CHEM2100J
Chemistry
Autumn 2024

Chapter 03
Chemical Bonds

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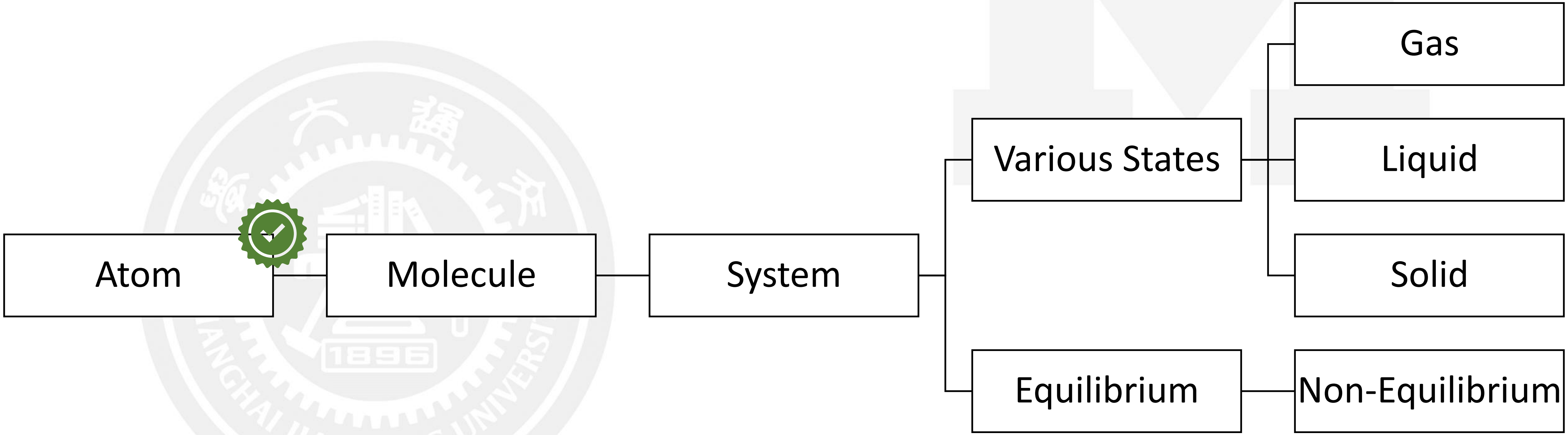
The Journey So Far



Bonds between Atoms

Each atom is unique due to their differing:

- sizes,
- electron affinities,
- ionization energies.

Atoms minimize these imbalances by forming bonds.

Bonds between Atoms

Atoms strive to fill their outer shells with electrons just like a noble gas does.

In a generalized way, atoms can achieve satisfaction by forming two types of bonds: ionic and covalent.

Ionic is gaining and losing electrons.

Covalent is sharing electrons.

The resulting bond is lower in energy than the separate atoms.

Ionic Bonds

If electrons transfer from one or more atoms, the entire compound is held together by **electrostatic attractions** between all the ions.

This attraction is called an **ionic bond**.

The new ionic partnership is lower in energy than the separate atoms.

Ionic Bonds

Binary ionic compounds form between **metals** and a **non-metallic** element.

Cations and anions stack into alternating, <u>oppositely charged ions</u> that line up in three dimensions.

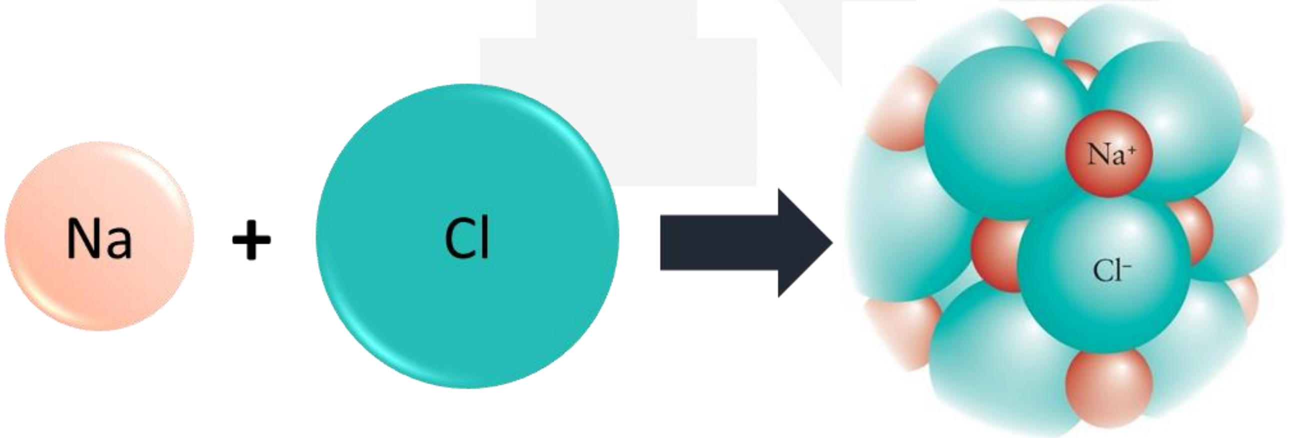


Figure 24.1
Atkins, Chemical Principles: The Quest for Insight, 7e
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Metals

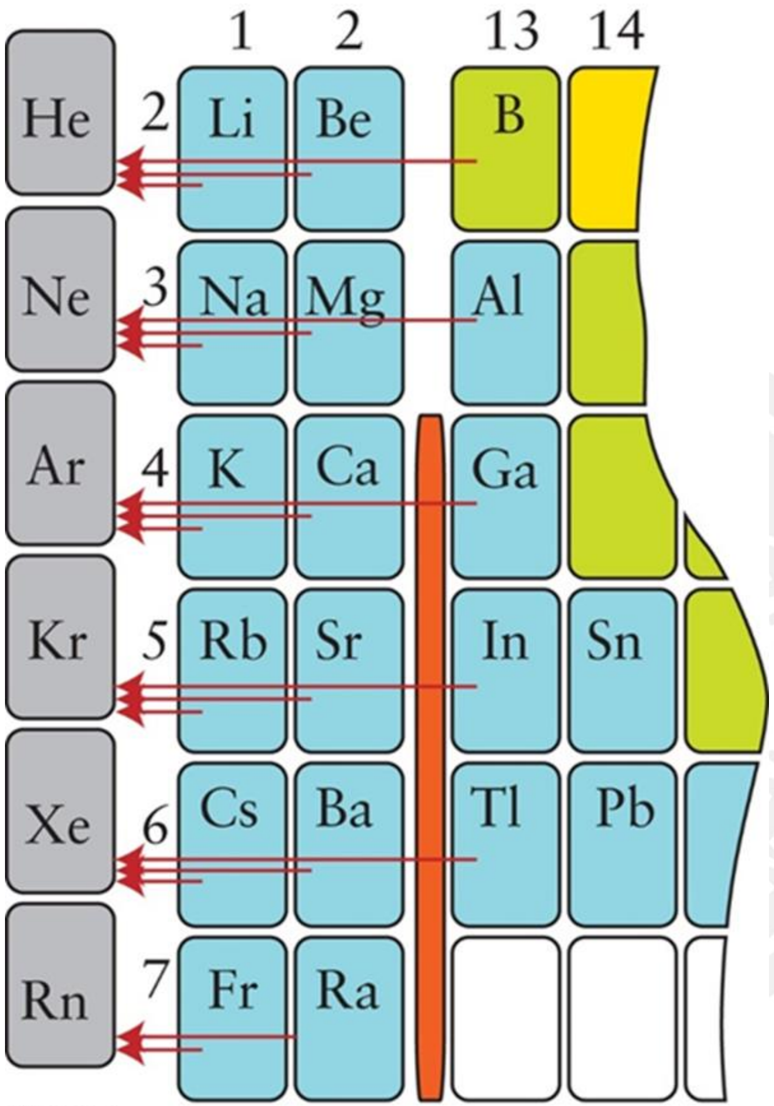

Figure 2A.2
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Metals form cations, by losing electrons to their **noble-gas core** or octet of electrons.

noble-gas core

Ion	Configuration
Li^+	[He] or $1s^2$
Be^{2+}	[He]
Na^+	[Ne] or [He] $2s^22p^6$
Mg^{2+}	[Ne]

Short Quiz

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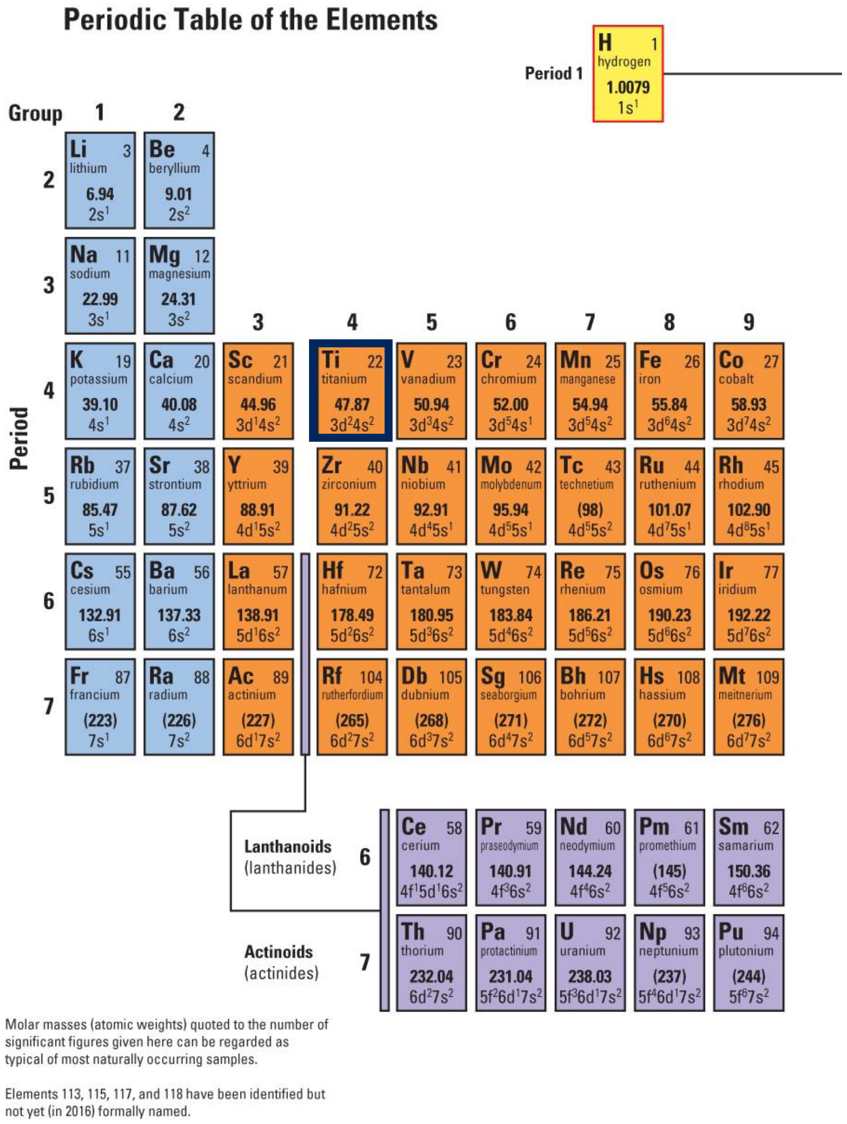
A Group 4 metal will:

A. Lose 2 electrons
B. Lose 4 electrons
C. Gain 4 electrons
D. Gain 14 electrons

Ti [Ar] $3d^{2}4s^{2} \rightarrow \mathrm{Ti}^{4+}$ [Ar]

Valence Electrons lost



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Short Quiz

What would the electron configuration be for V^{5+} (vanadium)?

