

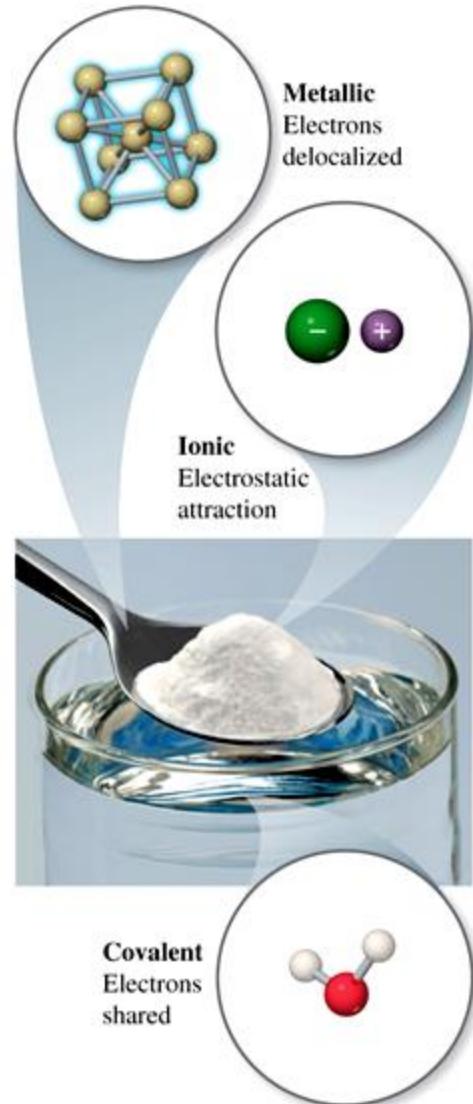
Chapter 8

Basic Concepts of Chemical Bonding

➤ Chemical Bonds

□ Three basic types of bonds

- **Ionic**-Electrostatic attraction between ions.
- **Covalent**-Sharing of electrons.
- **Metallic**-Metal atoms bonded to several other atoms.



➤ Lewis Symbols

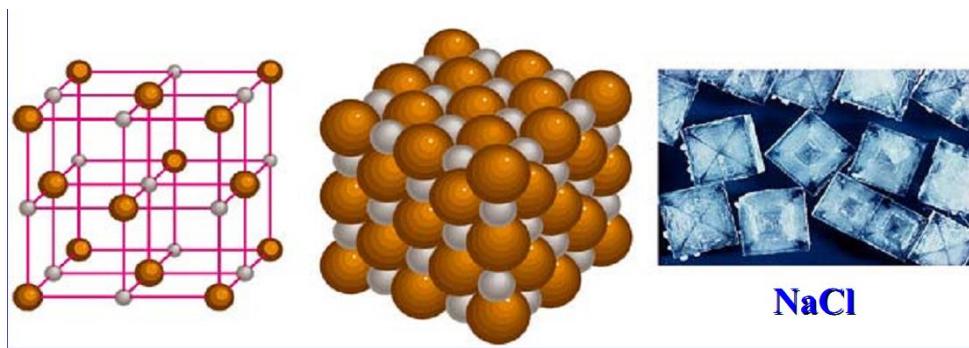
- Electrons in the outermost occupied shell---**valence electrons**
- G.N. Lewis pioneered the use of chemical symbols surrounded with dots to symbolize the valence electrons around an atom---Lewis symbol---
- When forming compounds, atoms tend to add or subtract electrons until they are surrounded by eight valence electrons (**the octet rule**八隅体规则).

TABLE 8.1 • Lewis Symbols

Group	Element	Electron Configuration	Lewis Symbol	Element	Electron Configuration	Lewis Symbol
1A	Li	[He]2s ¹	Li·	Na	[Ne]3s ¹	Na·
2A	Be	[He]2s ²	·Be·	Mg	[Ne]3s ²	·Mg·
3A	B	[He]2s ² 2p ¹	·B·	Al	[Ne]3s ² 3p ¹	·Al·
4A	C	[He]2s ² 2p ²	·C·	Si	[Ne]3s ² 3p ²	·Si·
5A	N	[He]2s ² 2p ³	·N·	P	[Ne]3s ² 3p ³	·P·
6A	O	[He]2s ² 2p ⁴	:O:	S	[Ne]3s ² 3p ⁴	:S:
7A	F	[He]2s ² 2p ⁵	·F·	Cl	[Ne]3s ² 3p ⁵	·Cl:
8A	Ne	[He]2s ² 2p ⁶	:Ne:	Ar	[Ne]3s ² 3p ⁶	:Ar:

➤ Ionic Bonding

- Typical Ionic compound-consist of a metal of low ionization energy and a nonmetal of high electron affinity.
- 电离能较小的金属原子（如碱金属与碱土金属）和电子亲和能较大的非金属原子（如卤素及氧族原子）靠近时，前者易失去电子变成正离子，后者易获得电子变成负离子，这样正、负离子便都具有类似稀有气体原子的稳定结构。它们之间靠库仑静电引力结合在一起而生成 力结合在一起而生成离子化合物。这种正负离子间的静电吸引力叫作离子键。



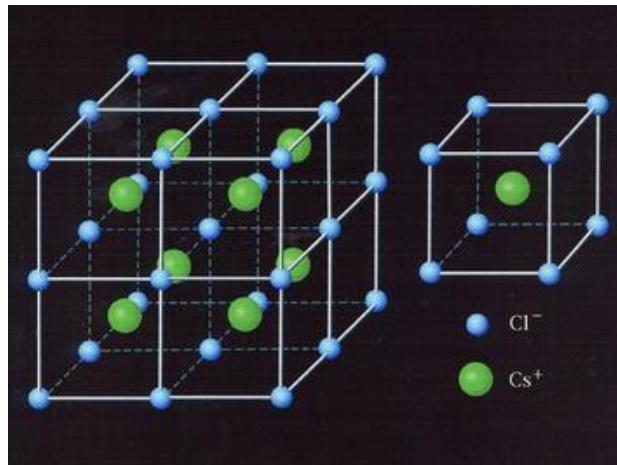
Crystalline, cleavable, rigid, three dimensional arrangement



The formation of Li⁺ and F⁻, the electron transfer from Li To F.

➤ 离子键的特点：

- 既没有方向性，也不具饱和性。
- 正负离子周围邻接的异电荷离子数目主要取决于正负离子的相对大小，而与它们所带电荷多少无直接关系。只要周围空间许可，一个负(正)离子可以尽量多地吸引异电荷离子。
- 实际上离子化合物没有独立的“分子单元”，因此无分子式，而只有化学式。例如， NaCl 并不代表氯化钠的分子式，只是表示在氯化钠晶体中 Na^+ 和 Cl^- 的摩尔比为 1:1。



➤ Energetics of Ionic Bonding

- As we saw in the last chapter, it takes 496 kJ/mol to remove electrons from sodium.

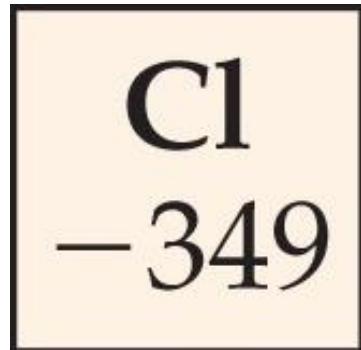


Element	I_1
Na	496

First Ionization Energy

➤ Energetics of Ionic Bonding

- We get 349 kJ/mol back by giving electrons to chlorine.



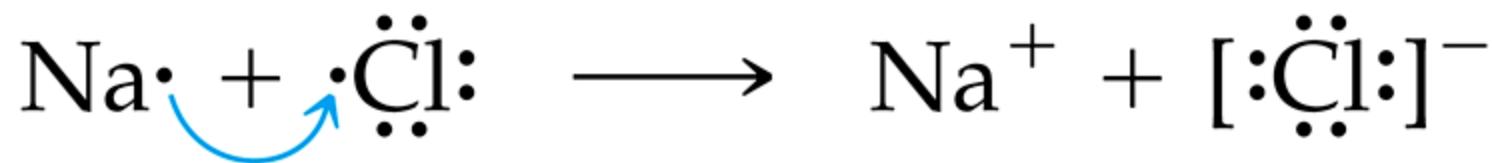
Electron Affinity

➤ Energetics of Ionic Bonding

- These numbers don't explain why the reaction of sodium metal and chlorine gas to form sodium chloride is so exothermic!



➤ Energetics of Ionic Bonding



$$\Delta H = +147 \text{ kJ/mol} \text{ endothermic}$$

- There must be a third piece to the puzzle.
- What is as yet unaccounted for is the electrostatic attraction between the newly formed sodium cation and chloride anion.

$$\Delta H = -788 \text{ kJ/mol}$$



$$\Delta H = 788 \text{ kJ/mol},$$

➤ Lattice Energy

- This third piece of the puzzle is the **lattice energy**(晶格能):
 - *The energy required to completely separate **a mole of a solid** ionic compound into its **gaseous ions**.*
 - The energy associated with electrostatic interactions is governed by Coulomb's law:

$$E_{\text{el}} = \kappa \frac{Q_1 Q_2}{d}$$

Where: κ is constant of $8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$

Q_1 and Q_2 are the charges on the particles

d is the distance between their centers

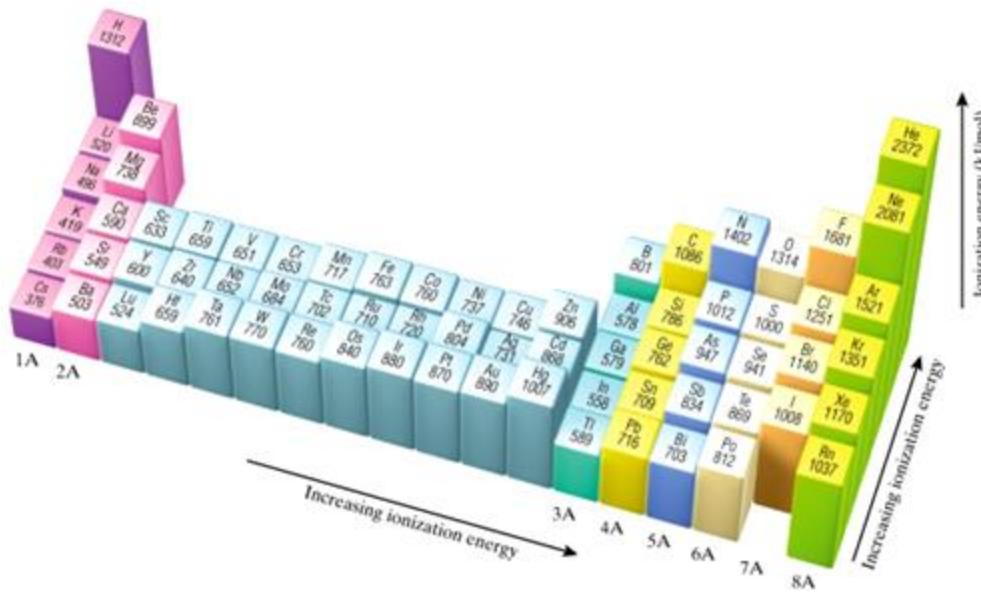
For a given arrangement of ions, the lattice energy increases as the charges on the ions increase and as their radii decrease.

GIVE IT SOME THOUGHT

Consider the trends in ionization energies of the alkali metals and electron affinities of the halogens shown in Figures 7.9 and 7.11. For which pair is electron transfer from the alkali metal atom to the halogen atom most likely to be an exothermic process?

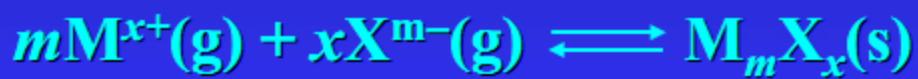
- A. No pair of an alkali metal with a halogen gives a sum of I_1 and EA that is negative, exothermic.
- B. Na and F
- C. K and Cl
- D. Rb and I

1A	2A	3A	4A	5A	6A	7A	8A
H -73	Be > 0	B -27	C -122	N > 0	O -141	F -328	Ne > 0
Li -60	Mg > 0	Al -43	Si -134	P -72	S -200	Cl -349	Ar > 0
K -48	Ca -2	Ga -30	Ge -119	As -78	Se -195	Br -325	Kr > 0
Rb -47	Sr -5	In -30	Sn -107	Sb -103	Te -190	I -295	Xe > 0

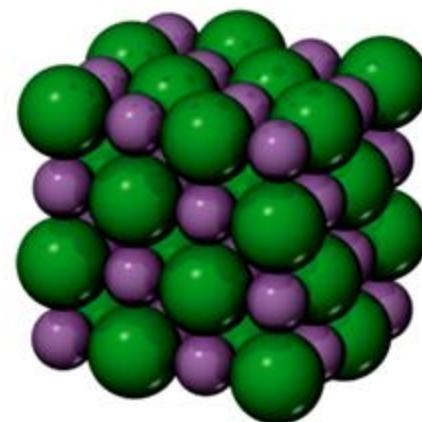


➤ 离子键的强度 —— 晶格能 (lattice energy)

- 离子键的强度可用晶格能，也称点阵能U的大小来衡量。晶格能表示相互远离的气态正离子和负离子结合成1mol离子晶体时所释放的能量，或1mol离子晶体解离成自由气态离子时所吸收的能量。在热化学计算中，正向反应释放的能量和逆向反应吸收的能量，数值相同，符号相反，取其绝对值称为晶格能 (U)。例如，对以下晶体生成反应，



晶格能: $U = -\Delta H$



➤ Lattice Energy

- Lattice energy, then, increases with the charge on the ions.
- It also increases with decreasing size of ions.

TABLE 8.2 • Lattice Energies for Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	MgCl ₂	2326
LiCl	834	SrCl ₂	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		



离子电荷、 r_0 对晶格能和晶体熔点、硬度的影响

NaCl型离子化合物	Z	r_0/pm	晶格能 $\text{kJ} \cdot \text{mol}^{-1}$	熔点/°C	Mohs硬度
NaF	1	231	923	993	3.2
NaCl	1	282	786	801	2.5
NaBr	1	298	747	747	<2.5
Nal	1	323	704	661	<2.5
MgO	2	210	3791	2852	6.5
CaO	2	240	3401	2614	4.5
SrO	2	257	3223	2430	3.5
BaO	2	256	3054	1918	3.3

离子化合物的晶格能越大，正负离子间结合力越强，相应晶体的熔点越高、硬度越大、热膨胀系数和压缩系数越小。

Sample Exercise 8.1 Magnitudes of Lattice Energies

Without consulting Table 8.2, arrange the ionic compounds NaF, CsI, and CaO in order of increasing lattice energy.

Solution

Analyze From the formulas for three ionic compounds, we must determine their relative lattice energies.

Plan We need to determine the charges and relative sizes of the ions in the compounds. We then use Equation 8.4 qualitatively to determine the relative energies, knowing that (a) the larger the ionic charges, the greater the energy and (b) the farther apart the ions are, the lower the energy.

$$E_{el} = \frac{\kappa Q_1 Q_2}{d} \quad [8.4]$$

Solve NaF consists of Na^+ and F^- ions, CsI of Cs^+ and I^- ions, and CaO of Ca^{2+} and O^{2-} ions. Because the product $Q_1 Q_2$ appears in the numerator of Equation 8.4, the lattice energy increases dramatically when the charges increase. Thus, we expect the lattice energy of CaO, which has $2+$ and $2-$ ions, to be the greatest of the three.

The ionic charges are the same in NaF and CsI. As a result, the difference in their lattice energies depends on the difference in the distance between ions in the lattice. Because ionic size increases as we go down a group in the periodic table (Section 7.3), we know that Cs^+ is larger than Na^+ and I^- is larger than F^- . Therefore, the distance between Na^+ and F^- ions in NaF is less than the distance between the Cs^+ and I^- ions in CsI. As a result, the lattice energy of NaF should be greater than that of CsI. In order of increasing energy, therefore, we have $\text{CsI} < \text{NaF} < \text{CaO}$.

Sample Exercise 8.1 Magnitudes of Lattice Energies

Continued

Check Table 8.2 confirms our predicted order is correct.

TABLE 8.2 • Lattice Energies for Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	MgCl ₂	2326
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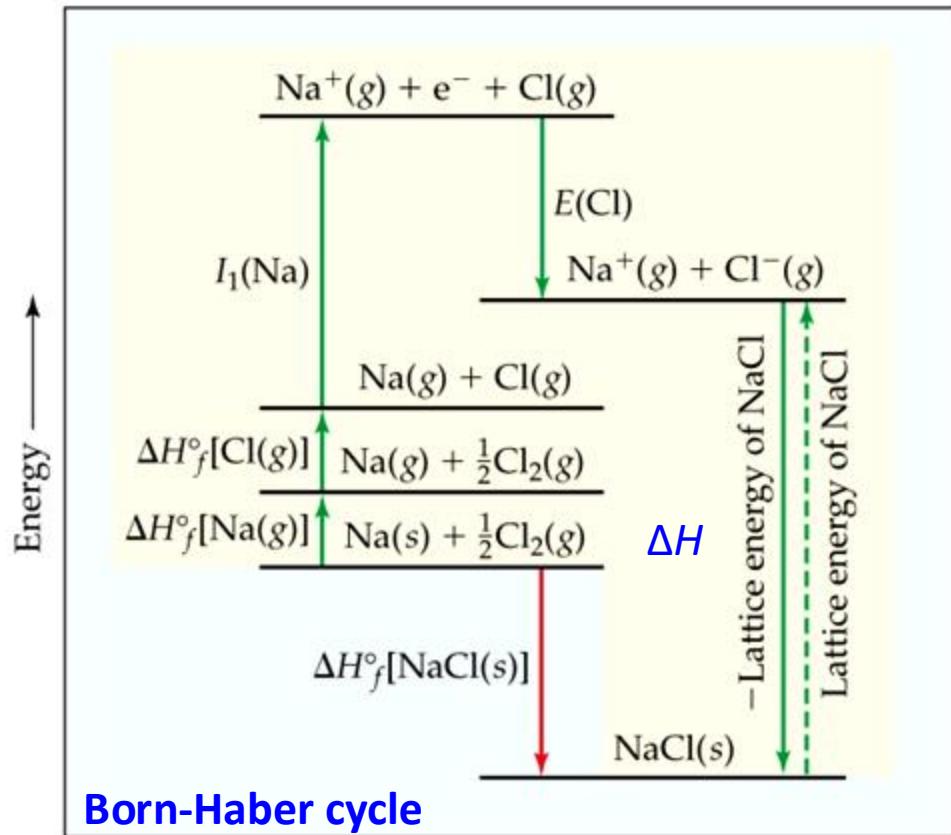
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Practice Exercise

Which substance do you expect to have the greatest lattice energy, MgF₂, CaF₂, or ZrO₂?

Answer: ZrO₂

➤ Energetics of Ionic Bonding



□ Lattice energies can not be determined directly by experiment. However, it can be calculated by envisioning in a series of well-defined steps.

$$\Delta H = -\Delta H_{\text{lattice}}$$

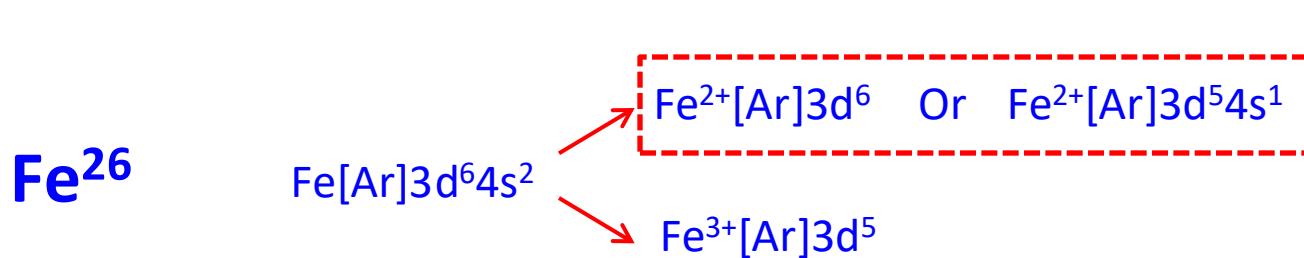
According to Hess's law:

$$\Delta H_f^\circ[\text{NaCl}(s)] = \Delta H_f^\circ[\text{Na}(g)] + H_f^\circ[\text{Cl}(g)] + I_1(\text{Na}) + E(\text{Cl}) + \Delta H_{\text{lattice}}$$

$$\begin{aligned} \Delta H_{\text{lattice}} &= \Delta H_f^\circ[\text{Na}(g)] + H_f^\circ[\text{Cl}(g)] + I_1(\text{Na}) + E(\text{Cl}) - \Delta H_f^\circ[\text{NaCl}(s)] \\ &= 108 + 122 + 496 + (-349) - (-411) = 788 \text{ kJ} \end{aligned}$$

➤ Electron Configuration of Ion of the s- and p-Block Elements

- The Second electron removed have to come from an inner shell of sodium atom, require a very large amount of energy.
- The increase in lattice energy is not enough to compensate for the energy need to remove an inner shell electron.
- The case is similar to Cl atom.

