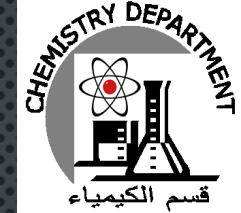




General Chemistry I



NAC 1101

Lecture 7

Chemical Bonding

Ahmad Alakraa

Outline

- Lewis Symbols and the Octet Rule
- Ionic Bonding
- Covalent Bonding
- Bond Polarity and
- Electronegativity
- Drawing Lewis Structures
- Formal Charge & Oxidation No.
- Resonance Structures
- Exceptions to the Octet Rule
- Strengths & Lengths of Covalent Bonds

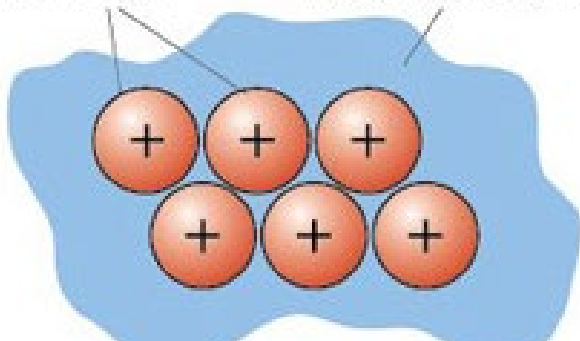
Lewis electron-dot symbols

a simple way (suggested by Lewis) of showing the valence e^- 's in an atom and tracking them during bond formation.

Metallic, Fe

positively charged metal ions

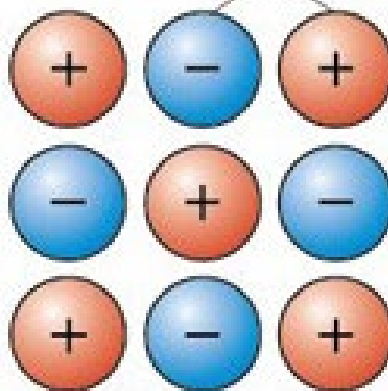
free electron 'sea' binds ions together



are formed by e^- 's that are relatively free to move from one atom to another

Ionic, NaCl

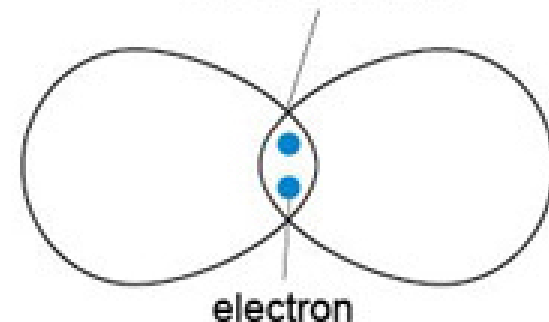
ions of opposite charge attract



formed due to electrostatic attractions between oppositely charged ions

Covalent, H₂O

orbitals overlap and share electrons



are formed by sharing e^- 's between atoms

Lewis Symbol

- consists of the element's chemical symbol plus a dot for each valence electron.
- Lewis symbol of ${}_{16}\text{S}$: $[\text{Ne}] 3s^2 3p^4$ (6 Ve's) is:



- The dots are placed on the 4 sides of the symbol—top, bottom, left, and right—and each side can accommodate up to 2 e's.
- All 4 sides are equivalent (choice of sides for placement of 2 e's rather than 1 e is arbitrary).
- Dots are spread out as much as possible. (Having 2 e's on 3 sides & none on 4th for S is not accepted).

1	2
Li [He]2s ¹ Li·	Be [He]2s ² ·Be·
Na [Ne]3s ¹ Na·	Mg [Ne]3s ² ·Mg·

13	14	15	16	17	18
B [He]2s ² 2p ¹ ·B·	C [He]2s ² 2p ² ·C·	N [He]2s ² 2p ³ ·N·	O [He]2s ² 2p ⁴ :O:	F [He]2s ² 2p ⁵ ·F·	Ne [He]2s ² 2p ⁶ :Ne:
Al [Ne]3s ² 3p ¹ ·Al·	Si [Ne]3s ² 3p ² ·Si·	P [Ne]3s ² 3p ³ ·P·	S [Ne]3s ² 3p ⁴ :S:	Cl [Ne]3s ² 3p ⁵ ·Cl·	Ar [Ne]3s ² 3p ⁶ :Ar:

Octet Rule

- Atoms tend to **gain**, **lose**, or **share e's** until they are surrounded by **8 Ve's**, *i.e.*, full **s** and **p** subshells.
- In a Lewis symbol, an **octet** is shown as **4** pairs of **Ve's** arranged around the element symbol as in **Ne** and **Ar**.
- The octet rule **mostly** applies to atoms that have **s** and **p Ve's**.

Exercise

Which is the correct Lewis symbol of As?



✗



✗



✗

Solution

${}_{33}\text{As}: [\text{Ar}] 4s^2 3d^{10} 4p^3$ (5 Ve's):