A. [Ar] $3d^3 4s^2$

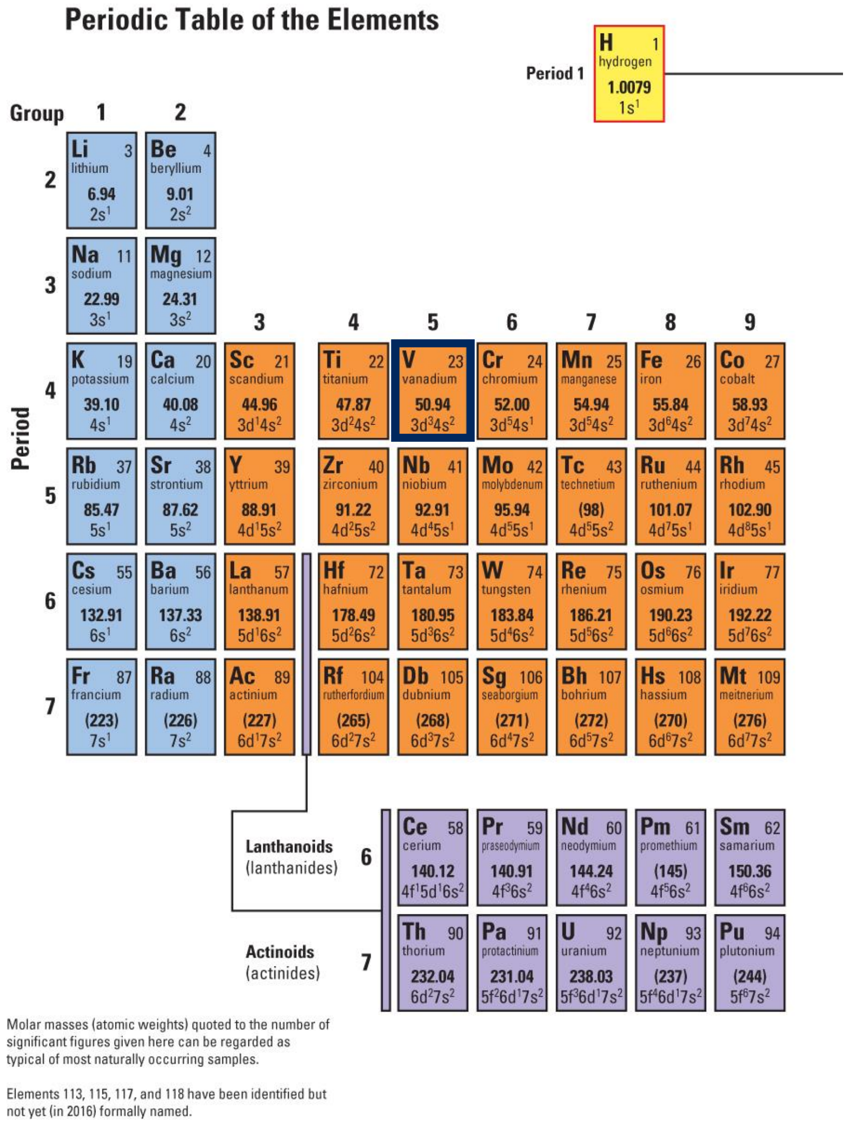
B. [Ar] $4s^2$

C. $\boxed{\text{[Ar]}}$

D. [Ar] $3d^{10} 4s^2 4p^6$

V [Ar] $3d^3 4s^2 \rightarrow V^{5+}$ [Ar]

Valence Electrons lost



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Non-metals

Nonmetals **rarely lose electrons** because their ionization and electron affinity energies are too high.

Instead, nonmetal atoms acquire electrons to fill their outer shell.

N ([He]$2s^22p^3$) + 3 e^- → N^{3-} ([Ne])

noble-gas core

Ion	Configuration
N^{3-}	[Ne] or $2s^22p^6$
O^{2-}	[Ne]
F^-	[Ne]
Cl^-	[Ar] or [Ne] $2s^22p^6$

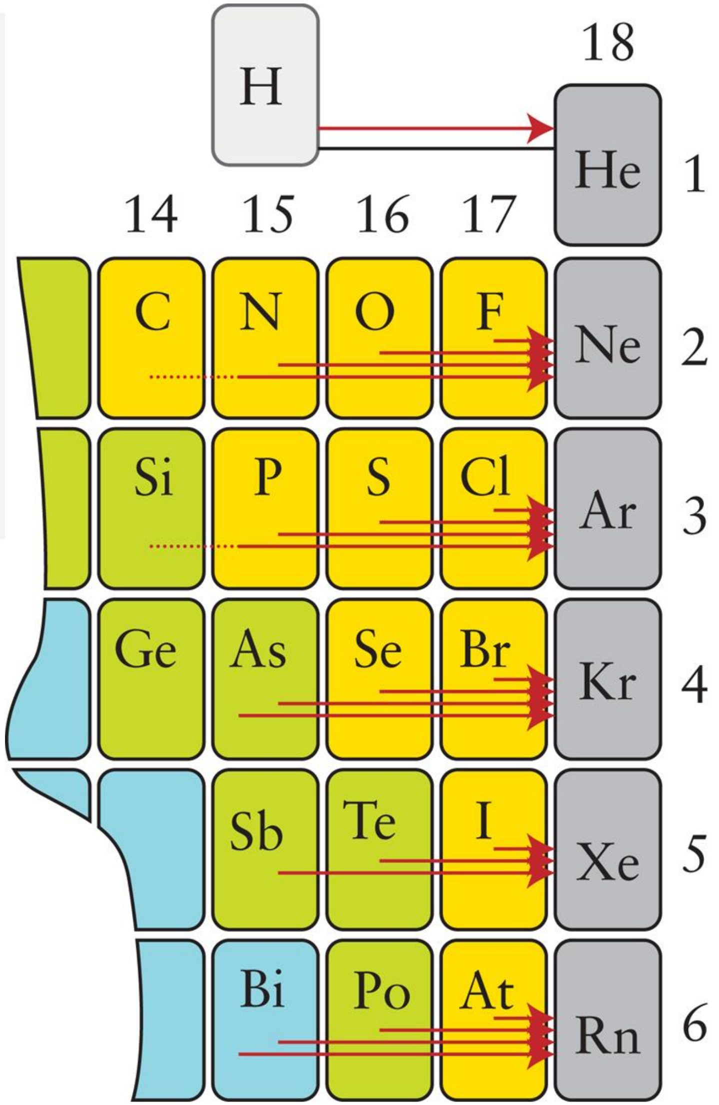

Figure 2A.4
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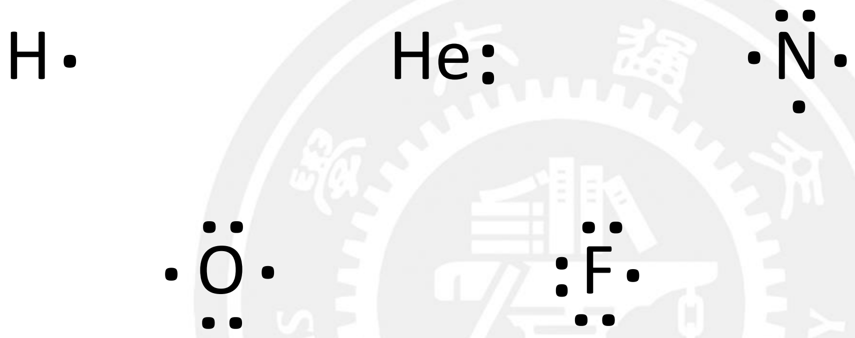
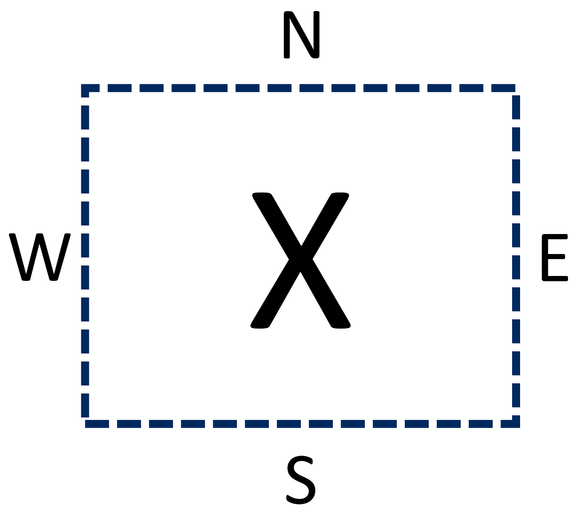
Lewis Dot Notation

A **single dot** represents a **valence electron**, the *outermost electron in the last shell*, in the atom.

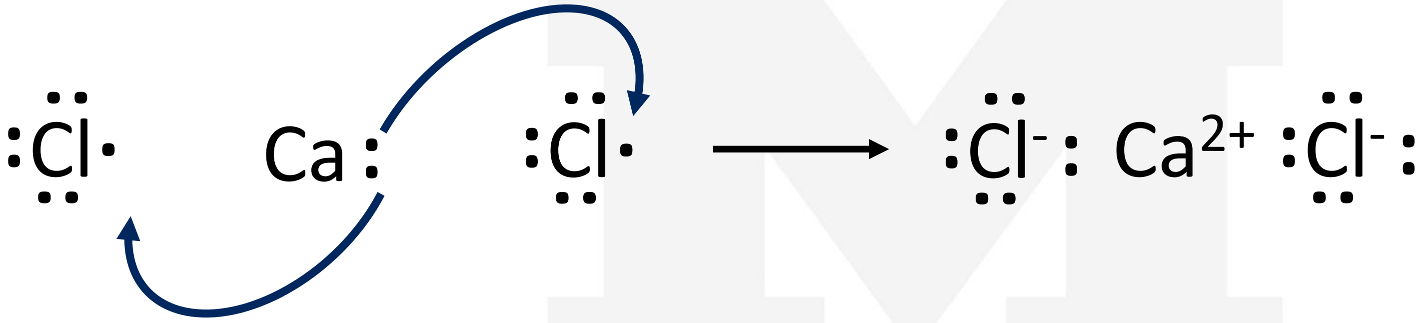


A **pair of dots** represents two paired electrons sharing an orbital.

Each symbol is thought of as having four sides, a north, south, east, and west position, where valance electrons are shown as dots.



Lewis Dot Notation



An ionic formula starts by removing valance electrons from the metal and transferring them to the nonmetal atom to complete its valence shell.

The **calcium** atom loses its two valence electrons.

Each **chlorine** atom has a vacancy for one electron, therefore it forms one bond.

Lewis Dot Notation

$:\ddot{\underset{\cdot\cdot}{Cl}}^{-}:\ Ca^{2+}\ :\ddot{\underset{\cdot\cdot}{Cl}}^{-}:$

Two chloride ions (Cl^-) ***balances the charge*** for **each** calcium ion (Ca^{2+}) resulting in the formula $CaCl_2$; the overall charge is zero.

There are **no** $CaCl_2$ molecules, only **crystals** of three-dimensional arrays of Ca^{2+} and Cl^- ions held by the vast array of opposite charges spread throughout the crystal—hence $CaCl_2$ is called a formula unit.

Crystal Formation

Crystal formation starts when large numbers of oppositely charged ions, **rush** together, releasing large amounts of energy.