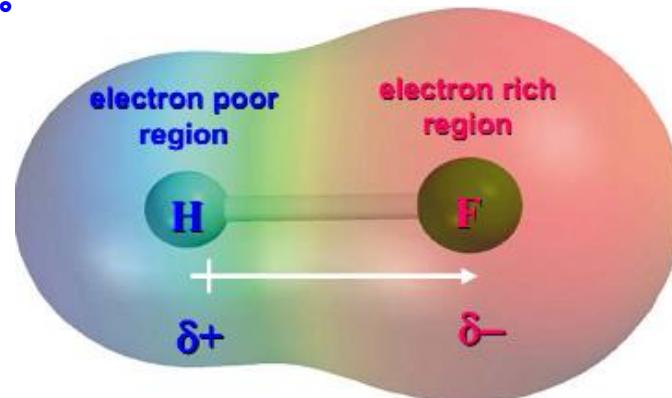
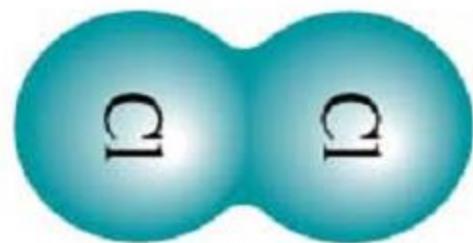


(n-1) d和ns轨道能量相差不大，可以逐个失去s电子和d电子造成氧化态的连续变化

➤ Covalent Bonding

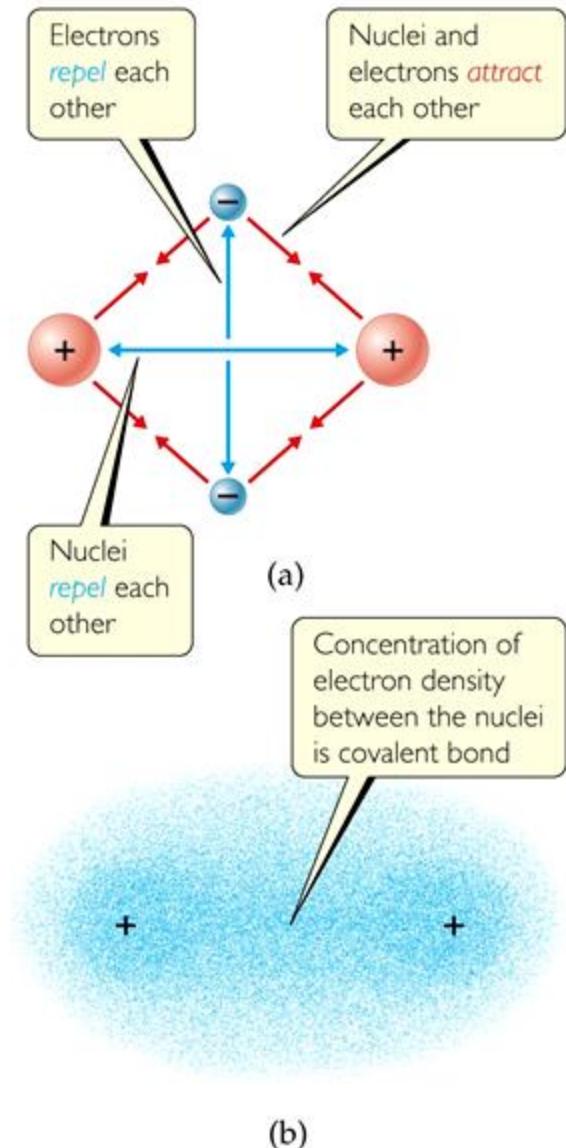
- G.N.Lewis reasoned that atoms might acquire a noble-gas electron configuration by sharing electrons with other atoms
- **Covalent bonds**-chemical bond by sharing a pair of electrons

1916 –1919年，美国化学家 G. N. Lewis和 I. Langmuir提出共价键理论(也称为路易斯–朗缪尔化键理论)。所依据的事实是化学性质不活泼的稀有气体原子的外层电子都具有 ns^2np^6 结构，即8电子层稳定结构。他们认为分子中原子之间可以通过共享电子对而使每一个原子具有稳定的稀有气体电子结构，这样构成的分子称为共价分子，原子通过共用电子对而形成的化学键称为**共价键**。



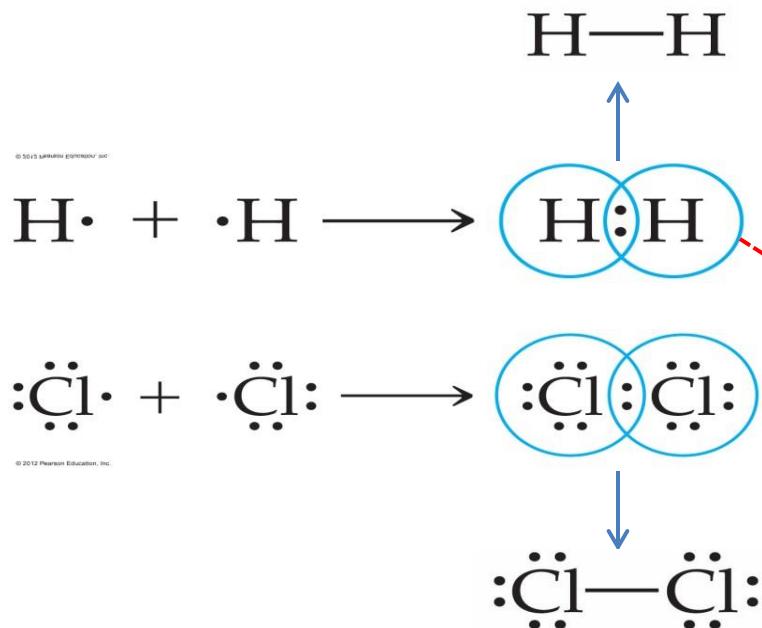
➤ Covalent Bonding

- There are several electrostatic interactions in these bonds:
 - Attractions between electrons and nuclei.
 - Repulsions between electrons.
 - Repulsions between nuclei.



- The formation of covalent bonds can be represented with **Lewis symbols**.

Single Bond



Lewis
structures or
Lewis electron-
dot structures

- The formation of covalent bonds can be represented with **Lewis symbols**.

Double Bond



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Triple Bond



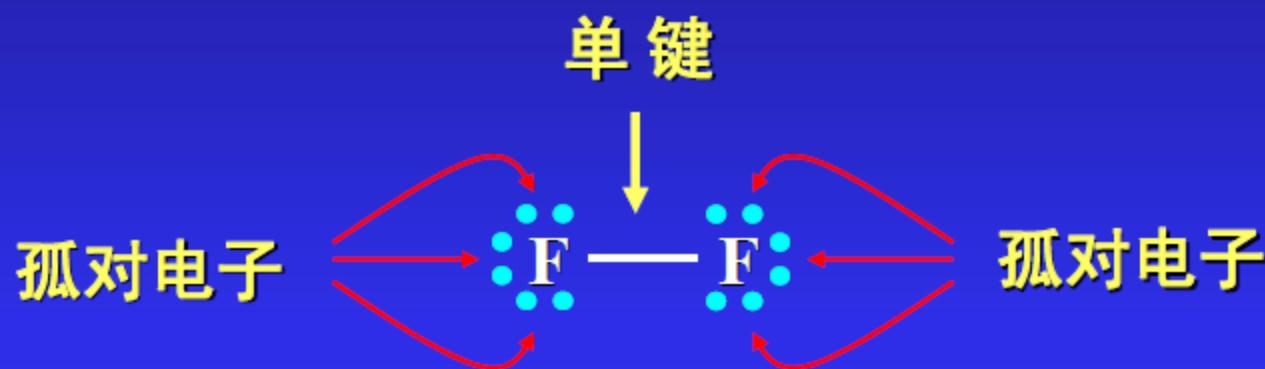
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2) 共价键的相关概念

➤ 价电子与Lewis结构 —— 原子中参与化学成键的外层电子称为价电子。一般用小黑点代表价电子，用短线代表原子之间的共享电子对，如此表达的电子结构称为Lewis结构。

Lewis Dot Symbols

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



F_2 分子的Lewis结构

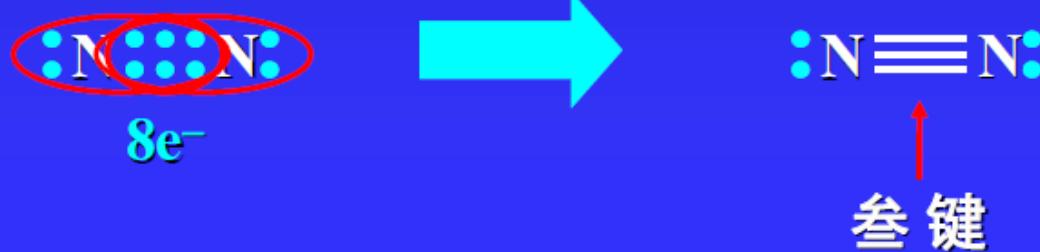
水的Lewis结构:



CO₂的Lewis结构:

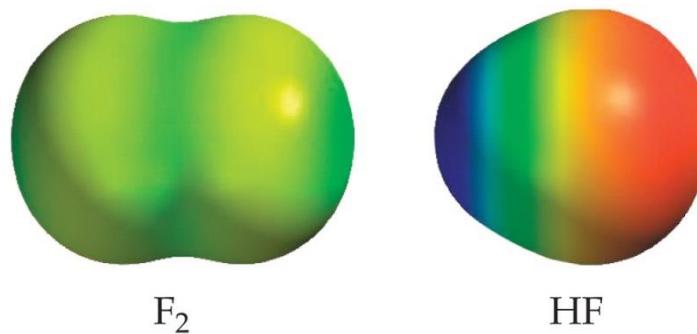


N₂的Lewis结构:



➤ Polar Covalent Bonds

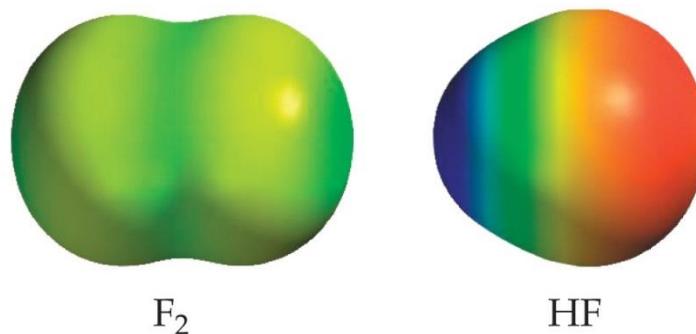
- Though atoms often form compounds by sharing electrons, the electrons are not always shared equally.
- **Bond Polarity** - Measurement of how equally or unequally the electrons in any covalent bond are share.
- Nonpolar covalent bond-In F_2 the electrons are shared equally



Computer-generated rendering shows the calculated electron-density on the molecules surface

➤ Polar Covalent Bonds

- Fluorine pulls harder on the electrons it shares with electrons than hydrogen does.
- Therefore, the fluorine end of the molecule has more electron density than the hydrogen end-polar covalent bond.



Computer-generated rendering shows the calculated electron-density on the molecules surface

Modern Valence Bond Theory



Prof. Sason Shaik



Prof. Philippe C. Hiberty



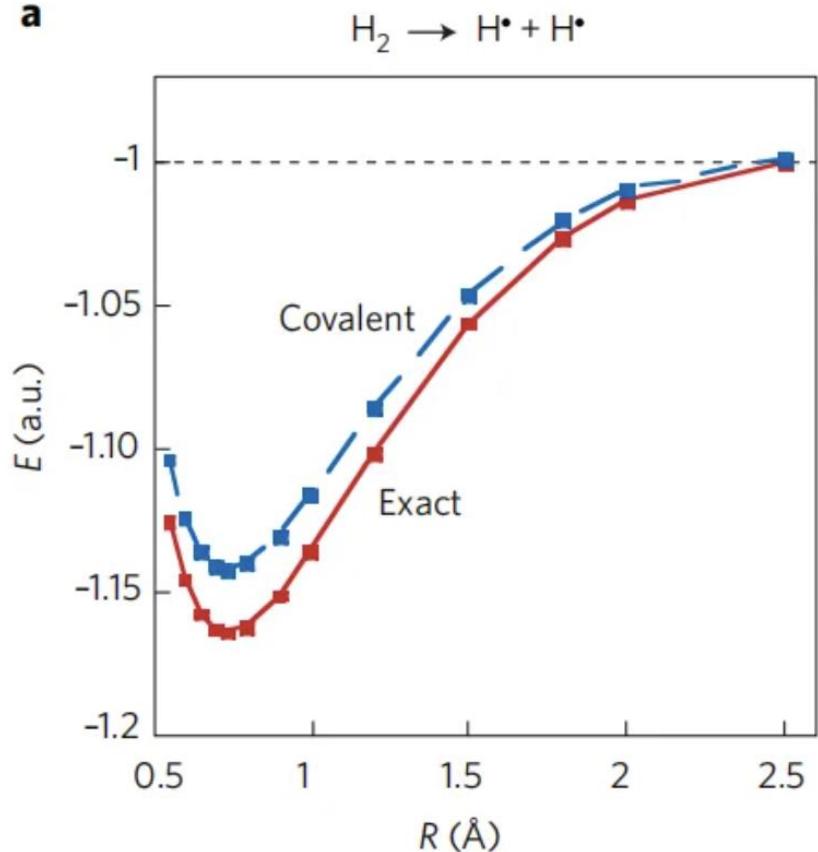
Prof. Wei Wu

$$\Psi(\text{VB}) = c_1 \Phi_{\text{cov}} + c_2 \Phi_{\text{ion}} + c_3 \Phi'_{\text{ion}}$$

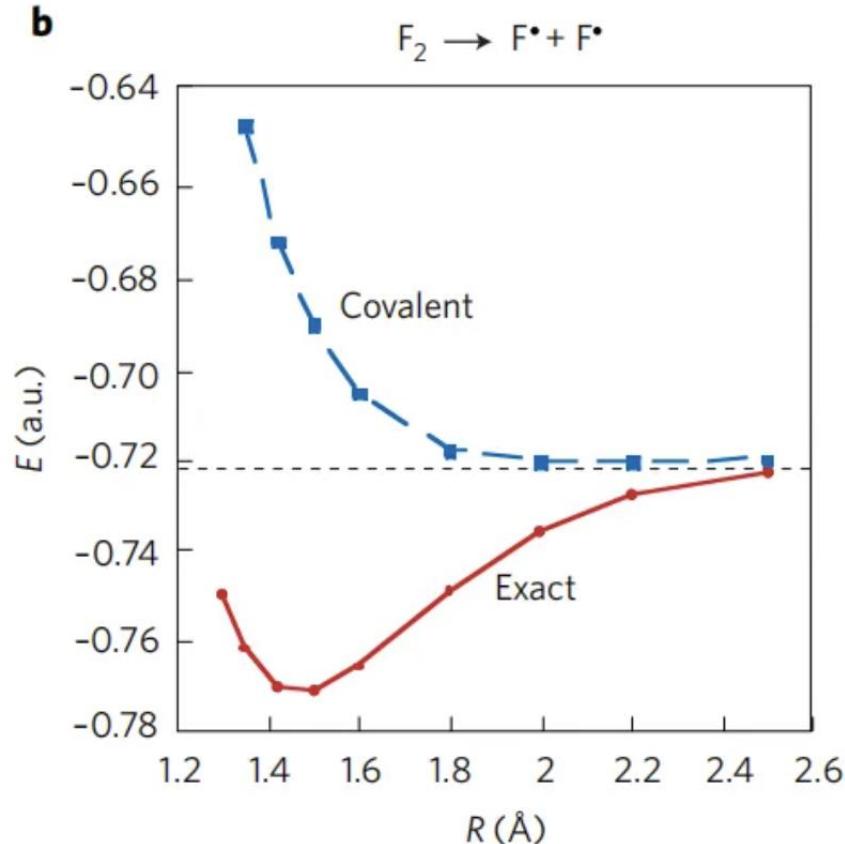
NaCl这样的分子中，离子键占主导；H-H这样的分子中，共价相互作用占主导。会不会有一种分子成键，是其他作用占主导呢？

Question Raised!

a



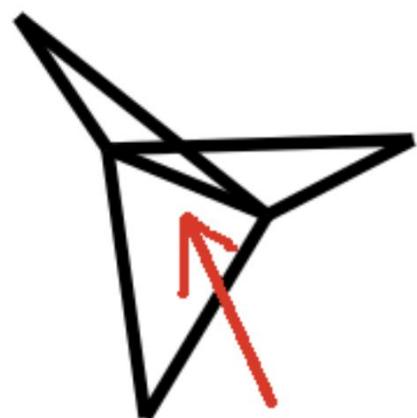
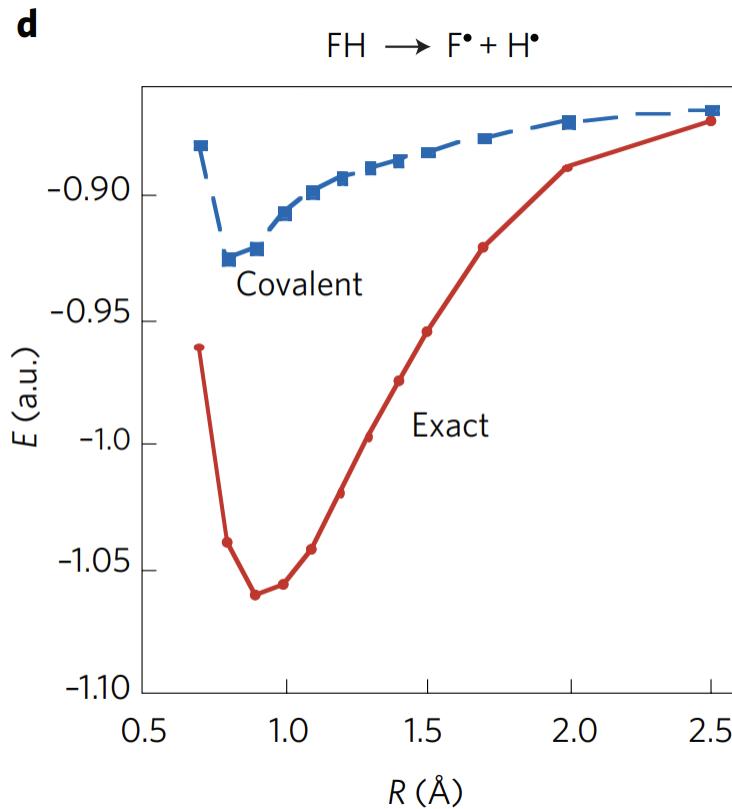
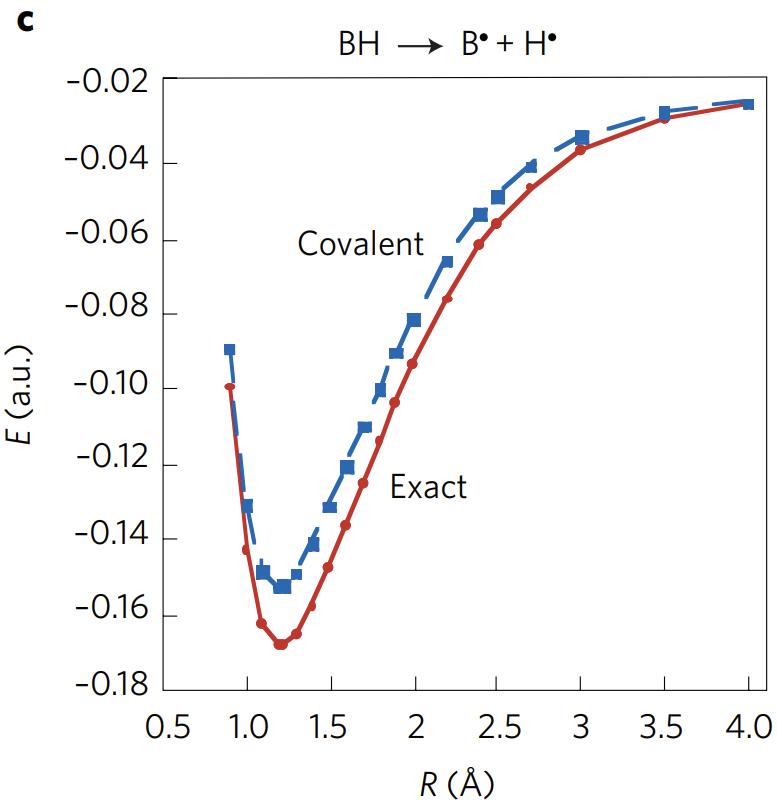
b



For F_2 , the covalent structure is entirely repulsive.

What determines the bonding energy and the equilibrium distance is the covalent–ionic mixing.

Question Raised!

