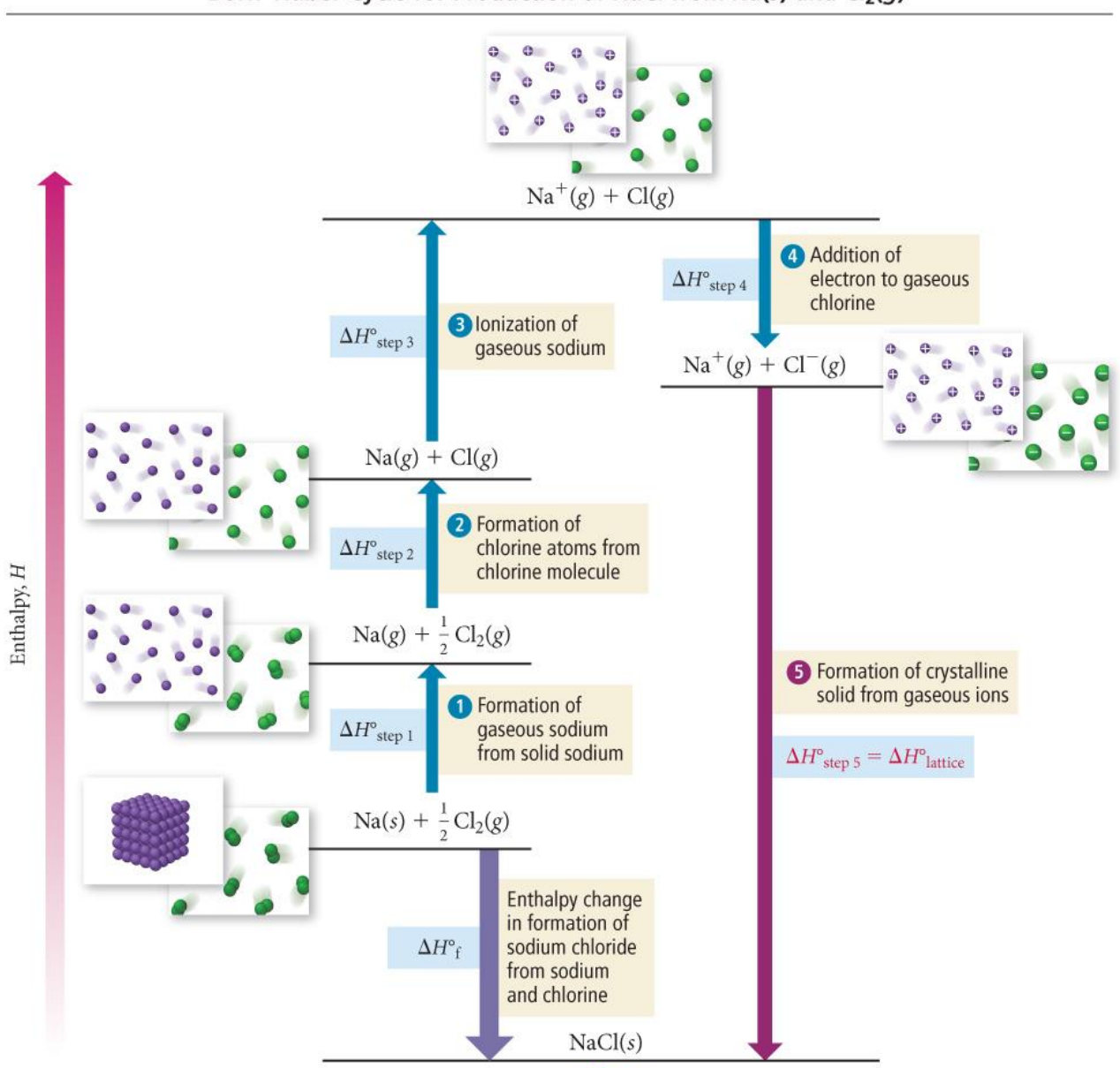
cmpd	lattice energy	
MgF_2	2957	Q= +2,-1
MgO	3938	Q= +2,-2
LiF	1036	r F < r Cl
LiCl	853	

Determining Lattice Energy: The Born–Haber Cycle

決定靜電能



$$\Delta H^o_{overall} = \Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4 + \Delta H^o_5$$



Enthalpy of standard formation:

$\Delta H_f^o = -411$ kJ

$Na_{(s)} + ½\ Cl_{2(g)} \rightarrow NaCl_{(s)}$

Born-Haber Cycle Explanation

1. Enthalpy of sublimation:
   $Na_{(s)} \rightarrow Na_{(g)}$ $\Delta H_1 = +107$ kJ
2. Bond dissociation energy:
   $\frac{1}{2}\ Cl_{2\,(g)} \rightarrow Cl_{\,(g)}$ $\Delta H_2 = +122$ kJ
3. First ionization energy:
   $Na_{(g)} \rightarrow Na^+_{(g)} + e^-$ $\Delta H_3 = +496$ kJ
4. Electron affinity:
   $Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$ $\Delta H_4 = -349$ kJ
5. Lattice energy:
   $Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$（計算才知道）$\Delta H_5 = -787$ kJ

---

6. Enthalpy of standard formation:
   $Na_{(s)} + \frac{1}{2}\ Cl_{2(g)} \rightarrow NaCl_{(s)}$ $\Delta H_f^o = -411$ kJ

$$\Delta H_f^o = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 = -411 \text{ kJ}$$

Born–Haber Cycle for NaCl

$Na(s) \rightarrow Na(g)$	$\Delta H_f(Na,g)$	$Na(s) \rightarrow Na(g)$	+108 kJ
$\frac{1}{2}\ Cl_2(g) \rightarrow Cl(g)$	$\Delta H_f(Cl,g)$	$\frac{1}{2}\ Cl_2(g) \rightarrow Cl(g)$	+½(244
$Na(g) \rightarrow Na^+(g)$	$\Delta H_f(Na^+,g)$	$Na(g) \rightarrow Na^+(g)$	+496 kJ
$Cl\,(g) \rightarrow Cl^-(g)$	$\Delta H_f(Cl^-,g)$	$Cl\,(g) \rightarrow Cl^-(g)$	−349 kJ
$Na^+\,(g) + Cl^-(g) \rightarrow NaCl(s)$	ΔH (NaCl lattice)	$Na^+\,(g) + Cl^-(g) \rightarrow NaCl(s)$	ΔH (NaC
$Na(s) + \frac{1}{2}\ Cl_2(g) \rightarrow NaCl(s)$	ΔH_f (NaCl, s)	$Na(s) + \frac{1}{2}\ Cl_2(g) \rightarrow NaCl(s)$	−411 kJ

ΔH°_f(NaCl, s) = ΔH°_f(Na atoms,g) + ΔH°_f(Cl atoms, g) + ΔH°_f(Na^+,g) + ΔH°_f(Cl^-,g) + ΔH°(NaCl lattice)

ΔH°_f(NaCl, s) = ΔH°_f(Na atoms,g) + ΔH°_f(Cl–Cl bond energy) + Na 1st ionization energy + Cl electron affinity + NaCl lattice energy

NaCl lattice energy = ΔH°_f(NaCl, s) − [ΔH°_f(Na atoms, g) + ΔH°_f(Cl–Cl bond energy) + Na 1st ionization energy + Cl electron affinity]

NaCl lattice energy = (−411 kJ) − [(+108 kJ) + (+122 kJ) + (+496 kJ) + (−349 kJ)] = −788 kJ

Trends in Lattice Energy: Charge and Ion Size

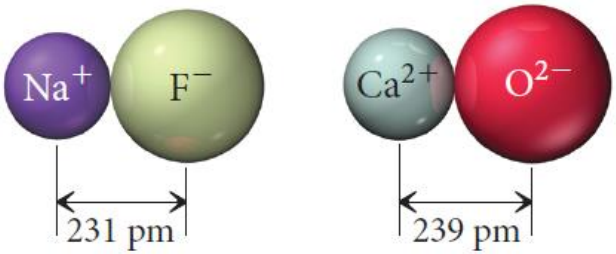
$$E = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r}$$

$$E = k\frac{Q_+ Q_-}{r}$$

Q_+ is the charge on the cation陽離子電荷

Q_- is the charge on the anion陰離子電荷

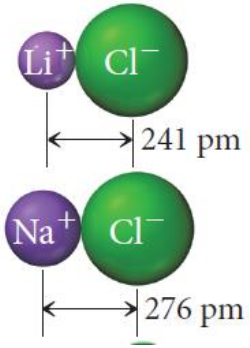
r is the distance between the ions
離子間的距離



cmpd	lattice energy	
NaF	910	Q= +1,-1
CaO	3414	Q= +2,-2

Lattice energy (E) increases as Q increases and/or as r decreases.當 **Q** 增加或 **r** 減少可以增加靜電能