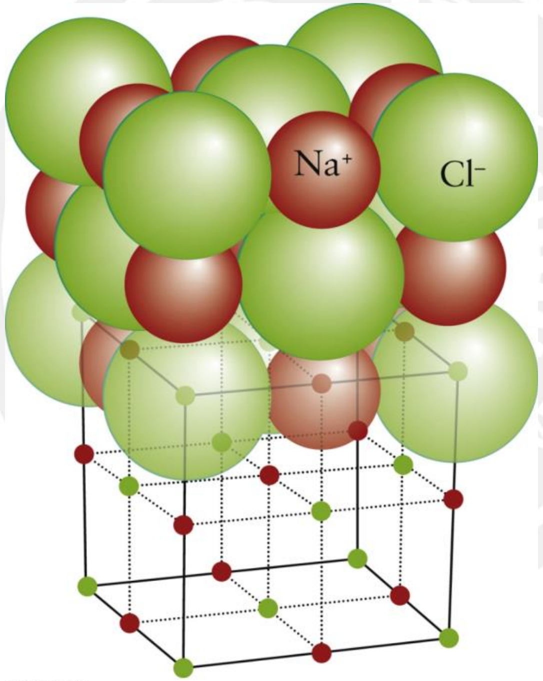


Figure 3H.28
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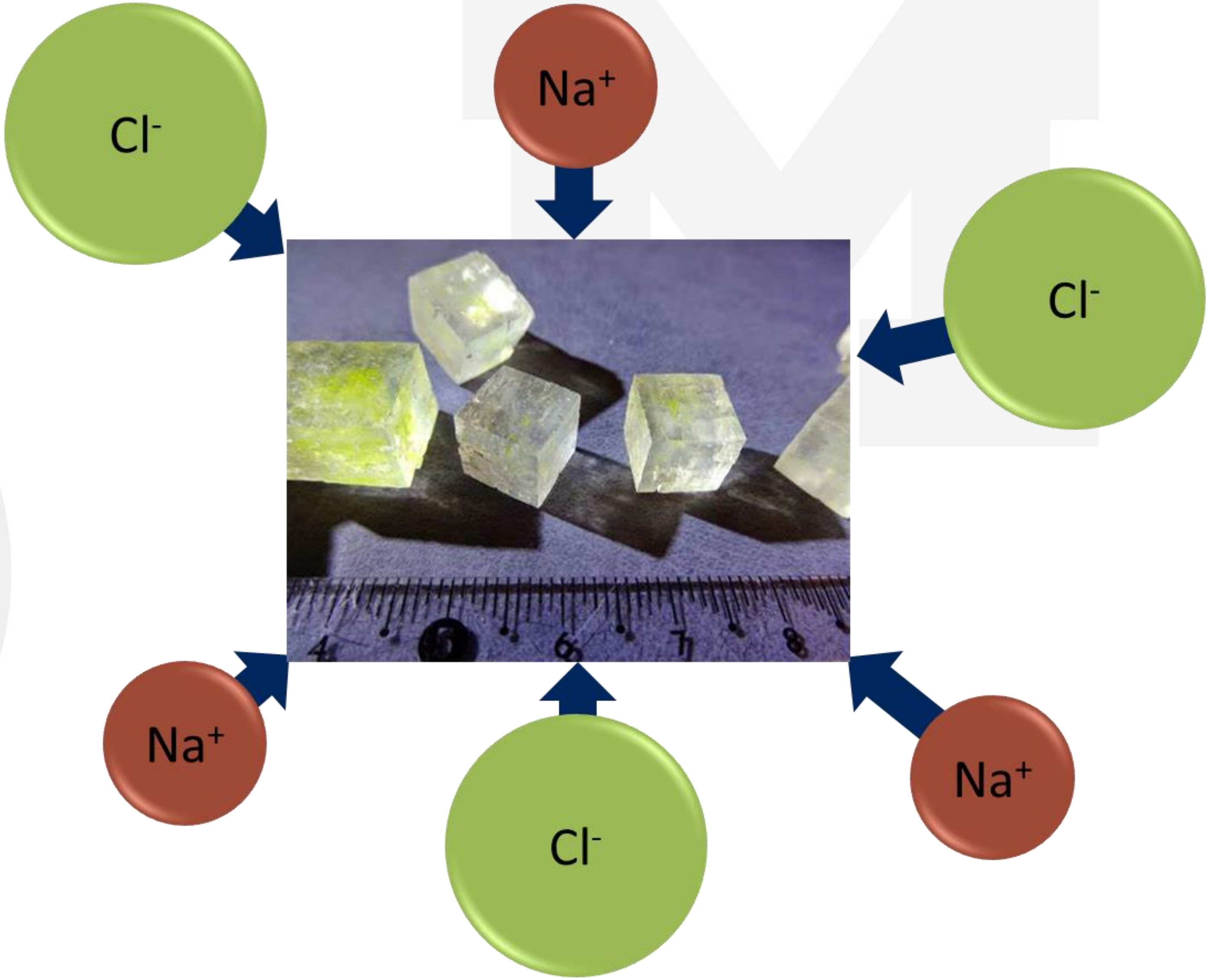

Crystal Formation

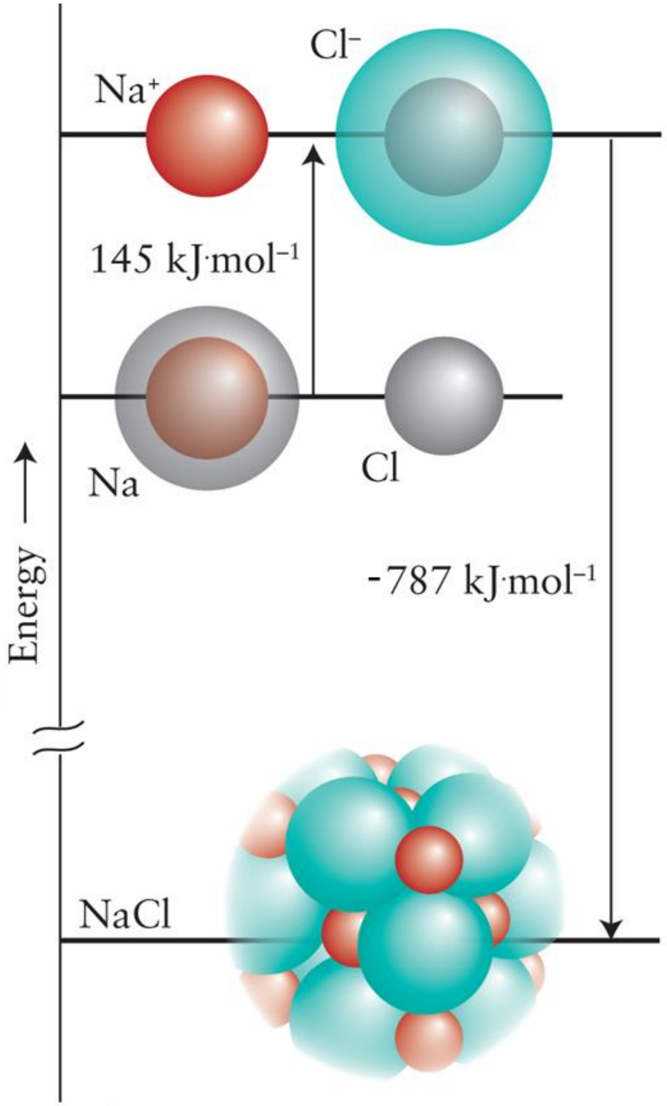

Figure 2A.5
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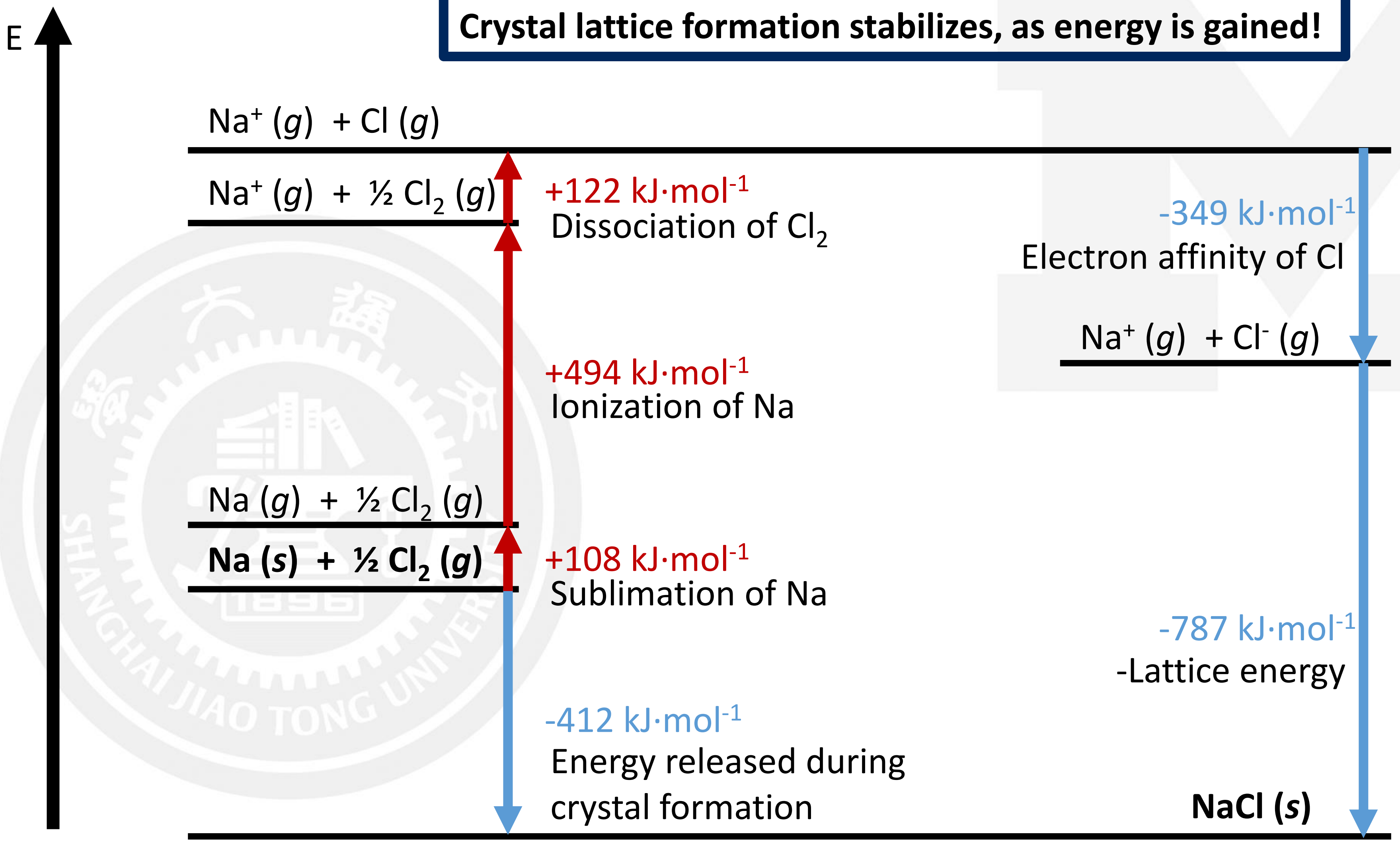
A **crystal** of sodium chloride has lower energy than separated sodium and chlorine atoms.

Formation of the solid takes place in three steps:

1. Sodium atoms release electrons.
2. These electrons attach to chlorine atoms.
3. Newly formed cations and anions clump together as a crystal.

Crystal Lattice Formation: Energy

Crystal lattice formation stabilizes, as energy is gained!



Lattice Energy

Lattice energy is a "**global**" characteristic of the **entire** crystal, a net lowering of energy in the entire crystal (once the cations and anions clump together as a crystal).

A **high lattice energy** value indicates **a stronger ion pair**, which produces a more tightly bonded solid.

Coulomb's potential energy measures the strength between individual ion pairs.

Note: Lattice energies describe the dispersion of a crystal into gaseous ions and are therefore **always positive**.

	Lattice energy / kJ·mol^{-1}
LiI	759
NaI	700
KI	645
RbI	632
CsI	601

Short Quiz

Which of the following compounds would be expected to have the strongest ionic bonds?

A. KI

B. NaI

C. CsF

D. LiF

Smaller ions have higher effective nuclear charges and are therefore bound together more tightly, which produces **higher lattice energies**.

	Lattice energy / kJ·mol^{-1}
LiI	759
NaI	700
KI	645
RbI	632
CsI	601

Macroscopic Consequences

The **strong attraction** (Coulomb's potential energy) between oppositely charged ions accounts for the typical properties of ionic solids:

- **high melting points** and
- **brittleness**.

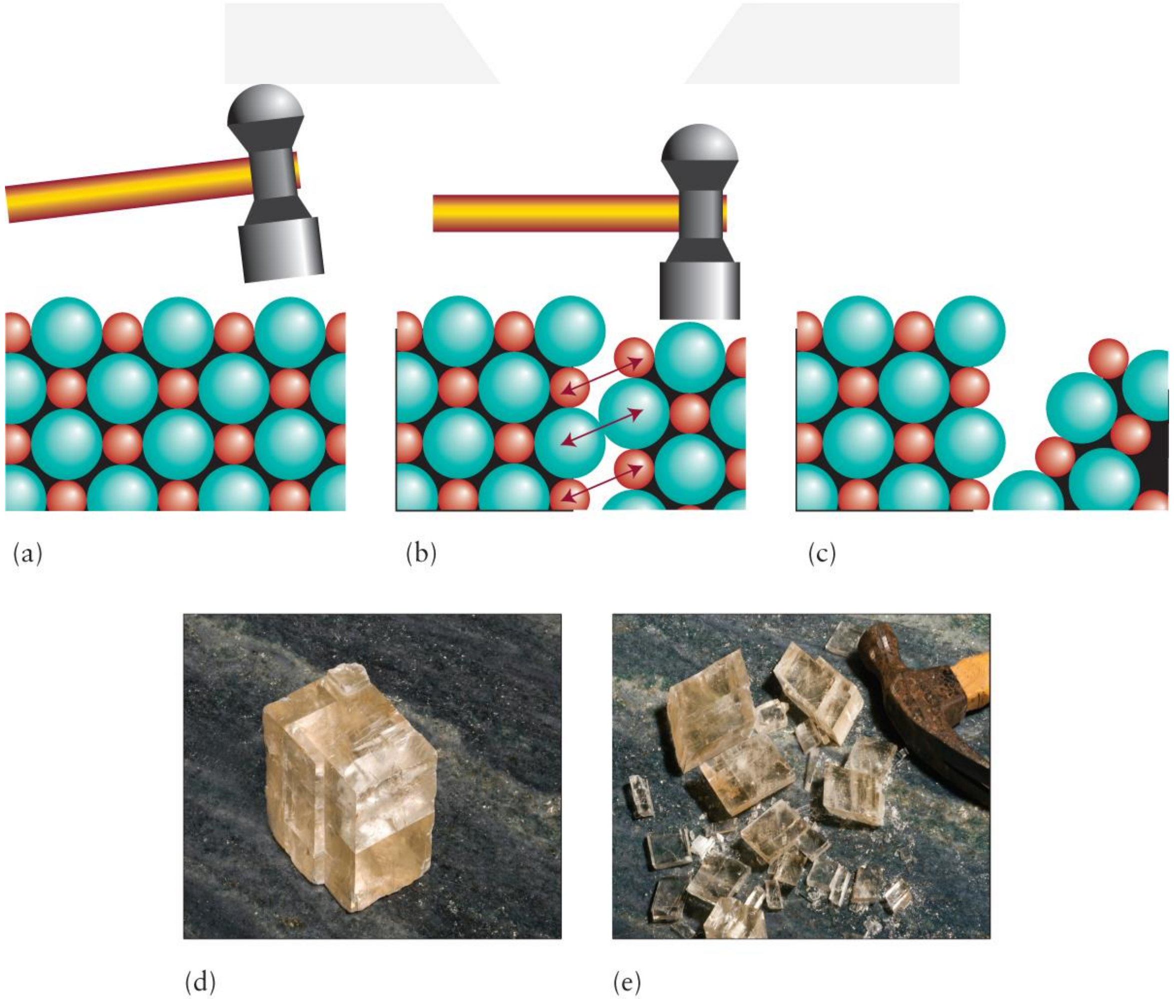


Figure 2A.6
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Coulomb Interactions