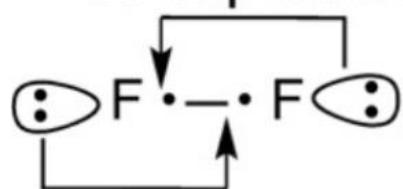


[1.1.1]propellane
螺桨烷

Similarity

(a)

3e repulsion

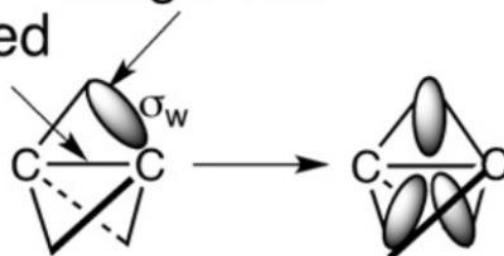


3e repulsion

(b)

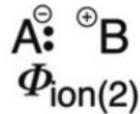
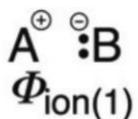
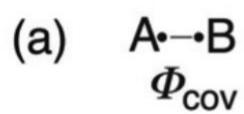
wing bond

inverted
bond

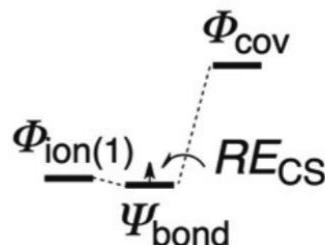
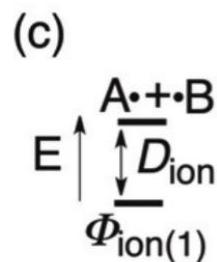
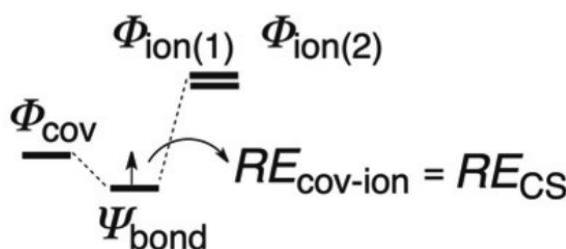
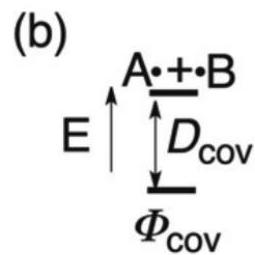


Φ_{cov}

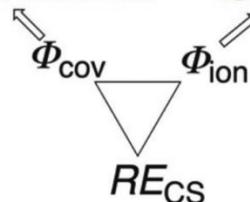
Charge Shift Bonding



根据Pauling的理论，化学键被分为两种，共价键和离子键。



covalent bonds ionic bonds



charge shift bonds

D_{cov} 描述了两个片段结合形成共价键后释放的能量(其实就是两个自旋相反的电子配对放出的能量)。

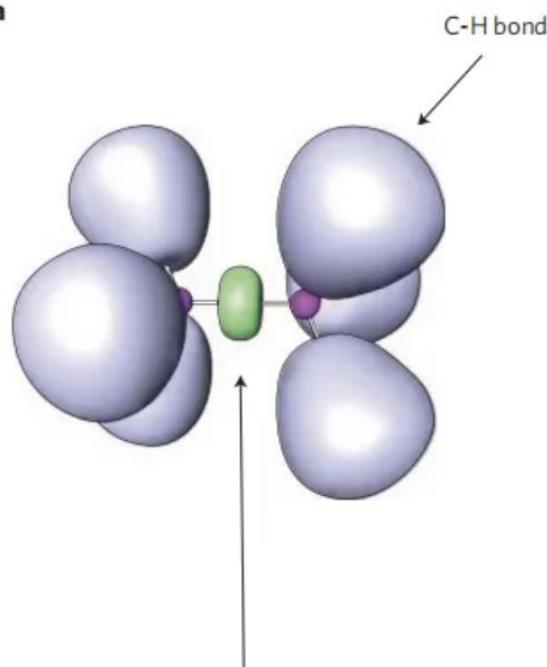
但是，电子自旋配对后，我们还是能画出这个AB分子电荷分离形式的两个共振式。

这两个离子化的共振式可以给出一个额外的稳定化能，进一步稳定AB这个分子。

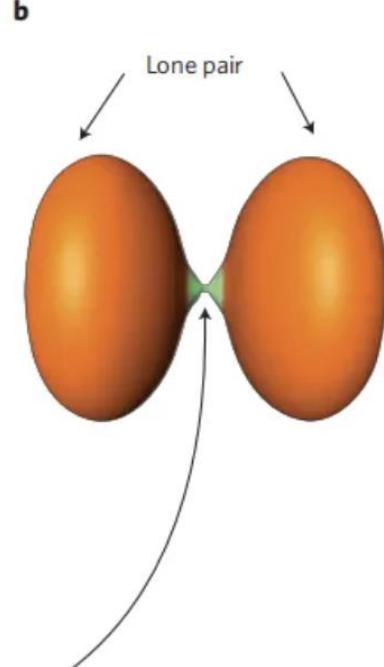
这部分能量，就是 charge-shift resonance energy, RE_{CS} 。

Character

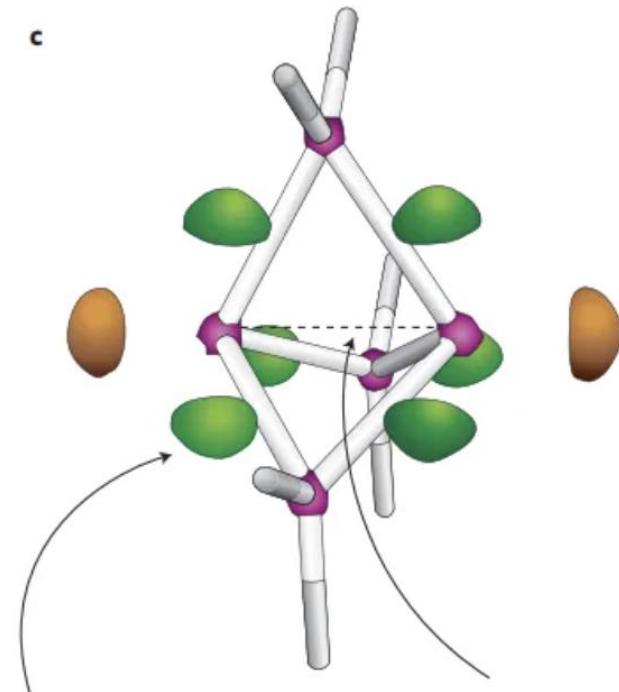
a



b



c



C-C bond

$$RE_{CS} = 27.7$$

$$\bar{N}_{CC} = 1.81$$

$$\sigma^2 = 0.96$$

$$\rho = 0.25$$

$$\nabla^2\rho = -0.62$$

F-F bond

$$RE_{CS} = 62.2$$

$$\bar{N}_{FF} = 0.44$$

$$\sigma^2 = 0.42$$

$$\rho = 0.25$$

$$\nabla^2\rho = +0.58$$

Wing bond

$$-$$

$$\bar{N}_{CC} = 1.76$$

$$-$$

$$\rho = 0.25$$

$$\nabla^2\rho = -0.51$$

Central bond

$$RE_{CS} = 72.2$$

$$\bar{N}_{CC} = 0.13$$

$$\sigma^2 = 0.12$$

$$\rho = 0.19$$

$$\nabla^2\rho = +0.43$$

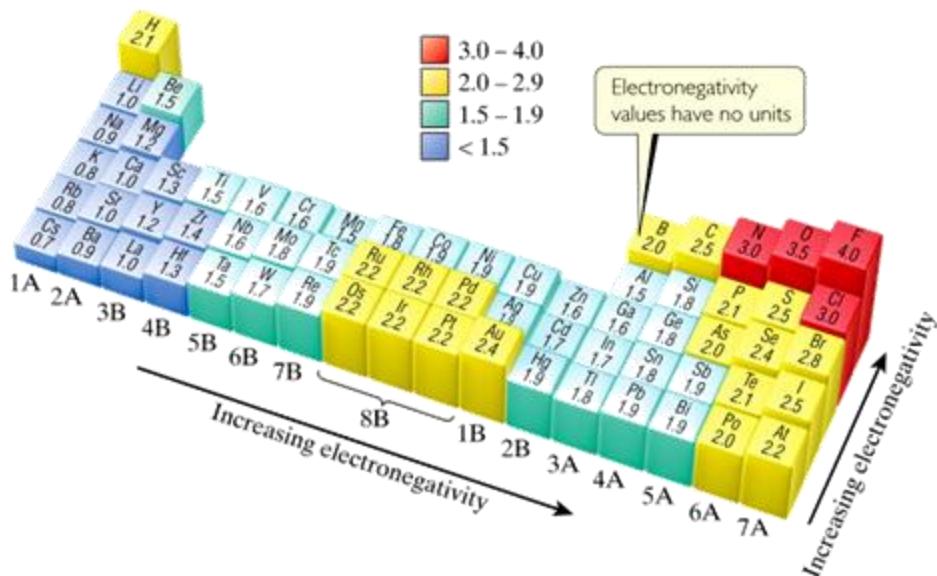
➤ Bond Polarity and Electronegativity(电负性)



Linus Carl Pauling
(1901-1994)

➤ Electronegativity

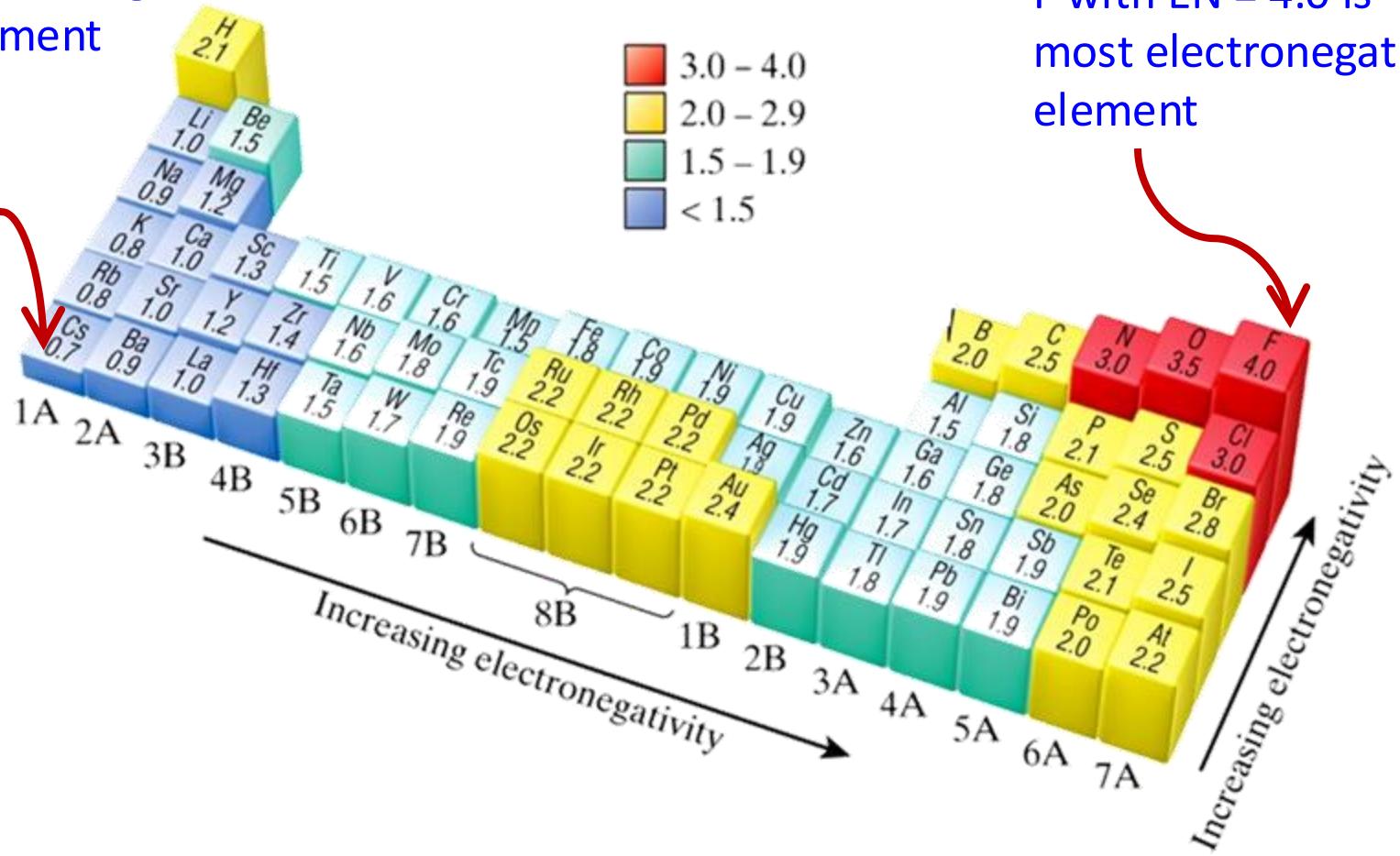
- Electronegativity is the ability of atoms in a molecule to attract electrons to themselves.
- More negative electron affinity and high ionization energy lead to highly electronegative



On the periodic chart, electronegativity increases as you go...
...from left to right across a row.
...from the bottom to the top of a column.

➤ Electronegativity

Cs (EN = 0.7) is least
electronegative
element



F with EN = 4.0 is
most electronegative
element

➤ Electronegativity and Bonding

Electronegativity tells us what kind of bonding we have, i.e. whether it is ionic or covalent. The greater the difference in EN between the two elements forming the bond, the more ionic is the bond. Typical ranges for EN differences are:

EN difference	bonding type	Example	EN
> 2.0	Ionic	LiF	4.0-1.0 = 3.0
0.5-2.0	polar covalent	HF	4.0-2.1 = 1.9
<0.5	covalent	F–F	4.0-4.0 = 0.0
	covalent	C–H	2.5-2.1 = 0.4
	covalent	Li –Li	1.0-1.0 = 0.0
	covalent	Au–C	2.5-2.4 = 0.1

Shortcoming: Electronegativity do not take into account changes in bonding that accompany changes in the oxidation state of the metal: Manganese and oxygen as $3.5-1.5=2$, it is considered to be ionic, however Manganese (VII) oxide, Mn_2O_7 , is covalent rather than ionic. (Metals In high oxidation states tend to be molecular substances rather than ionic compounds.

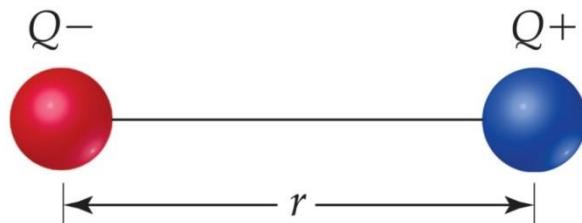
➤ Polar Covalent Bonds

- When two electrical charges of **equal magnitude** but opposite sign are separated by a distance, a **bond dipole(键偶极)** results.
- The **dipole moment(偶极矩)**, μ , produced by two equal but opposite charges separated by a distance, r , is calculated:

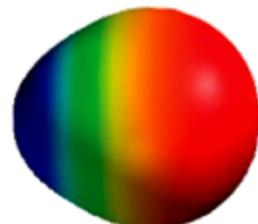
$$\mu = Qr$$

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

- It is measured in **debyes (D)**, a unit that equals to 3.34×10^{-30} coulomb·meter (C·m).



$$\text{Dipole moment } \mu = Qr$$



分子极性的表示方法——偶极矩 (dipole moment, μ)

分子极性的强弱可以用偶极矩表示。偶极矩是表示分子电荷分布情况的物理量，等于极性分子正负电荷之重心间的距离 d (又称偶极长)与偶极电荷量 q 的乘积，

$$\mu = q \cdot d$$

偶极矩的单位：

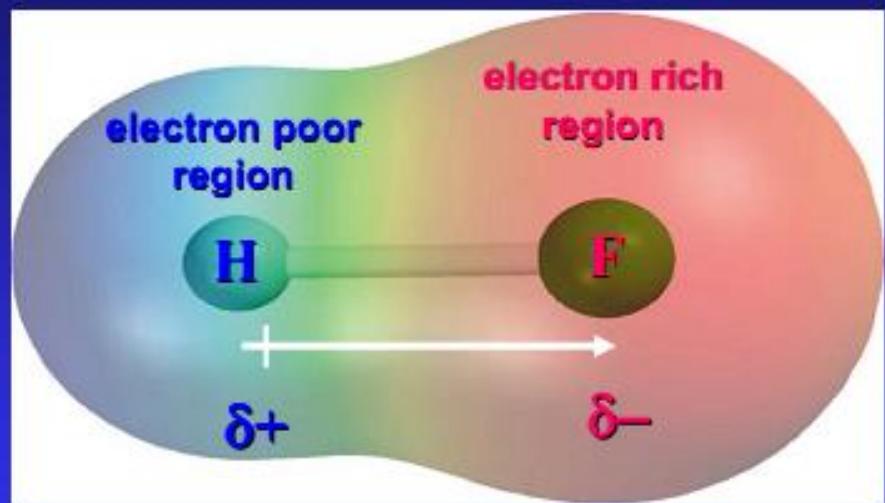
1) 德拜 (Debye)，

以D表示， $1D = 10^{-18} \text{ cm} \cdot \text{esu}$ 。

2) C·m (SI制)。

$$1D = 3.336 \times 10^{-30} \text{ C} \cdot \text{m}.$$

偶极矩的方向：矢量，化学上习惯规定其方向是由正到负。



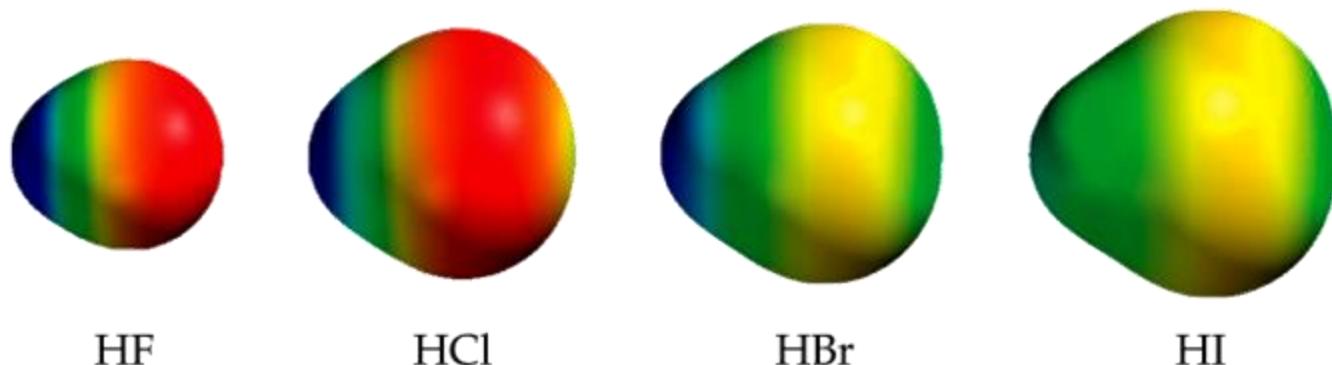
须指出，键长 R 与偶极长 d 是两个不同的概念。用现代实验技术可以测定分子的键长(即分子中原子间的距离)以及分子的偶极矩，但无法单独测定偶极长 d 及偶极电荷量 q 。

➤ Polar Covalent Bonds

- The greater the difference in electronegativity, the more polar is the bond.

TABLE 8.3 • Bond Lengths, Electronegativity Differences, and Dipole Moments of the Hydrogen Halides

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44



Sample Exercise 8.4 Bond Polarity

In each case, which bond is more polar: (a) B—Cl or C—Cl, (b) P—F or P—Cl? Indicate in each case which atom has the partial negative charge.

Solution

Analyze We are asked to determine relative bond polarities, given nothing but the atoms involved in the bonds.

Plan Because we are not asked for quantitative answers, we can use the periodic table and our knowledge of electronegativity trends to answer the question.

Solve

(a) The chlorine atom is common to both bonds. Therefore, the analysis reduces to a comparison of the electronegativities of B and C. Because boron is to the left of carbon in the periodic table, we predict that boron has the lower electronegativity. Chlorine, being on the right side of the table, has a higher electronegativity. The more polar bond will be the one between the atoms having the lowest electronegativity (boron) and the highest electronegativity (chlorine). Consequently, the B—Cl bond is more polar; the chlorine atom carries the partial negative charge because it has a higher electronegativity.

(b) In this example phosphorus is common to both bonds, and the analysis reduces to a comparison of the electronegativities of F and Cl. Because fluorine is above chlorine in the periodic table, it should be more electronegative and will form the more polar bond with P. The higher electronegativity of fluorine means that it will carry the partial negative charge.

Sample Exercise 8.4 Bond Polarity

Continued

Check

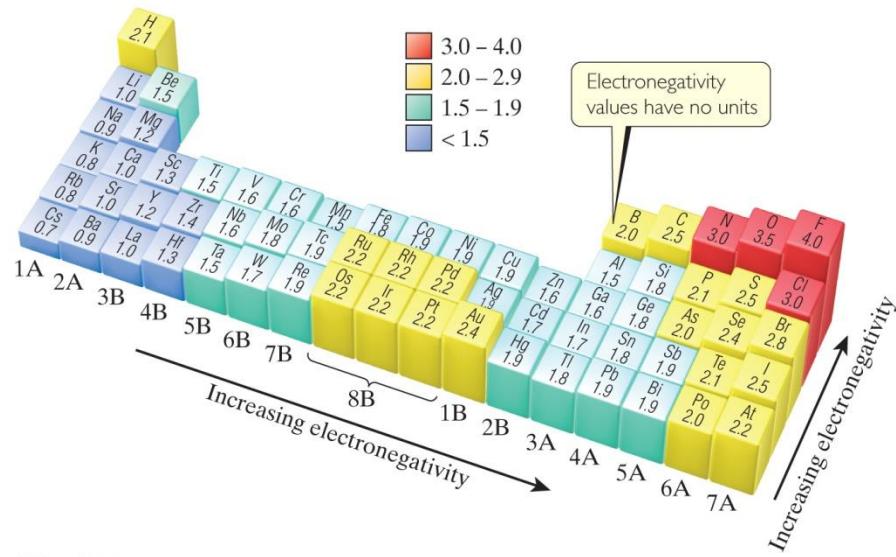
(a) Using Figure 8.7: The difference in the electronegativities of chlorine and boron is $3.0 - 2.0 = 1.0$; the difference between chlorine and carbon is $3.0 - 2.5 = 0.5$. Hence, the B—Cl bond is more polar, as we had predicted.

(b) Using Figure 8.7: The difference in the electronegativities of chlorine and phosphorus is $3.0 - 2.1 = 0.9$; the difference between fluorine and phosphorus is $4.0 - 2.1 = 1.9$. Hence, the P—F bond is more polar, as we had predicted.

Practice Exercise

Which of the following bonds is most polar: S—Cl, S—Br, Se—Cl, or Se—Br?

Answer: Se—Cl



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Sample Exercise 8.5 Dipole Moments of Diatomic Molecules

The bond length in the HCl molecule is 1.27 Å. (a) Calculate the dipole moment, in debyes, that results if the charges on the H and Cl atoms were +1 and -1, respectively. (b) The experimentally measured dipole moment of HCl(g) is 1.08 D. What magnitude of charge, in units of e , on the H and Cl atoms leads to this dipole moment?

Solution

Analyze and Plan We are asked in (a) to calculate the dipole moment of HCl that would result if there were a full charge transferred from H to Cl. We can use Equation 8.11 to obtain this result. In (b), we are given the actual dipole moment for the molecule and will use that value to calculate the actual partial charges on the H and Cl atoms.

(a) The charge on each atom is the electronic charge,

$$e = 1.60 \times 10^{-19} \text{ C}$$

The separation is 1.27 Å. The dipole moment is therefore

(b) We know the value of μ , 1.08 D, and the value of r , 1.27 Å. We want to calculate the value of Q :

$$\mu = Qr = (1.60 \times 10^{-19} \text{ C})(1.27 \text{ Å}) \left(\frac{10^{-10} \text{ m}}{1 \text{ Å}} \right) \left(\frac{1 \text{ D}}{3.34 \times 10^{-30} \text{ C-m}} \right) = 6.08 \text{ D}$$

$$Q = \frac{\mu}{r} = \frac{(1.08 \text{ D}) \left(\frac{3.34 \times 10^{-30} \text{ C-m}}{1 \text{ D}} \right)}{(1.27 \text{ Å}) \left(\frac{10^{-10} \text{ m}}{1 \text{ Å}} \right)} = 2.84 \times 10^{-20} \text{ C}$$

$$\text{Charge in } e = (2.84 \times 10^{-20} \text{ C}) \left(\frac{1 \text{ e}}{1.60 \times 10^{-19} \text{ C}} \right) = 0.178e$$

We can readily convert this charge to units of e :

在偶极矩公式 $\mu = q \times r$ 中, q 代表的是正电荷中心 (H^+) 和负电荷中心 (Cl^-) 所带电荷的绝对值。

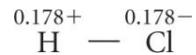
既然假设的电荷是 +1 和 -1, 那么这个电荷的绝对值 q 就是 1 个元电荷 (elementary charge, e) 的大小。

$$q = 1e = 1.602 \times 10^{-19} \text{ C}$$

Sample Exercise 8.5 Dipole Moments of Diatomic Molecules

Continued

Thus, the experimental dipole moment indicates that the charge separation in the HCl molecule is



Because the experimental dipole moment is less than that calculated in part (a), the charges on the atoms are much less than a full electronic charge. We could have anticipated this because the H—Cl bond is polar covalent rather than ionic.