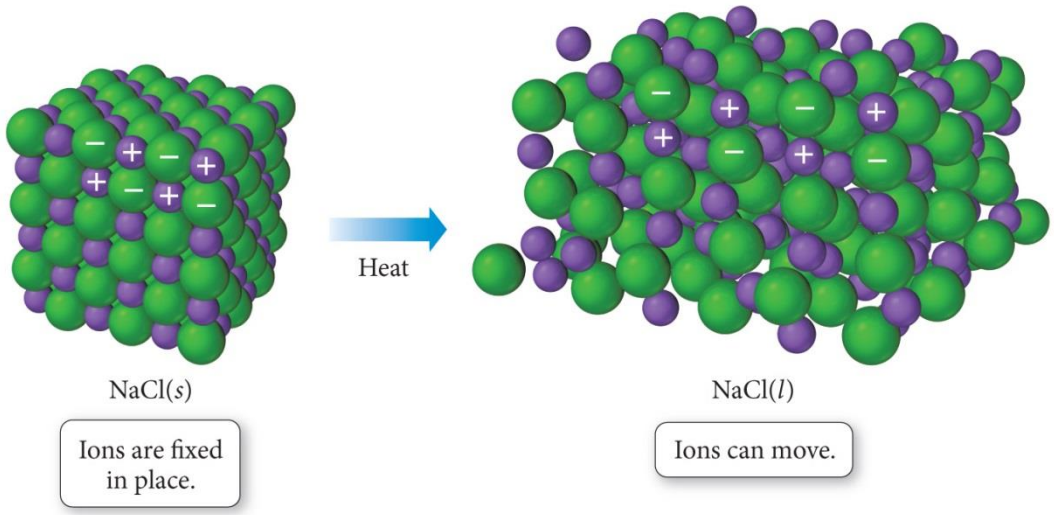
LiCl	834	r Li < r Na
NaCl	788	



9.3

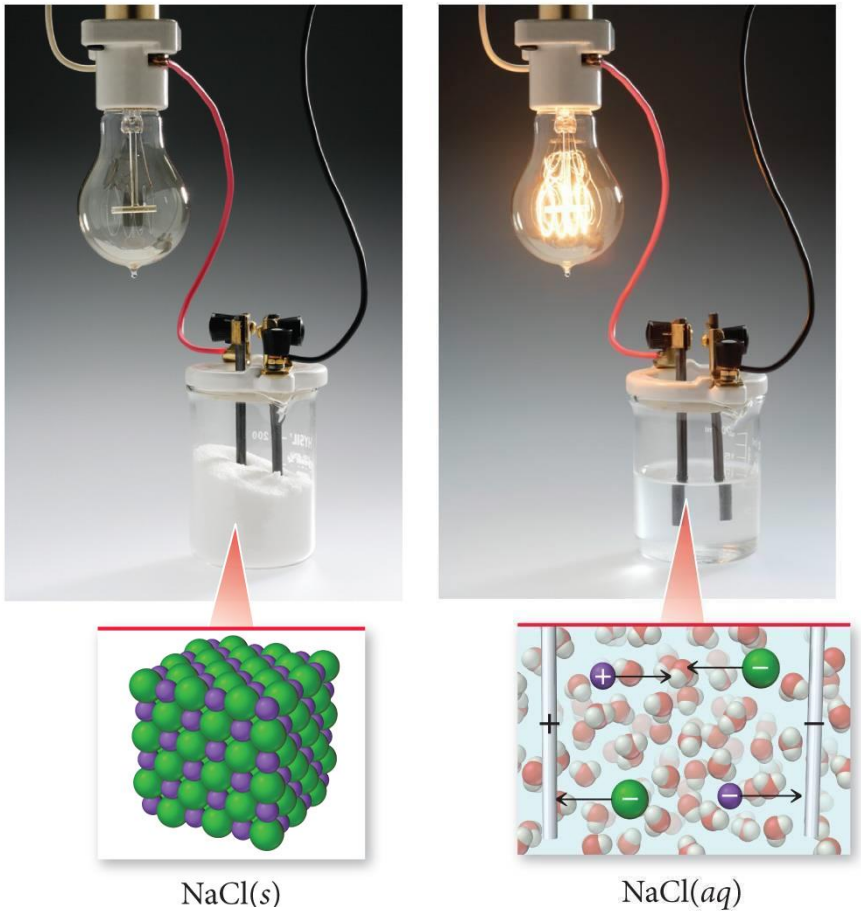
Properties of Ionic Compounds

- Hard and brittle crystalline solids
  - All are solids at room temperature
- Melting points generally > 300 °C
- The liquid state conducts electricity
  - The solid state does not conduct electricity
- Many are soluble in water
  - The solution conducts electricity well



Conductivity of NaCl

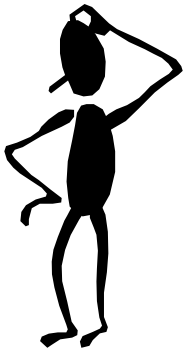
In NaCl(*s*), the ions are stuck in position and not allowed to move to the charged rods.



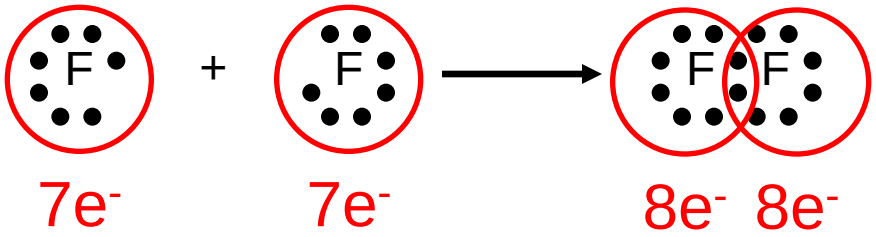
In NaCl(*aq*), the ions are separated and allowed to move to the charged rods.

9.5 Lewis Theory of Covalent Bonding

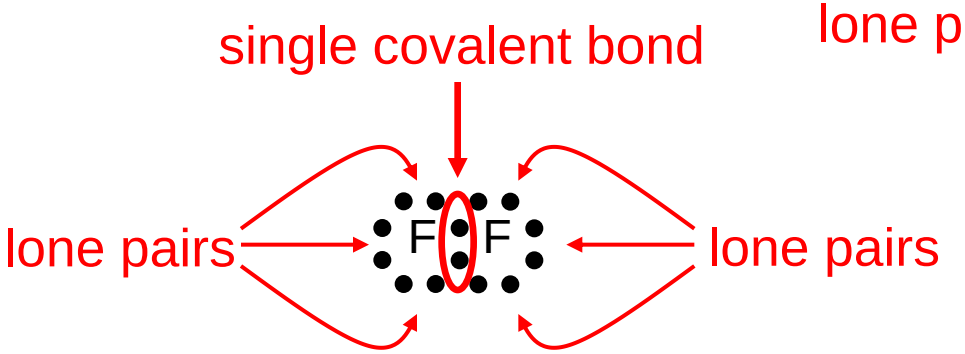
The **covalent bonding** is a chemical bond in which two or more electrons are shared by two atoms.共價鍵是兩個原子共用兩個或更多電子的化學鍵

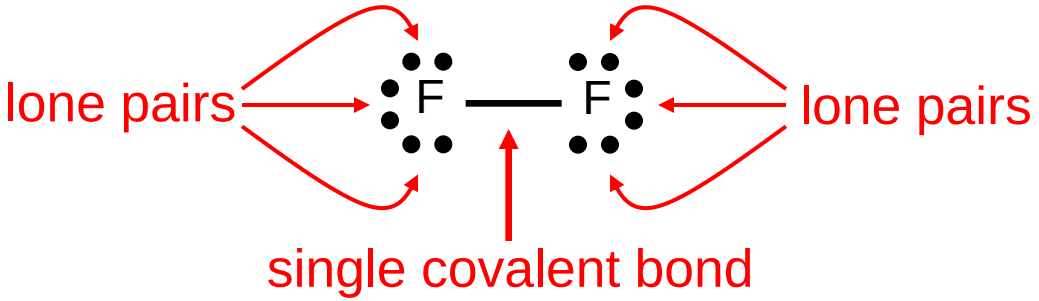


Why should two atoms share electrons?
為什麼兩個原子能夠分享電子**?**



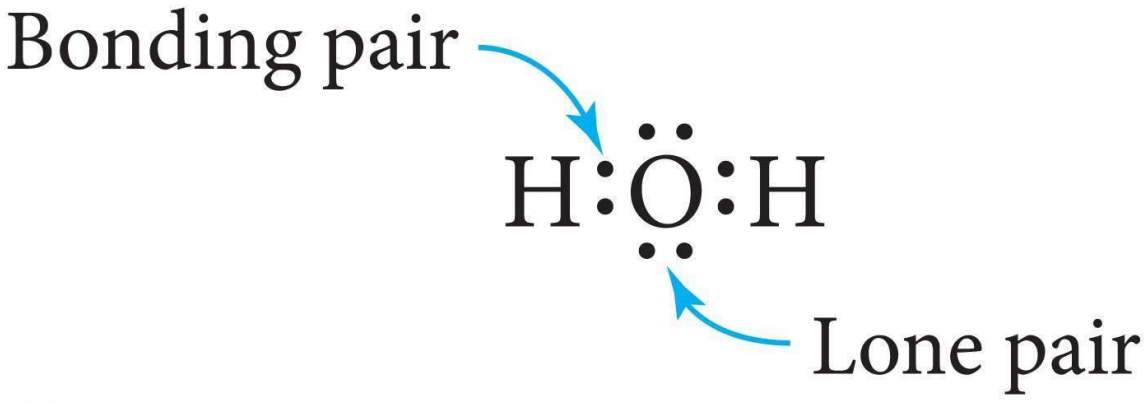
Lewis structure of F_2





Covalent Bonding: Bonding and Lone Pair Electrons

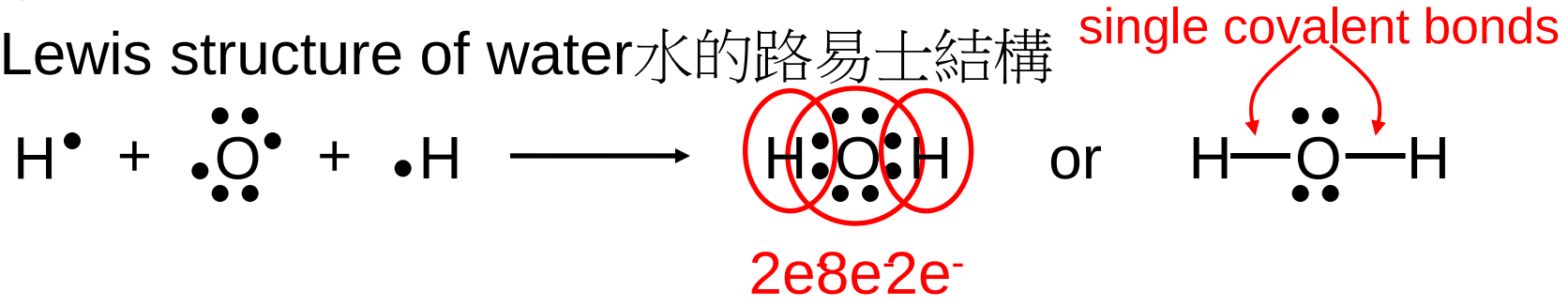
- Electrons that are shared by atoms are called **bonding pairs**.
- Electrons that are not shared by atoms but belong to a particular atom are called **lone pairs**.
  - ✓Also known as **nonbonding pairs**



Single bond – two atoms share one pairs of electrons

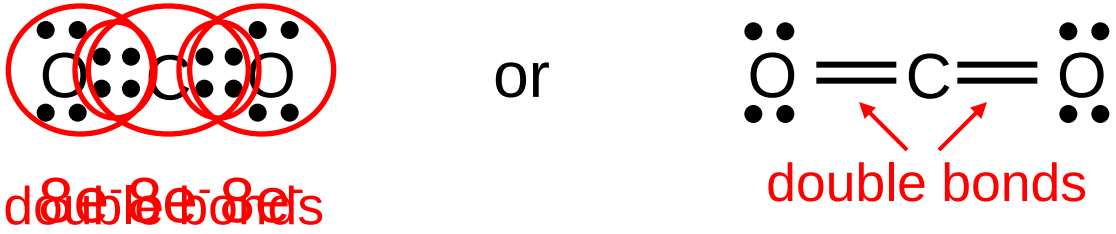
單鍵 – 兩個原子分享一個電子對

Lewis structure of water水的路易士結構



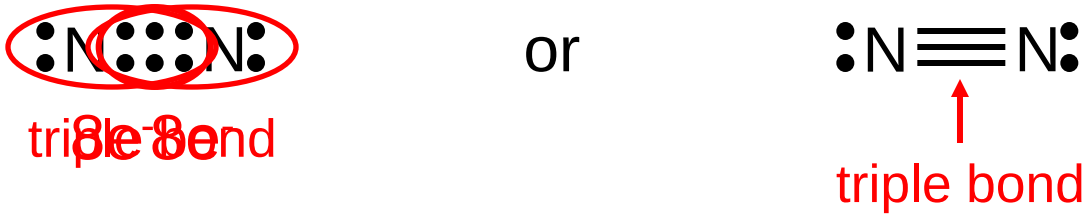
Double bond – two atoms share two pairs of electrons