Measure of the ion–ion force

$$\boxed{E_{P,12} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 d_{12}}}$$

- e is the fundamental charge (the absolute value of the charge of an electron)
- z_1 and z_2 are the charge numbers of the two ions, e.g., +2,+ 1, -1…
- d_{12} is the distance between the centers of the ions
- ε_0 is the vacuum permittivity

As ***d***↑ ***E***↓

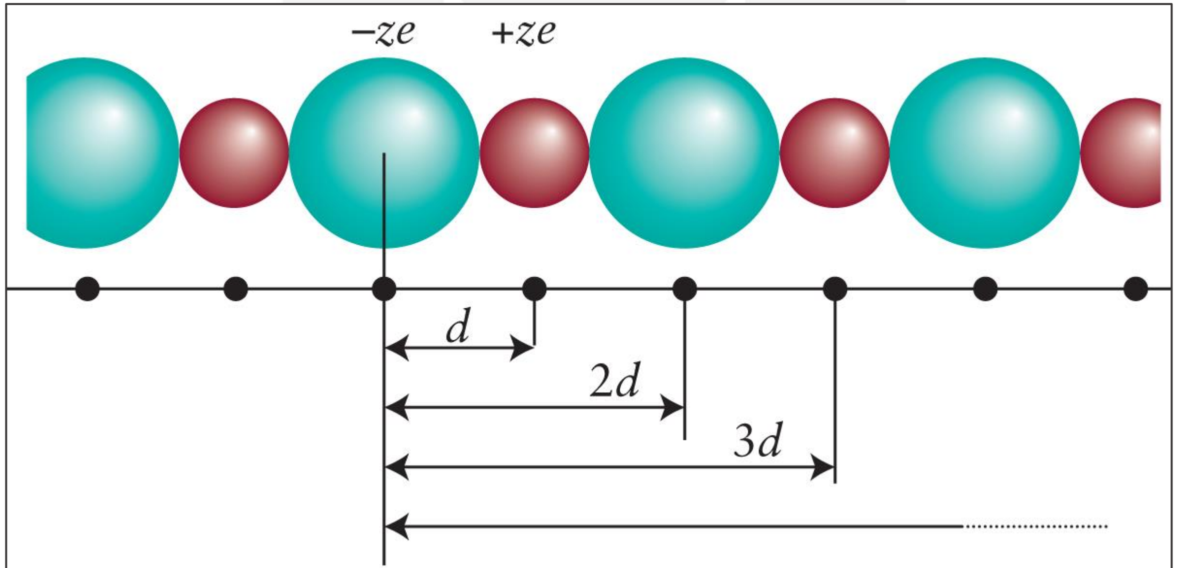

Figure 2A.7
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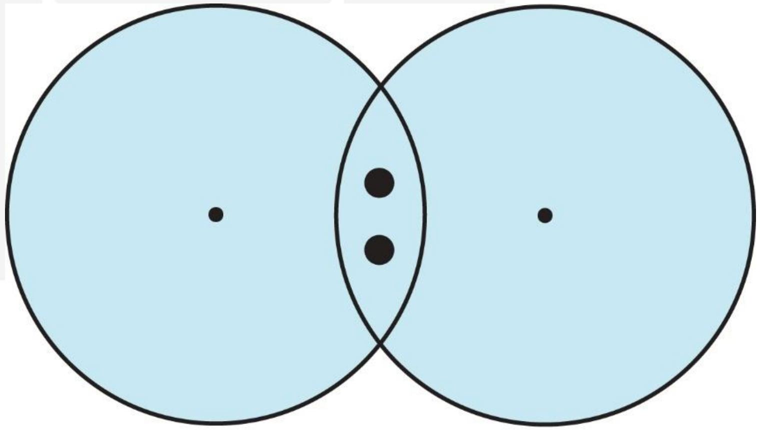
Covalent Bonds

Covalent bonds form between **two non-metals** that **do not form ions**.

The nature of nonmetal bonds *puzzled* scientists until 1916, when **G. N. Lewis** published his explanation.

A brilliant insight, before anyone knew anything about quantum mechanics



1 Shared electron pair

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Lewis' Octet Rule

Lewis called this principle the **octet rule**, reaching a ***noble-gas configuration.***

Ionic bonds form when one element **loses** electrons and the other atom **gains** electrons, until both atoms reach a ***noble-gas configuration***.

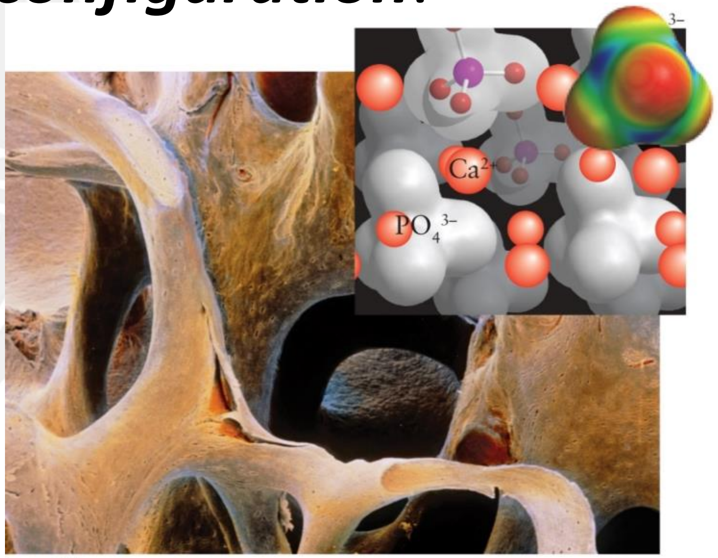
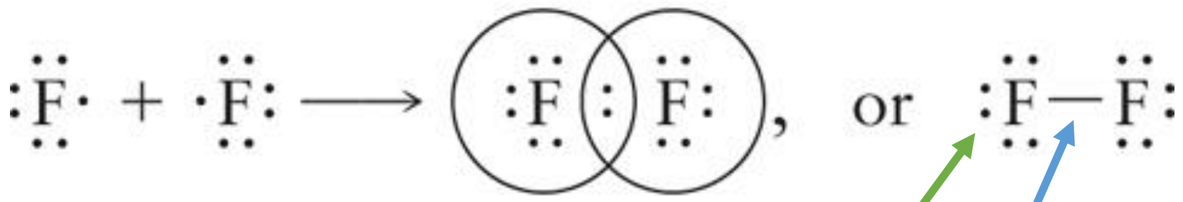


Figure 2A.8
Atkins, *Chemical Principles: The Quest for Insight*, 7e
Prof. P. Motta/Science Source

Covalent bonds form by atoms **sharing** electrons until they reach a ***noble-gas configuration***.

Covalent Bonds

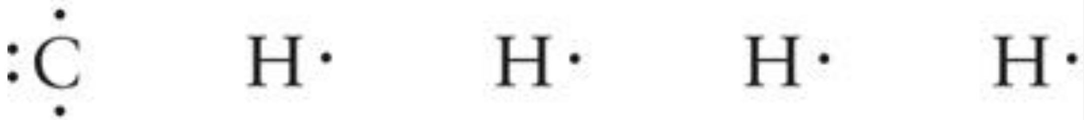
A fluorine atom can achieve an octet by accepting a share in an electron from another fluorine atom.



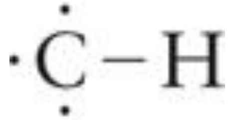
The **octet** (or duplet) shows **lines** (bonding pairs) and **dots** (lone pairs).

Methane CH_4

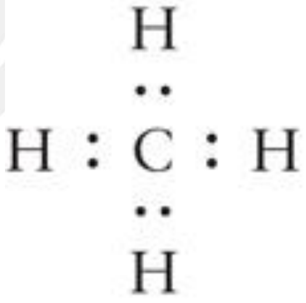
The Lewis dot symbols for carbon and hydrogen:

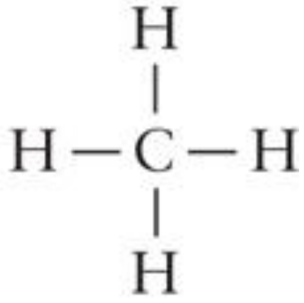


The first element is the central atom. Arrange other atoms in a North, South, West, and East position.



Because the carbon atom is linked by four bonds, the carbon is *tetravalent*: It has a valence of 4.

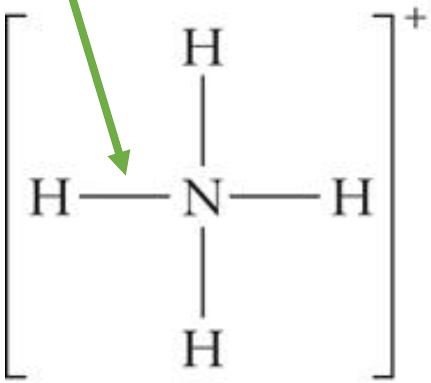




Lewis Dot Structures

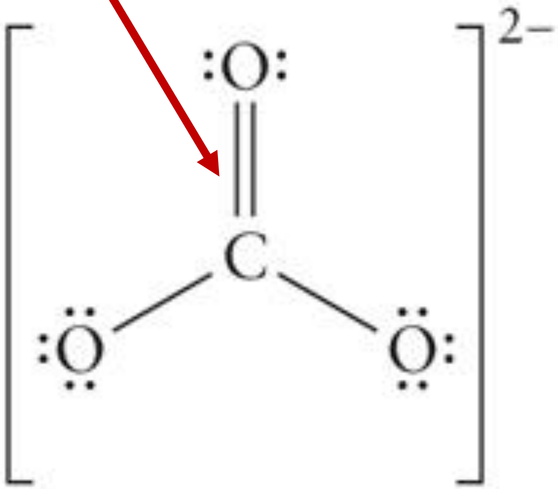
Single bonds

represents two electrons



Double bonds

represents four electrons

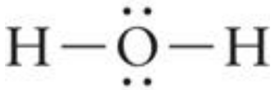
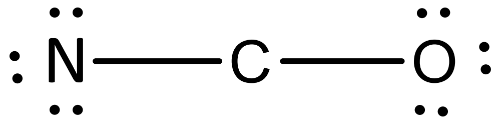
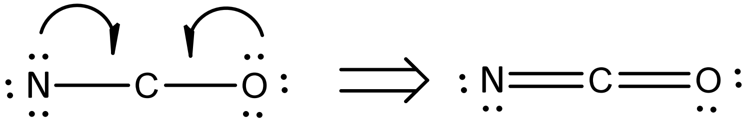
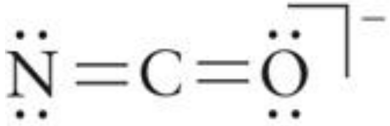


Triple Bonds

represents six electrons

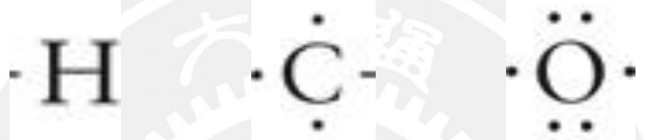
Lone pair

Example: Lewis Dot Structures

	H_2O	Cyanate CNO^-
Step 1: Count valence electrons, adjust for charge of ions	$1 + 1 + 6 = 8$ H + H + O	$4 + 5 + 6 + 1 = 16$ C + N + O + e^-
Step 2: Arrange atoms, the first atom is typically the central atom, except hydrogen	H O H	N C O
Step 3: Connect atoms with bonds	H — O — H	N — C — O
Step 4: Electrons on the outside first		
Step 5: Complete octet		
Step 6: Add charge if needed		

Helpful Hints

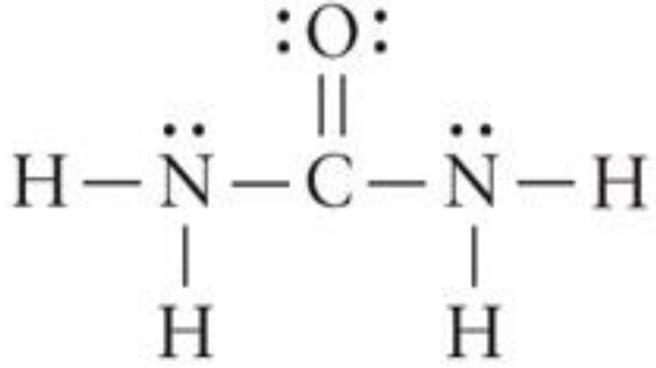
1. Remember **simple** Lewis dot structures