✓

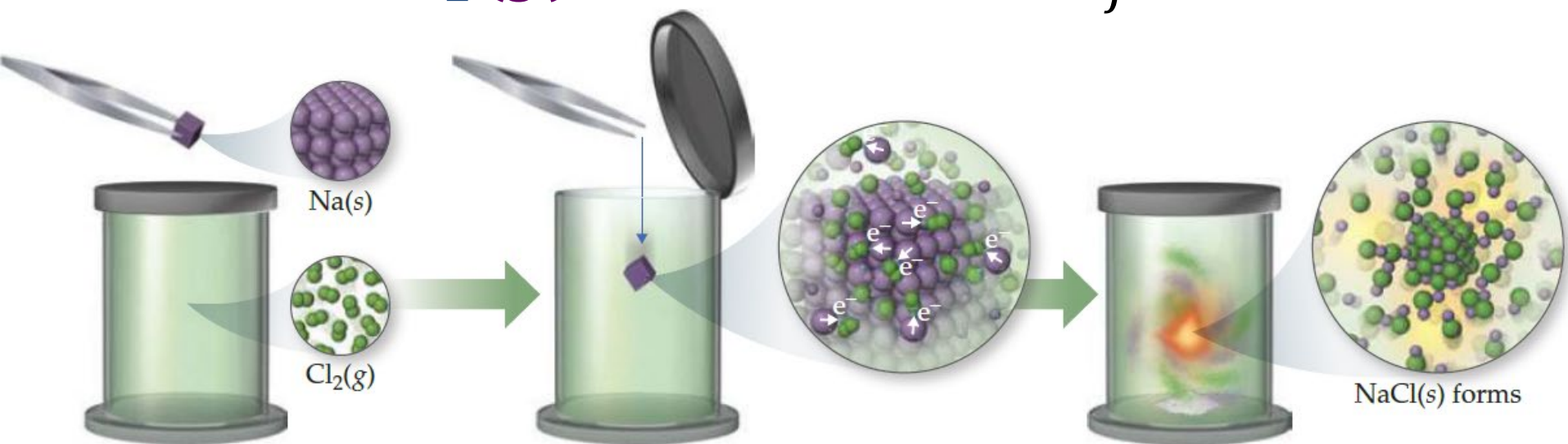


✓



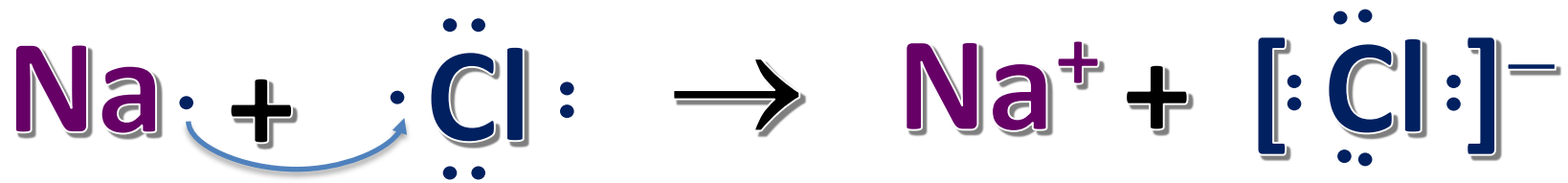
Ionic Bonding

- Ionic substances generally result from the interaction of **metals** on the left side of the periodic table with **nonmetals** on the right side (excluding the noble gases, Group 18).



e⁻s transfer from Na to Cl₂

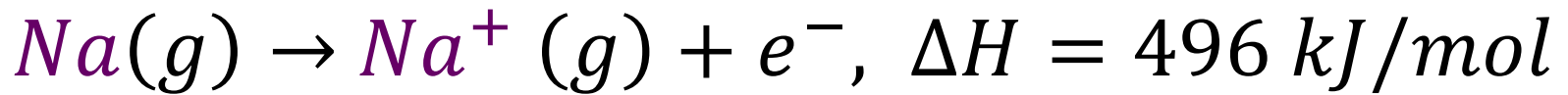
Highly exothermic



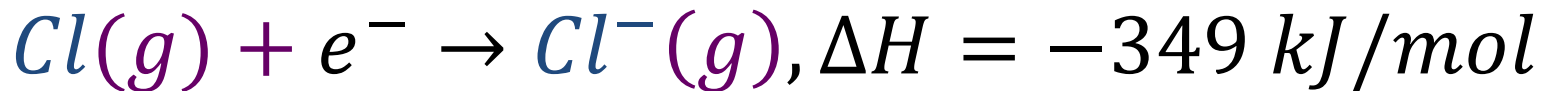
- The **low** I_1 of **Na** and the **high** electron affinity of Cl_2 indicates how easily an electron can be removed from **Na** to Cl_2 to form NaCl that is a typical ionic compound.
- Each ion (Na^+ & Cl^-) has an octet of **es**, yet, a bracket is put around Cl^- ion to emphasize that all **8 es** are located on it.
- Ionic substances are usually **brittle**, of **high** melting points & **crystalline** (often can be cleaved “break apart” along smooth, flat surfaces) as a result of the electrostatic forces that maintain the ions in a **rigid**, well-defined, **three-dimensional** arrangement

Energetics of Ionic Bond Formation

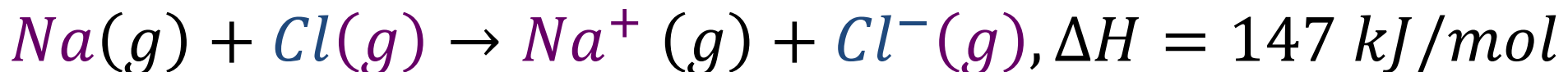
- Loss of **e**s from an atom is always an endothermic (**ionization**).



- Gaining an **e**s by a nonmetal is generally **exothermic** (negative electron affinities of the elements).



- Transfer of an **e** from an $Na(g)$ atom to a $Cl(g)$ atom would not be **exothermic !!!!!!!**.



- This **endothermic** process corresponds to the formation of Na^+ & Cl^- ions that are infinitely **far apart**—the positive energy change assumes that the ions **do not interact** with each other, which is quite different from the situation in ionic solids.

Lattice Energy

- energy required to completely **separate** one mole of a solid ionic compound into its gaseous ions.
- Ionic compounds are stable due to the attraction between ions of opposite charge that draws the ions together, releasing **lattice energy** and causing many ions to form a solid array, or lattice.



- The released **lattice energy** is more than **makes up** for the **endothermic** nature of ionization energies, making the formation of ionic compounds an **exothermic**.
- The strong attractions cause most ionic materials to be **hard** and **brittle** with **high** melting points—e.g., NaCl melts at **801 °C**.



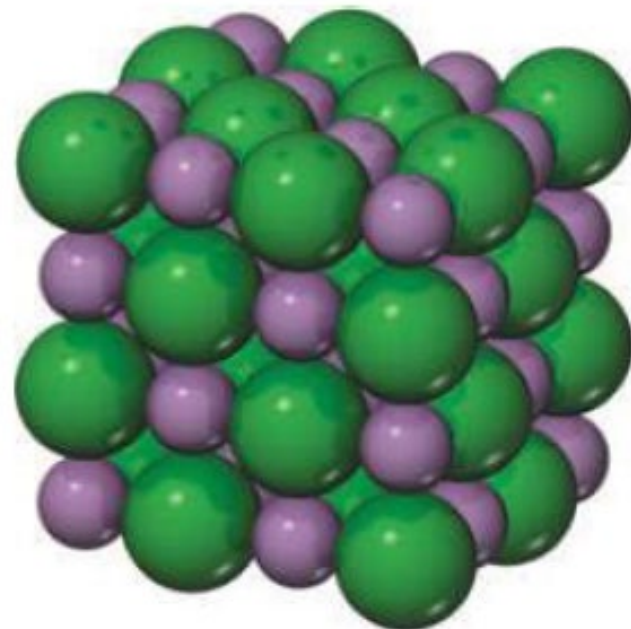
= Na⁺



= Cl⁻

Each Na⁺ ion
surrounded by
six Cl⁻ ions

Each Cl⁻ ion
surrounded by
six Na⁺ ions



Lattice Energy for Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	MgCl ₂	2526
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		

- The magnitude of the **lattice energy** of an ionic solid depends on the **charges** of the ions, their **sizes**, and their **arrangement** in the solid.