雙鍵 – 兩個原子分享兩個電子對



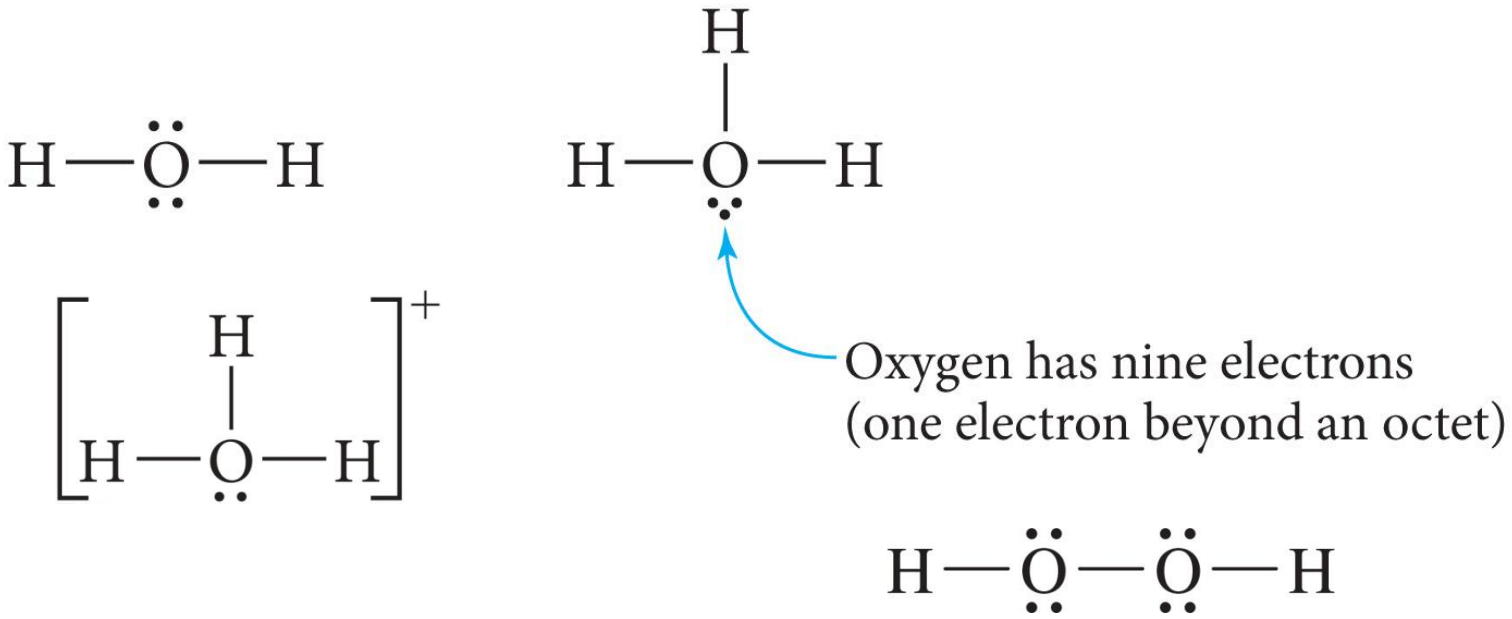
Triple bond – two atoms share three pairs of electrons

三鍵 – 兩個原子分享三個電子對



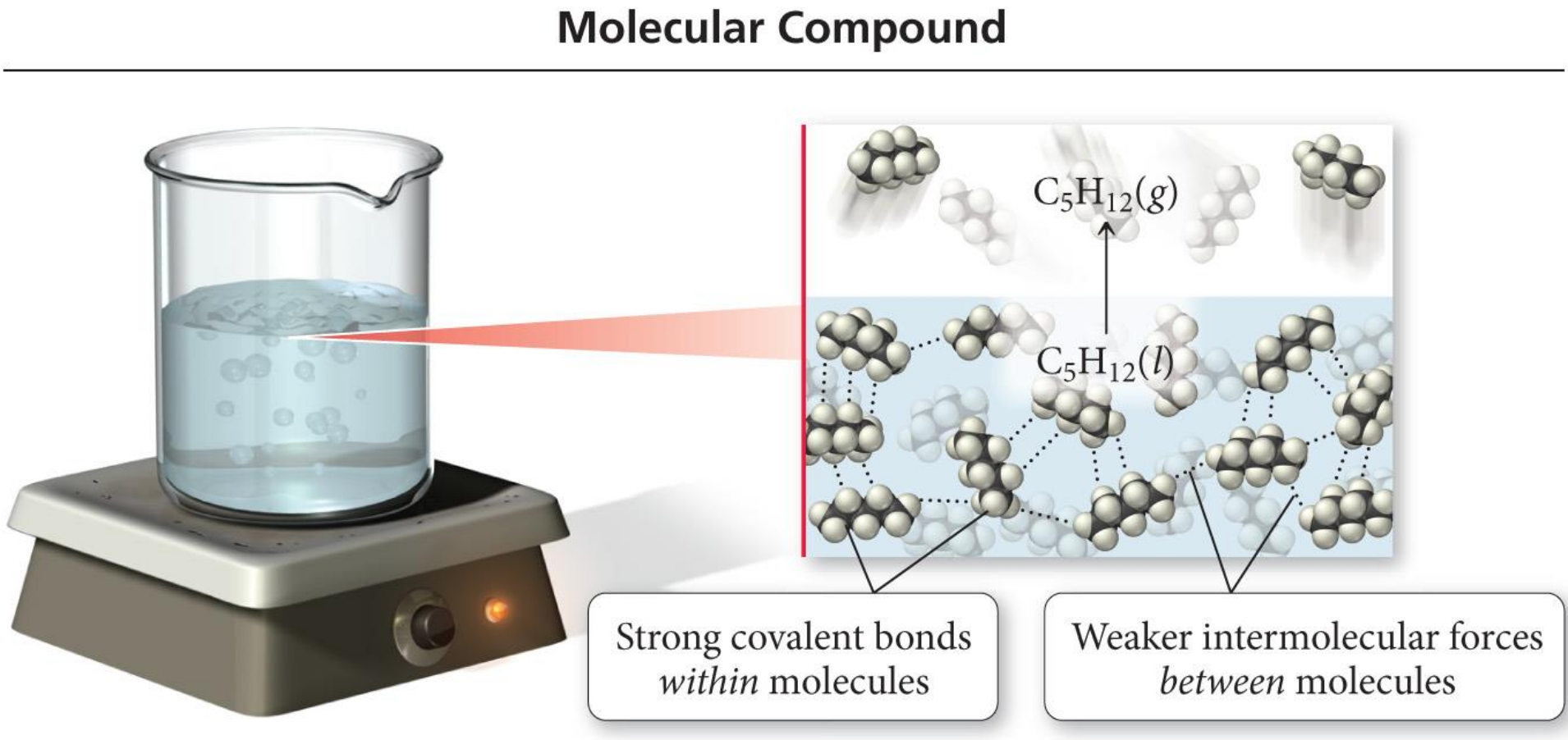
Predictions of Molecular Formulas by Lewis Theory

Oxygen is more stable when it is singly bonded to two other atoms



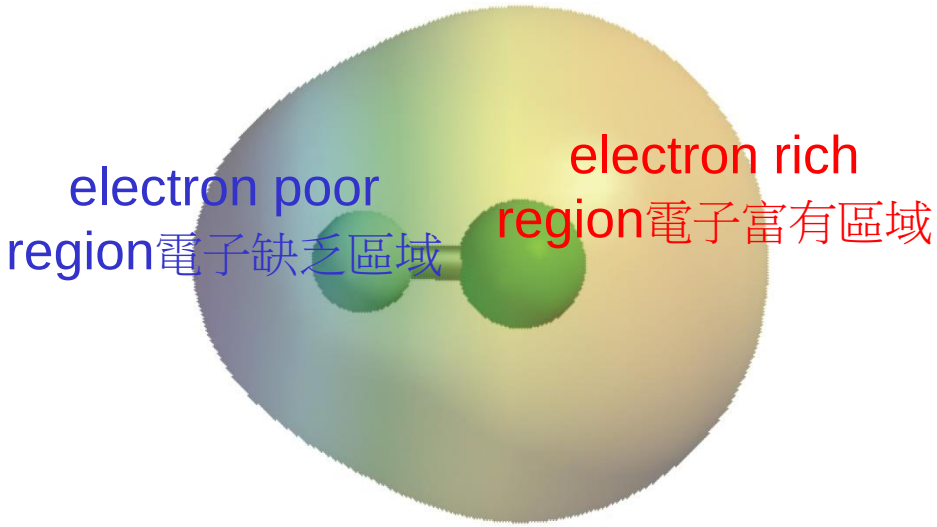
- Molecular compounds have low melting points and boiling points.
  - MP generally < 300 °C
  - Molecular compounds are found in all three states at room temperature.

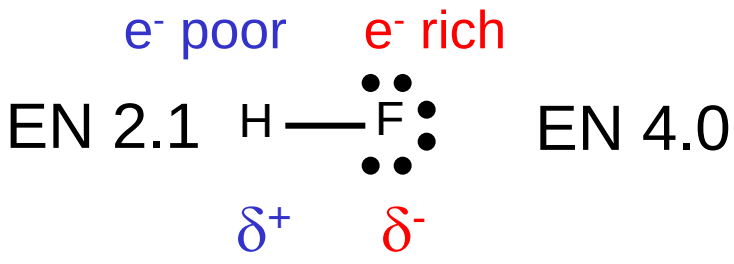
Intermolecular Attractions versus Bonding

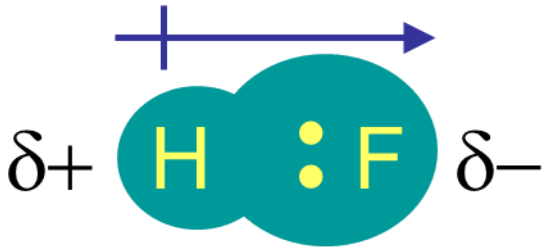


9.6 Electronegativity and Bond Polarity
Polar Covalent Bonding

Polar covalent bond is a covalent bond with greater electron density around one of the two atoms*極性共價鍵*或*極性鍵結*是一個共價鍵中兩個原子的一方原子周圍有較高電子密度。