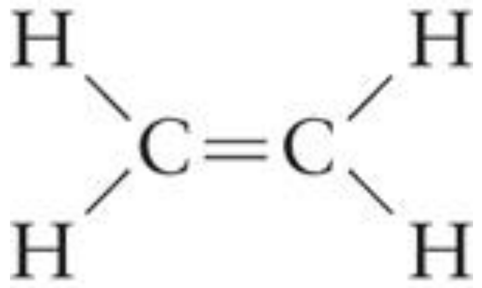
one bond, four bonds, two bonds to complete their octet

2. Molecules have **symmetry**

Urea, $(NH_2)_2CO$



C_2H_4

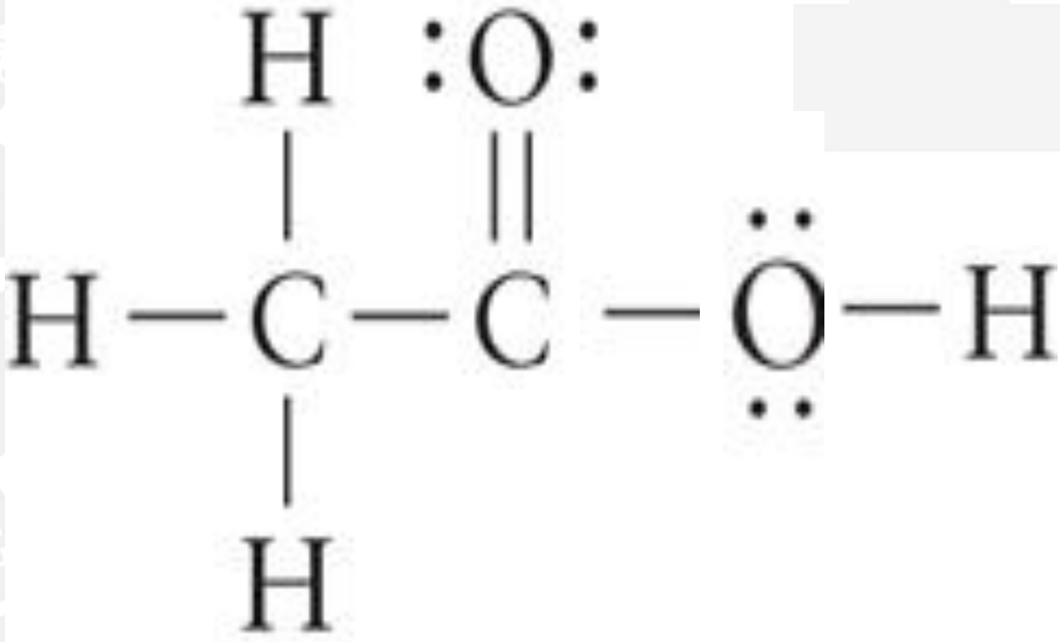


Helpful Hints

3. Read the formula for order of atom attachment

Acetic acid

$$CH_3COOH$$



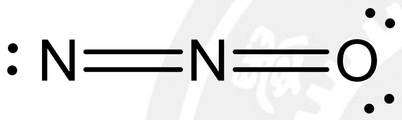
Short Quiz

Which of the following is the correct Lewis structure for N_2O?

N: 5 VE × 2 = 10

O: 6 VE = 6

total 16 VE



A.

Only 14 VE

B.

C.

Exceeds the Octet

D.

Exceeds the Octet

Example: Lewis Dot Structures

NO_3^-

Step 1: Count valence electrons, adjust for charge of ions

$5 + 3(6) + 1 = 24$

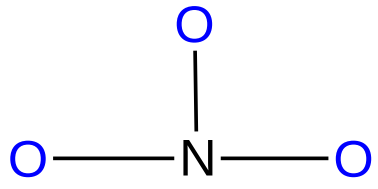
$N + 3(O) + e^-$

Step 2: Arrange atoms, the first atom is typically the central atom, except hydrogen

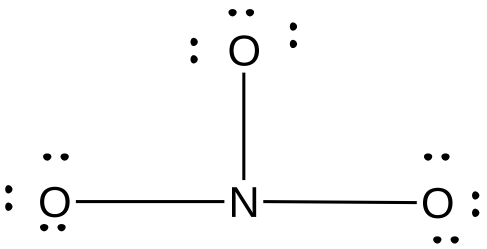
O

O N O

Step 3: Connect atoms with bonds

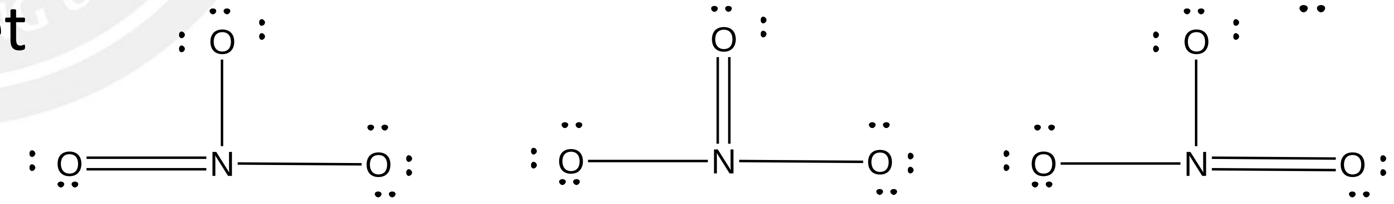


Step 4: Electrons on the outside first



Step 5: Complete octet

Step 6: Add charge if needed



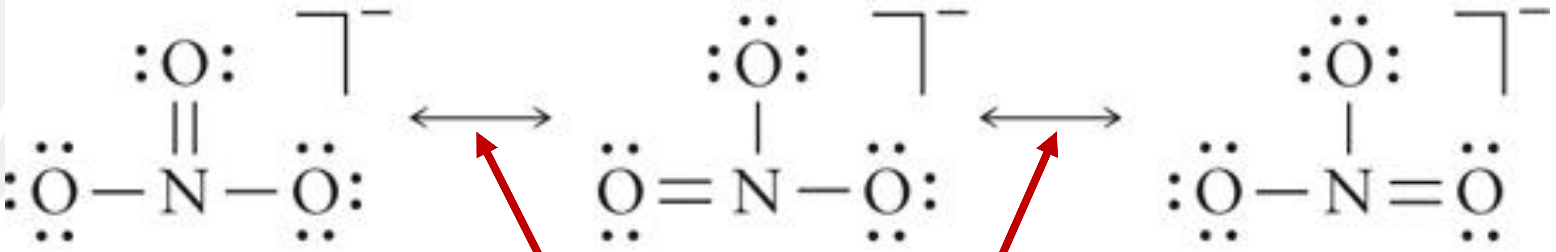
which one should we use?

Resonance Structures

Delocalized electrons ***hop*** from one atom to another; no discretion as long as it's the *same atom pair*.

Nitrate ion, NO_3^-

Resonance Structures



Resonance arrows

Formal Charge

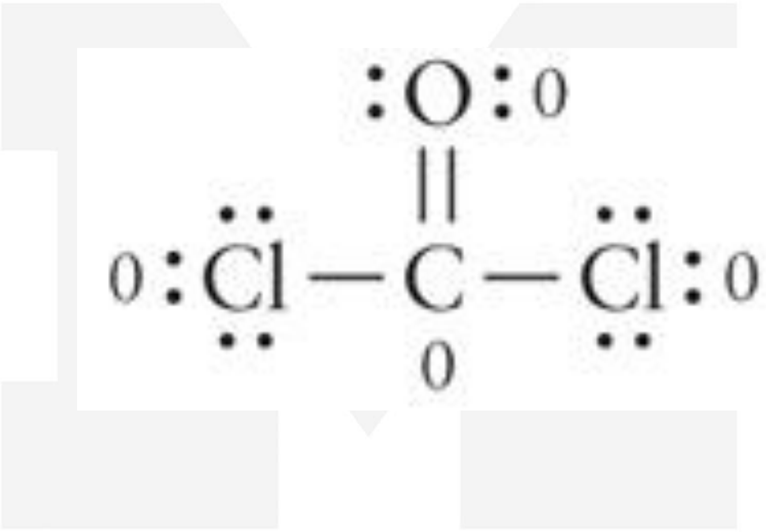
$$Formal\ Charge = V - \left(L + \frac{1}{2}B\right)$$

Valence electrons

Lone-pair electrons

Bonding electrons

The sum of formal charges is equal to the overall charge of the molecule or ion; electrically neutral molecules have a formal charge of zero.



O 6 - (4 + ½ 4) = 0

Cl 7 - (6 + ½ 2) = 0

C 4 - (0 + ½ 8) = 0

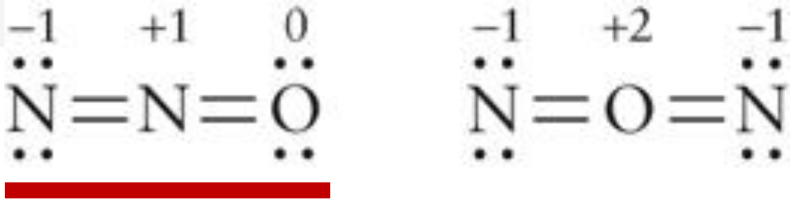
Formal Charge Calculations

$$Formal\ Charge = V - \left(L + \frac{1}{2}B\right)$$

Formal charges can predict the most *favourable* Lewis structure:

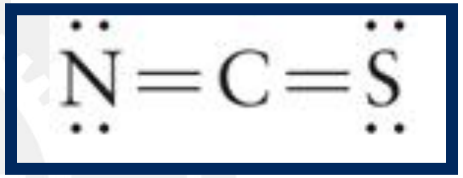
The structure with the lowest formal charges (absolute value) on each atom is the most favourable (lowest energy) structure.

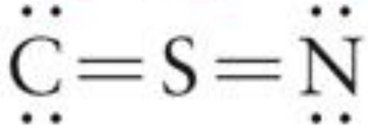
NNO



Short Quiz

Predict the most *favourable* Lewis structure for CNS^-:





A.

B.

Exceptions to the Octet Rule

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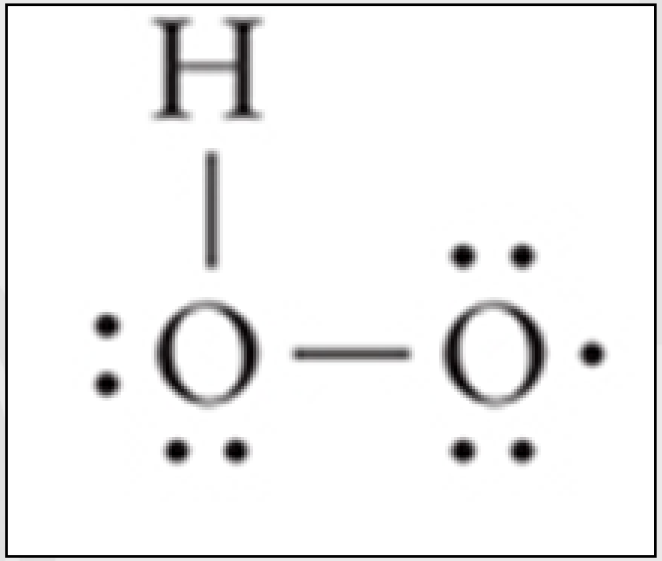
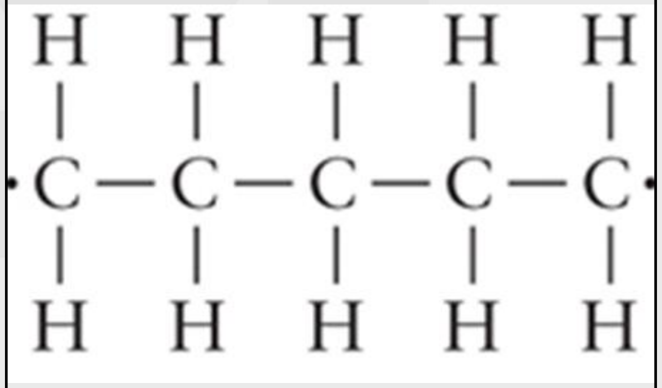
Radicals are something you cannot isolate, are very unstable, and are highly reactive.