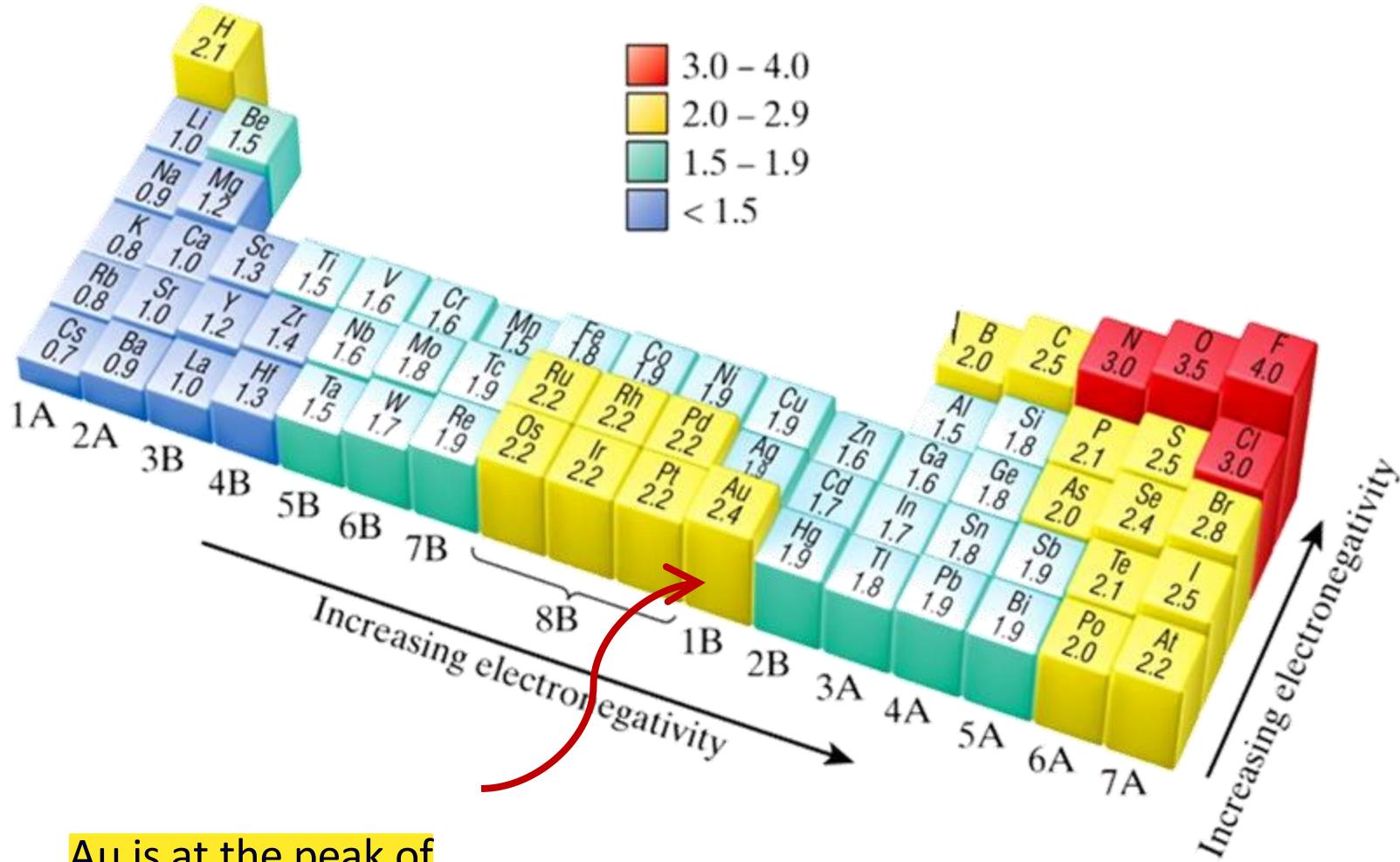
Practice Exercise

The dipole moment of chlorine monofluoride, ClF(g), is 0.88 D. The bond length of the molecule is 1.63 Å.

(a) Which atom is expected to have the partial negative charge? (b) What is the charge on that atom in units of e^- ?

Answers: (a) F, (b) 0.11 e^-

➤ Electronegativity



Au is at the peak of
an island of electronegativity,
and is most electronegative metal



GIVE IT SOME THOUGHT

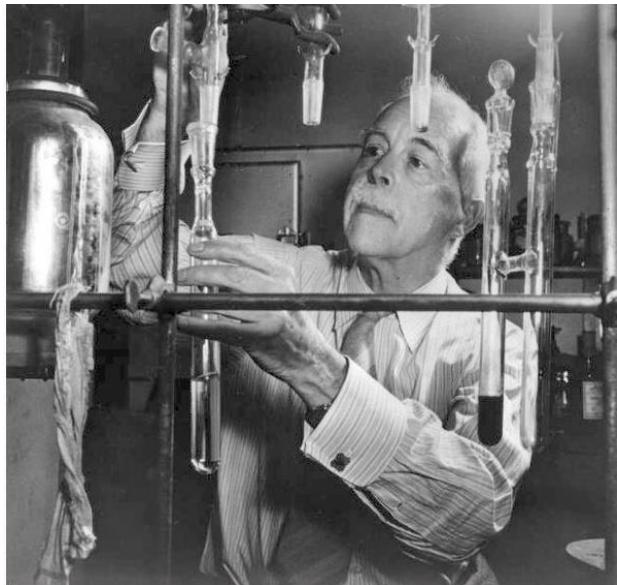
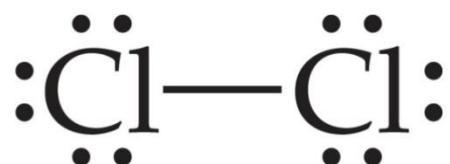
How does the *electronegativity* of an element differ from its *electron affinity*?

- A. EN and EA are the same; they both measure the same characteristic.
- B. EA measures the energy released when an isolated atom/ion gains an electron; EN measures the ability of an atom in a molecule to attract electrons to itself.
- C. EN values of neutral atoms are just the negative of EA values of neutral atoms.
- D. EN measures the energy released when an isolated atom/ion gains an electron; EA measures the ability of an atom in a molecule to attract electrons to itself.



➤ Lewis Structures

- Lewis structures are representations of **molecules** showing all electrons, bonding and nonbonding.



G. N. Lewis was probably the best chemist who never won the Nobel Prize.

Gilbert Newton Lewis (1875–1946)

➤ Writing Lewis Structures

- Find the sum of **valence electrons** of all atoms in the polyatomic ion or molecule.
 - If it is an anion, add one electron for each negative charge.
 - If it is a cation, subtract one electron for each positive charge.



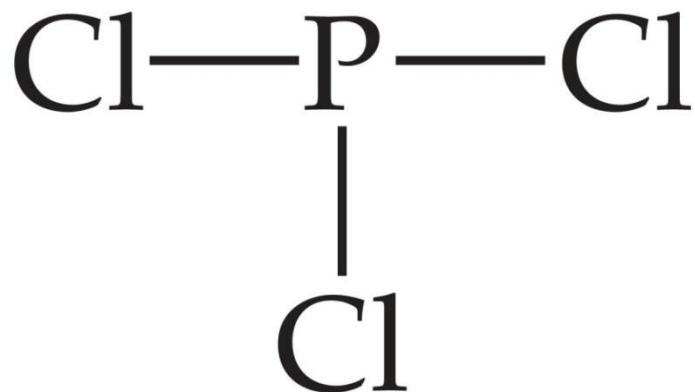
Keep track of the electrons:

$$5 + 3(7) = 26$$



➤ Writing Lewis Structures

- The central atom is the *least electronegative* element that isn't hydrogen. Connect the outer atoms to it by single bonds.

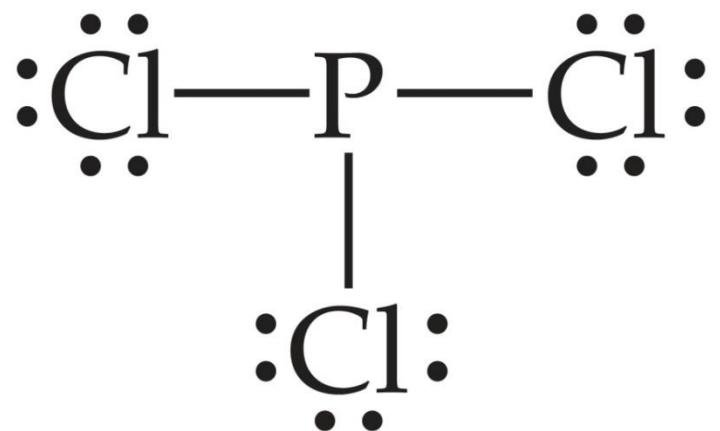


Keep track of the electrons:

$$26 - 6 = 20$$

➤ Writing Lewis Structures

- Fill the octets of the outer atoms.

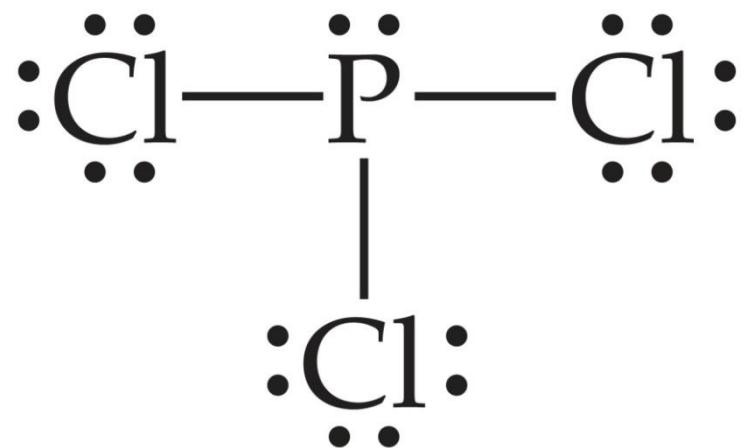


Keep track of the electrons:

$$26 - 6 = 20; 20 - 18 = 2$$

➤ Writing Lewis Structures

- Place any leftover electrons on the central atom.(Even if doing so results in more than an octet of electrons around the atom)



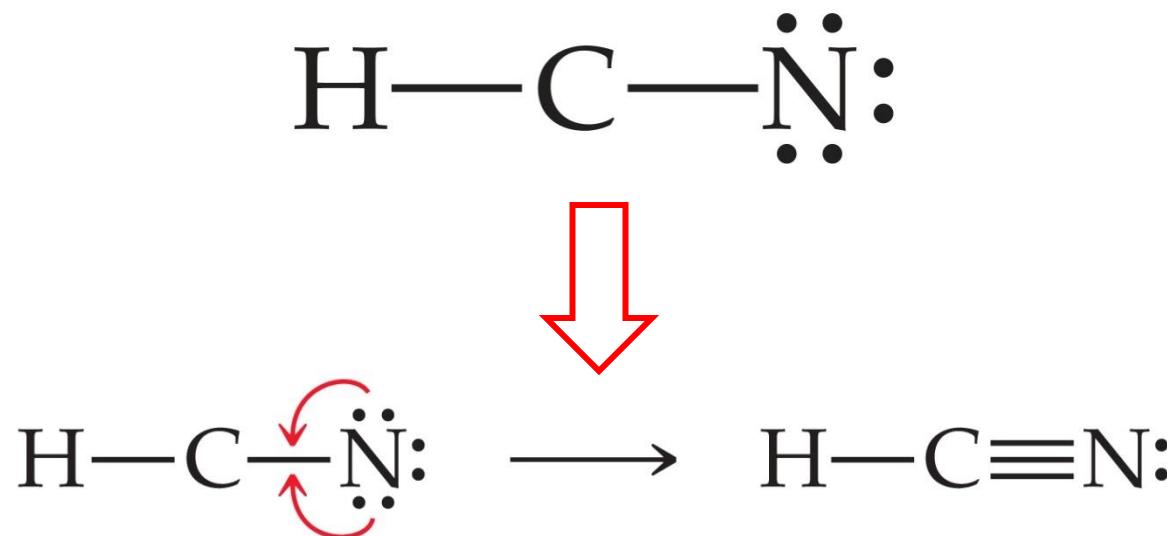
Keep track of the electrons:

$$26 - 6 = 20; 20 - 18 = 2;$$
$$2 - 2 = 0$$

➤ Writing Lewis Structures

- If you run out of electrons before the central atom has an octet...

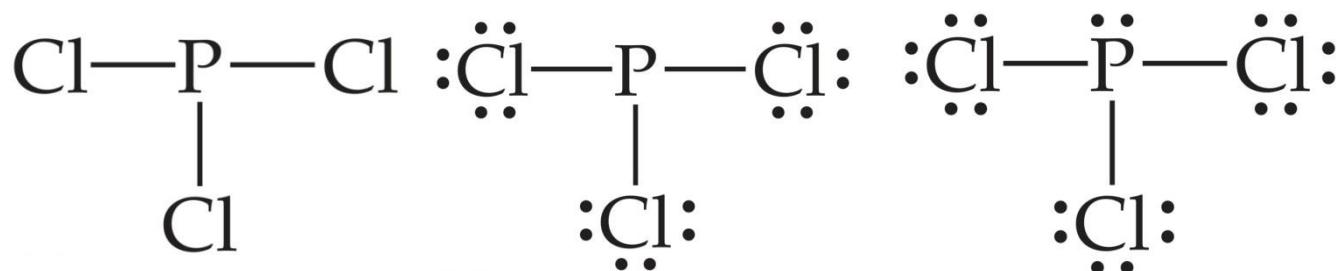
...form multiple bonds until it does.



➤ Lewis Lewis结构式的写法规则 (八隅体规则, octet rule):

- 根据分子式或离子式计算出总的价电子数目。对于多原子阴离子的价电子总数，除各原子的价电子数外还要加上阴离子的负电荷数。对于多原子阳离子，则必须从各原子价电子数中减去阳离子正电荷数。
- 画出分子或离子的骨架结构，用单键将原子联结起来。每一个单键扣除2个价电子。然后将其余电子当作未共用电子对（即孤对电子）分配在原子周围，以便尽可能使每个原子具有孤对电子）分配在原子周围，以便尽可能使每个原子具有8个电子。如缺2个电子，则以形成一个双键来补偿；如缺4个电子，则以形成一个叁键来补偿。但需注意，在结构式中每个原子提供的电子数要与它的价电子数相符。

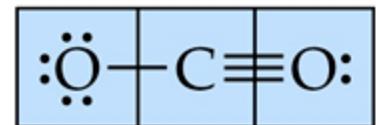
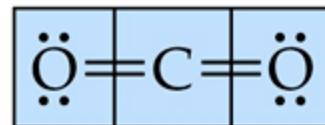
PCl₃



➤ Writing Lewis Structures

- In some cases, more than one Lewis structure obey the octet rule
- **Formal charge(形式电荷)**
- Assign electron:
 - All unshared electrons are assigned to the atom on which they are found
 - Half of the bonding electrons are assigned to each atom in the bond.
 - the difference between assigned electrons and valence electrons is its **formal charge** and used to identify the dominant Lewis structure.

Dominant, formal
charge closest to 0



Valence electrons:

6 4 6

6 4 6

-(Electrons assigned to atom):

6 4 6

7 4 5

Formal charge:

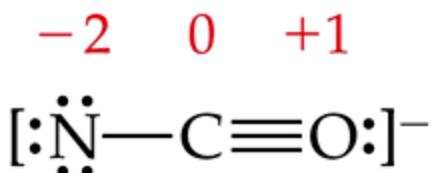
0 0 0

-1 0 +1

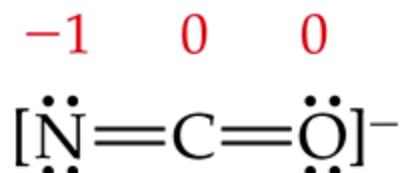
➤ Writing Lewis Structures

□ The best Lewis structure...

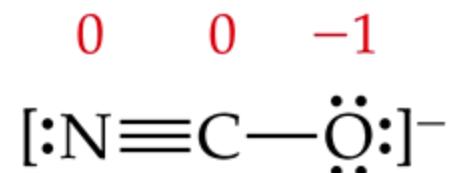
- ...is the one in which the atoms bear formal charges closest to zero.
- ...any negativity formal charge reside on the more electronegative atoms.



(i)



(ii)



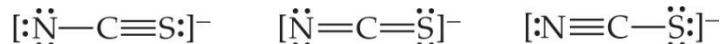
(iii)



Dominant
Structure

Sample Exercise 8.9 Lewis Structures and Formal Charges

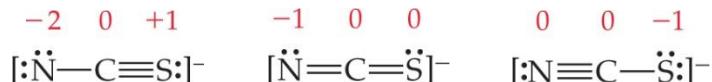
Three possible Lewis structures for the thiocyanate ion, NCS^- , are



- (a) Determine the formal charges in each structure. (b) Based on the formal charges, which Lewis structure is the dominant one?

Solution

(a) Neutral N, C, and S atoms have five, four, and six valence electrons, respectively. We can determine the formal charges in the three structures by using the rules we just discussed:



As they must, the formal charges in all three structures sum to 1–, the overall charge of the ion. (b) The dominant Lewis structure generally produces formal charges of the smallest magnitude (guideline 1). That rules out the left structure as the dominant one. Further, as discussed in Section 8.4, N is more electronegative than C or S. Therefore, we expect any negative formal charge to reside on the N atom (guideline 2). For these two reasons, the middle Lewis structure is the dominant one for NCS^- .

Sample Exercise 8.9 Lewis Structures and Formal Charges

Continued

Practice Exercise

The cyanate ion, NCO^- , has three possible Lewis structures. (a) Draw these three structures and assign formal charges in each. (b) Which Lewis structure is dominant?

-2 0 +1

Answers: (a) $[\ddot{\text{N}}-\text{C}\equiv\text{O}]^-$

(i)

-1 0 0

$[\ddot{\text{N}}=\text{C}=\ddot{\text{O}}]^-$

(ii)

0 0 -1

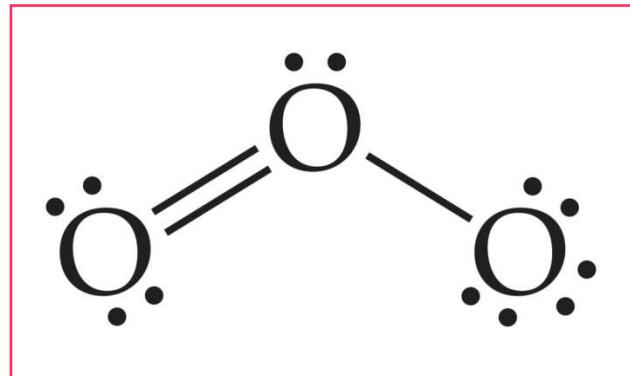
$[\text{:N}\equiv\text{C}-\ddot{\text{O}}:]^-$

(iii)

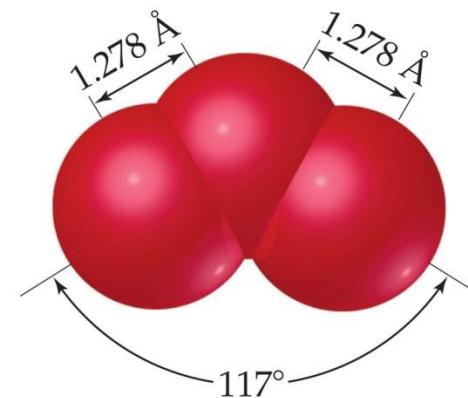
(b) Structure (iii), which places a negative charge on oxygen, the most electronegative element in the ion, is the dominant Lewis structure.

➤ Resonance(共振)

- This is the Lewis structure we would draw for ozone, O₃.

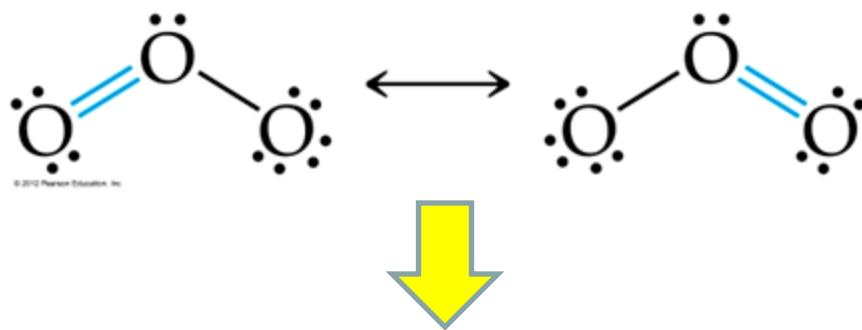


- But this is at odds with the true, observed structure of ozone, in which...
 - ...both O–O bonds are the same length.



➤ Resonance

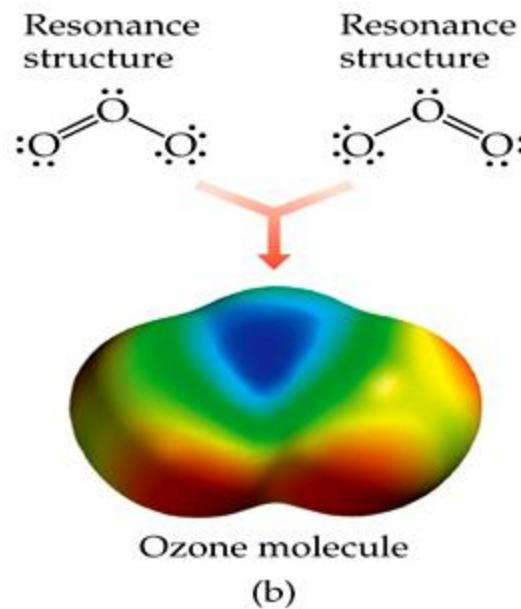
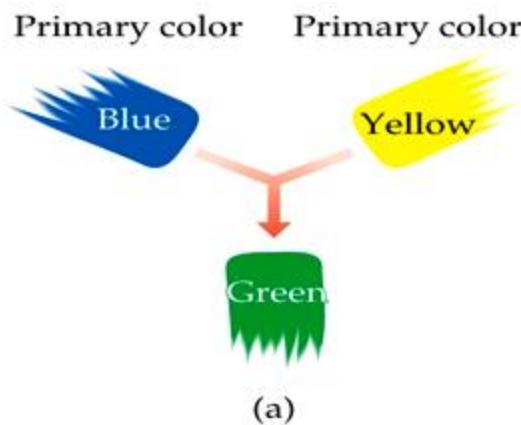
- One Lewis structure cannot accurately depict a molecule like ozone.
- We use multiple structures, **resonance structures**, to describe the molecule.