Electrostatic potential energy of 2 interacting charged particles

$$E_{el} = \frac{k Q_1 Q_2}{d}$$

- Q_1 and Q_2 are the charges on the particles in Coulombs, with their signs;
- d is the distance between their centers in meters;
- $k(= 8.99 \times 10^9 \text{ J.m C}^2)$ is a constant.

- The attractive interaction between two oppositely charged ions **increases** as the magnitudes of their **charges** increase and as the **distance** between their centers decreases.
- For a given arrangement of ions, the **lattice energy increases** as **charges** (more influence) on ions increase and as their **radii (less)** decrease.

Exercise

✚ Arrange the ionic compounds NaF , CsI , and CaO in order of increasing lattice energy.

Solution

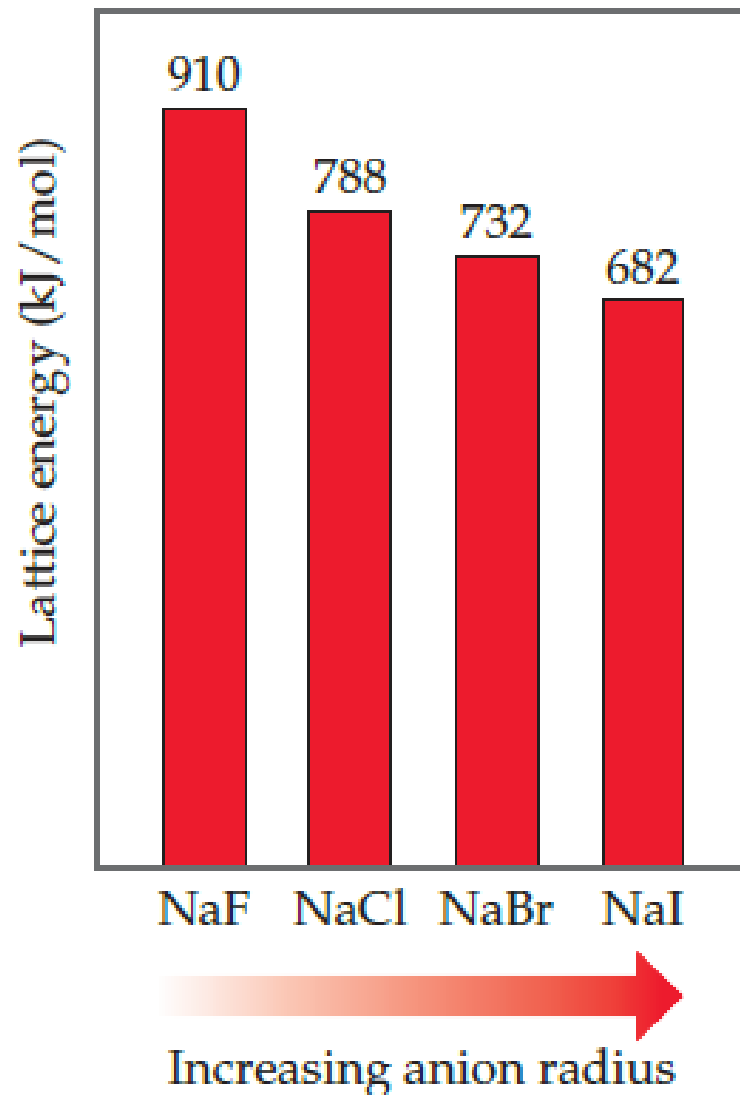
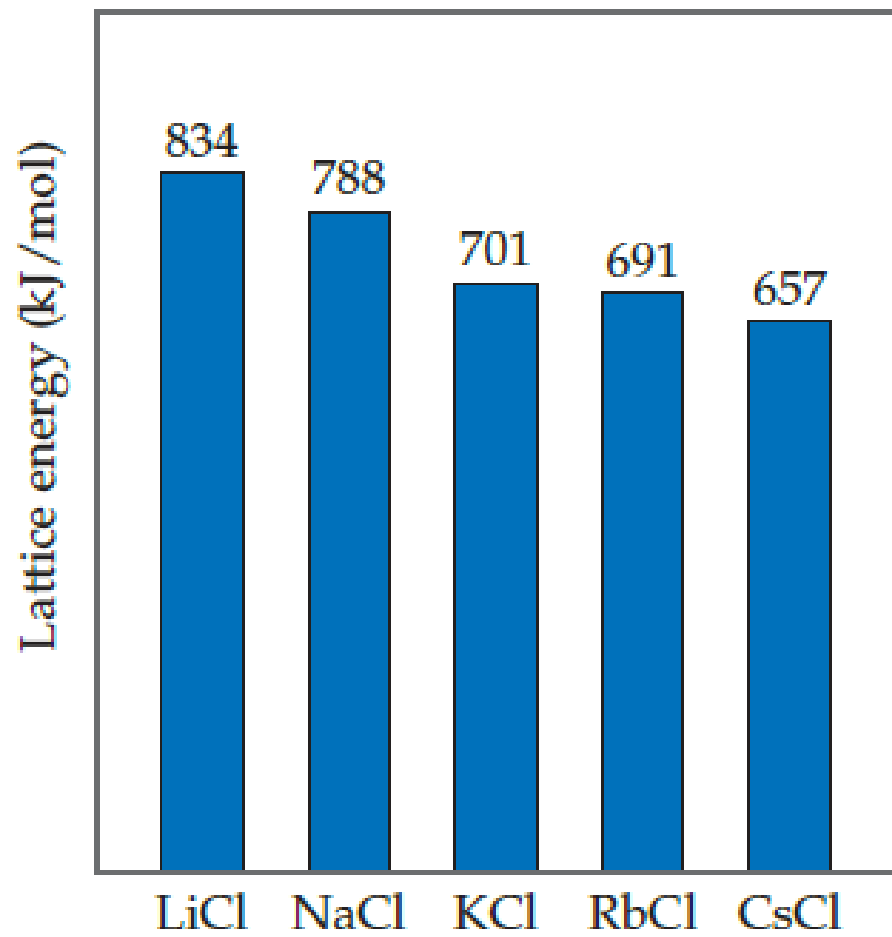
✚ $Q_1Q_2 = (2+)(2-)$ for CaO , which increases lattice energy dramatically.

✚ Q_1 & Q_2 of NaF and CsI are the same. The difference in their lattice energies thus depends on d . Because ionic size increases as we go down a group in PT, 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 .