Hydrogenperoxyl, $HO_2\cdot$



A biradical

Piranha Solution

- Mixture of H_2SO_4 and H_2O_2
  - 3:1 H_2SO_4 conc. and 30 wt% H_2O_2
  - Add H_2O_2 to acid very slowly, never in reverse order!
  - Mixing is extremely exothermic
  - Prone to explosions
    (*T* too high, $c_{H_2O_2}$ too high, too much contaminant)
- Strong oxidizing agent
  - Will decompose most organic matter
  - Will hydroxylate most surfaces (adding OH groups)
- Easily dissolves fabric and skin
  - High risk of severe chemical burns

https://en.wikipedia.org/wiki/Piranha_solution
https://www.youtube.com/watch?v=CTVd_WxblGI

Exceptions to the Octet Rule

Dissociation of PCl_5

$$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$$

Carbon, **nitrogen**, **oxygen**, and **fluorine** **obey the octet rule rigorously**. *Period 3* and subsequent periods can accommodate *more than 8 electrons* in its valence shell, up to **18 electrons**.

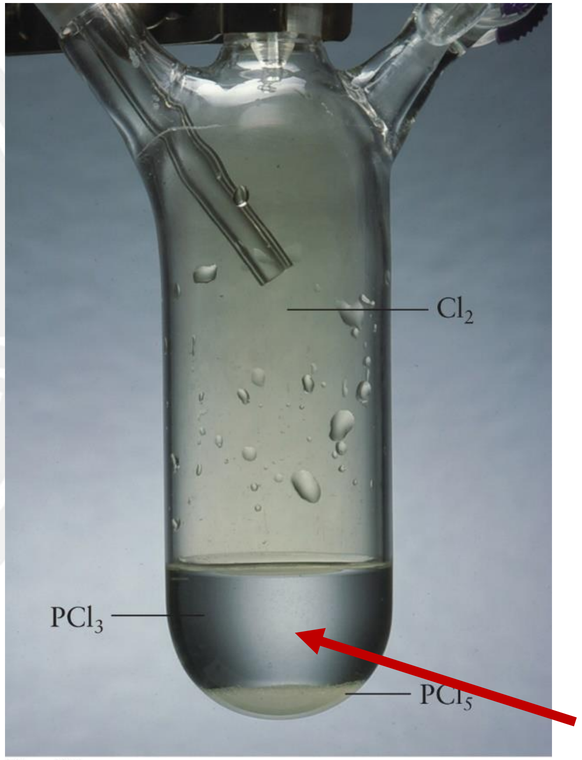
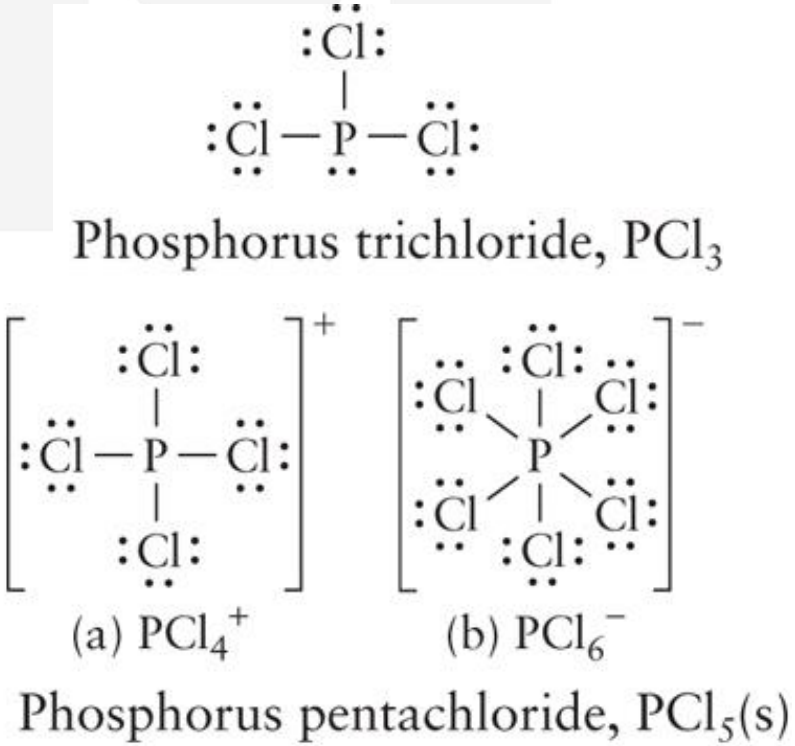


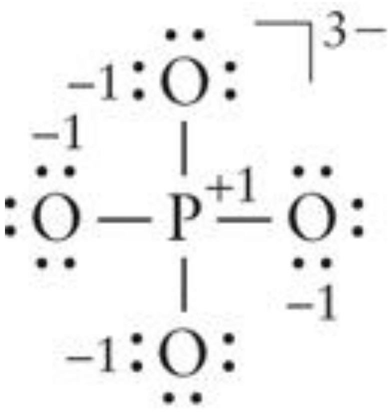
Figure 2C.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman photo by Ken Karp

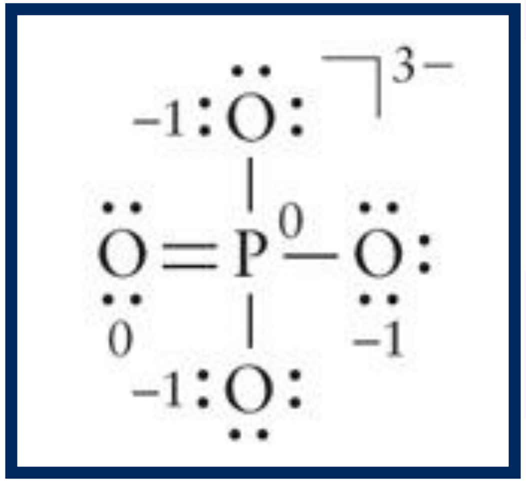
PCl_5

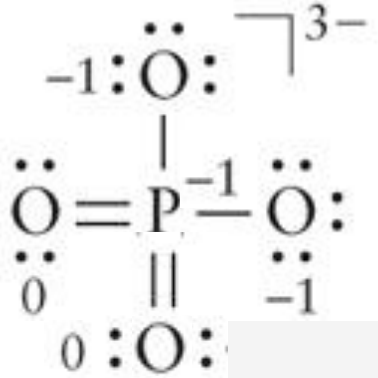


Exceptions to the Octet Rule

Determine the most stable structure







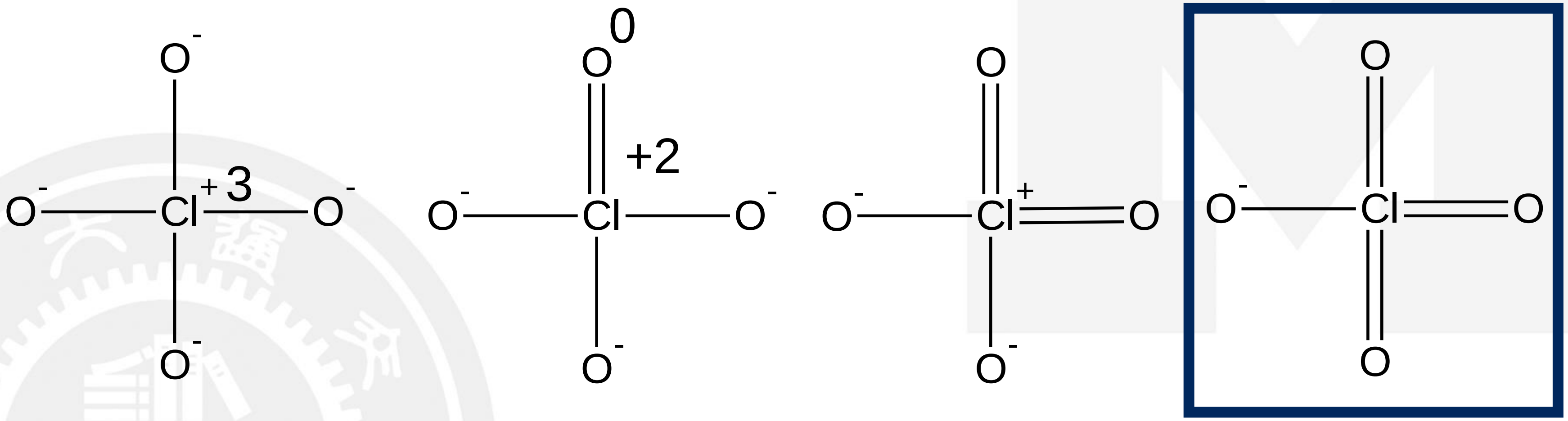
P: $5 - (0 + ½×8) = +1$
O: $6 - (6 + ½×1) = -1$

P: $5 - (0 + ½×10) = 0$
O: $6 - (4 + ½×4) = 0$
O: $6 - (6 + ½×1) = -1$

P: $5 - (0 + ½×12) = -1$
O: $6 - (4 + ½×4) = 0$
O: $6 - (6 + ½×1) = -1$

Exceptions to the Octet Rule

ClO_4^- (VE 7+24+1=32)



Cl: 7-4=+3

O: 6-7= (-1)4

net -1

All atoms have a charge

Cl: 7-5=+2

O: 6-6=0

O: 6-7= (-1)3

net: -1

High charge for Cl

Cl: 7-6=+1

O: 6-6=0

O: 6-7= (-1)2

net -1

Charge for Cl and O

Cl: 7-7=0

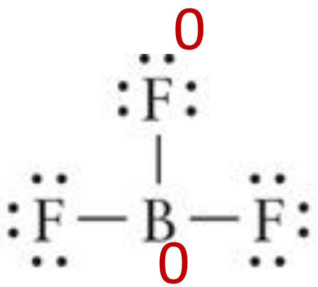
O:6-6=0

O: 6-7= -1

net -1

Short Quiz

Which is the correct Lewis structure for BF_3?

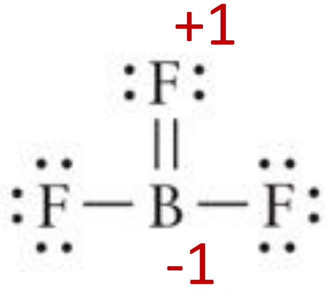


Boron trifluoride, BF_3

A.

F: $7 - (6 + \frac{1}{2}\,2) = 0$

B: $3 - (0 + \frac{1}{2}\,6) = 0$



Boron trifluoride, BF_3

B.

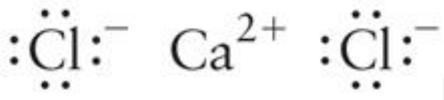
F: $7 - (4 + \frac{1}{2}\,4) = +1$

B: $3 - (0 + \frac{1}{2}\,8) = -1$

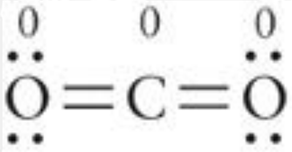
C. Neither of these

Ionic or Covalent?

Ionic and covalent bonding are **two extreme bonding models**. Most bonds lie somewhere between purely ionic and purely covalent.

Ionic 

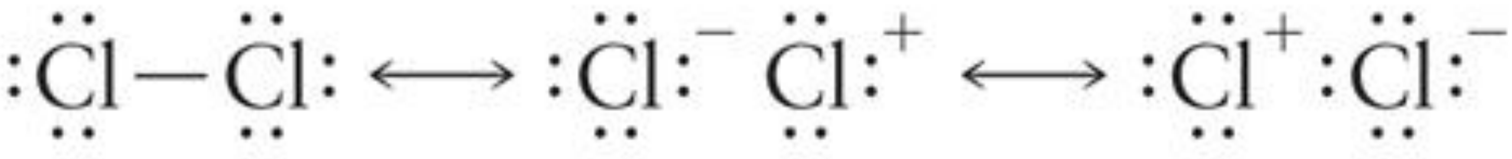
Bonds between a metal and non-metal are present in ionic compounds.

Covalent 

In bonds between non-metals, covalent bonding is a good model.

Can we describe these bonds more accurately by improving the two basic models?

Correcting the Covalent Model

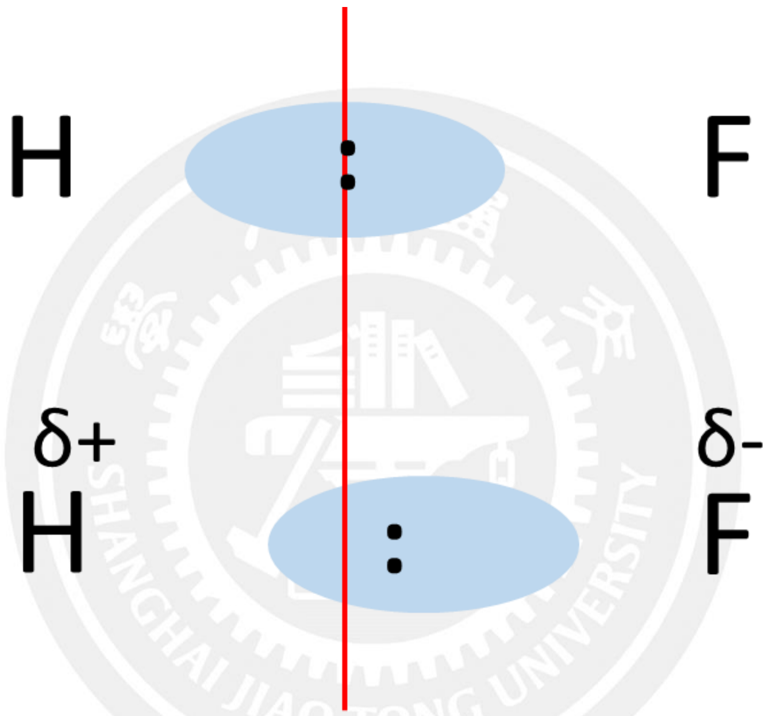


Both ionic structures **have the same** resonance hybrid energy.