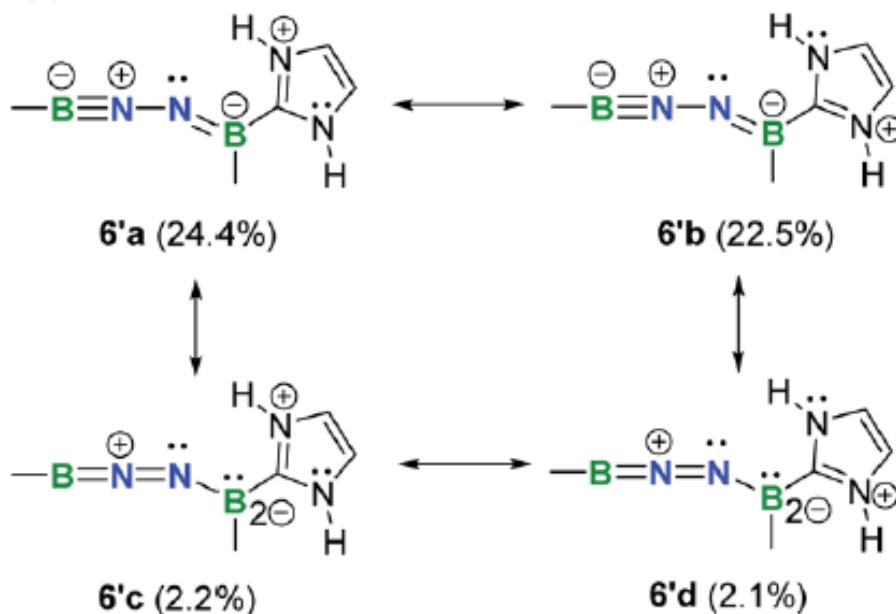
Write both resonance structure, Use a double-head arrow to indicate the real molecule is described by an average of the two

➤ Resonance structures are equivalent dominant

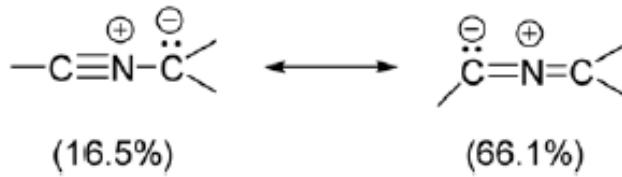
- Just as green is a synthesis of blue and yellow...
...ozone is a synthesis of these two resonance structures.



(a)

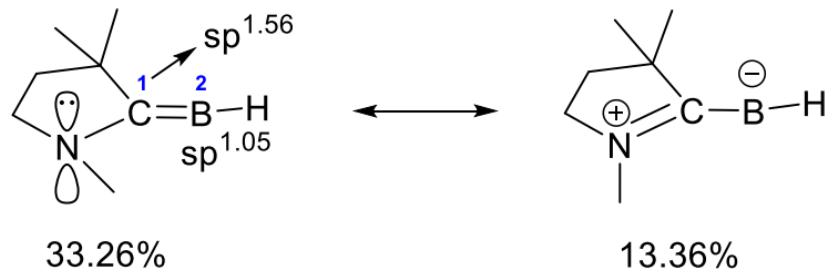


(b)



R. Guo, J. Jiang, C. Hu, L. L. Liu, P. Cui, M. Zhao, Z. Ke, C.-H. Tung, L. Kong, *Chem. Sci.*
2020, *11*, 7053-7059.

(a)



(b)

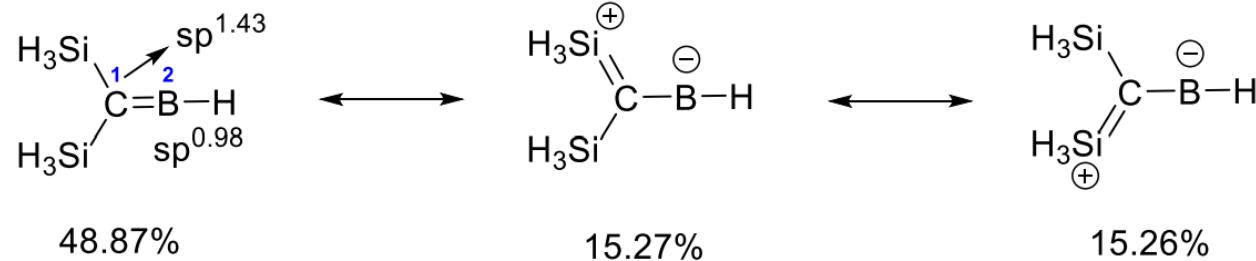
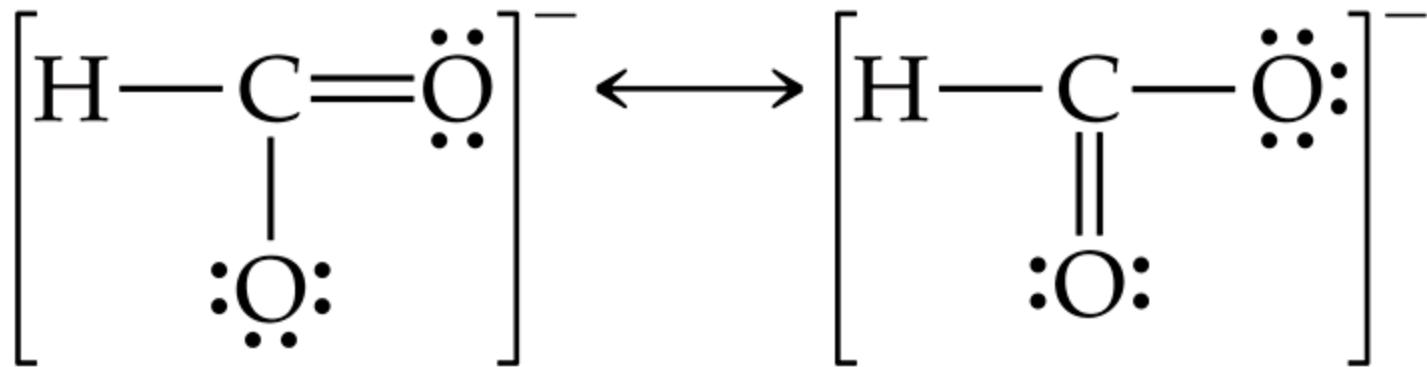


图 2.3 亚甲基硼烷的主要共振结构

Figure 2.3 The leading resonance structures of methyleneboranes

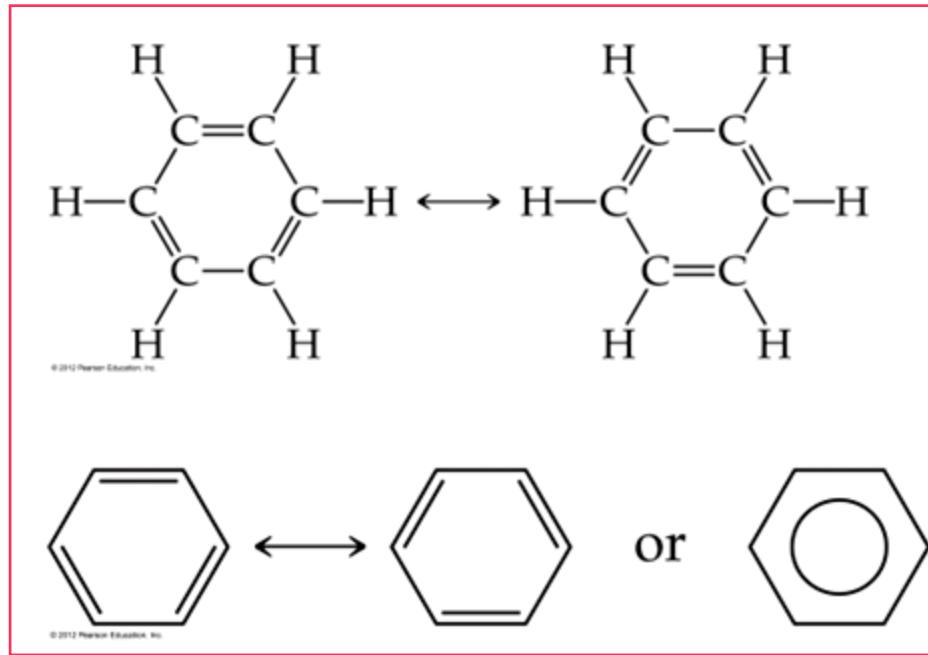
➤ Resonance

- In truth, the electrons that form the second C—O bond in the double bonds below do not always sit between that C and that O, but rather can move among the two oxygens and the carbon.
- They are not **localized** but **delocalized**(离域).



➤ Resonance

- The organic compound benzene, C_6H_6 , has two resonance structures.
- It is commonly depicted as a hexagon with a circle inside to signify the delocalized electrons in the ring.



➤ 共振体的概念

- 为解释分子或离子中的单键和双键的键长相等而且键长数值一般介于单、双键键长之间的实验事实，1931–1933年Pauling提出了共振体(resonance form)的概念，即这些分子或离子的真实结构实际上是两种或两种以上结构式的共振体。
- 共振结构概念建立在经典结构概念的基础上，能够解释一些实验现象，特别对讨论有机分子的结构和性质很有帮助。它扩大了电子对的概念。
- 价键理论过分强调了成键电子对的定域性，但实际上电子可以离域运动，即电子可以在成键的两个原子间的范围以外运动。在书写分子的共振结构时，虽然不能移动原子，但在结构式中可以移动电子，因此共振结构概念反映了电子的离域性。有几种合理的 Lewis结构，就可能有几种共振体。

Resonance structures represent different ways to arrange electrons (specifically, lone pairs and pi bonds) in a molecule without changing the position of the atoms themselves. Moving atoms would create a different compound (an isomer).

- ## ➤ Exceptions to the Octet Rule
- There are three types of ions or molecules that do not follow the octet rule:
 - ions or molecules with an odd number of electrons,
 - ions or molecules with less than an octet,
 - ions or molecules with more than eight valence electrons (**an expanded octet**).

➤ Odd Number of Electrons

- Though relatively rare and usually quite unstable and reactive, there are ions and molecules with an odd number of electrons.

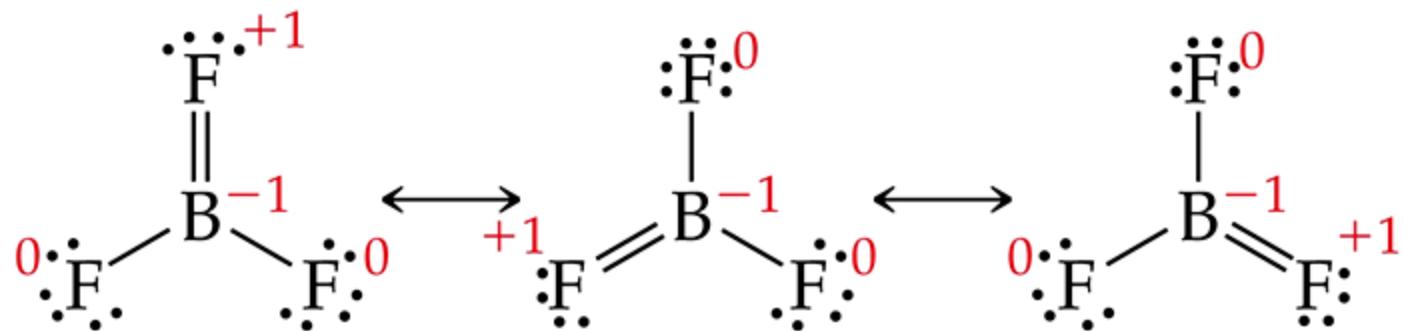


Valence electron:	5	6	5	6
Electron assigned to atom:	5	6	6	5
<hr/>				
Formal charge:	0	0	-1	1

➤ Fewer Than Eight Electrons

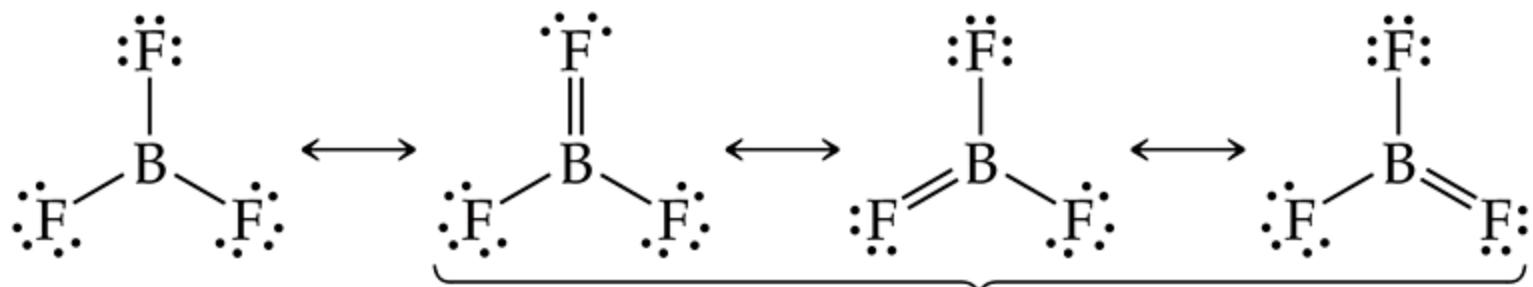
□ Consider BF_3 :

- Giving boron a filled octet places a *negative* charge on the boron and a *positive* charge on fluorine.
- This would not be an accurate picture of the distribution of electrons in BF_3 .



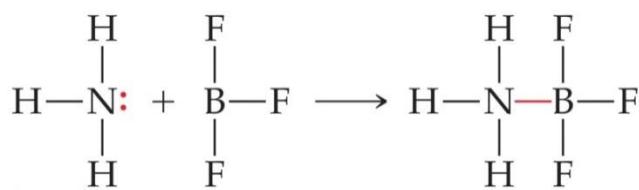
➤ Fewer Than Eight Electrons

- Therefore, structures that put a double bond between boron and fluorine are much less important than the one that leaves boron with only 6 valence electrons.



Dominant

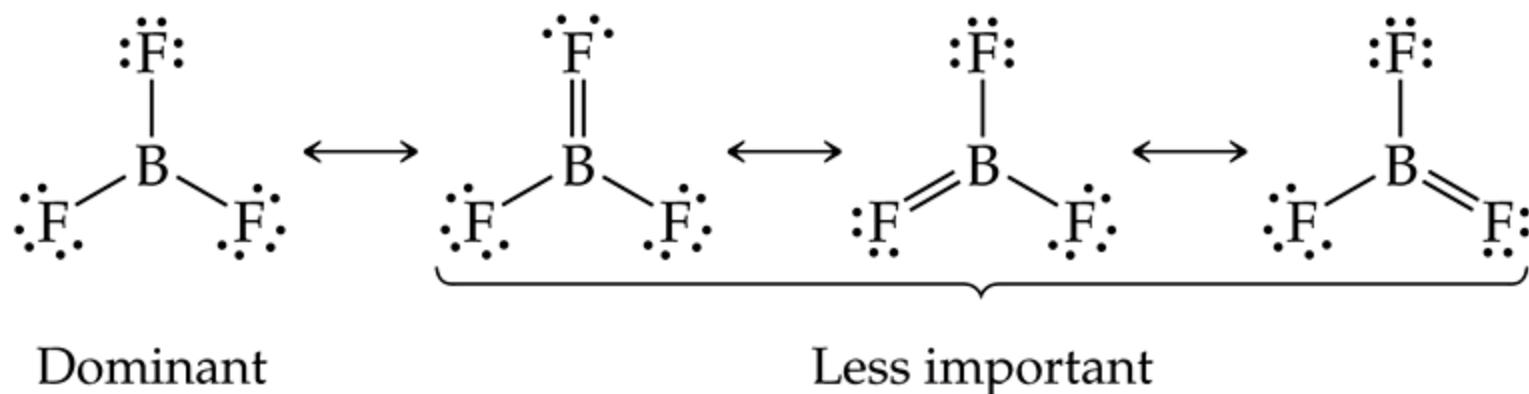
Less important



BF₃ reacts energetically with molecules having an unshared pair of electron that can be used to form a bond with boron.

➤ Fewer Than Eight Electrons

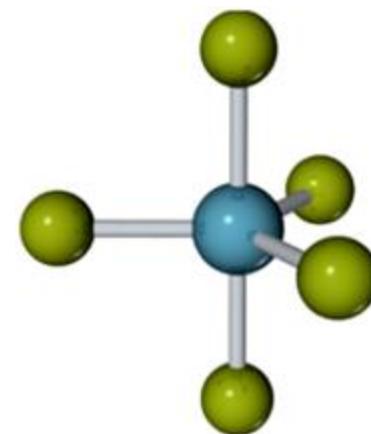
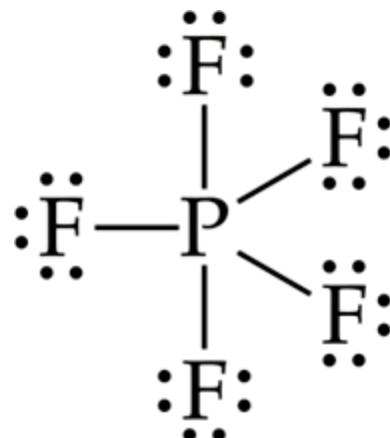
- The lesson is: If filling the octet of the central atom results in a negative charge on the central atom and a positive charge on the more electronegative outer atom, don't fill the octet of the central atom.



➤ More Than Eight Electrons

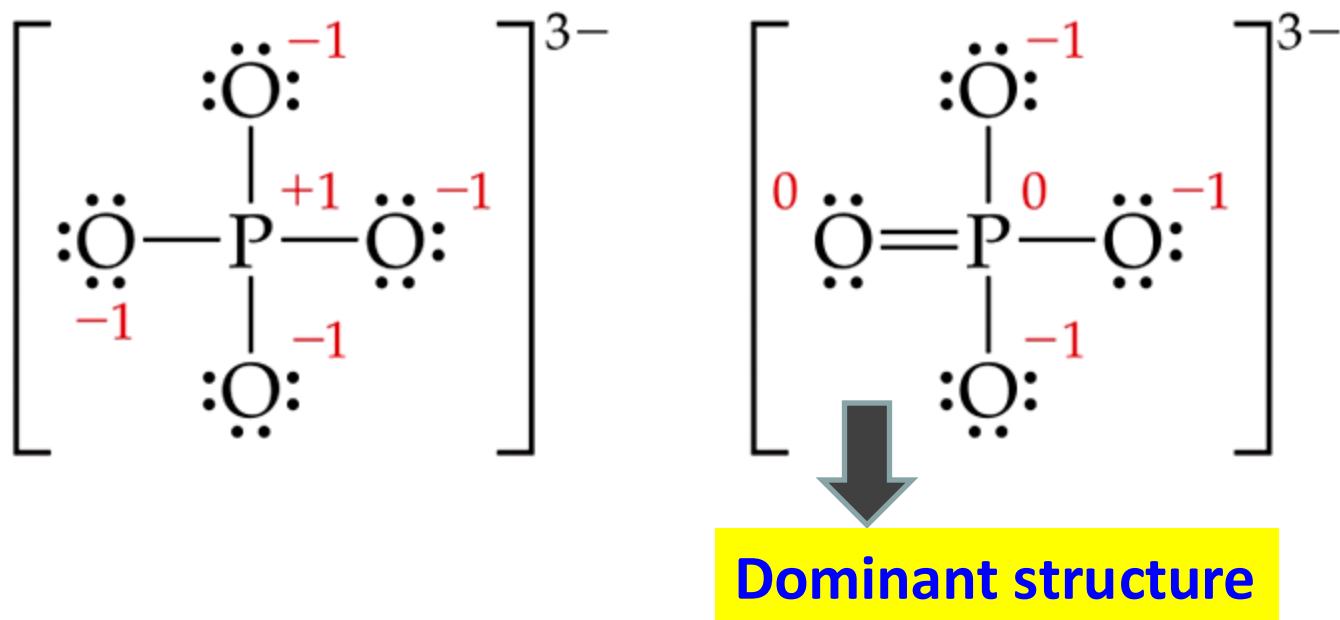
- The only way PCl_5 can exist is if phosphorus has 10 electrons around it.
- More than an octet of electrons around the central atom are called **hypervalent(高价)**.
- It is allowed to expand the octet of atoms on the third row or below.
 - Presumably **unfilled *d* orbitals** in these atoms participate in bonding.

P $1s^2 2s^2 2p^6 3s^2 3p^3 3d$



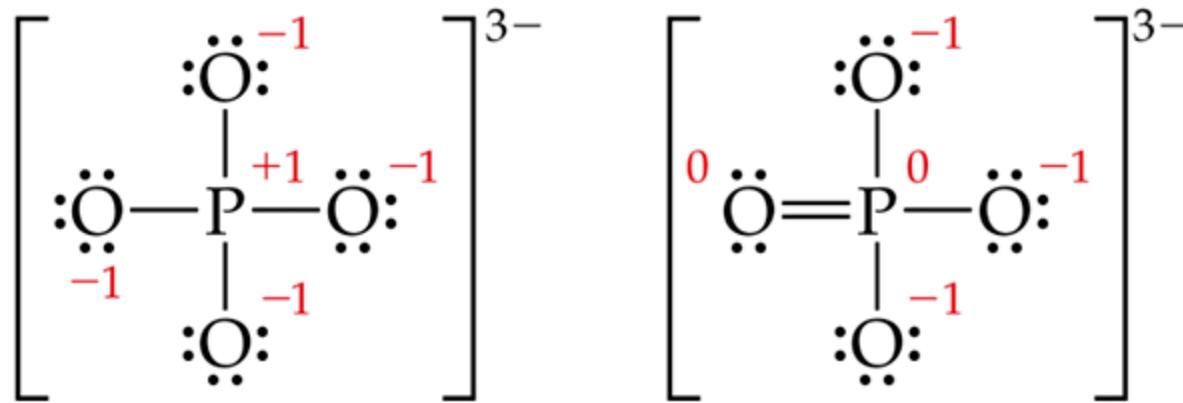
➤ More Than Eight Electrons

- Even though we can draw a Lewis structure for the phosphate ion that has only 8 electrons around the central phosphorus, the better structure puts a double bond between the phosphorus and one of the oxygen.