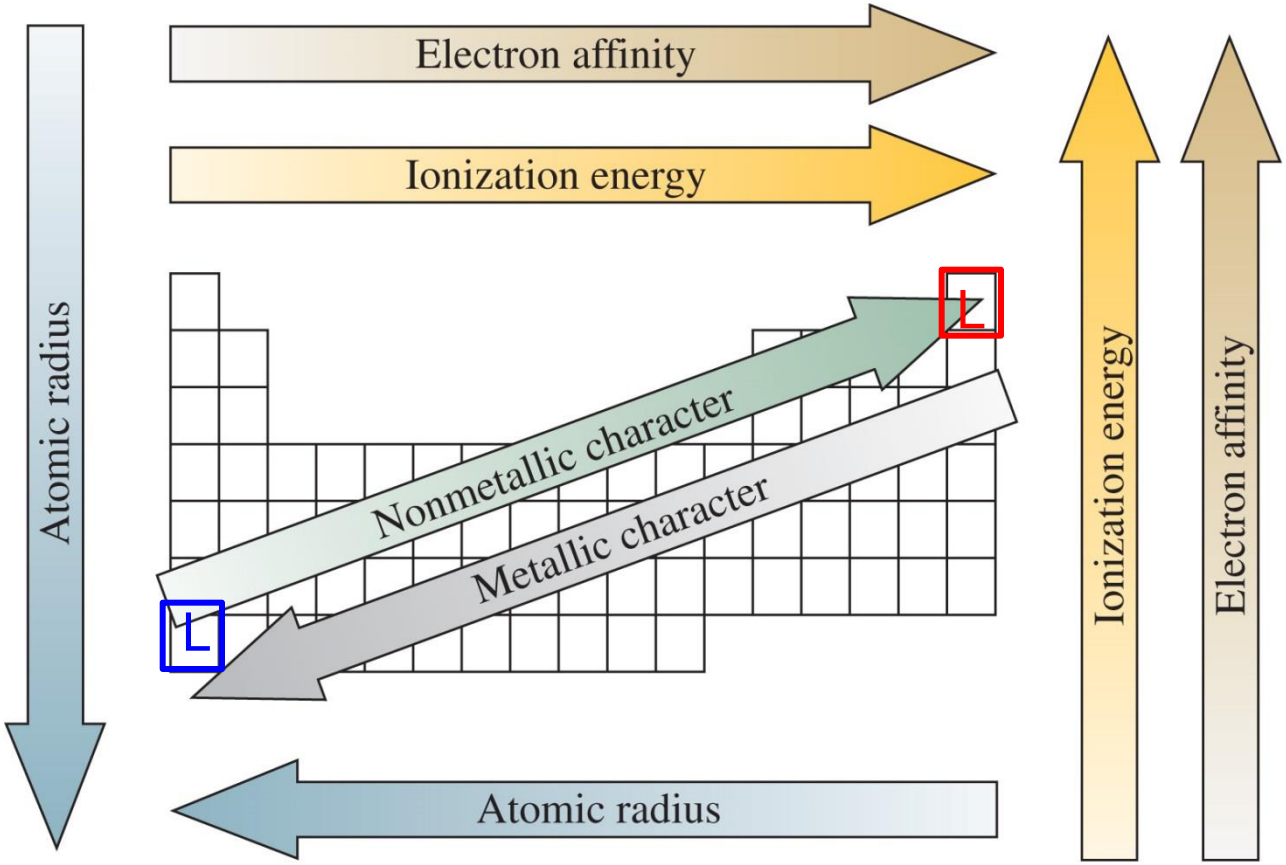


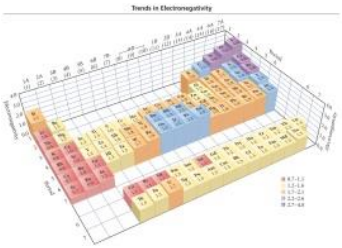
Electronegativity

Electronegativity 電負度

The ability of an atom to attract bonding electrons to itself is called **electronegativity**.*電負度*是在一個化學鍵中一個原子吸引接近它自己的電子的能力

Large: Ionization energy游離能
Electron affinity電子親和力
Nonmetallic 非金屬





arge: atomic radius（原子半徑）
Metallic (金屬)

Bond Polarity

Classification of bonds by difference in electronegativity
鍵結的分類是依照電負度的差異

TABLE 9.1 The Effect of Electronegativity Difference on Bond Type

Electronegativity Difference (ΔEN)		Bond Type	Example
Small (0–0.4)	共價	Covalent	Cl_2
Intermediate (0.4–2.0)	極性共價	Polar covalent	HCl
Large (2.0+)	離子	Ionic	NaCl

Increasing difference in electronegativity增加電負度的差異

Covalent

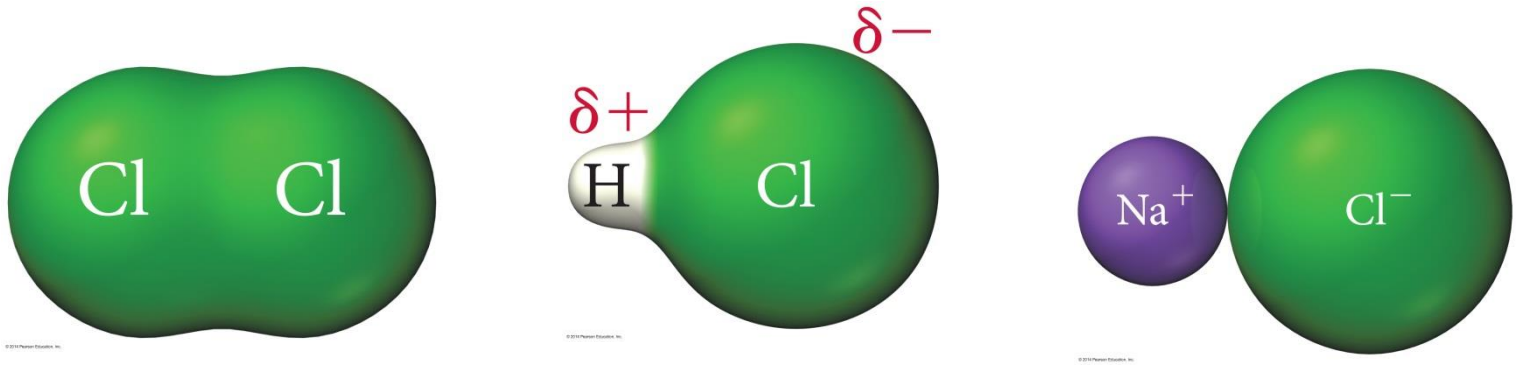
share e^-
共享電子

Polar Covalent

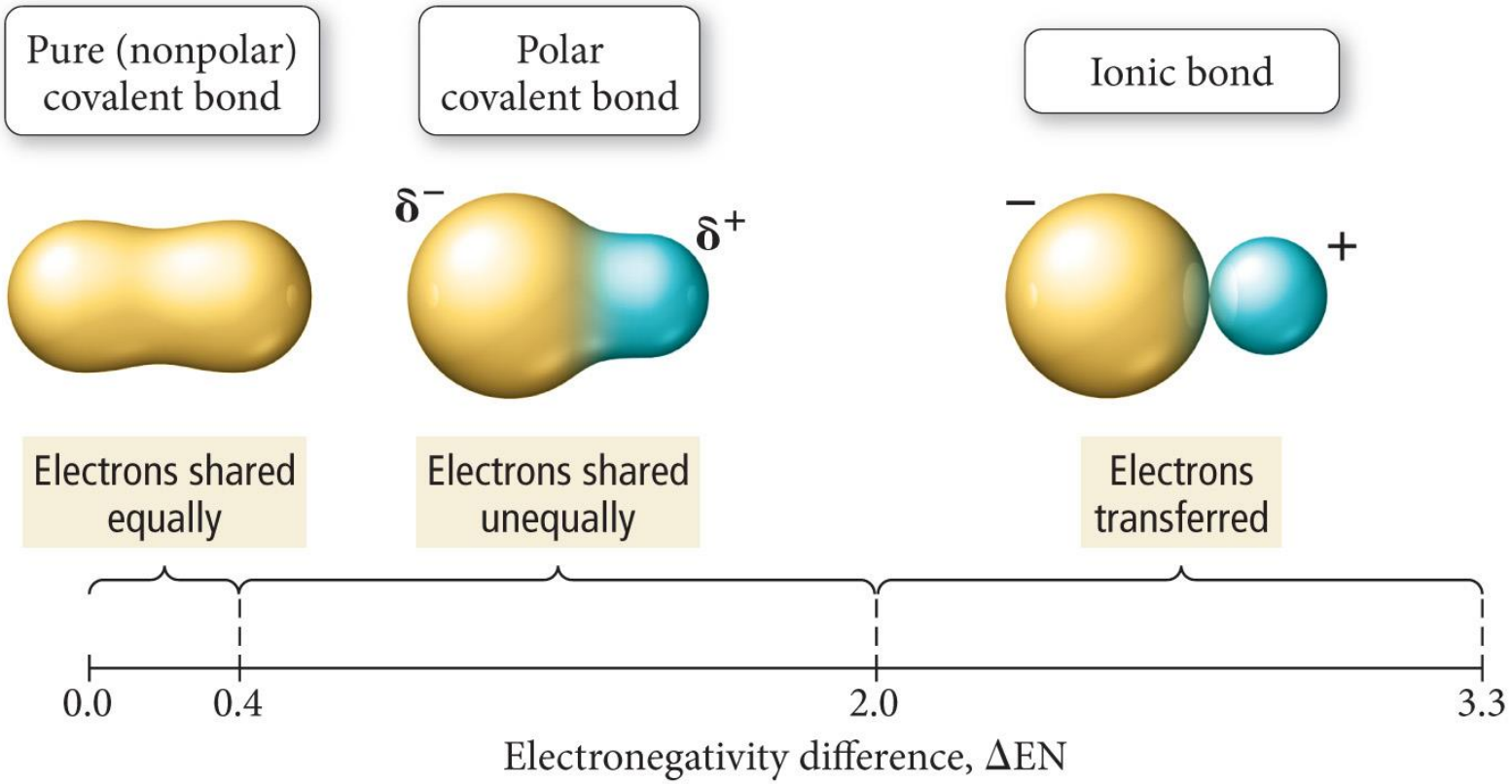
partial transfer of e^-
電子的局部轉移

Ionic

transfer e^-
電子轉移



The Continuum of Bond Types



Bond Dipole Moments

- **Dipole moment**, μ, is a measure of bond polarity.

$\mu = (q)(r)$ Measured in Debyes, D

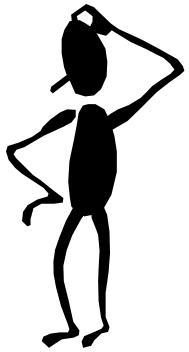
TABLE 9.2 Dipole Moments of Several Molecules in the Gas Phase

Molecule	ΔEN	Dipole Moment (D)
Cl_2	0	0
ClF	1.0	0.88
HF	1.9	1.82
LiF	3.0	6.33

9.7 Lewis Structures of Molecular Compounds and Polyatomic Ions

Writing Lewis Structures for Molecular Compounds

1. **Write the correct skeletal structure for the molecule.** Put least electronegative element in the center.
2. Calculate total number of valence e^-. Add 1 for each negative charge. Subtract 1 for each positive charge.
3. Complete an octet for all atoms ***except*** hydrogen
4. **If any atoms lack an octet, form double or triple bonds as necessary to give them octets.**



Write the Lewis structure of nitrogen trifluoride (NF_3).

Step 1 – N is less electronegative than F, put N in center

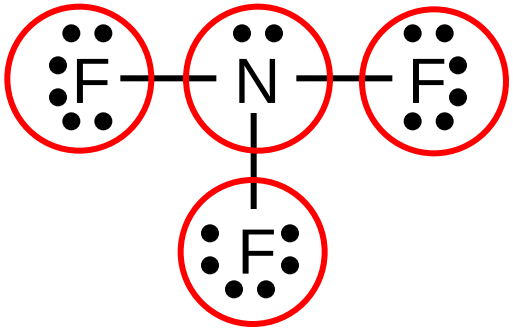
Step 2 – Count valence electrons N - 5 ($2s^2 2p^3$) and F - 7 ($2s^2 2p^5$)

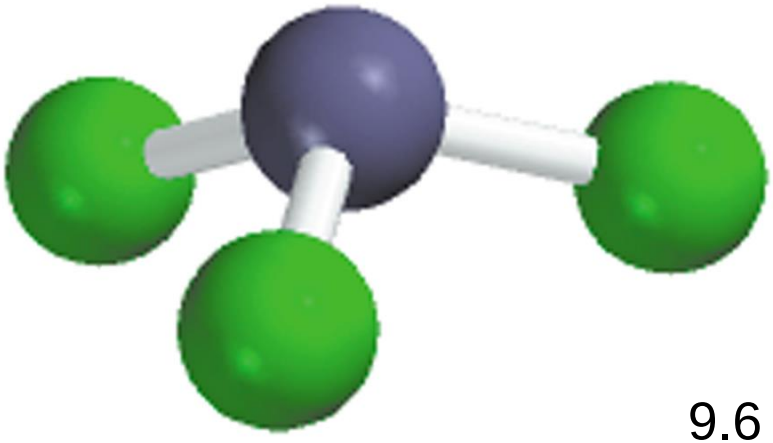
5 + (3 x 7) = 26 valence electrons

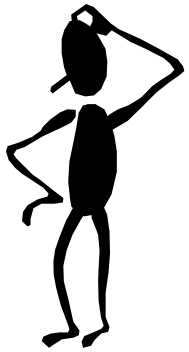
Step 3 – Draw single bonds between N and F atoms and complete octets on N and F atoms. 26 - (3 x 2) = 20 valence electrons

Step 4 - Check, are # of e^- in structure equal to number of valence e^- ?