Heterodiatomic molecules **do not** have the same **resonance** hybrid energy.

Experiments show a small net negative charge on the Cl atom and positive on the H. This is a limitation of formal charge which estimates a net zero charge.

Electronegativity



Linus Pauling proposed a quantitative **electron-pulling power ability** of an atom in a molecule, called its **electronegativity** *χ*.

Red line shows pure (top) *versus* actual (bottom) offset **electron cloud distribution** due to an atom with a greater electronegativity.

Electronegativity Values

If an atom gives up an electron reluctantly it has **high ionization energy**, and if the electron attaches favourably, it has **high electron affinity**.

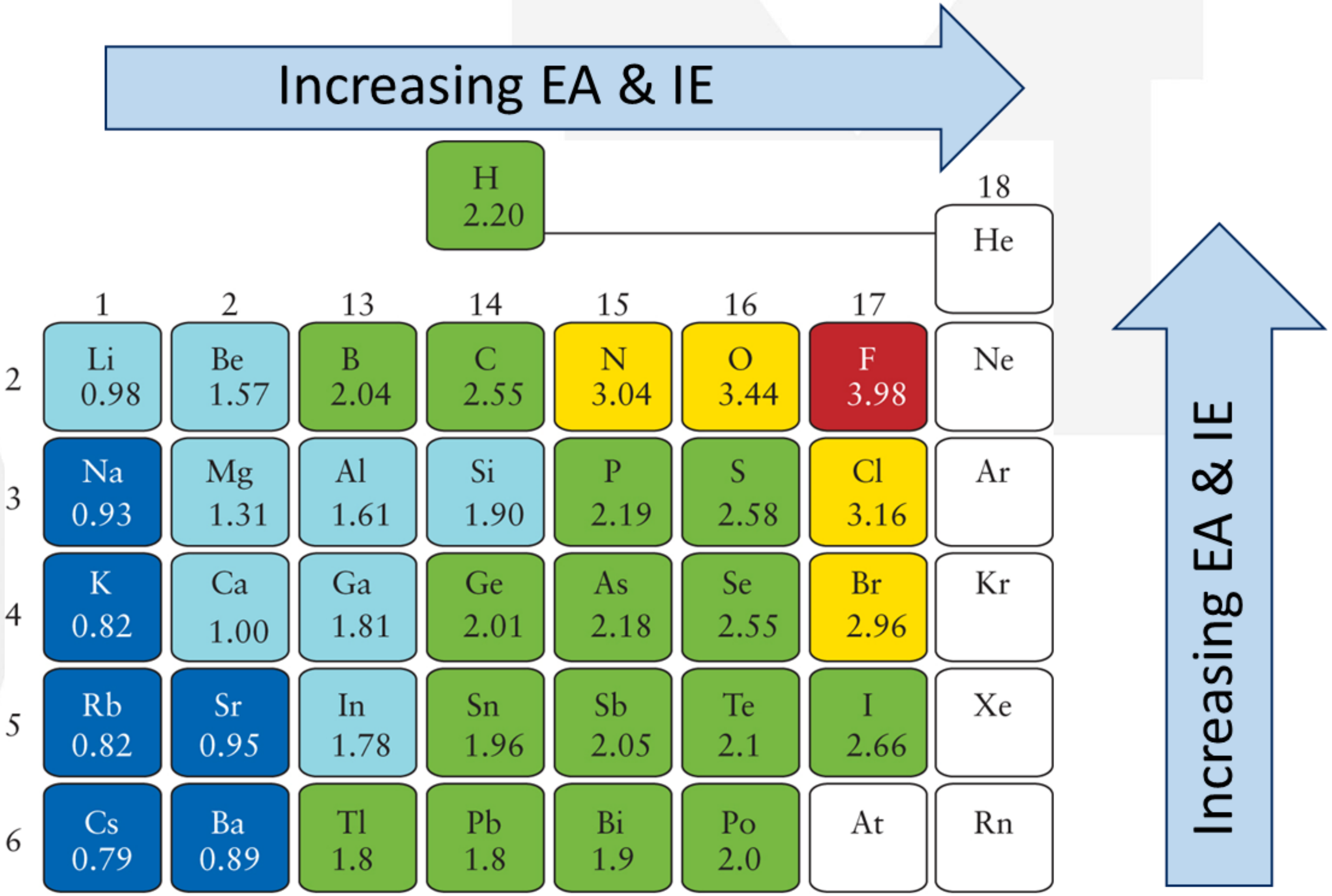


Figure 2D.2
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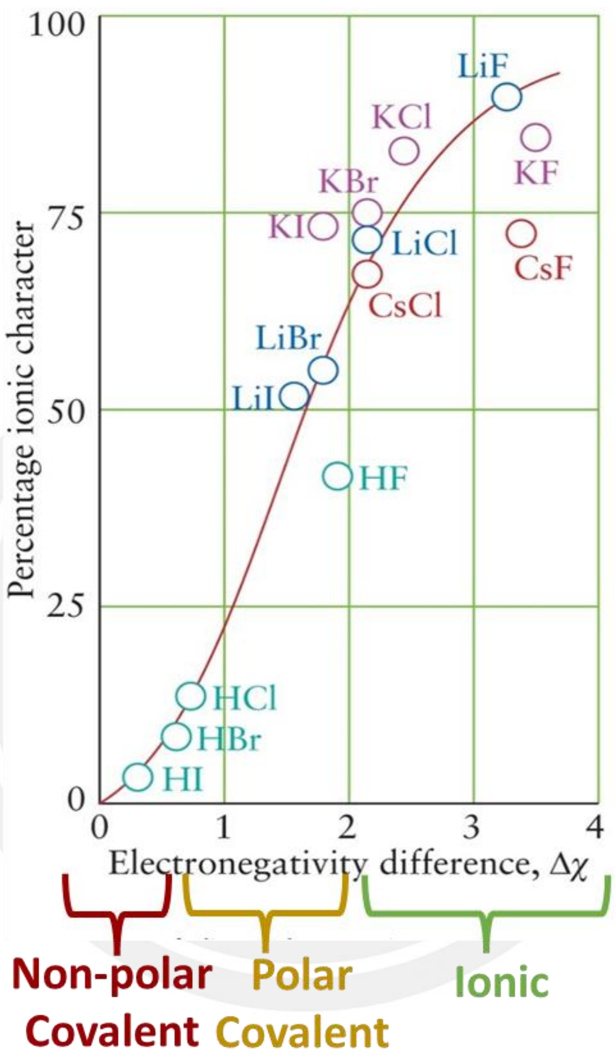
Electronegativity Difference, Δχ



Li-F

$|0.98 - 3.98| = 3.00$

H-Cl

$|2.20 - 3.16| = 0.96$

Polarization

Polarization by small, highly charged cations of larger, nearby anions.

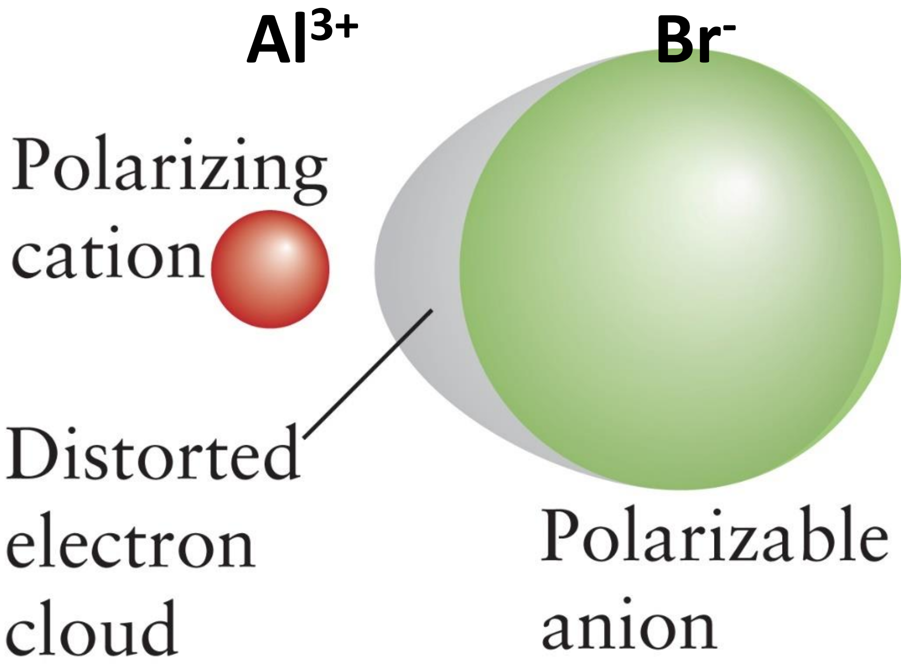


Figure 2D.4
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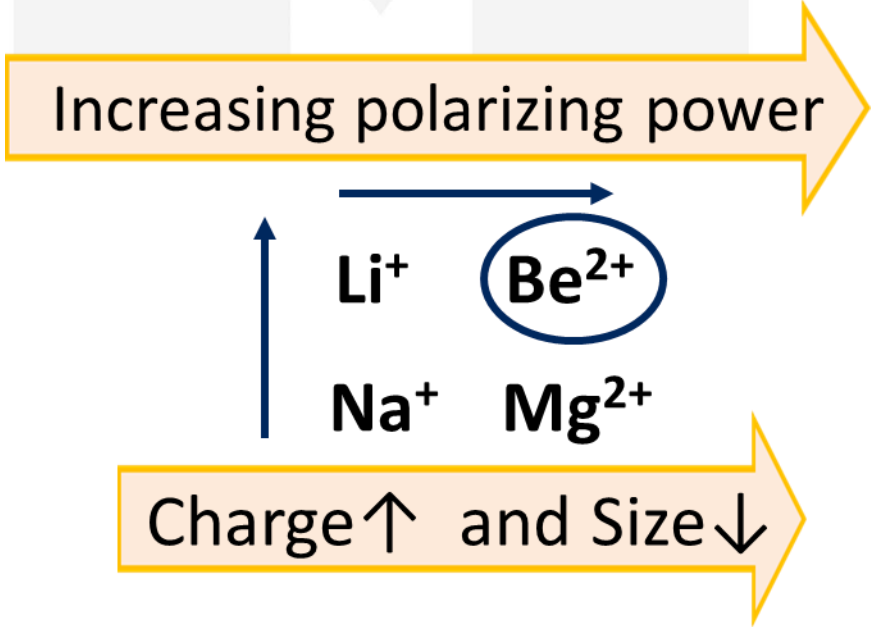