➤ More Than Eight Electrons

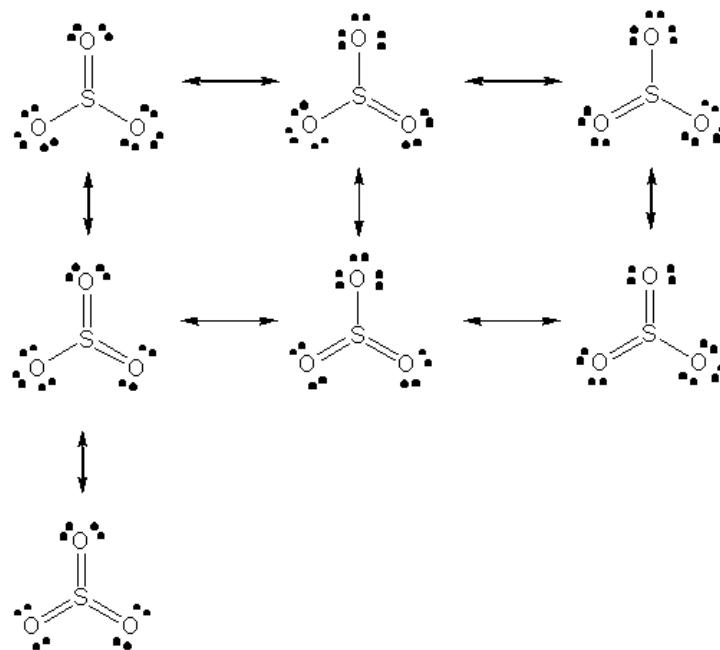
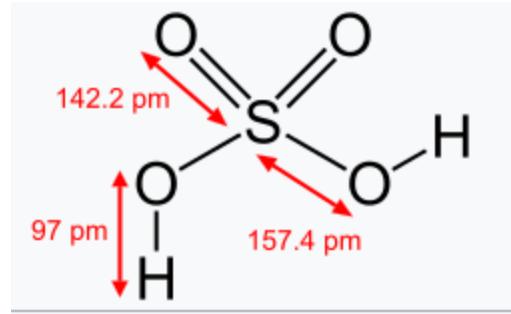
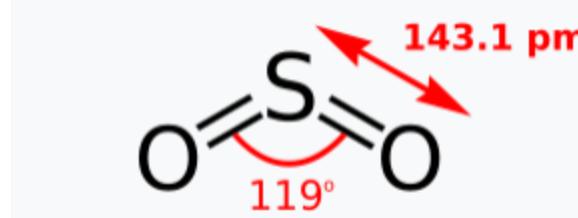
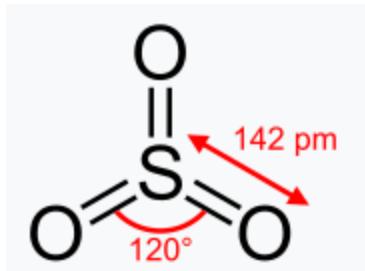
- This eliminates(消除) the charge on the phosphorus and the charge on one of the oxygens.
- The lesson is: When the central atom is **on the third row** or below and expanding its octet eliminates some formal charges, do so.



Debate: Theoretical calculation based on quantum mechanics suggest left structure is dominant; other research claim bond length in right structure are more consistent.

SO_3 Lewis structure

https://en.wikipedia.org/wiki/Sulfur_trioxide



PCl_5

SF_6

BeF_2

BF_3

NO

NO_2

SO_2

NO_3^-

SO_3

► 经典Lewis学说的不足:

作为化学键的经典电子理论，共价键理论在化学键理论发展史上起到了继往开来的作用。Lewis共价概念初步解释了一些简单非金属原子间形成共价分子的过程及其与离子键的区别。所以一些简单分子的Lewis结构式至今仍为化学家们所采用。但Lewis共价概念有其局限性，它存在几方面的不足：

- 1) Lewis结构未能阐明共价键的本质和特性。不能说明为什么共用电子对就能使两个原子牢固结合。
- 2) 八隅体规则的例外很多。该规则能较好地适用于第二周期元素原子，而其它周期某些元素的原子并不完全遵守此规则。
- 3) 不能解释某些分子的一些性质。如 O_2 的顺磁性问题以及 NO_2 分中的N-O键长问题等。

Sample Exercise 8.11 Lewis Structure for an Ion with More than an Octet of Electrons

Draw the Lewis structure for ICl_4^- .

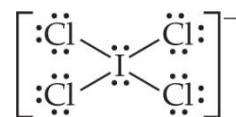
Solution

Iodine (group 7A) has seven valence electrons. Each chlorine atom (group 7A) also has seven. An extra electron is added to account for the 1^- charge of the ion. Therefore, the total number of valence electrons is

$$7 + (4 \times 7) + 1 = 36$$

The I atom is the central atom in the ion. Putting eight electrons around each Cl atom (including a pair of electrons between I and each Cl to represent the single bond between these atoms) requires $8 \times 4 = 32$ electrons.

We are thus left with $36 - 32 = 4$ electrons to be placed on the larger iodine:



Iodine has 12 valence electrons around it, four more than needed for an octet.

Sample Exercise 8.11 Lewis Structure for an Ion with More than an Octet of Electrons

Continued

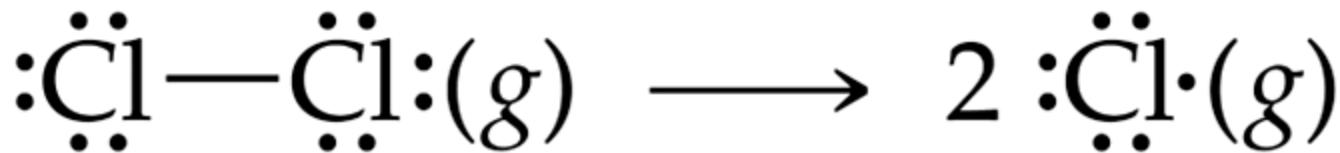
Practice Exercise

- (a) Which of the following atoms is never found with more than an octet of valence electrons around it: S, C, P, Br? (b) Draw the Lewis structure for XeF₂.

Answers: (a) C, (b) :F—[Xe]—F:

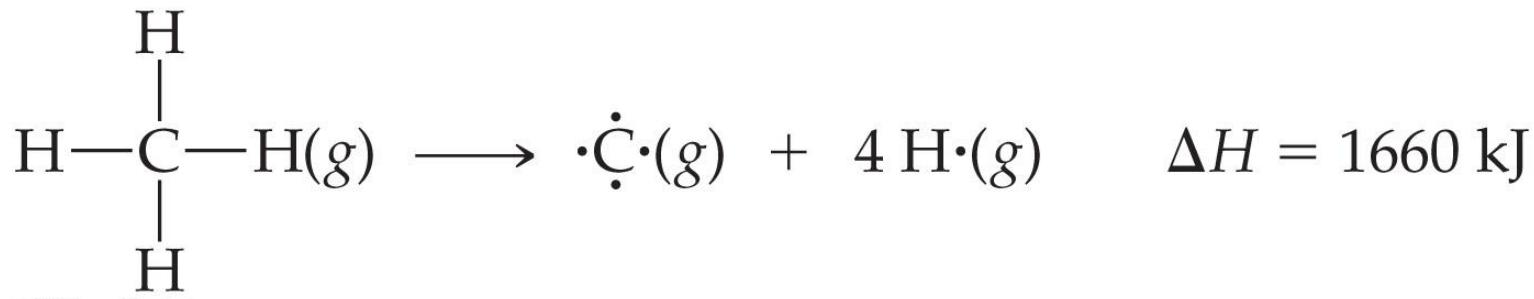
➤ Covalent Bond Strength

- Most simply, the strength of a bond is measured by determining how much energy is required to break the bond.
- **Bond enthalpy** is the enthalpy change, ΔH for the breaking of a particular bond in **one mole of a gaseous substance**.
- The bond enthalpy for a Cl—Cl bond, $D(\text{Cl}—\text{Cl})$, is measured to be 242 kJ/mol.



➤ Average bond enthalpy

- In polyatomic molecules, when molecule is decomposed into its atom (atomization), numerous equivalent bonds are broken, the enthalpy of atomization is equal to the sum of all the bond enthalpies.



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Average C-H bond enthalpy:

$$D(\text{C-H}) = (1660/4)\text{kJ/mol} = 415 \text{ kJ/mol}$$

➤ Average bond enthalpy

- Table 8.4 lists the average bond enthalpies for many different types of bonds.
- Average bond enthalpies are positive, because bond breaking is an endothermic process.

TABLE 8.4 • Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						

Multiple Bonds

C=C	614	N=N	418	O ₂	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

Average bond enthalpy

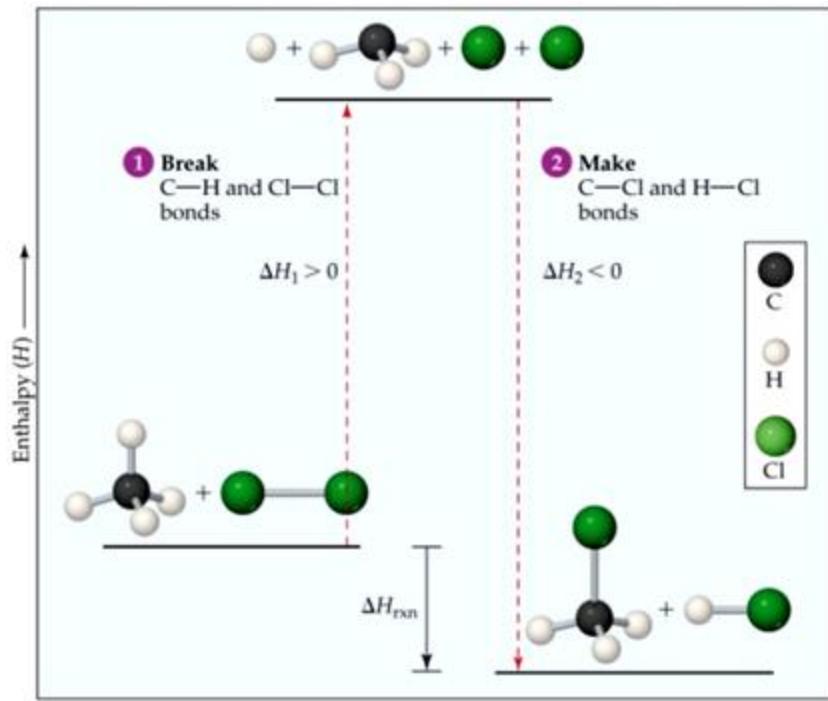
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C=O	799						
C≡O	1072						

Note: These are average bond enthalpies, not absolute bond enthalpies; the C—H bonds in methane, CH₄, will be a bit different than the C—H bond in chloroform, CHCl₃.

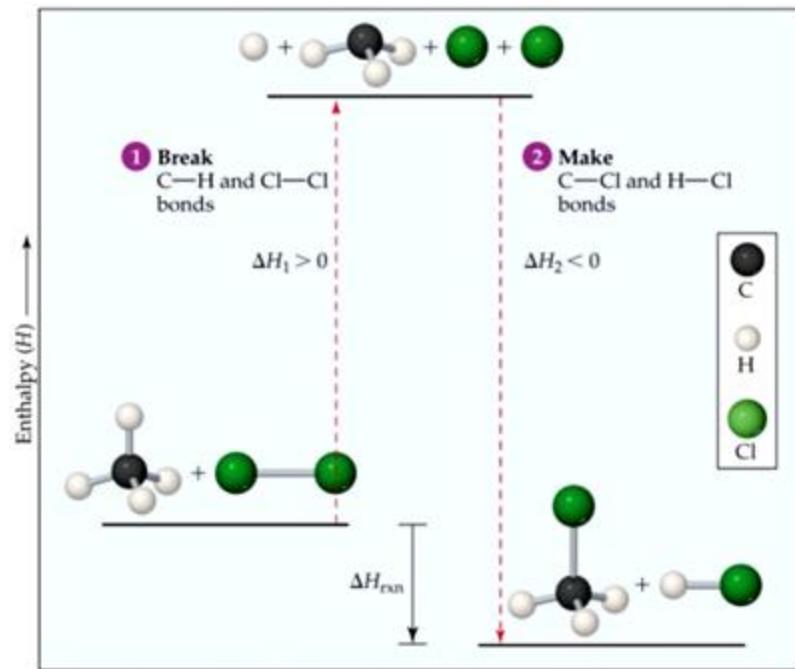
➤ Enthalpies of Reaction

- Using average bond enthalpies to estimate the enthalpies of reaction to quickly estimate a given reaction will be endothermic ($\Delta H > 0$) or exothermic ($\Delta H < 0$);
- Application of Hess's Law: Breaking bond-endothermic; forming bond-exothermic;
- Supply energy-enthalpies increased by the sum of the bond enthalpies of the bond are broken;
- Release energy-enthalpies lowered by the sum of the bond enthalpies of the bonds that are formed



➤ Enthalpies of Reaction

- One way to estimate ΔH for a reaction is to compare the bond enthalpies of bonds broken to the bond enthalpies of the new bonds formed.

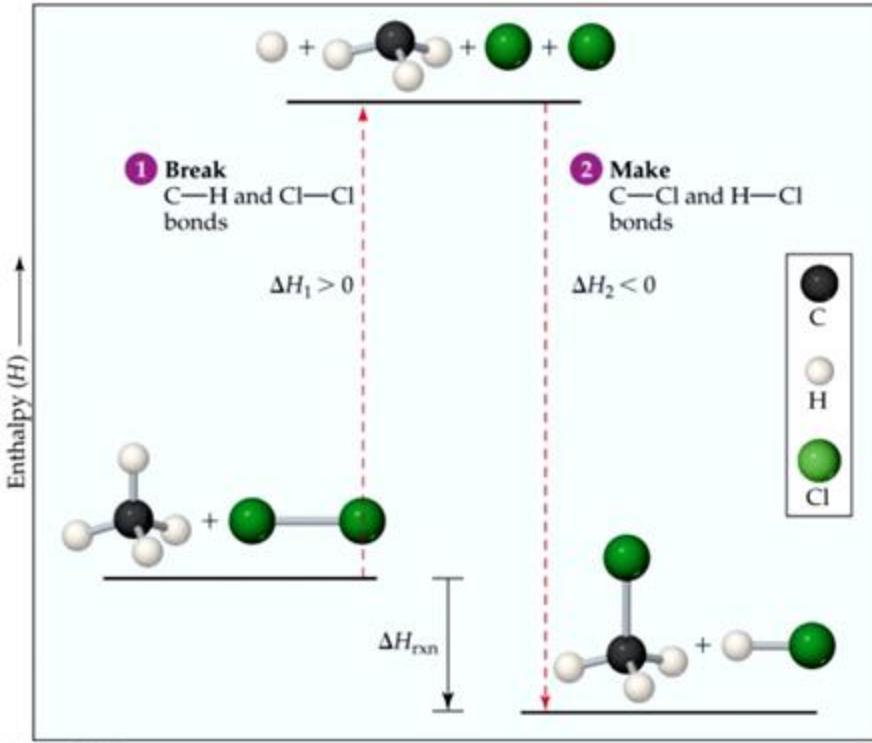


- In other words,
$$\Delta H_{rxn} = \Sigma(\text{bond enthalpies of bonds broken}) - \Sigma(\text{bond enthalpies of bonds formed})$$

➤ Enthalpies of Reaction

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2$$

In this example, one mol C—H bond and one mol Cl—Cl bond are broken; one mol C—Cl and one mol H—Cl bond are formed.

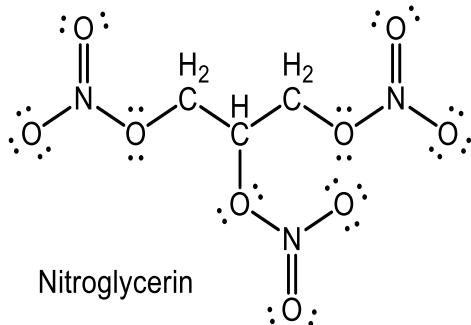
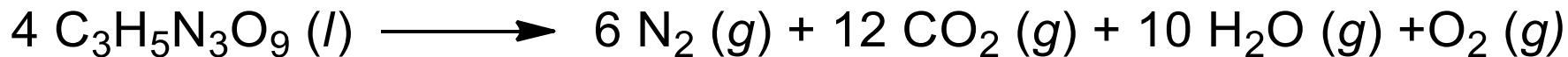


➤ Enthalpies of Reaction

So,

$$\begin{aligned}\Delta H &= [D(\text{C—H}) + D(\text{Cl—Cl})] - [D(\text{C—Cl}) + \\&\quad D(\text{H—Cl})] \\&= [(413 \text{ kJ/mol}) + (242 \text{ kJ/mol})] - [(328 \text{ kJ/mol}) \\&\quad + (431 \text{ kJ/mol})] \\&= (655 \text{ kJ/mol}) - (759 \text{ kJ/mol}) \\&= -104 \text{ kJ/mol}\end{aligned}$$

➤ Explosives and Bond Enthalpies



硝酸甘油

TABLE 8.4 • Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146	Cl—F	253
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Multiple Bonds

C=C	614	N=N	418	O ₂	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

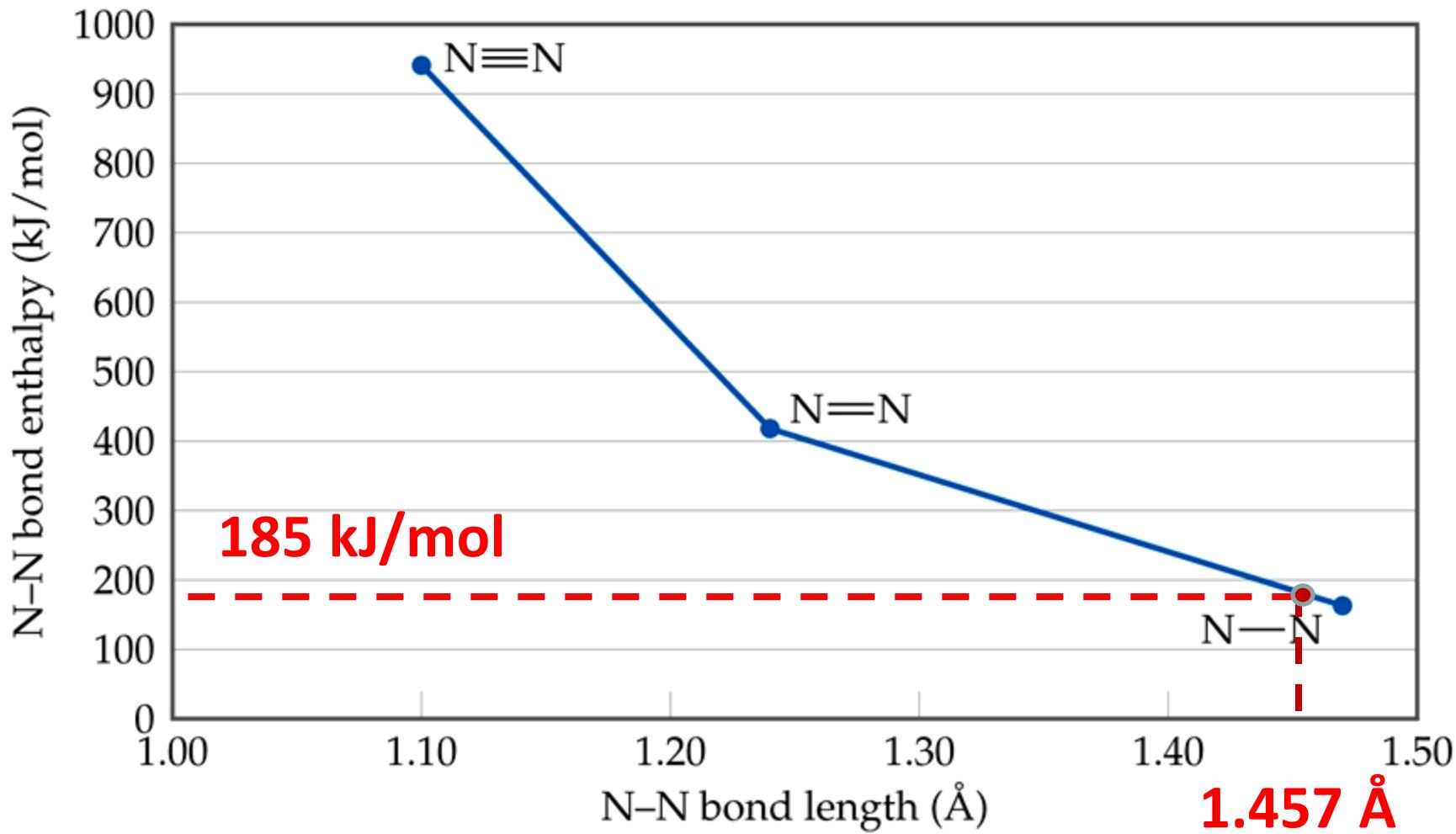
$$\Delta H_{rxn} = \Sigma(\text{bond enthalpies of bonds broken}) - \Sigma(\text{bond enthalpies of bonds formed})$$

➤ Bond Enthalpy and Bond Length

- We can also measure an average bond length for different bond types.
- As the number of bonds between two atoms increases, the bond length decreases.