Trends in Lattice Energy

- Because lattice energy decreases as distance between ions increases, lattice energies follow trends that parallel those in ionic radius.
- Because ionic radius increases as we go down a group of PT, the lattice energy of ionic compounds decreases as we go down a group.



Electron Configurations of Ions

- The energetics of **ionic** bond formation helps explain why many ions tend to have noble-gas electron configurations.
- Na readily loses **1 e** to form Na^+ , which has the same electron configuration as Ne: $1s^2 2s^2 2p^6$.
- Even though **lattice energy** increases with increasing ionic charge, we never find ionic compounds that contain Na^{2+} ions: as the removal of the **2nd electron (inner-shell)** would require a very large amount of energy that can not be compensated from the **lattice energy**. Thus, Na and the other **Group 1** metals are found in ionic substances only as **1+** ions.

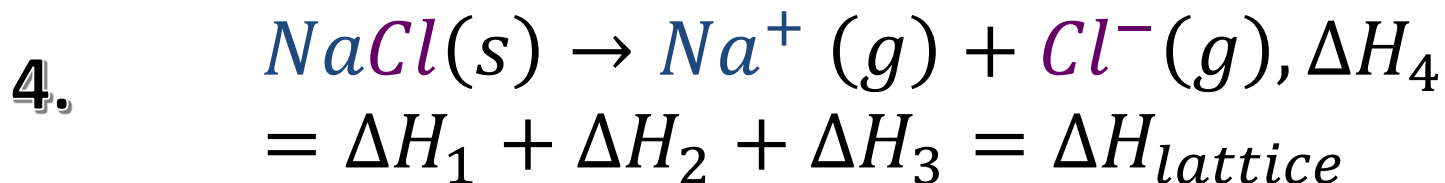
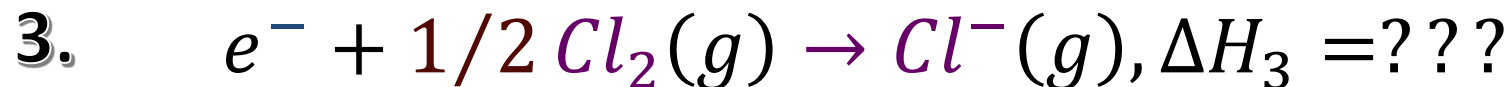
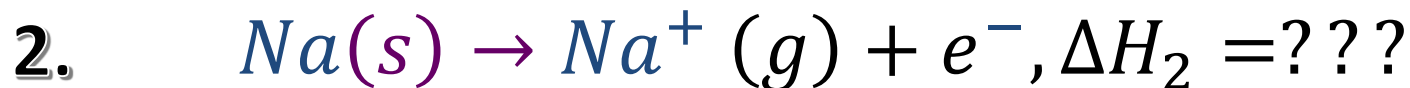
Electron Configurations of Ions

- adding **es** to nonmetals is either **exothermic** or only slightly **endothermic** if **es** are added to the valence shell. Thus, a **Cl** atom easily adds **e** to form **Cl⁻**, which has same electron configuration as Ar: **[Ne] 3s² 3p⁶**.
- To form a **Cl²⁻** ion, the **2nd** **e** would have to be added to the next higher shell of the **Cl** atom, an addition that is **energetically** very **unfavorable**.
- We expect ionic compounds of **representative metals** from Groups **1**, **2**, and **13** to contain **1+**, **2+**, and **3+** cations, respectively, and ionic compounds of the representative nonmetals of Groups **15**, **16**, and **17** to contain **3-**, **2-**, and **1-** anions, respectively.

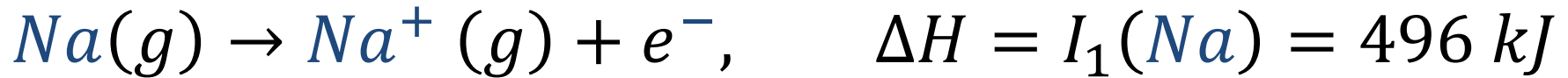
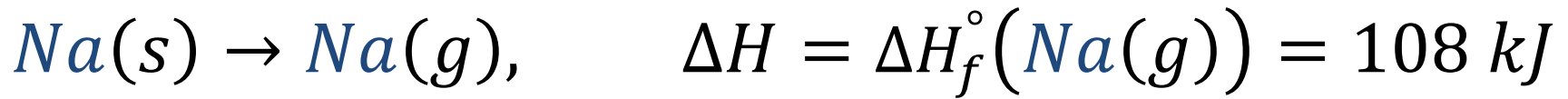
Calculation of Lattice Energy



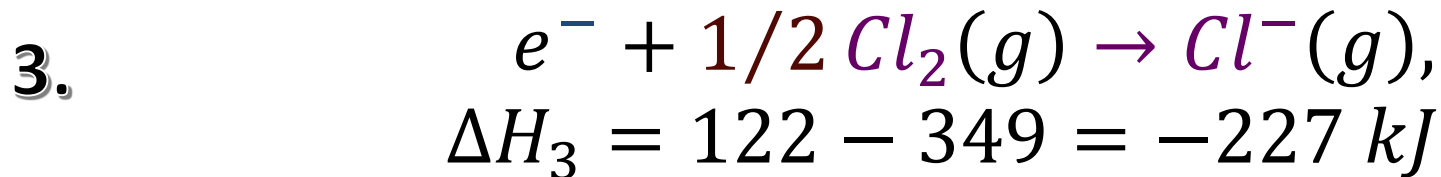
- Hess's Law is applied to estimate the lattice energy of the above equation.

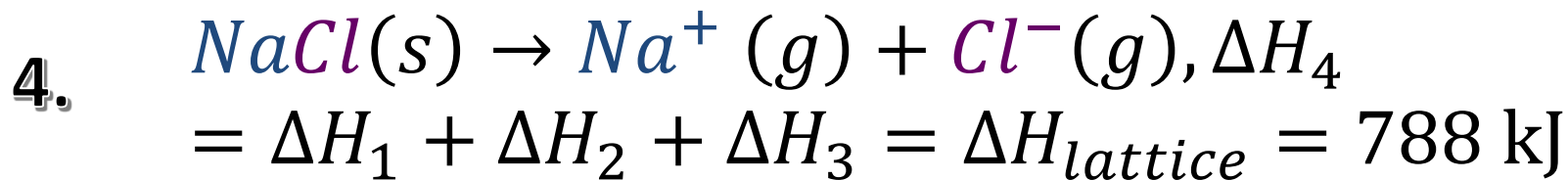
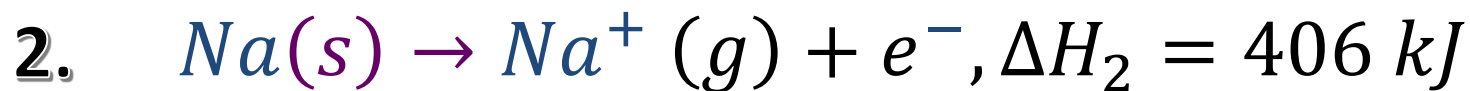
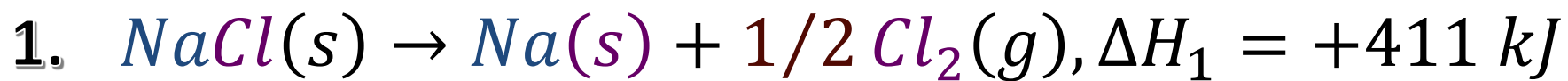