3 single bonds (3x2) + 10 lone pairs (10x2) = 26 valence electrons







Write the Lewis structure of the carbonate ion (CO_3^{2-}).

Step 1 – C is less electronegative than O, put C in center

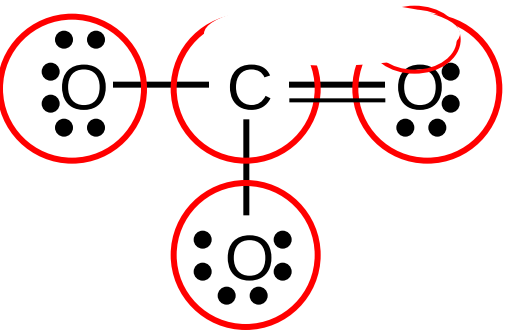
Step 2 – Count valence electrons C - 4 ($2s^2 2p^2$) and O - 6 ($2s^2 2p^4$)
-2 charge – $2e^-$

4 + (3 x 6) + 2 = 24 valence electrons

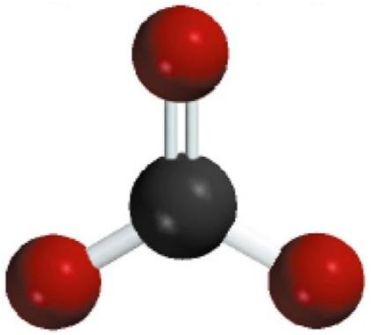
Step 3 – Draw single bonds between C and O atoms and complete octet on C and O atoms. 24 - (3 x 2) = 18 valence electrons

Step 4 - Check every atom satisfied octet rule,

Step 5 - central atom C is not for octet rule, we move a lone pair from one of the O atoms to form another bond with C. Now the octet rule also satisfied for te C atom.



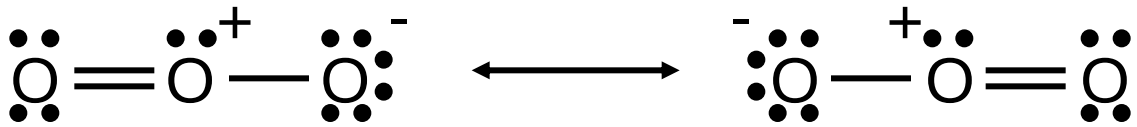
2 single bonds (2x2) = 4
1 double bond = 4
8 lone pairs (8x2) = 16
Total = 24

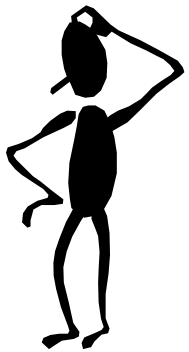


9.8 Resonance and Formal Charge

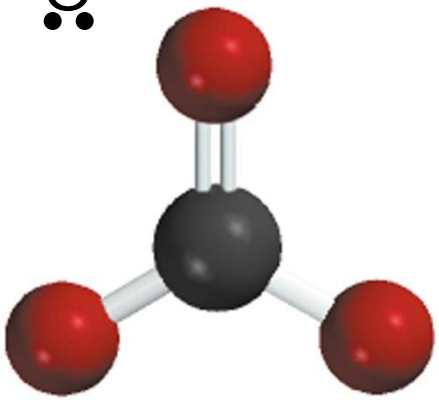
Resonance

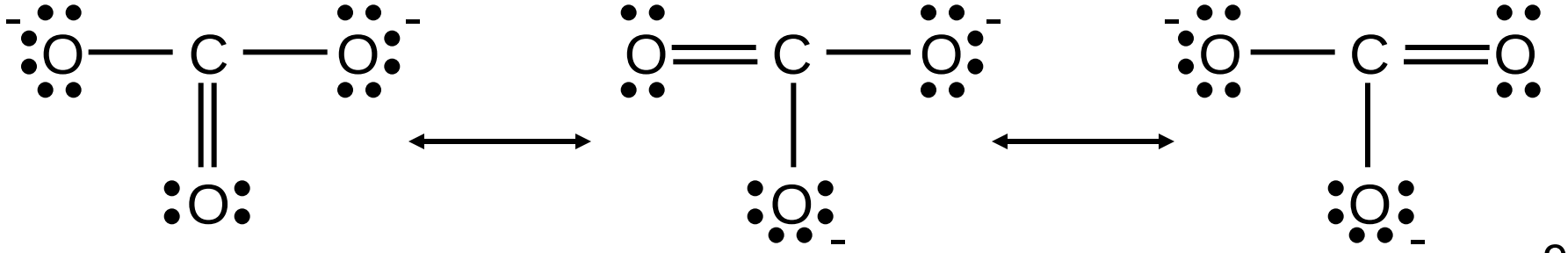
A ***resonance structure*** is one of two or more Lewis structures for a single molecule that cannot be represented accurately by only one Lewis structure.





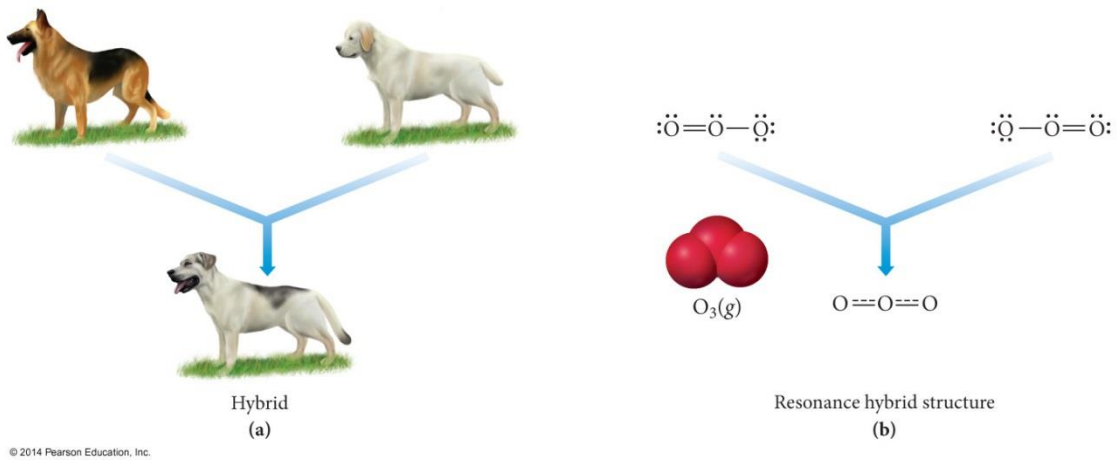
What are the resonance structures of the carbonate (CO_3^{2-}) ion?





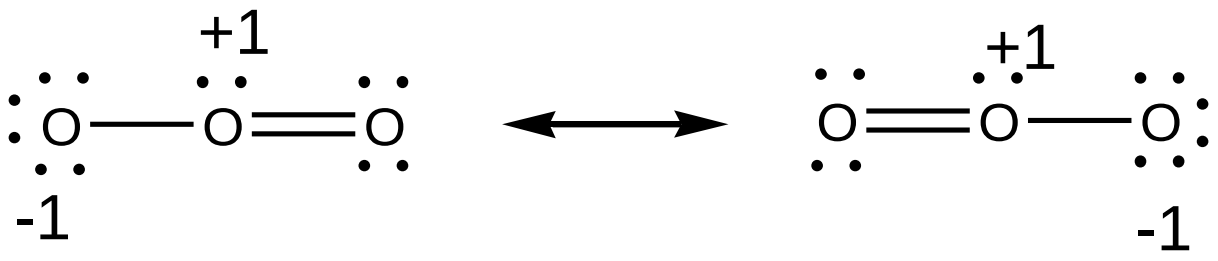
Resonance

- The actual molecule is a combination of the resonance forms—a **resonance hybrid**.
  - ✓The molecule does **not** resonate between the two forms, though we often draw it that way.



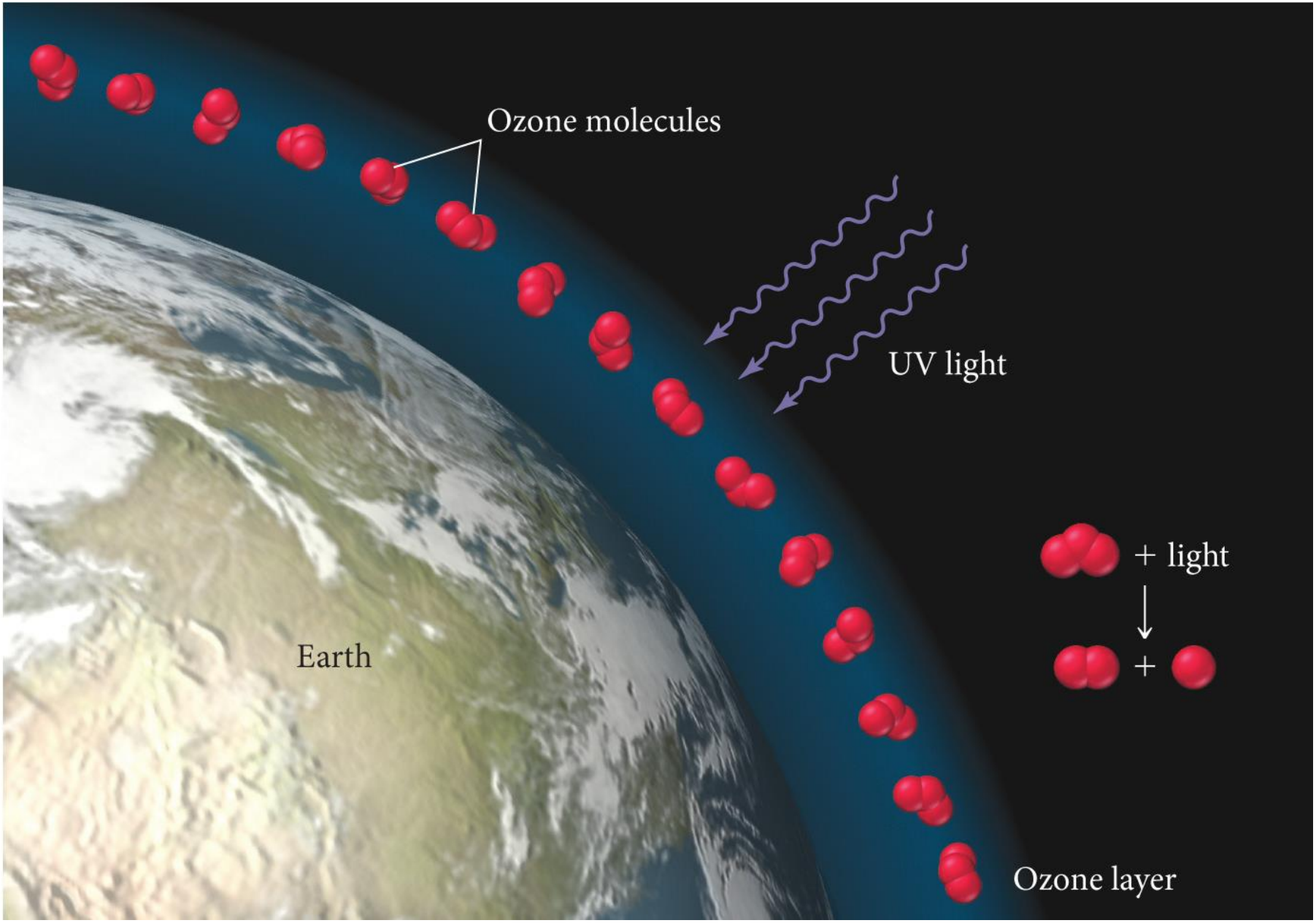
Q：Within each of the following species all bonds are equivalent. To show this, for which one of these compounds must we draw <u>two</u> resonance structures?