TABLE 8.5 • Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (Å)		Bond	Bond Length (Å)	
C—C	1.54	348 kJ/mol	N—N	1.47	163 kJ/mol
C=C	1.34	614 kJ/mol	N=N	1.24	418 kJ/mol
C≡C	1.20	839 kJ/mol	N≡N	1.10	941 kJ/mol
C—N	1.43	293 kJ/mol	N—O	1.36	201 kJ/mol
C=N	1.38	615 kJ/mol	N=O	1.22	607 kJ/mol
C≡N	1.16	891 kJ/mol	O—O	1.48	146 kJ/mol
C—O	1.43	358 kJ/mol	O=O	1.21	495 kJ/mol
C=O	1.23	799 kJ/mol			
C≡O	1.13	1072 kJ/mol			



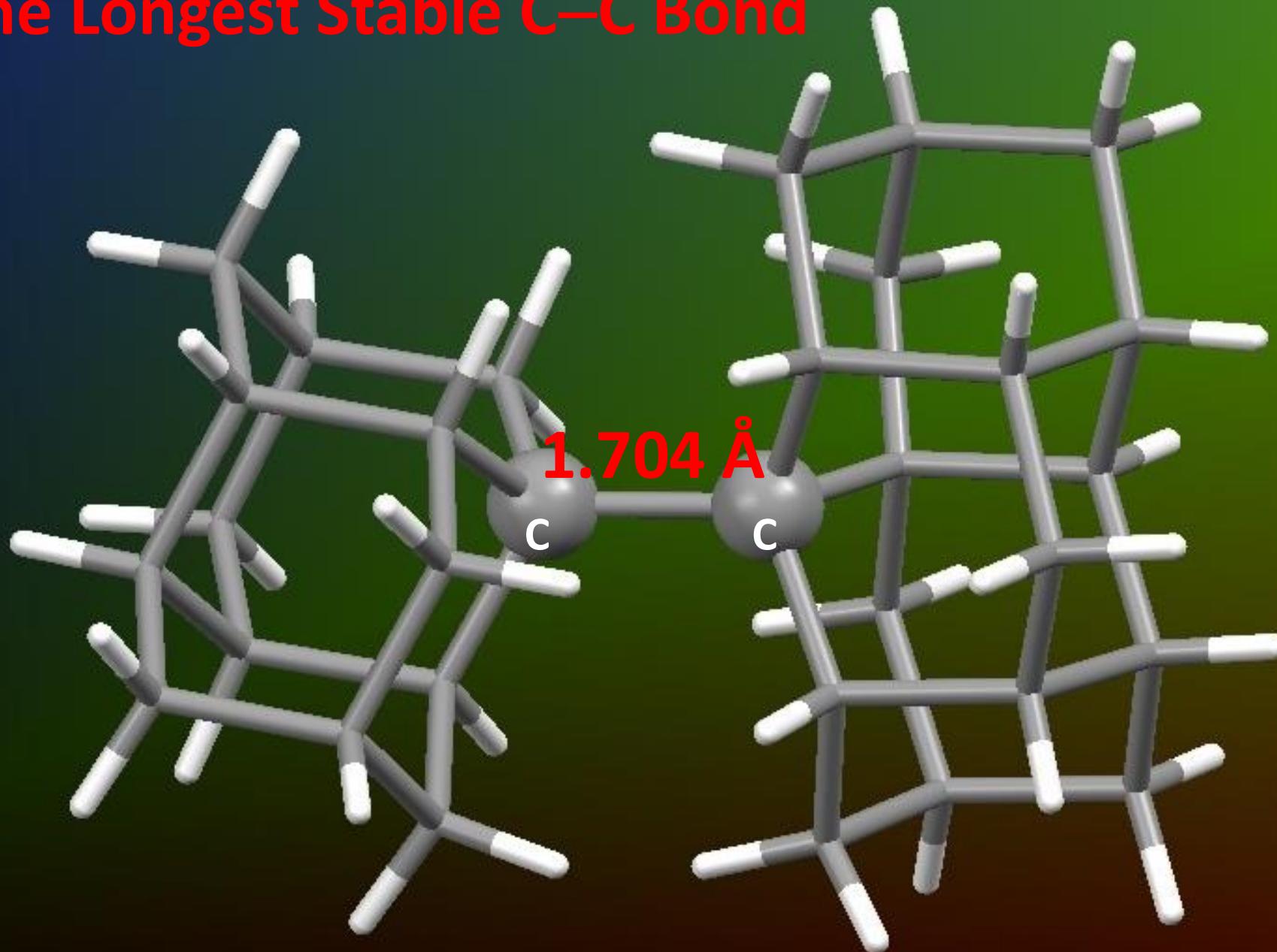
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C=N	1.38	615 kJ/mol	N=O	1.22	607 kJ/mol
C≡N	1.16	891 kJ/mol			
			O—O	1.48	146 kJ/mol
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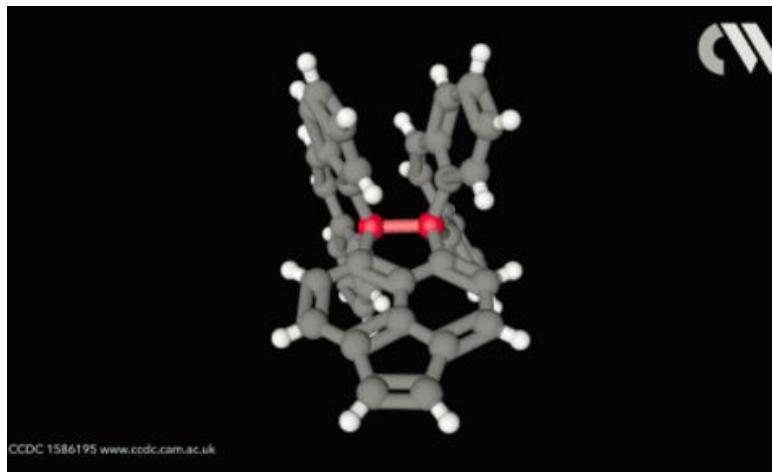
The Longest Stable C–C Bond



Longest C–C Single Bond among Neutral Hydrocarbons with a Bond Length beyond 1.8 Å



New record for longest C–C bond: 1.806 Å



碳-碳单键是有机化合物中最常见的共价键，大多数有机物中的碳-碳单键键长约在1.54Å。对于碳-碳单键的极限究竟在哪里这一问题，Ishigaki和Suzuki表示具有类似结构化合物的“超共价键”键长也许能达到2Å。

Chem, 2018, DOI: 10.1016/j.chempr.2018.01.011

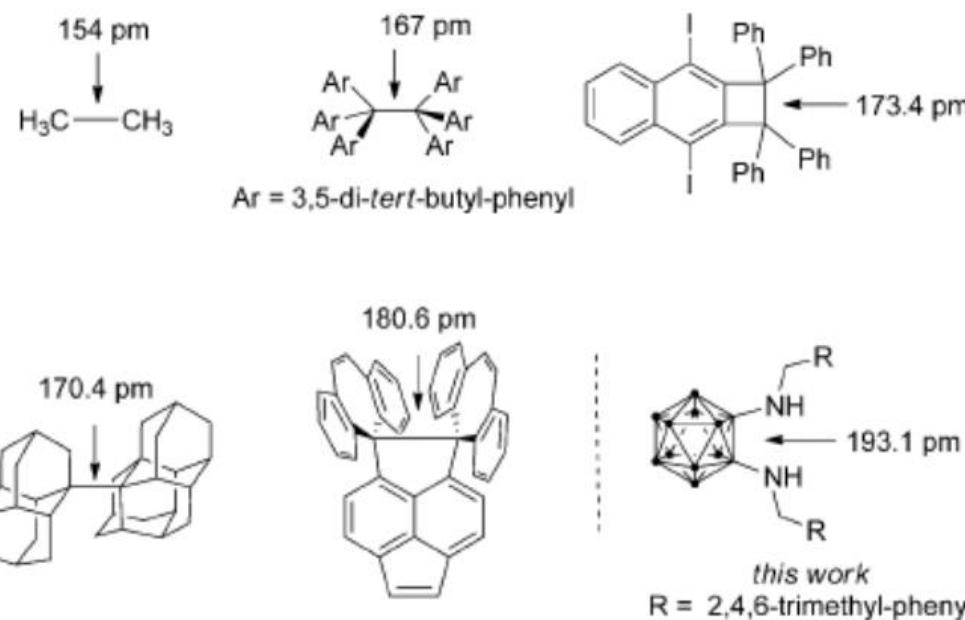
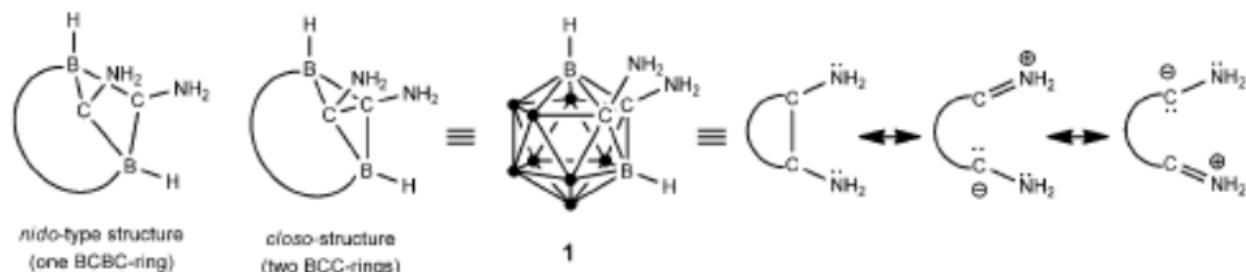


Figure 1. Compounds with normal and ultra-long C–C bonds.



Scheme 2. Resonance forms describing the negative hyperconjugation in **1** are shown on the right. *Closo-*- and *nido*-type structures of **1** are shown on the left.

Angew. Chem., Int. Ed.
2019, **58**, 1397–1401.



GIVE IT SOME THOUGHT

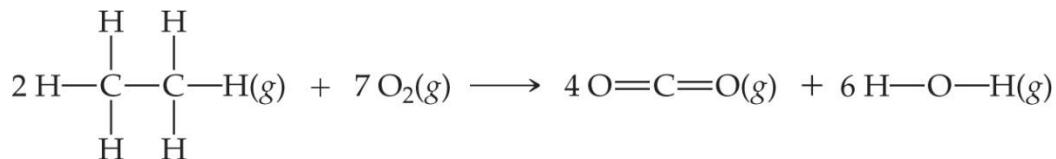
The C—O bond length in carbon monoxide, CO, is 1.13 Å, whereas the C—O bond length in CO₂ is 1.24 Å. Without drawing a Lewis structure, do you think that CO contains a single, double, or triple bond?

- A. Single covalent bond
- B. Double covalent bond
- C. Triple covalent bond



Sample Exercise 8.12 Using Average Bond Enthalpies

Using data from Table 8.4, estimate ΔH for the reaction



Solution

Analyze We are asked to estimate the enthalpy change for a chemical reaction by using average bond enthalpies for the bonds broken and formed.

Plan In the reactants, we must break twelve C—H bonds and two C—C bonds in the two molecules of C_2H_6 and seven O₂ bonds in the seven O₂ molecules. In the products, we form eight C=O bonds (two in each CO₂) and twelve O—H bonds (two in each H₂O).

TABLE 8.4 • Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
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Multiple Bonds

C=C	614	N=N	418	O ₂	495
C≡C	839	N≡N	941		
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Sample Exercise 8.12 Using Average Bond Enthalpies

Continued

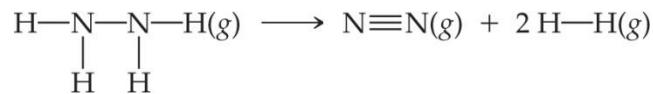
Solve Using Equation 8.12 and data from Table 8.4, we have

$$\begin{aligned}\Delta H &= [12D(C-H) + 2D(C-C) + 7D(O_2)] - [8D(C=O) + 12D(O-H)] \\ &= [12(413 \text{ kJ}) + 2(348 \text{ kJ}) + 7(495 \text{ kJ})] - [8(799 \text{ kJ}) + 12(463 \text{ kJ})] \\ &= 9117 \text{ kJ} - 11948 \text{ kJ} \\ &= -2831 \text{ kJ}\end{aligned}$$

Check This estimate can be compared with the value of -2856 kJ calculated from more accurate thermochemical data; the agreement is good.

Practice Exercise

Using Table 8.4, estimate ΔH for the reaction



Answer: -86 kJ

TABLE 8.4 • Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
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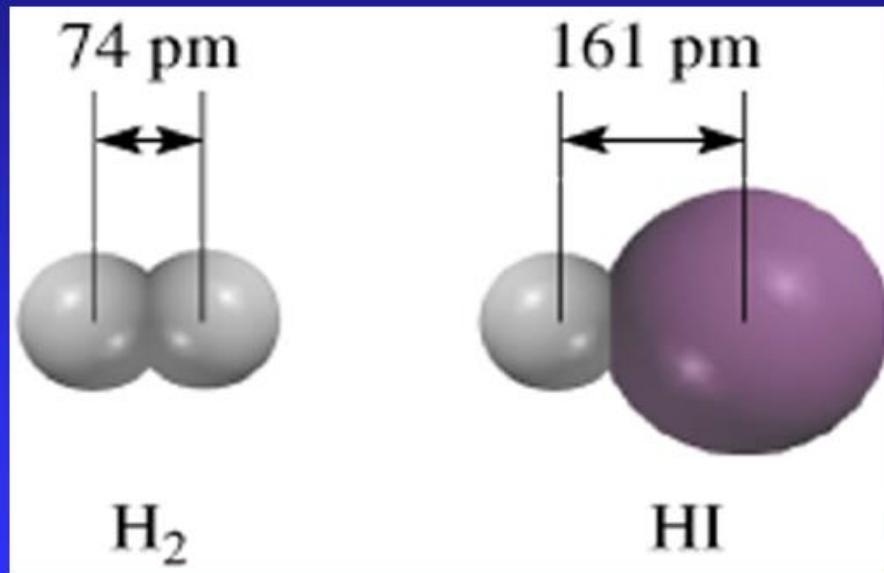
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C=O	799				
C≡O	1072				

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➤ 键长与键级:

共价分子中两个成键原子的核间距称为键长；原子之间共享电子对的数目称为键级。



Bond Type	Bond Length (pm)
C-C	154
C=C	133
C≡C	120
C-N	143
C=N	138
C≡N	116

Bond Lengths

Triple bond < Double Bond < Single Bond

➤ 键能

也称键焓。在温度 T 与标准压力时，气态分子断开1 mol化
学键的焓变。通常用符号B.E.表示。

	N ₂	O ₂	F ₂
键 级	3	2	1
键 能 / kJ·mol ⁻¹	945	498	155
键 长 / pm	110	121	142



Bond Energies

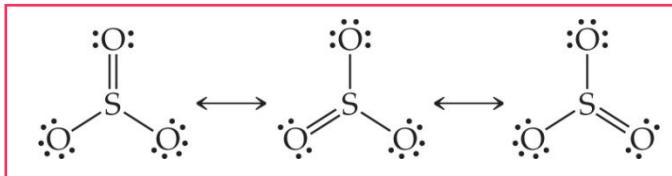
Single bond < Double bond < Triple bond

Sample Exercise 8.10 Resonance Structures

Which is predicted to have the shorter sulfur–oxygen bonds, SO_3 or SO_3^{2-} ?

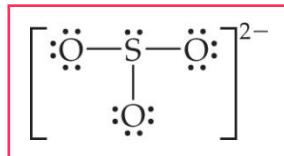
Solution

The sulfur atom has six valence electrons, as does oxygen. Thus, SO_3 contains 24 valence electrons. In writing the Lewis structure, we see that three equivalent resonance structures can be drawn:



As with NO_3^- , the actual structure of SO_3 is an equal blend of all three. Thus, each S—O bond length should be about one-third of the way between the length of a single bond and the length of a double bond. That is, they should be shorter than single bonds but not as short as double bonds.

The SO_3^{2-} ion has 26 electrons, which leads to a dominant Lewis structure in which all the S—O bonds are single:



Our analysis of the Lewis structures leads us to conclude that SO_3 should have the shorter S—O bonds and SO_3^{2-} the longer ones. This conclusion is correct: The experimentally measured S—O bond lengths are 1.42 Å in SO_3 and 1.51 Å in SO_3^{2-} .

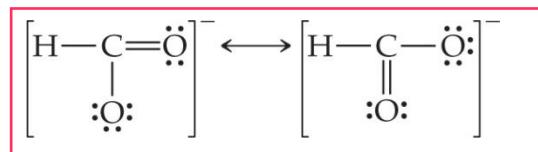
Sample Exercise 8.10 Resonance Structures

Continued

Practice Exercise

Draw two equivalent resonance structures for the formate ion, HCO_2^- .

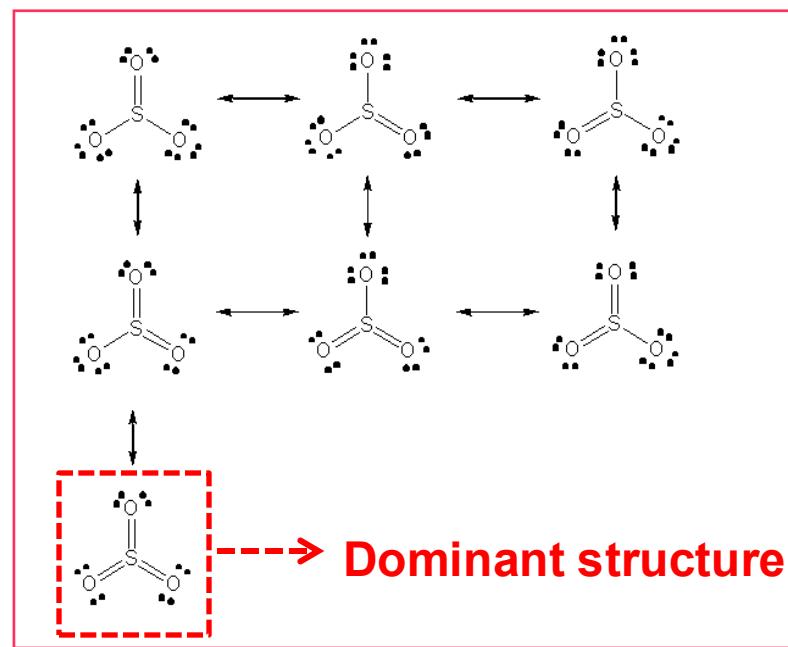
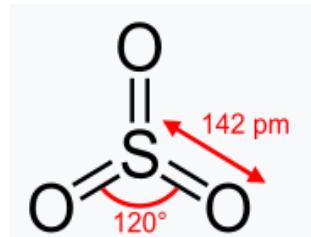
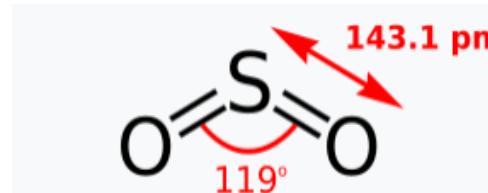
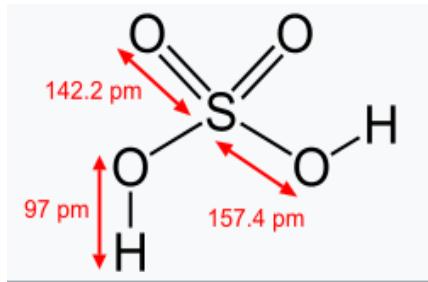
Answer:



SO_3 Lewis structure

<http://geometryofmolecules.com/so3-lewis-structure-polarity/>

<https://socratic.org/questions/what-are-all-resonance-structures-for-so3>



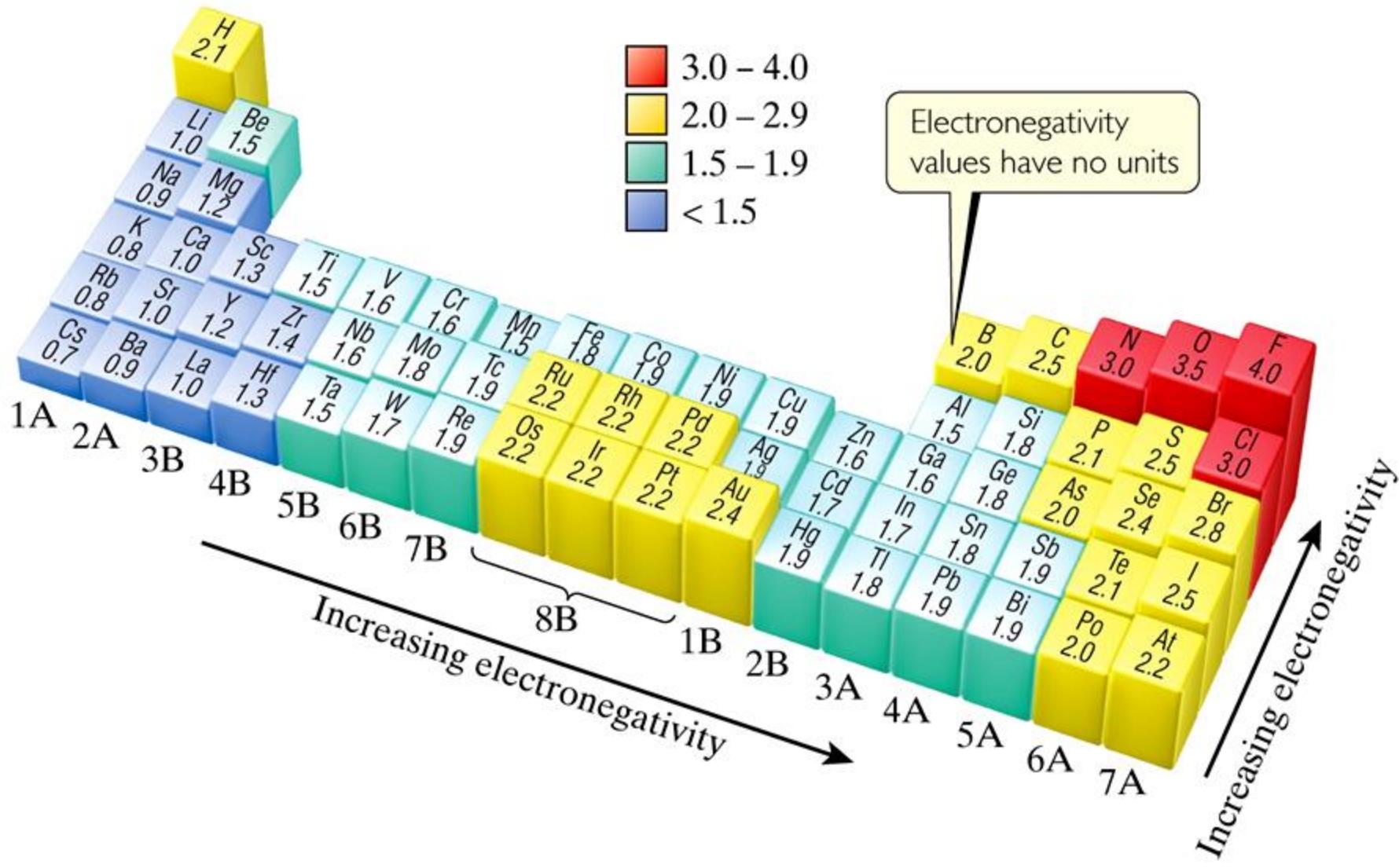


GIVE IT SOME THOUGHT

Based on differences in electronegativity, how would you characterize the bonding in sulfur dioxide, SO_2 ? Do you expect the bonds between S and O to be nonpolar, polar covalent, or ionic?

- A. Nonpolar, because both S and O are in the same family.
- B. Polar covalent, because the difference in electronegativity values is 1.0.
- C. Ionic, because the difference in electronegativity values is -1.0 .
- D. Ionic, because the difference in electronegativity values is >0.9 .