To calculate ΔH_2

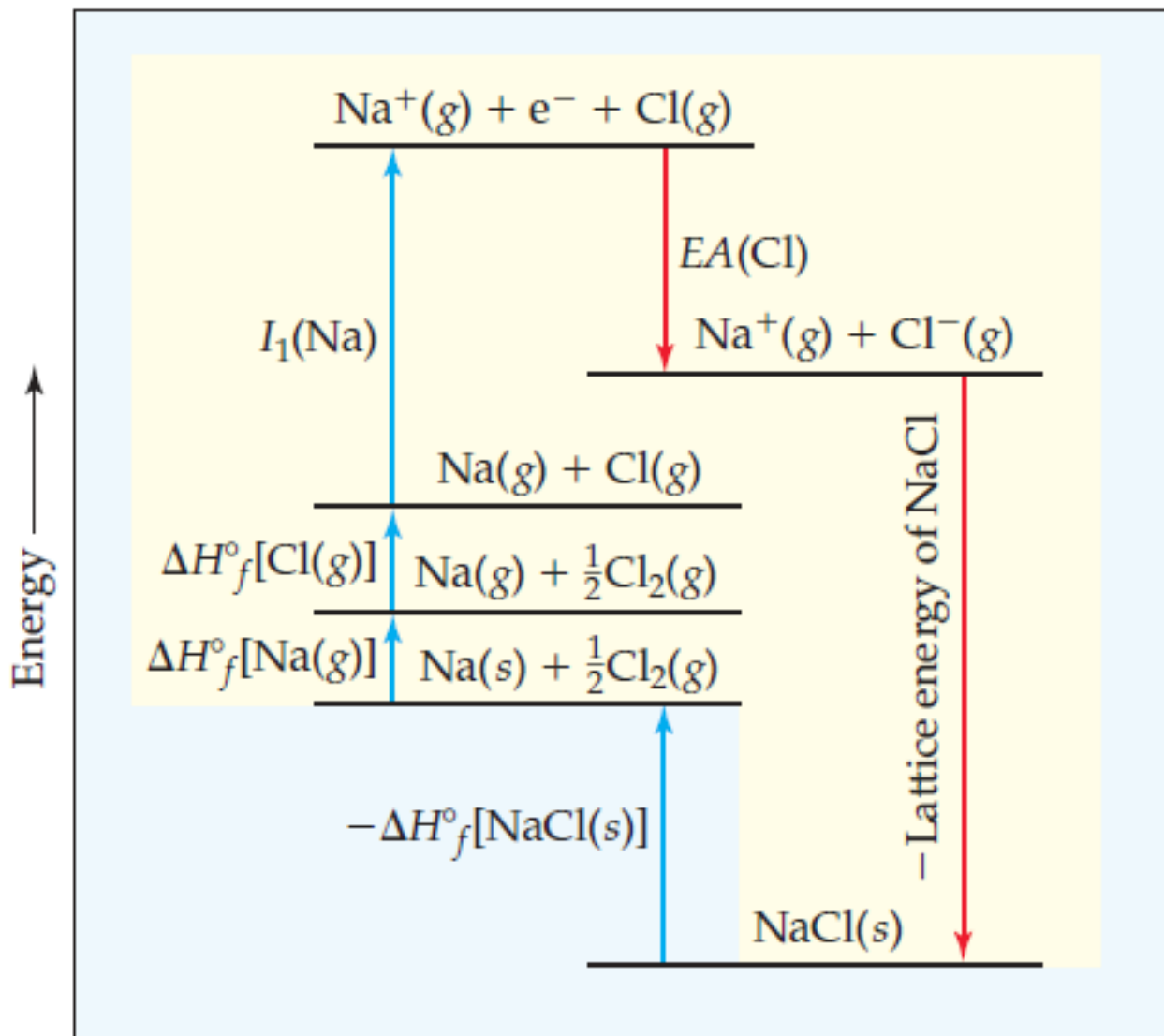


To calculate ΔH_3





This process is described as a “cycle”