A. CO_2
B. O_3
C. CO
D. NO
E. H_2S



Answer: B

Ozone Layer



Formal Charge

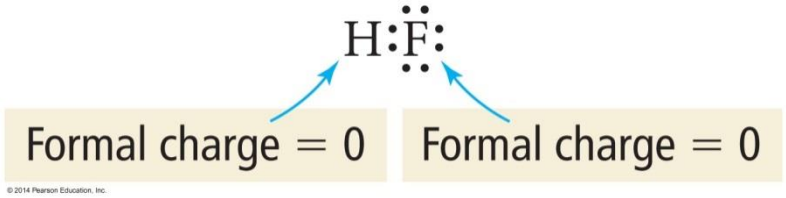
- During bonding, atoms may end with more or fewer electrons than the valence electrons they brought in order to fulfill octets.
- His results in atoms having a **formal charge**.

FC = valence e⁻ – nonbonding e⁻ – ½ bonding e⁻

$$\text{Formal charge} = 1 - \underbrace{[0 + \tfrac{1}{2}(2)]}_{} = 0$$

Number of valence electrons for H

Number of electrons that H "owns" in the Lewis structure



$$\text{Formal charge} = 7 - \underbrace{[6 + \tfrac{1}{2}(2)]}_{} = 0$$

Number of valence electrons for F

Number of electrons that F "owns" in the Lewis structure

	Structure A					Structure B				
	H	—	C	≡	N:	H	—	N	≡	C:
number of valence e^-	1		4		5	1		5		4
− number of nonbonding e^-	−0		−0		−2	−0		−0		−2
$-\frac{1}{2}$(number of bonding e^-)	$-\frac{1}{2}(2)$		$-\frac{1}{2}(8)$		$-\frac{1}{2}(6)$	$-\frac{1}{2}(2)$		$-\frac{1}{2}(8)$		$-\frac{1}{2}(6)$
Formal charge	**0**		**0**		**0**	**0**		**+1**		**−1**

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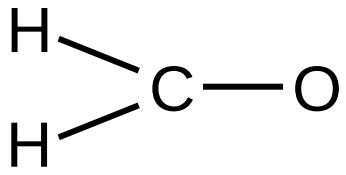
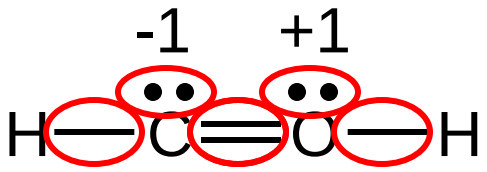
Two possible skeletal structures of formaldehyde (CH_2O)



An atom's ***formal charge*** is the difference between the number of valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.

$$\text{formal charge on an atom in a Lewis structure} = \text{total number of valence electrons in the free atom} - \text{total number of nonbonding electrons} - \frac{1}{2}\left(\text{total number of bonding electrons}\right)$$

The sum of the formal charges of the atoms in a molecule or ion must equal the charge on the molecule or ion.



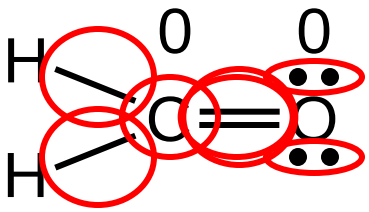
C – 4 e^-
O – 6 e^-
2H – 2x1 e^-
12 e^-

2 single bonds (2x2) = 4
1 double bond = 4
2 lone pairs (2x2) = 4
Total = 12

formal charge on an atom in a Lewis structure = total number of valence electrons in the free atom - total number of nonbonding electrons - $\frac{1}{2}$ (total number of bonding electrons)

formal charge on C = 4 -2 -½ x 6 = -1

formal charge on O = 6 -2 -½ x 6 = +1



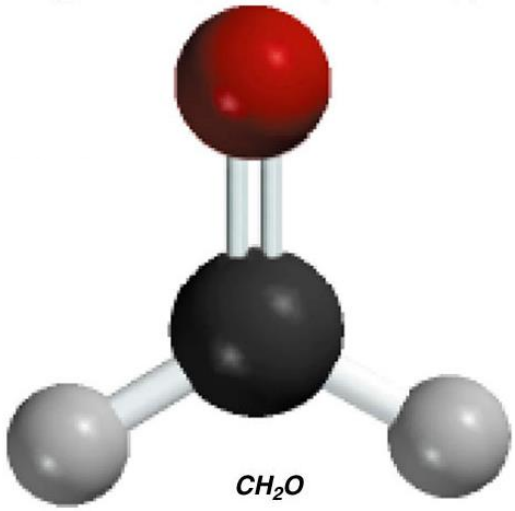
C – 4 e^-
O – 6 e^-
2H – 2x1 e^-
12 e^-

2 single bonds (2x2) = 4
1 double bond = 4
2 lone pairs (2x2) = 4
Total = 12

$$\text{formal charge on an atom in a Lewis structure} = \text{total number of valence electrons in the free atom} - \text{total number of nonbonding electrons} - \frac{1}{2}\left(\text{total number of bonding electrons}\right)$$

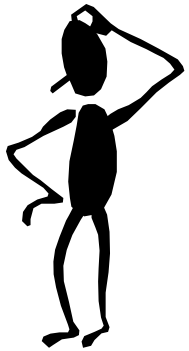
formal charge on C = 4 - 0 - ½ x 8 = 0

formal charge on O = 6 - 4 - ½ x 4 = 0

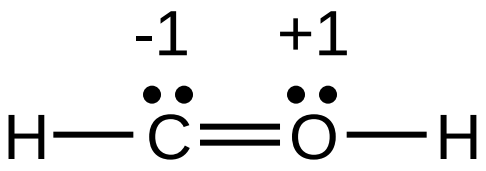


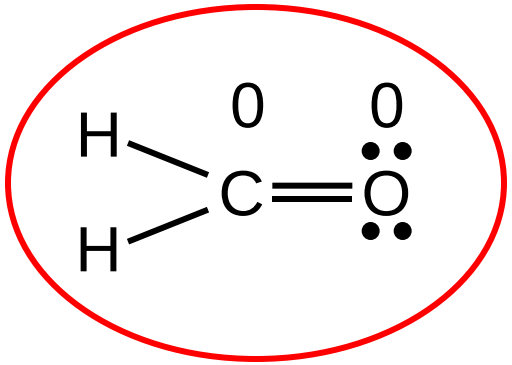
Formal Charge and Lewis Structures

1. For neutral molecules, a Lewis structure in which there are no formal charges is preferable to one in which formal charges are present.
2. Lewis structures with large formal charges are less plausible than those with **small formal** charges.
3. Among Lewis structures having similar distributions of formal charges, the most plausible structure is the one in which **negative formal charges** are placed on the **more electronegative atoms.**



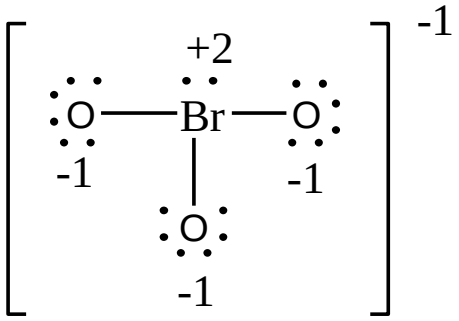
Which is the most likely Lewis structure for CH_2O?





Q：What is the formal charge on the bromine atom in BrO_3^- , drawn with three single bonds?

A. -2
B. -1
C. 0
D. +1
E. +2



Answer: E

9.9 Exceptions to the Octet Rule: Odd-Electron Species, Incomplete Octets, and Expanded Octets

- Odd number electron species (e.g., NO)
  - Will have one unpaired electron
  - Free-radical
  - Very reactive
- Incomplete octets
  - B, Al
- Expanded octets
  - Elements with empty *d* orbitals can have more than eight electrons.

Exceptions to the Octet Rule

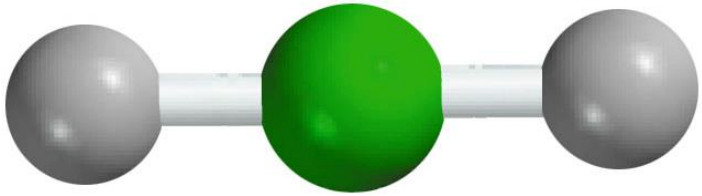
The Incomplete Octet (2A,3A)

BeH_2

Be – $2e^-$

2H – $2x1e^-$

$4e^-$

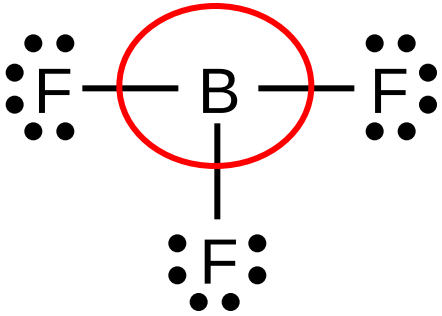


BF_3

B – $3e^-$

3F – $3x7e^-$

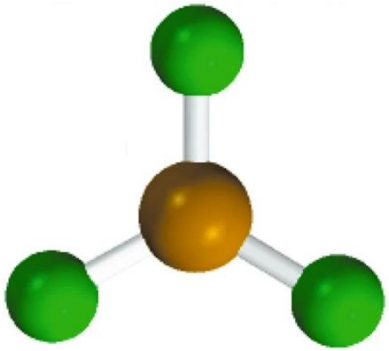
$24e^-$



3 single bonds (3x2) = 6

9 lone pairs (9x2) = 18

Total = 24

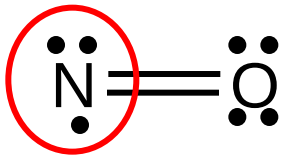


Exceptions to the Octet Rule

Odd-Electron Molecules

NO

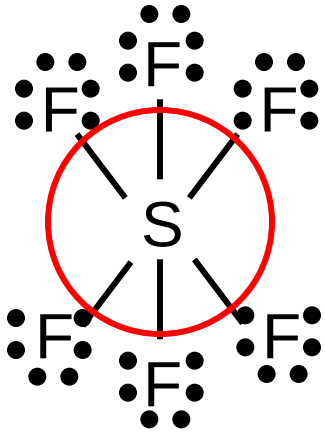
N – $5e^-$
O – $6e^-$
$11e^-$



The Expanded Octet (central atom with principal quantum number n > 2)