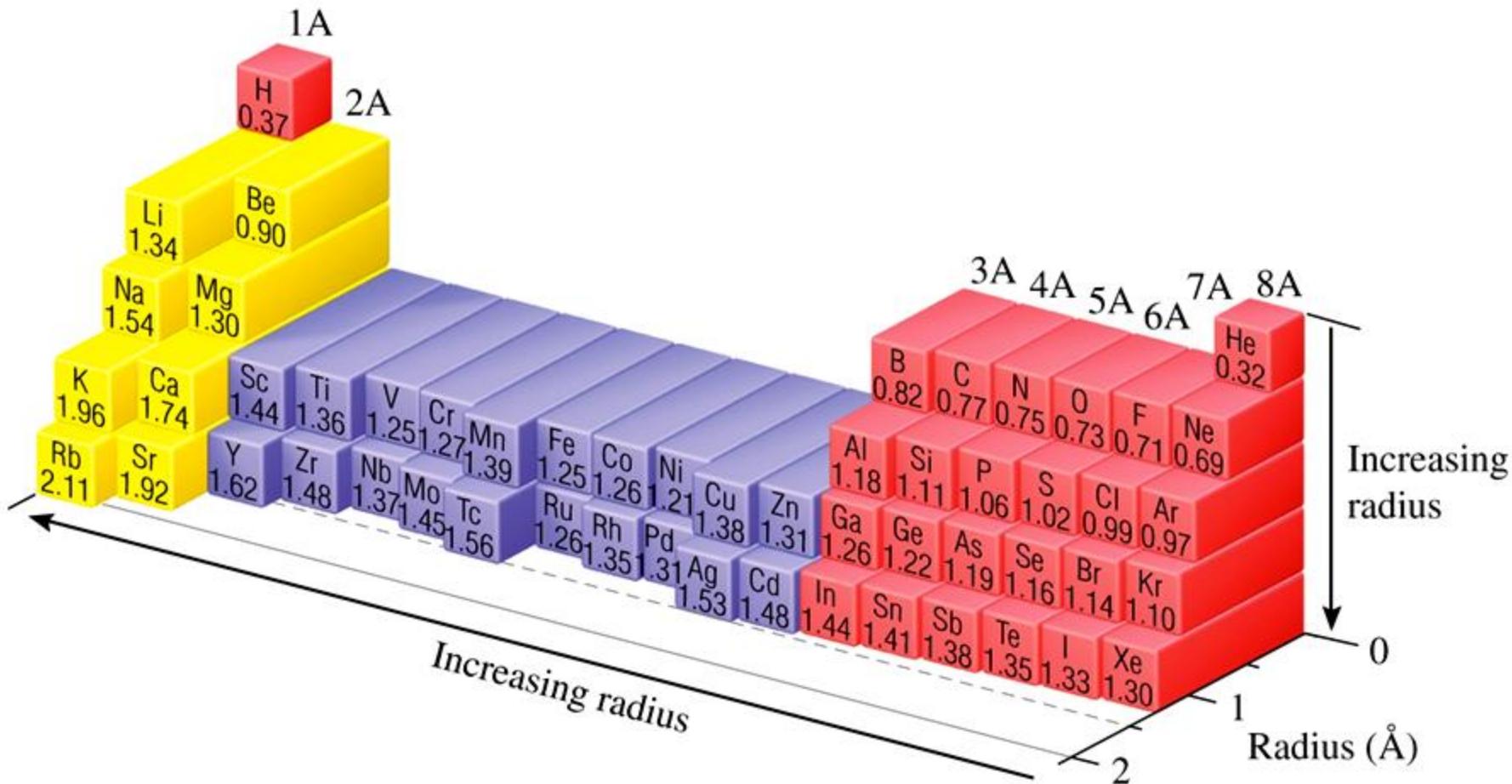
GIVE IT SOME THOUGHT

Chlorine monofluoride, ClF, and iodine monofluoride, IF, are *interhalogen* compounds—compounds that contain bonds between different halogen elements. Which of these molecules has the larger dipole moment?

- A IF
- B. ClF
- C. They have the same dipole moment.
- D. Neither has a dipole moment; they are both nonpolar.

电荷分离量 (q)：这取决于两个成键原子之间的电负性 (electronegativity) 差异 (ΔEN)。电负性差异越大，电子越偏向电负性强的一方，导致正负电荷中心的分离程度 (q) 越大。





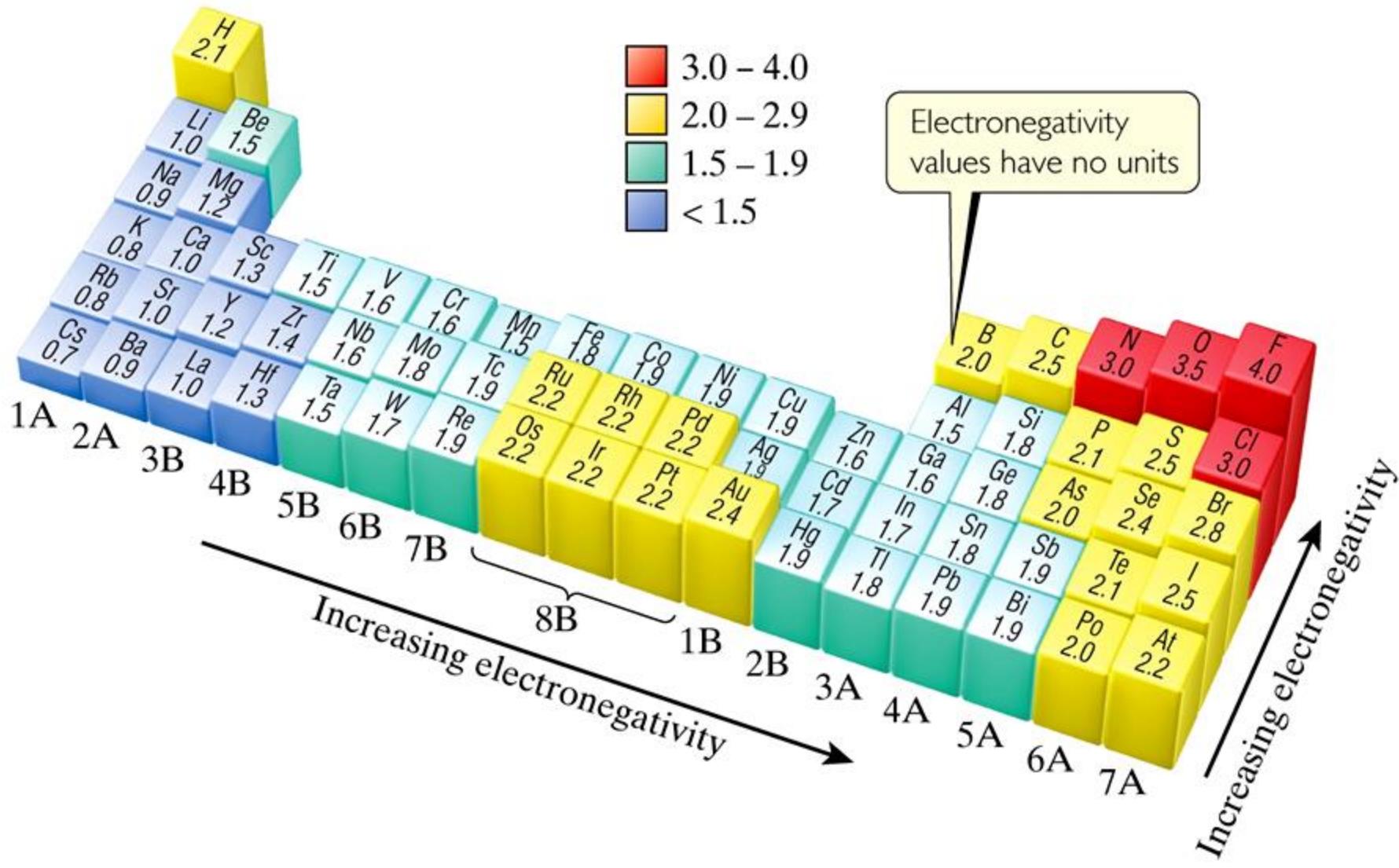


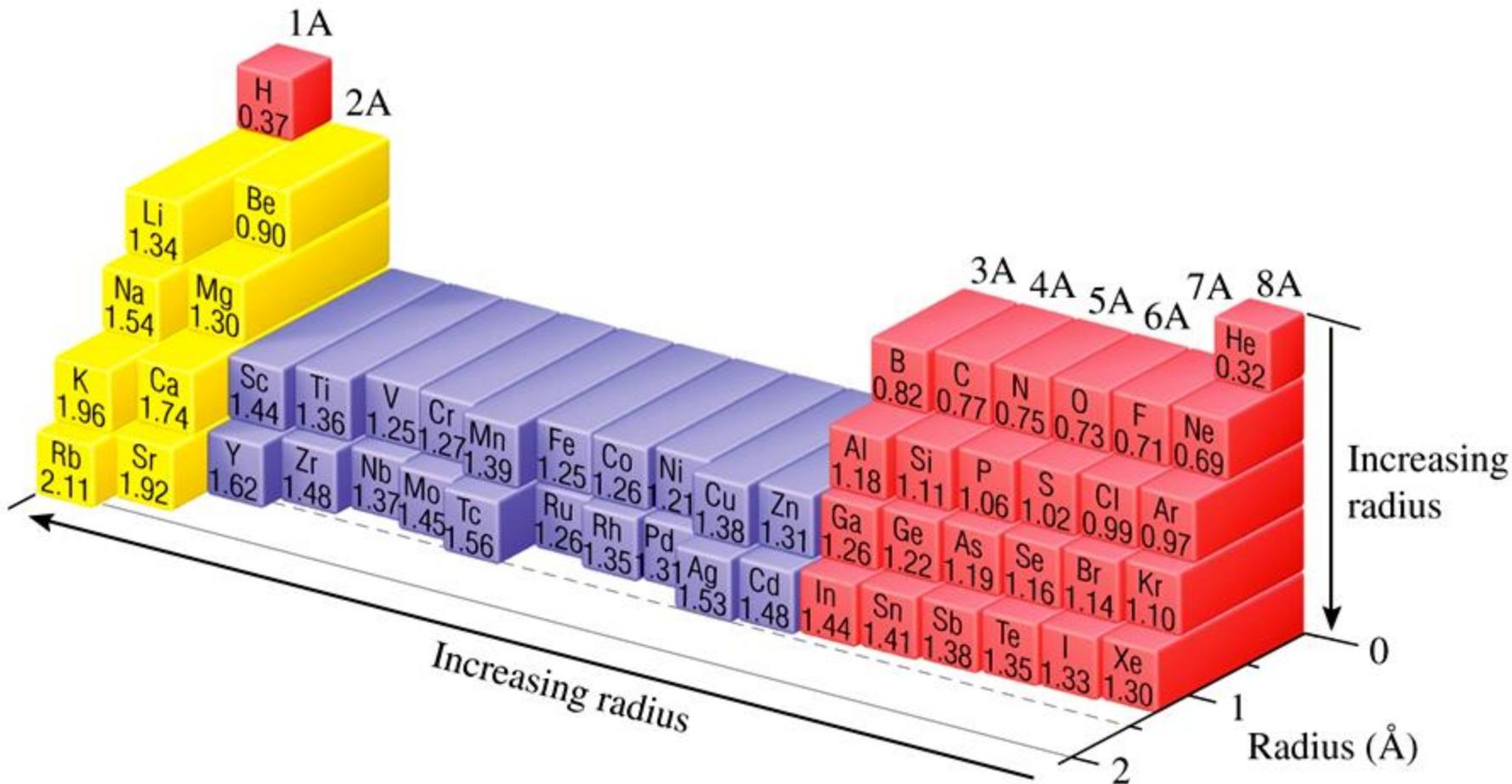
GIVE IT SOME THOUGHT

The bond between carbon and hydrogen is one of the most important types of bonds in chemistry. The length of a H—C bond is approximately 1.1 Å. Based on this distance and differences in electronegativity, do you expect the dipole moment of an individual H—C bond to be larger or smaller than that of the H—I bond?

- A. H—C has the same bond dipole moment as H—I, because the magnitude of Q and r in $\mu=Qr$ are about the same for both.
- B. H—C has the larger bond dipole moment, because Q and r are larger in H—C than in H—I.
- C. H—I has the smaller bond dipole moment, because Q is about the same for both, but r is larger in H—C than in H—I.
- D. H—I has the larger bond dipole moment, because Q is about the same for both, but r is larger in H—I than in H—C.

电荷分离量 (q): 这取决于两个成键原子之间的电负性 (electronegativity) 差异 (ΔEN)。电负性差异越大，电子越偏向电负性强的一方，导致正负电荷中心的分离程度 (q) 越大。







GIVE IT SOME THOUGHT

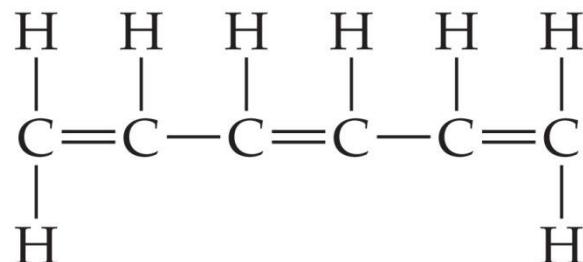
The O—O bonds in ozone are often described as “one-and-a-half” bonds. Is this description consistent with the idea of resonance?

- A Yes, because in each of the two resonance forms there is one O=O bond and one O—O bond, giving an overall average of 1.5 bonds per O—O bond.
- B No, because a half bond cannot exist in a bonding situation.



GIVE IT SOME THOUGHT

Each Lewis structure of benzene has three C=C double bonds. Another hydrocarbon containing three C=C double bonds is *hexatriene*, C₆H₈. A Lewis structure of hexatriene is



Do you expect hexatriene to have multiple resonance structures? If not, why is this molecule different from benzene with respect to resonance?

- A. Yes, because it has multiple Lewis resonance structures.
- B. Yes, because it has three C=C bonds that can be moved throughout the structure.
- C. No, because the carbon chain is linear.
- D. No, because we cannot write other reasonable Lewis structures.



GIVE IT SOME THOUGHT

Which of the Lewis structures for NO is dominant based on analysis of the formal charges?



- A. The first NO structure, because all atoms have zero formal charge.
- B. The first NO structure, because N and O have equal but opposite formal charges.
- C. The second NO structure, because all atoms have zero formal charge.
- D. The second NO structure, because N should not have a positive formal charge.



GIVE IT SOME THOUGHT

How can you use the enthalpy of atomization of the hydrocarbon ethane, $\text{C}_2\text{H}_6(g)$, along with the value $D(\text{C}—\text{H}) = 413 \text{ kJ/mol}$ to estimate the value for $D(\text{C}—\text{C})$?

- A. The enthalpy of atomization / 7 bonds broken = a good estimate of $D(\text{C}—\text{C})$.
- B. The enthalpy of atomization – 6 [$D(\text{C}—\text{H})$] = a good estimate of $D(\text{C}—\text{C})$.
- C. The enthalpy of atomization + 6 [$D(\text{C}—\text{H})$] = a good estimate of $D(\text{C}—\text{C})$.
- D. The enthalpy of atomization / 7 bonds broken – 6[$D(\text{C}—\text{H})$] = a good estimate of $D(\text{C}—\text{C})$.



GIVE IT SOME THOUGHT

Based on bond enthalpies, which do you expect to be more reactive, oxygen, O₂, or hydrogen peroxide, H₂O₂?

- A. O₂ is more reactive, because the O=O bond enthalpy is less than that of the O—O bond enthalpy in hydrogen peroxide.
- B. O₂ is more reactive, because the O=O bond enthalpy is greater than that of the O—O bond enthalpy in hydrogen peroxide.
- C. H₂O₂ is more reactive, because the O—O bond enthalpy is less than that of the O=O bond enthalpy in O₂.
- D. H₂O₂ is more reactive, because the O—O bond enthalpy is greater than that of the O=O bond enthalpy in O₂.

TABLE 8.4 • Average Bond Enthalpies (kJ/mol)**Single Bonds**

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						

Multiple Bonds

C=C	614	N=N	418	O ₂	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

1. Which of these molecules has the same number of shared electron pairs as unshared electron pairs?

- A) HCl B) PF₃ C) H₂S D) CCl₂F₂ E) Br₂

2. Calculate the dipole moment for HF (bond length 0.917 Å), assuming that the bond is completely ionic. ($1D = 3.34 \times 10^{-30} \text{ C} \cdot \text{m}$; $1 e = 1.6 \times 10^{-19} \text{ C}$)

- A) 0.917 D B) 1.91 D C) 2.75 D D) 4.39 D E) 7.37 D

3. How many dots should be shown in the Lewis symbol for phosphorus?

- A) One B) Seven C) Six D) Five E) Two

4. Phosphorus oxychloride has the chemical formula POCl₃, with P as the central atom. To minimize formal charge, how many bonds does phosphorus make to the other atoms in the molecule? (Count each single bond as one, each double bond as two, and each triple bond as three.)

- A) 3 B) 4 C) 5 D) 6 E) 7

5. Consider the covalent bond each of the following elements forms with *hydrogen: chlorine, phosphorus, sulfur, and silicon*. Which will form the most polar bond with hydrogen?

- A) Si B) S C) Cl D) P

6. Lattice energy is _____.

- A) the sum of electron affinities of the components in an ionic solid
- B) the energy given off when gaseous ions combine to form one mole of an ionic solid
- C) the energy required to produce one mole of an ionic compound from its constituent elements in their standard states
- D) the sum of ionization energies of the components in an ionic solid
- E) the energy required to convert a mole of ionic solid into its constituent ions in the gas phase

7. Which of the following does not have eight valence electrons?

- A) V^{5+}
- B) He
- C) Br^-
- D) Sr^{2+}
- E) Rb^+

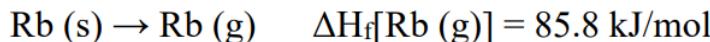
8. Electronegativity _____ from left to right within a period and _____ from top to bottom within a group.

- A) decreases, increases
- B) increases, decreases
- C) stays the same, increases
- D) increases, stays the same
- E) increases, increases

9. Predict the order of the N—O bond lengths in NO^+ , NO_2^- , and NO_3^- .

- A) NO^+ shortest, NO_3^- longest
- B) NO_3^- shortest, NO_2^- longest
- C) NO^+ shortest, NO_2^- longest
- D) NO^+ longest, NO_2^- shortest

10. (2 points) calculate the lattice energy of RbCl , given the following pertinent information:



Answer:

$$\Delta H_{\text{lattice}} = (403 + 85.8 + 121.7 + 403 - 349) \text{ kJ/mol} = 692 \text{ kJ/mol}$$

11. (3 points) The iodine monobromide molecule, IBr, has a bond length of 2.49 Å and a dipole moment of 1.21 D. (a) Which atom of the molecule is expected to have a negative charge? (b) Calculate the effective charges on the I and Br atoms in IBr in units of the electronic charge, e. (1 debye = 3.34×10^{-30} coulomb-meters; 1 e = 1.6×10^{-19} coulombs)

Answer:

(a) Br atom of the molecule is expected to have a negative charge.

$$(b) Q = \mu/r = 1.21 \times 3.34 \times 10^{-30} \div (2.49 \times 10^{-10}) \div (1.6 \times 10^{-19}) = 0.10e$$

effective charges on the I is $+0.10 e$

effective charges on the Br is $-0.10 e$

12. (2 points) According to their expected lattice energies, listing them from lowest lattice energy to the highest: MgS, KI, GaN, LiBr.

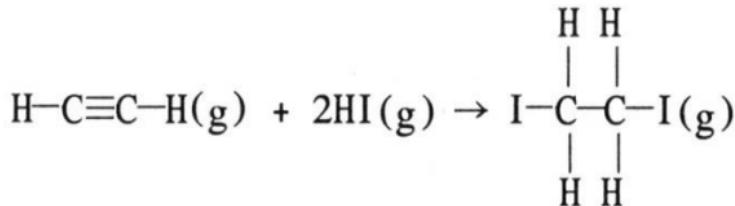
$$U_L \propto \frac{|Q_1 \cdot Q_2|}{r}$$

Answer:

KI, LiBr, MgS, GaN

1. 离子的电荷 (Q_1, Q_2): 离子所带电荷的乘积。电荷越高, 吸引力越强, 晶格能越大。这是最重要的决定因素。
2. 离子间距 (r): 阳离子和阴离子核之间的距离 (即它们的离子半径之和)。离子越小, 距离 (r) 越短, 吸引力越强, 晶格能越大。

13. (3 points) Using the table of average bond energies below, to estimate the enthalpy change (kJ) for the following gas-phase reaction:



Bond:	$\text{C}\equiv\text{C}$	$\text{C}-\text{C}$	$\text{H}-\text{I}$	$\text{C}-\text{I}$	$\text{C}-\text{H}$
D (kJ/mol):	839	348	299	240.	413

Answer:

Answer:

$$\begin{aligned}\Delta H_{\text{rxn}} &= [D(\text{C}\equiv\text{C}) + 2D(\text{C-H}) + 2D(\text{H-I})] - [D(\text{C-C}) + 2D(\text{C-I}) + 4D(\text{C-H})] \\ &= (839 + 2 \times 413 + 2 \times 299) - (348 + 2 \times 240. + 4 \times 413) \\ &= -217 \text{ kJ}\end{aligned}$$

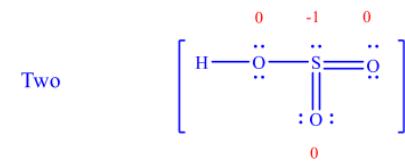
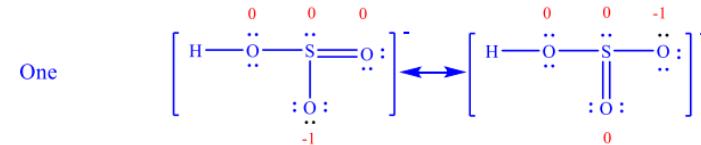
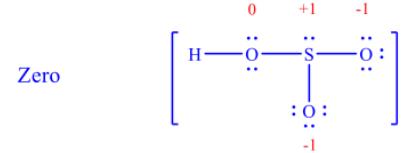
14. (5 points)

(a) (3 points) Describe the ion, HSO_3^- (the H atom is bonded to one of the O atoms), using three possible Lewis structures, one each with zero, one, or two S = O double bonds (indicate all resonance structures if there are) and determine the formal charges of oxygen and sulfur atoms in each structure.

(b) (1 points) Based on the formal charges, which Lewis structure is the dominant one?

(c) (1 points) Indicate the structure that obeys the octet rule for sulfur atom in part (a).

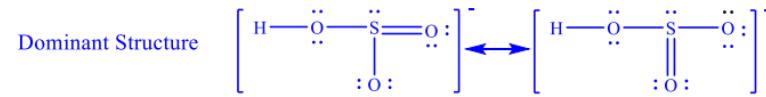
(a) (3 points)



判断最稳定（占主导地位）的结构，我们遵循以下规则：

1. 形式电荷的总和最接近 0。
2. 如果必须有非零的形式电荷，负的形式电荷应分布在电负性最强的原子上。

(b) (2 points)



(c) (2 points)