Born-Haber cycle for formation of NaCl

Transition Metal Ions

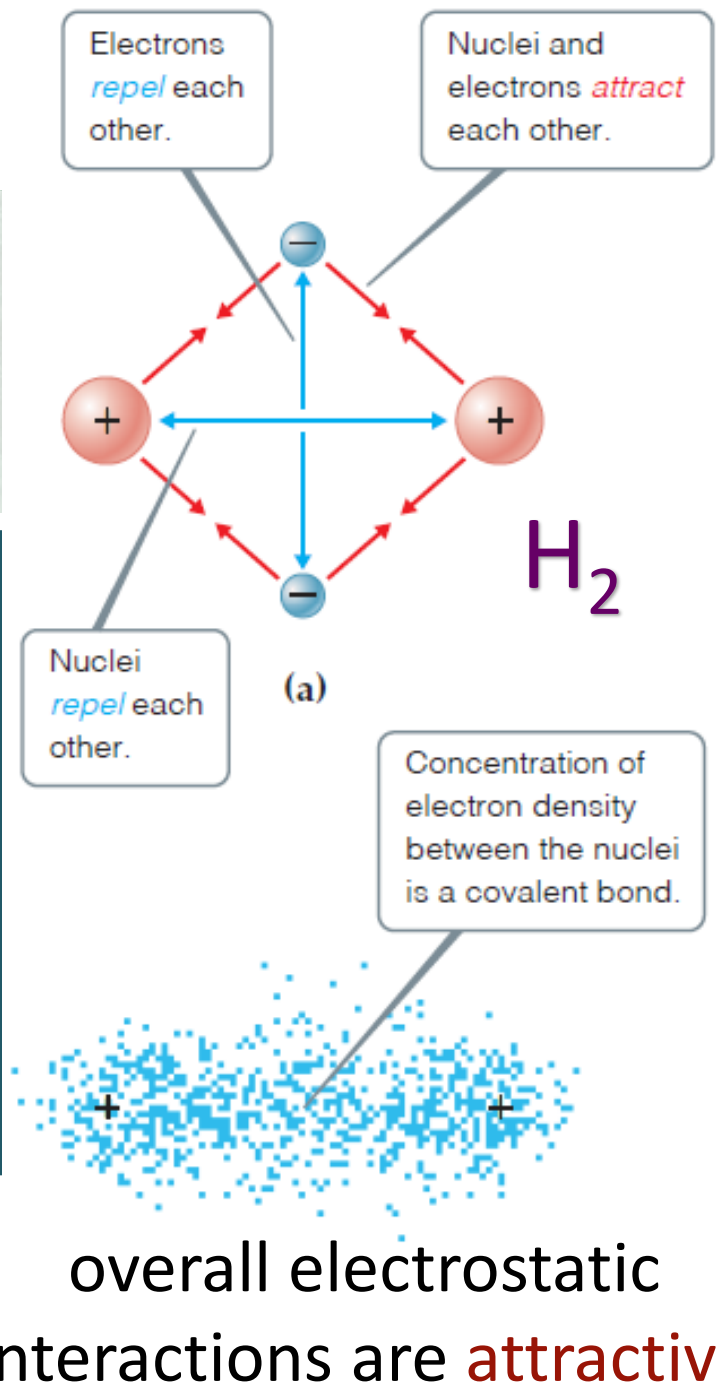
- Because **IEs** increase rapidly for each successive **e** removed, the **lattice energies** of ionic compounds are generally large enough to compensate for the loss of up to only **3 e**s from atoms. Thus, we find cations with charges of **1+**, **2+**, or **3+** in ionic compounds.
- Most transition metals, however, have more than **3 e**s beyond a noble-gas core, as **Ag**: [Kr] $4d^{10}5s^1$.
- Metals of Group 11 (**Cu**, **Ag**, **Au**) often occur as **1+** ions (as in **CuBr** and **AgCl**).
- To form **Ag⁺**, **5s e** is lost, leaving a filled **4d** subshell.
- Transition metals generally do not form ions that have a noble-gas configuration.
- The octet rule, although useful, is clearly limited in scope.

Covalent Bonding

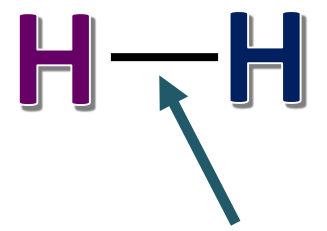
A chemical bond formed by **sharing** a pair of electrons is a covalent bond

- Most of the substances with which we come into daily contact—as water, air, foods, and indeed our own composition—are not **ionic** but **molecular** materials.

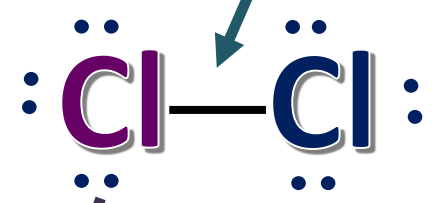
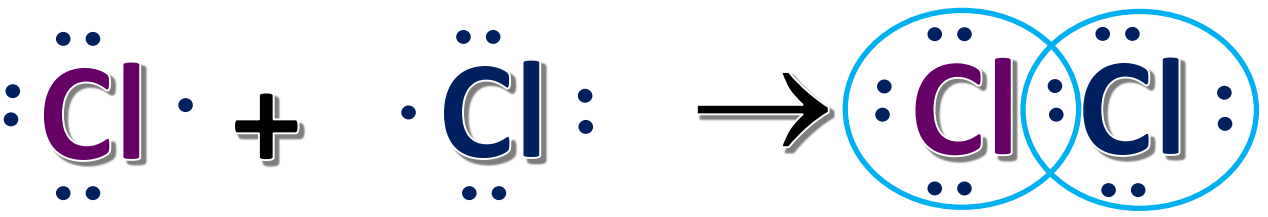
Shared pair of **es** act as a kind of “**glue**” to bind atoms together.