SF_6

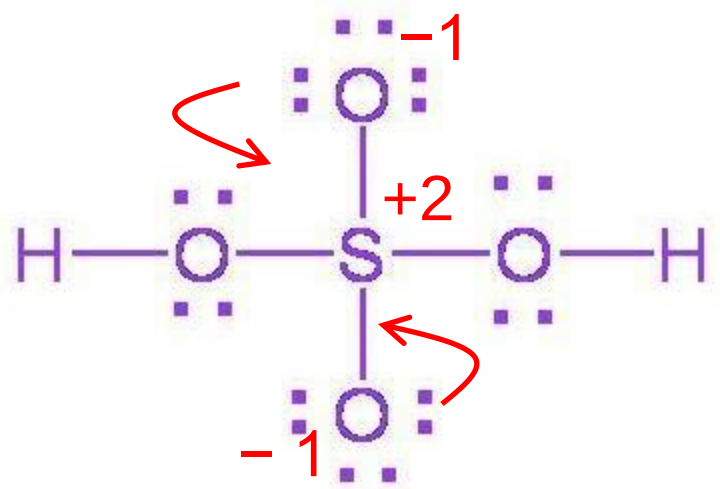
S – $6e^-$
6F – $42e^-$
$48e^-$

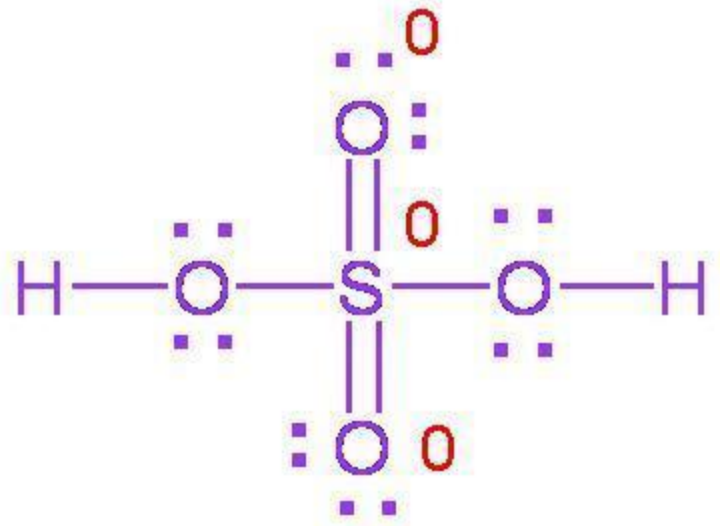


6 single bonds (6x2) = 12
18 lone pairs (18x2) = 36
Total = 48

Drawing Resonance Structures

1. Draw the first Lewis structure that maximizes octets.
2. Assign formal charges.
3. Move electron pairs from atoms with (−) formal charge toward atoms with (+) formal charge.
4. If (+) formal charge atom second row, only move in electrons if you can move out electron pairs from multiple bond.
5. If (+) formal charge atom third row or below, keep bringing in electron pairs to reduce the formal charge, even if get expanded octet.





Q : Which response includes all the molecules below that do not follow the octet rule?

(1) H_2S (2) BCl_3 (3) PH_3 (4) SF_4

A. 2,4
B. 2,3
C. 1,2
D. 3,4
E. 1,4

Answer: A

9.10 Bond Energies and Bond Lengths

Bond Energies

The enthalpy change required to break a particular bond in one mole of gaseous molecules is the ***bond energy***.

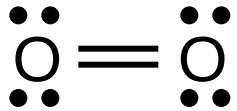
Bond Energy

$H_{2\,(g)} \longrightarrow H_{(g)} + H_{(g)} \quad \Delta H^0 = 436.4\ kJ$

$Cl_{2\,(g)} \longrightarrow Cl_{(g)} + Cl_{(g)} \quad \Delta H^0 = 242.7\ kJ$

$HCl_{(g)} \longrightarrow H_{(g)} + Cl_{(g)} \quad \Delta H^0 = 431.9\ kJ$

$O_{2\,(g)} \longrightarrow O_{(g)} + O_{(g)} \quad \Delta H^0 = 498.7\ kJ$



$N_{2\,(g)} \longrightarrow N_{(g)} + N_{(g)} \quad \Delta H^0 = 941.4\ kJ$

Bond Energies

Single bond < Double bond < Triple bond

Trends in Bond Energies

- In general, the more electrons two atoms share, the stronger the covalent bond.
  - Must be comparing bonds between like atoms
  - **C≡C (837 kJ) > C═C (611 kJ) > C—C (347 kJ)**
  - C≡N (891 kJ) > C ═ N (615 kJ) > C—N (305 kJ)
- In general, the shorter the covalent bond, the stronger the bond.
  - Must be comparing similar types of bonds
  - Br—F (237 kJ) > Br—Cl (218 kJ) > Br—Br (193 kJ)
  - Bonds get weaker down the column.
  - Bonds get stronger across the period.

Average ***bond energy*** in polyatomic molecules

$$H_2O_{(g)} \longrightarrow H_{(g)} + OH_{(g)} \quad \Delta H^0 = 502 \text{ kJ}$$

$$OH_{(g)} \longrightarrow H_{(g)} + O_{(g)} \quad \Delta H^0 = 427 \text{ kJ}$$

$$\text{Average OH bond energy} = \frac{502 + 427}{2} = 464 \text{ kJ}$$

TABLE 9.3 Average Bond Energies

Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)
H—H	436	N—N	163	Br—F	237
H—C	414	N=N	418	Br—Cl	218
H—N	389	N≡N	946	Br—Br	193
H—O	464	N—O	222	I—Cl	208
H—S	368	N=O	590	I—Br	175
H—F	565	N—F	272	I—I	151
H—Cl	431	N—Cl	200	Si—H	323
H—Br	364	N—Br	243	Si—Si	226
H—I	297	N—I	159	Si—C	301
C—C	347	O—O	142	S—O	265
C=C	611	O=O	498	Si=O	368
C≡C	837	O—F	190	S= O	523
C—N	305	O—Cl	203	Si—Cl	464
C=N	615	O—I	234	S= S	418
C≡N	891	F—F	159	S—F	327
C—O	360	Cl—F	253	S—Cl	253
C=O	736*	Cl—Cl	243	S—Br	218
C≡O	1072			S—S	266
C—Cl	339				

*799 in CO_2.

Using Bond Energies to Estimate ΔH°_{rxn}

- The actual bond energy depends on the surrounding atoms and other factors.
- We often use **average bond energies** to estimate the ΔH_{rxn}.
  - Works best when all reactants and products in gas state
- Bond breaking is endothermic, ΔH(breaking) = +.
- Bond making is exothermic, ΔH(making) = −.

$$\Delta H_{rxn} = \sum (\Delta H(\text{bonds broken})) + \sum (\Delta H(\text{bonds formed}))$$

Using Bond Energies to Estimate ΔH°_{rxn}

Bond Energies (BE) and Enthalpy changes in reactions

Imagine reaction proceeding by breaking all bonds in the reactants and then using the gaseous atoms to form all the bonds in the products.

ΔH^0 = total energy input – total energy released

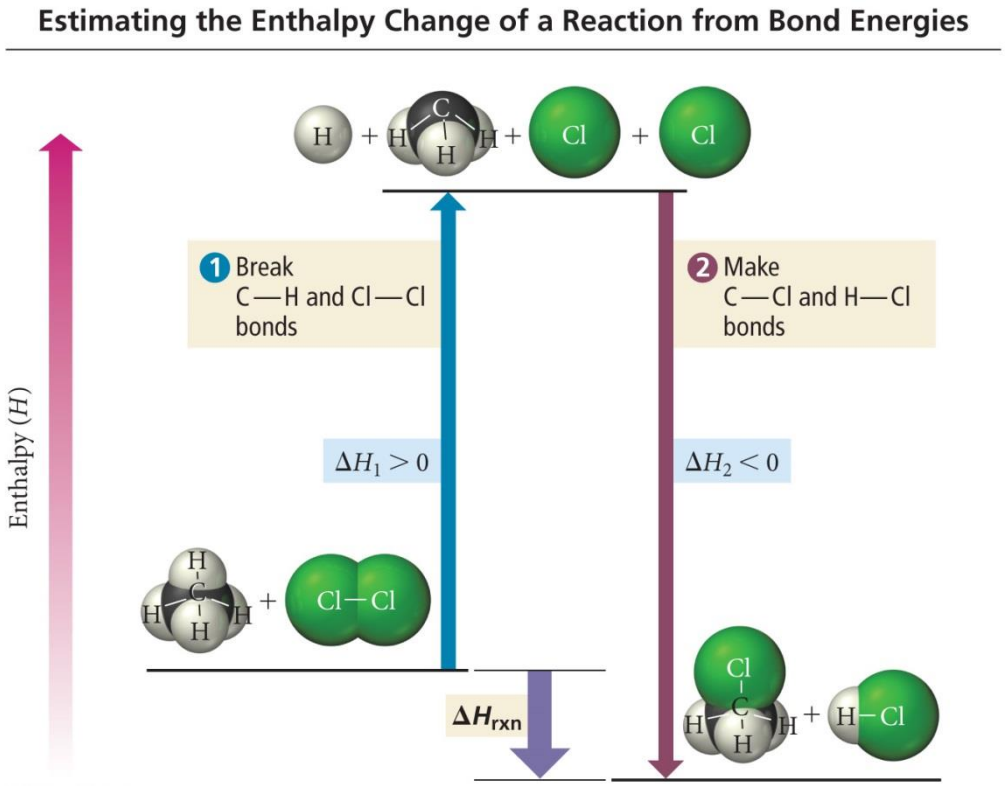
= ΣBE(reactants) – ΣBE(products)

$\Delta H_{rxn} = \sum (\Delta H(\text{bonds broken})) + \sum (\Delta H(\text{bonds formed}))$

- endothermic,

  $-\Delta H$(breaking) = +.
- exothermic,

  $-\Delta H$(making) = −.



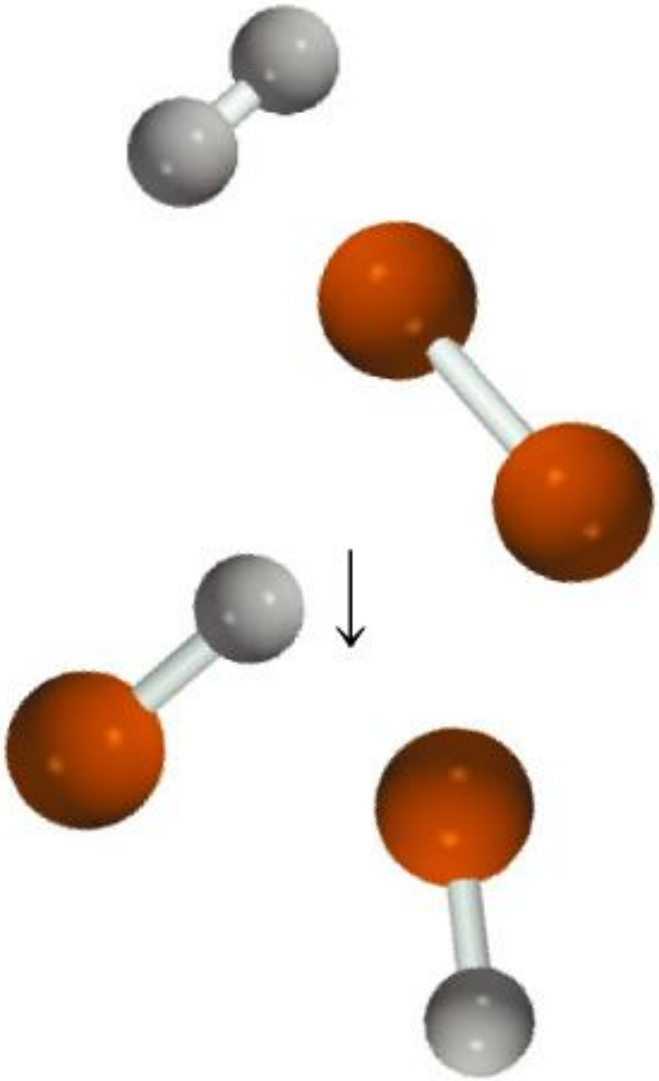
$$H_3C{-}H(g) + Cl{-}Cl(g) \longrightarrow H_3C{-}Cl(g) + H{-}Cl(g)$$