Bond Strength

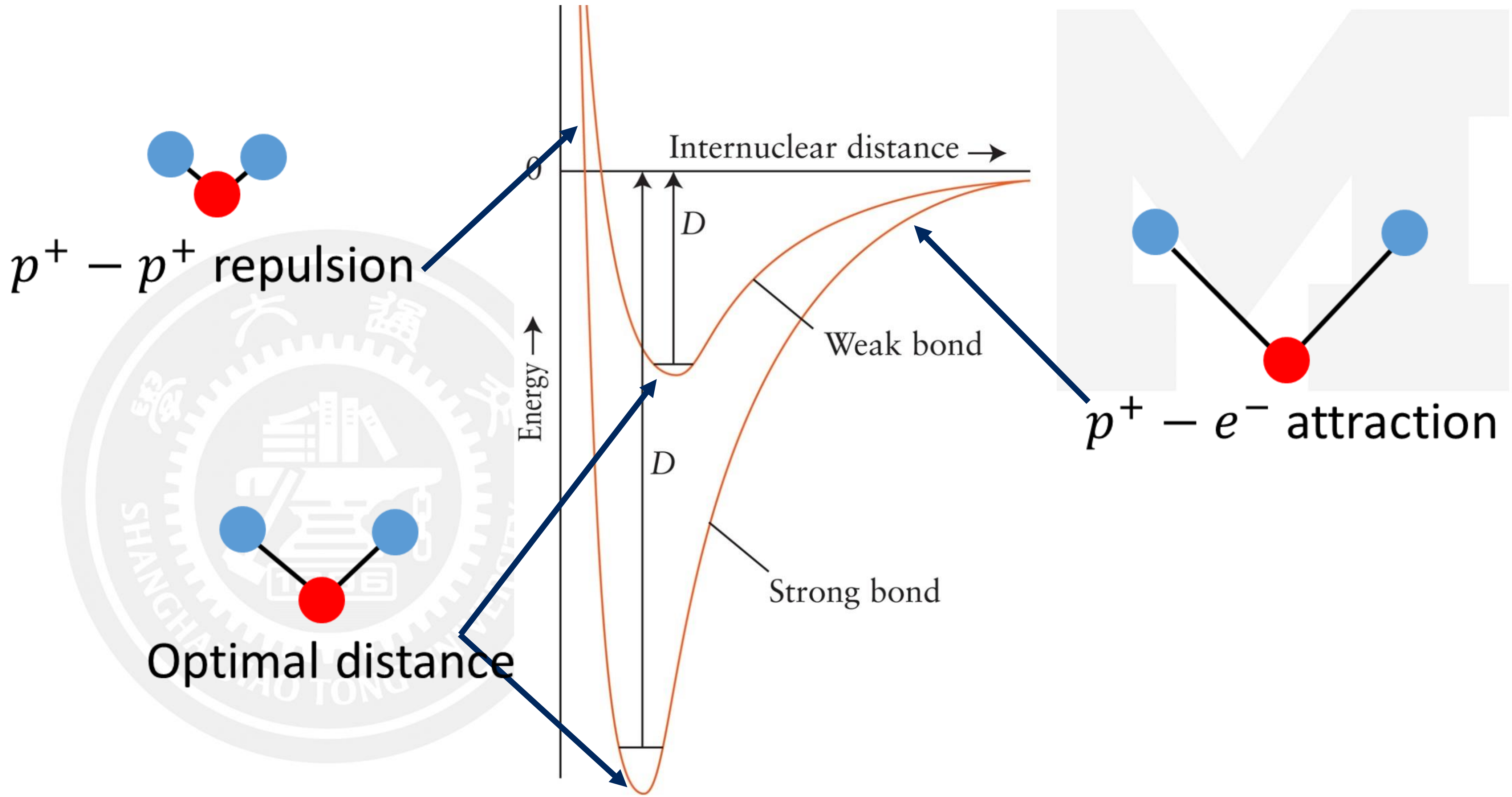

Figure 2D.5
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Bond Energy

Electrons in **double** and **triple bonds** are **not as concentrated (located)** between two atoms as they are in a single bonds.

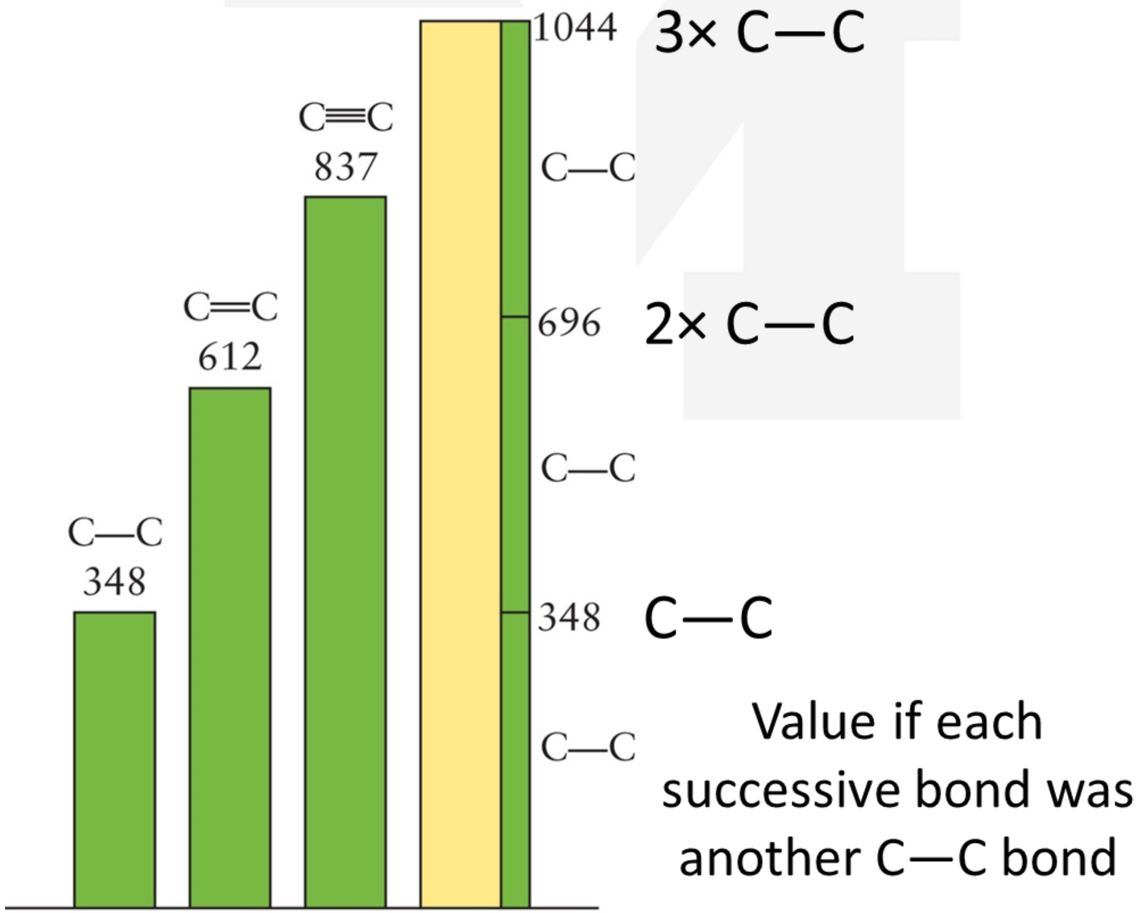

Figure 2D.7
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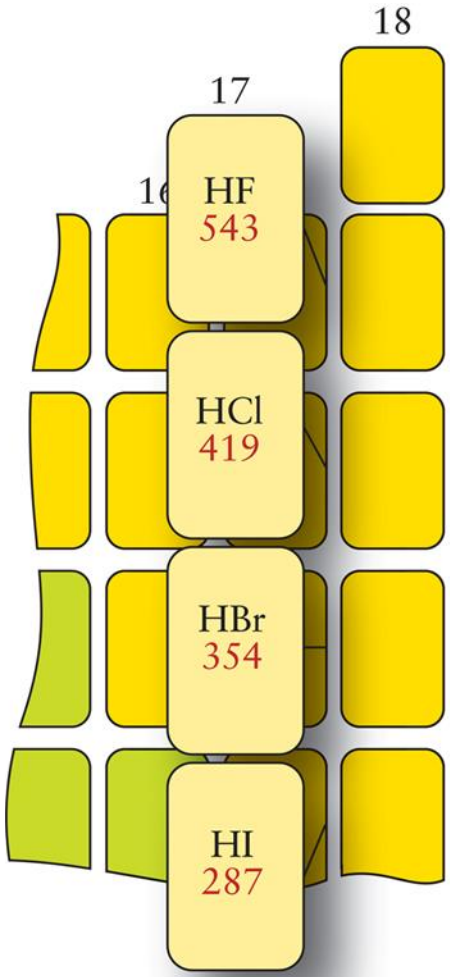
Bond Strength vs. Atomic Radius



Bond Strength / kJ

Figure 2D.8
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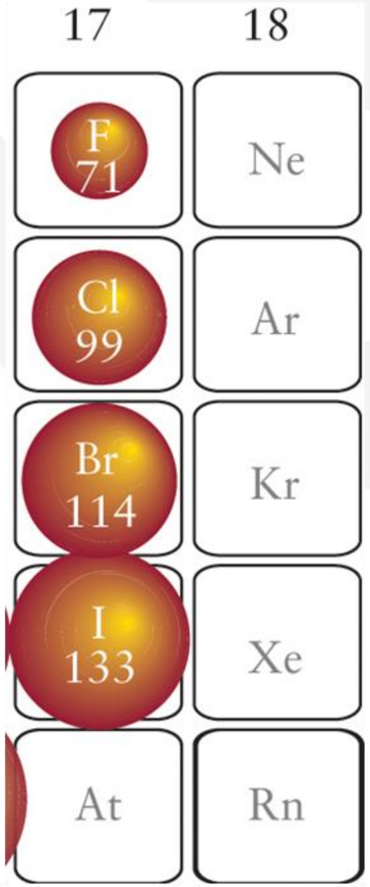
Strength↓ as Size↑



Atomic Radii / pm

Figure 1F.4
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Bond Length vs. Atomic Radius

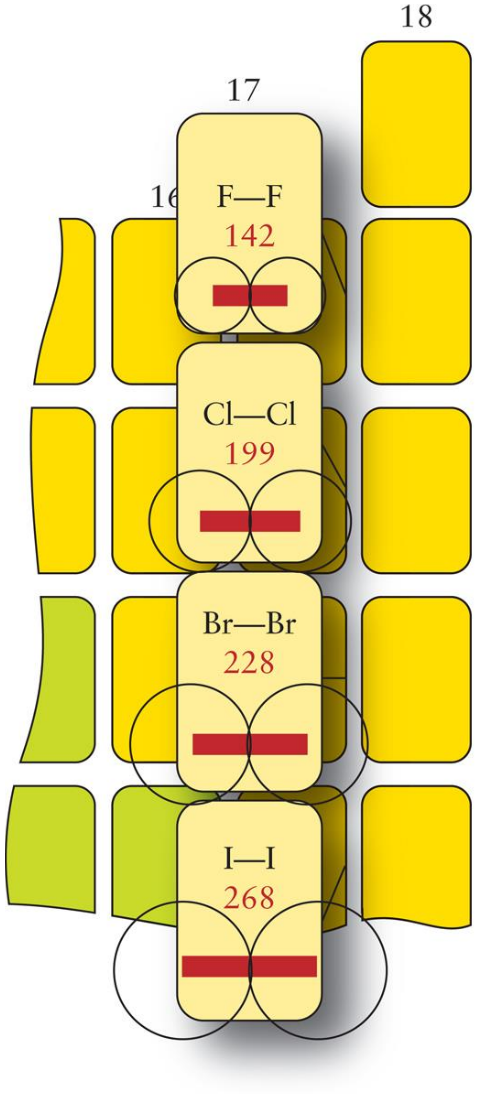

Figure 2D.10
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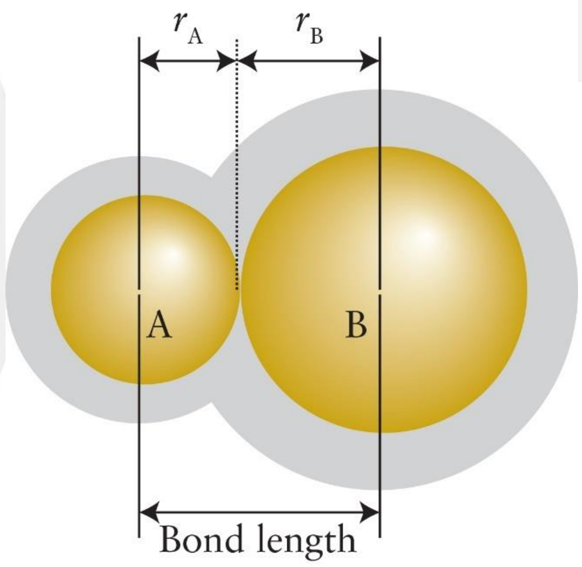
Bond Lengths↑ as Size↑



3 Covalent radii

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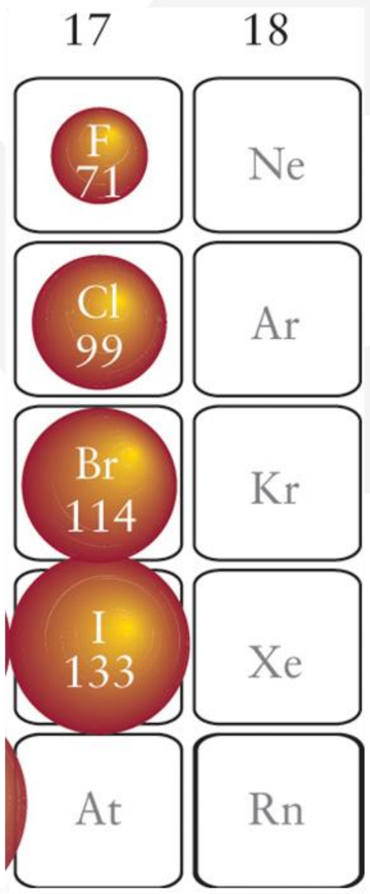

Atomic Radii / pm

Figure 1F.4
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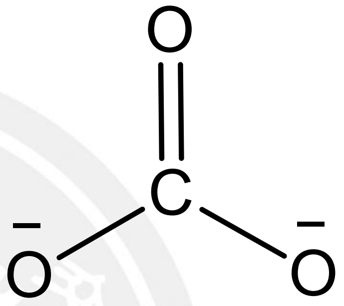
Short Quiz

Which molecule has the shortest C—O bond?

1.



2.

3.

4.

Triple bonds are shorter and stronger than double bonds, which are shorter and stronger than single bonds.