Lewis Structures



bonding pair

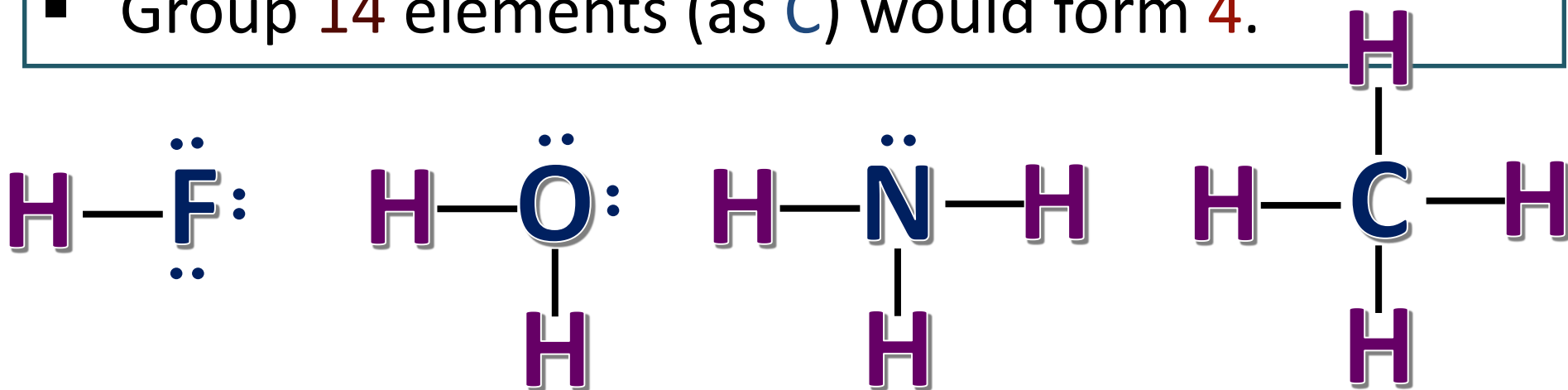


○ Lone pair

○ nonbonding pair

Non-metals

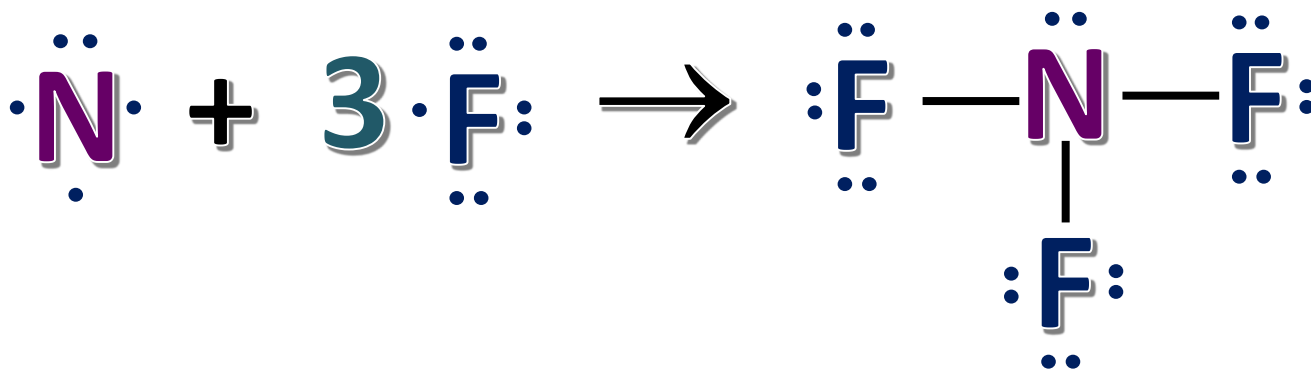
- No. of **Ves** in a neutral atom is the same as the group number **minus 10**.
- Group **17** elements (as **F**) would form **one** covalent bond to achieve an octet.
- Group **16** elements (as **O**) would form **2** covalent bonds.
- Group **15** elements (as **N**) would form **3**.
- Group **14** elements (as **C**) would form **4**.



Exercise

- Using the Lewis symbols for nitrogen and fluorine, predict the formula of the stable binary compound (a compound composed of two elements) formed when nitrogen reacts with fluorine and draw its Lewis structure.

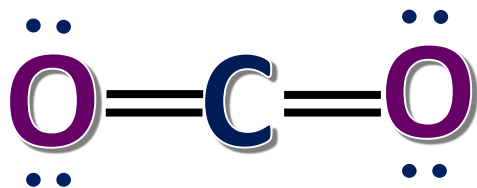
Solution



N must share a pair of **es** with 3 F atoms to complete its octet. Thus, the binary compound must be **NF₃**

Multiple Bonds

- A shared e pair constitutes a **single** covalent bond (simply, a single bond).
- In many molecules, atoms attain complete octets by sharing **more** than one pair of es.



Double Bond



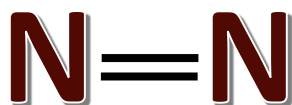
Triple Bond

Nitrogen

- N_2 is a diatomic gas with exceptionally **low reactivity** that results from the very stable nitrogen–nitrogen bond (**110 pm**).
- The short separation distance (**110 pm**) between the two **N** atoms is a result of the **triple** bond between the atoms.
- The structures of many different substances in which **N** atoms share **one** or **two** electron pairs were found to have **variable** average distance between bonded nitrogen atoms.



147 pm



124 pm



110 pm

Bond Polarity

is a measure of how **equally** or **unequally** the **electrons** in any covalent bond are **shared**.

- A **nonpolar** covalent bond is one in which **es** are shared equally, as in **Cl₂** and **N₂**.
- A **polar** covalent bond is one in which one of the atoms exerts a greater attraction for the bonding **es** than the other.
 - If the **difference** in relative ability to attract **es** is **large** enough, an **ionic** bond is formed.

Electronegativity, EN

is the **ability** of an atom in a molecule to attract **electrons** to itself.

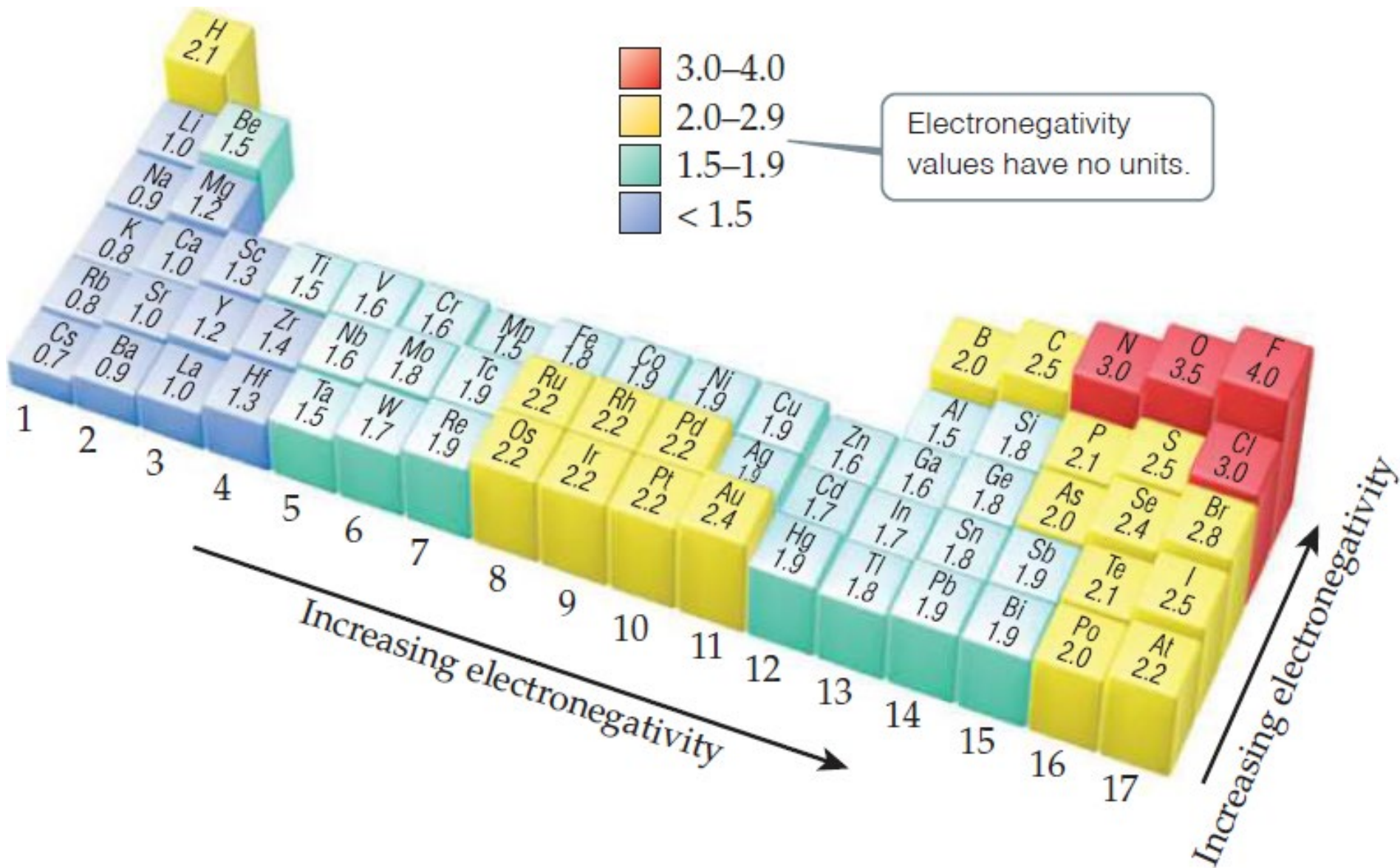
- The greater an atom's **EN**, the greater its ability to attract **es** to itself.
- The **EN** of an atom in a molecule is related to the atom's **ionization energy, IE**, and **electron affinity, EA**, which are **properties** of **isolated** atoms.
- An atom with a very negative **EA** and a high **IE** both attracts **es** from other atoms and resists having its **es** attracted away; therefore, it is highly **electronegative**.