$$H_3C{-}H(g) + Cl{-}Cl(g) \longrightarrow H_3C{-}Cl(g) + H{-}Cl(g)$$

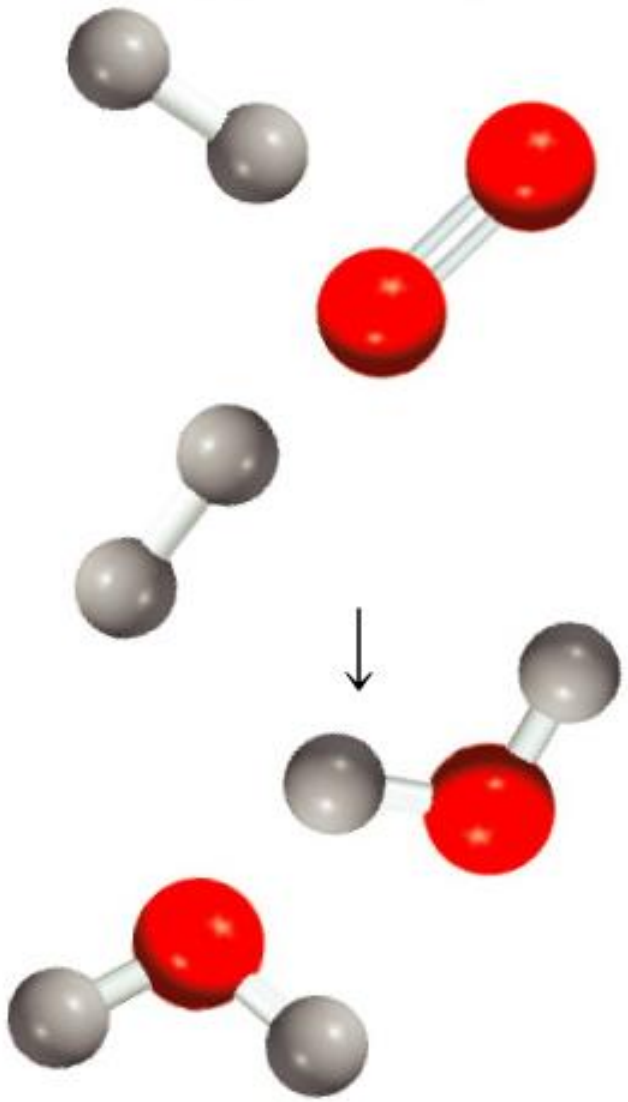
Bonds Broken		Bonds Formed	
C—H break	+414 kJ	C—Cl form	−339 kJ
Cl—Cl break	+243 kJ	H—Cl form	−431 kJ
Sum (Σ) ΔH's bonds broken:	+657 kJ	*Sum (Σ) ΔH's bonds formed:*	−770 kJ

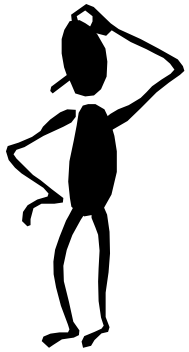
$$\begin{aligned}\Delta H_{rxn} &= \Sigma(\Delta H\text{'s bonds broken}) + \Sigma(\Delta H\text{'s bonds formed}) \\ &= +657\ \text{kJ} - 770\ \text{kJ} \\ &= -113\ \text{kJ}\end{aligned}$$

$H_2\ (g) + Cl_2\ (g) \longrightarrow 2HCl\ (g)$



$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (g)$





Use bond energies to calculate the enthalpy change for:

$$H_{2\,(g)} + F_{2\,(g)} \longrightarrow 2HF_{\,(g)}$$

$$\Delta H^0 = \Sigma BE(\text{reactants}) - \Sigma BE(\text{products})$$

Type of bonds broken	Number of bonds broken	Bond energy (kJ/mol)	Energy change (kJ)
H—H	1	436.4	436.4
F—F	1	156.9	156.9
Type of bonds formed	**Number of bonds formed**	**Bond energy (kJ/mol)**	**Energy change (kJ)**
H—F	2	568.2	1136.4

$$\Delta H^0 = 436.4 + 156.9 - 2 \times 568.2 = -543.1 \text{ kJ}$$

Q：Estimate the enthalpy change for the reaction

$2SO_2 + O_2 \rightarrow 2SO_3$

given the following bond energies

BE(S - O) = 347 kJ

BE(O=O) = 499 kJ

A. -152 kJ
B. +152 kJ
C. -195 kJ
D. +195 kJ
E. +846 kJ

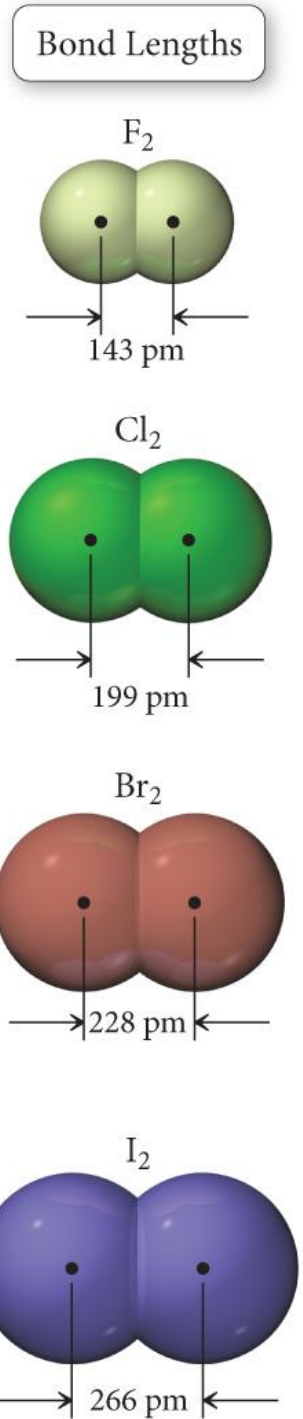
$\Delta H^0 = \Sigma BE(\text{reactants}) - \Sigma BE(\text{products})$

$\Delta H^0 = 2 \times 2 \times 347 + 499 - 2 \times 3 \times 347 = -195 \text{ kJ}$

Answer: C

Bond Lengths

- The distance between the nuclei of bonded atoms is called the **bond length**.
- Because the actual bond length depends on the other atoms around the bond we often use the **average bond length**.
  - Averaged for similar bonds from many compounds



Trends in Bond Lengths

- In general, the more electrons two atoms share, the shorter the covalent bond.
  - Must be comparing bonds between like atoms
  - C≡C (120 pm) < C═C (134 pm) < C—C (154 pm)
  - C≡N (116 pm) < C═N (128 pm) < C—N (147 pm)
- Generally, bond length decreases from left to right across period.
  - C—C (154 pm) > C—N (147 pm) > C—O (143 pm)
- Generally, bond length increases down the column.
  - F—F (144 pm) > Cl—Cl (198 pm) > Br—Br (228 pm)
- In general, as bonds get longer, they also get weaker.

Bond Lengths

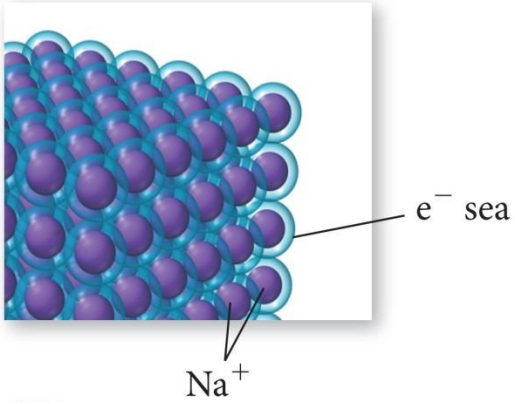
TABLE 9.4 Average Bond Lengths

Bond	Bond Length (pm)	Bond	Bond Length (pm)	Bond	Bond Length (pm)
H—H	74	C—C	154	N—N	145
H—C	110	C=C	134	N=N	123
H—N	100	C≡C	120	N≡N	110
H—O	97	C—N	147	N—O	136
H—S	132	C=N	128	N=O	120
H—F	92	C≡N	116	O—O	145
H—Cl	127	C—O	143	O=O	121
H—Br	141	C=O	120	F—F	143
H—I	161	C—Cl	178	Cl—Cl	199
				Br—Br	228
				I—I	266

9.11 **Bonding in Metals: The Electron Sea Model**

https://www.youtube.com/watch?v=Bjf9gMDP47s

- Metallic solids do conduct electricity well.
- As temperature increases, the electrical conductivity of metals decreases.
- Metallic solids do conduct heat well.
- Metallic solids do reflect light.
- Metallic solids are malleable and ductile.



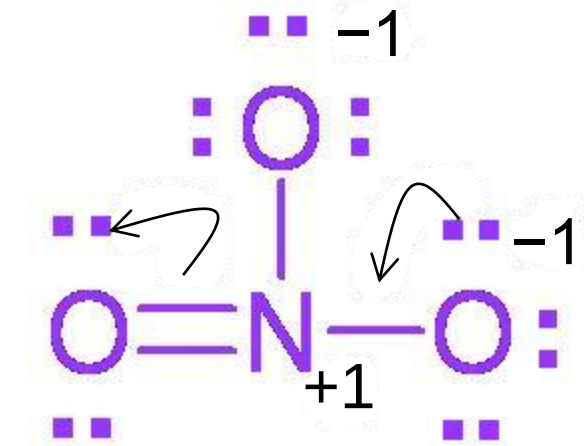
- Metals generally have high melting points and boiling points.
  - All but Hg are solids at room temperature.
- Melting points of metal generally increase left to right across period.（溶點右上角最大）

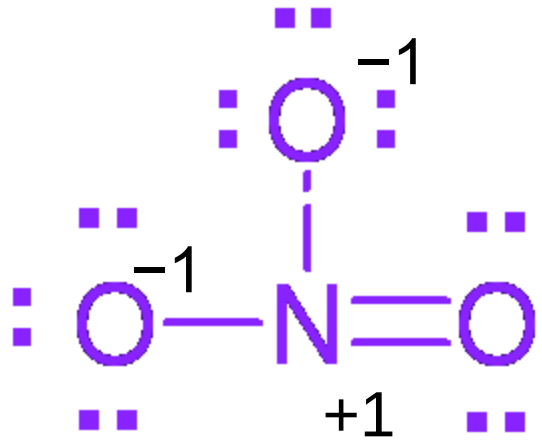
  -Na (97.72 ºC) < Mg (650 ºC) < Al (660.32 ºC)
- Melting points of metals generally decrease down column.

  -Li (180.54 ºC) > Na (97.72 ºC) > K (63.38 ºC)

Drawing Resonance Structures

1. Draw the first Lewis structure that maximizes octets.
2. Assign formal charges.
3. Move electron pairs from atoms with (−) formal charge toward atoms with (+) formal charge.
4. If (+) formal charge atom second row, only move in electrons if you can move out electron pairs from multiple bond.
5. If (+) formal charge atom third row or below, keep bringing in electron pairs to reduce the formal charge, even if get expanded octet.





Evaluating Resonance Structures

- Better structures have fewer formal charges.
- Better structures have smaller formal charges.
- Better structures have the negative formal charge on the more electronegative atom.