Trends in Electronegativity

Linus Pauling developed a scale for **EN**, which is based on thermochemical data .

- **EN** generally, increases from left (metals) to right (nonmetals) across a period.
- With some exceptions (especially in the transition metals), **EN** decreases with increasing atomic number in a group.
 - Because of the decrease in **IEs** & the little variation in **EAs**.

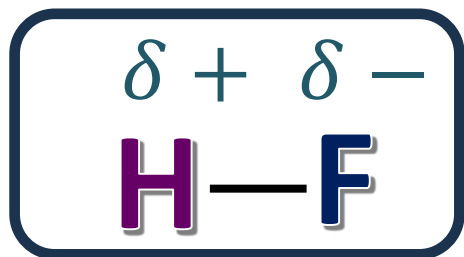
EN values based on Pauling's thermochemical data



EN & Bond Polarity

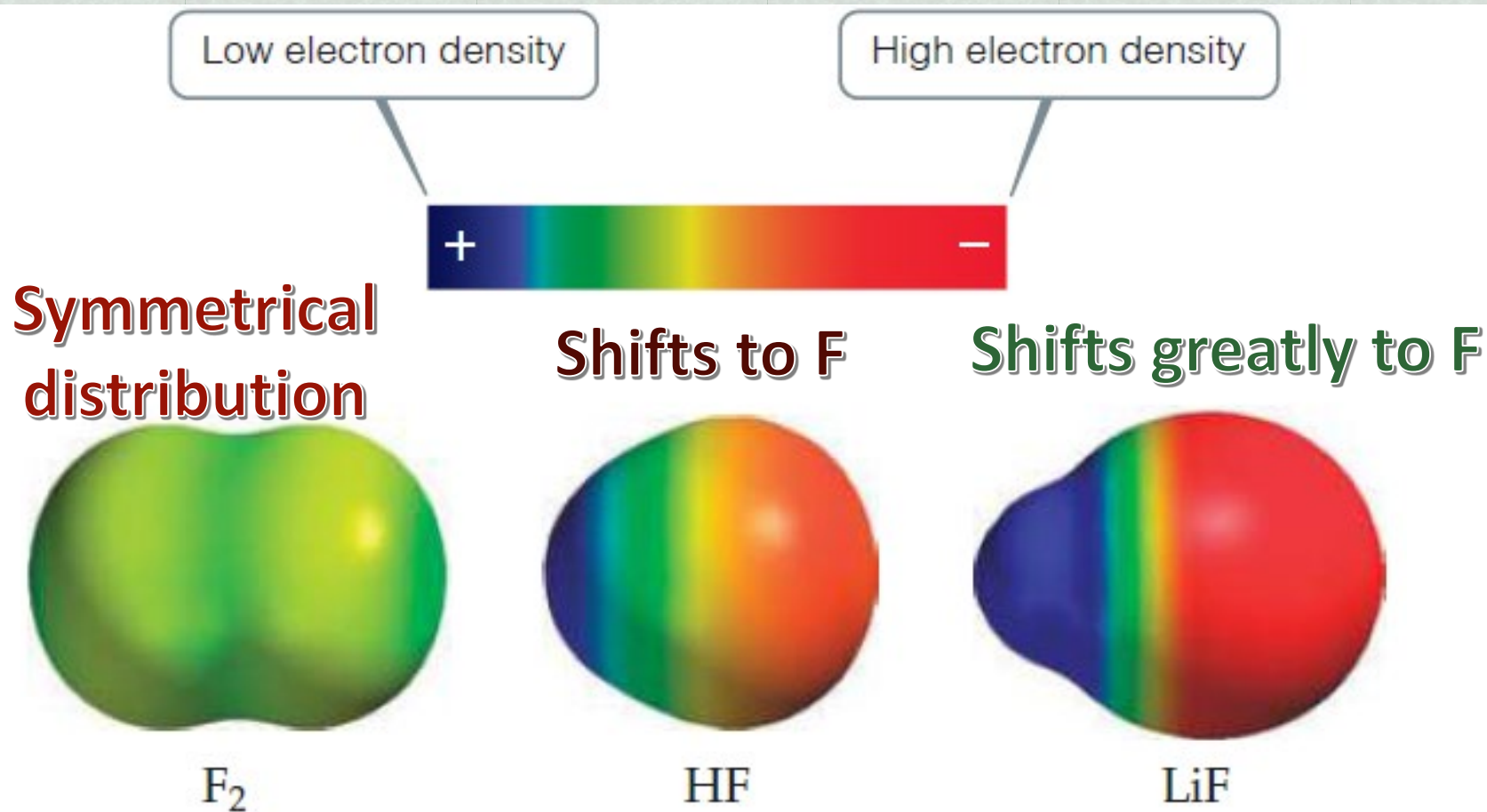
The difference in **EN** between two atoms I used to gauge the polarity of the bond the atoms form.

	<i>F₂</i>	<i>HF</i>	<i>LiF</i>
ΔEN	$4.0 - 4.0 = 0$	$4.0 - 2.1 = 1.9$	$4.0 - 1.0 = 3.0$
Bond's Type	Nonpolar covalent	Polar covalent	Ionic



$\delta +$ & $\delta -$ are less than the full charges of the ions.

Calculated electron-density distribution on the surface of molecules.



The *greater* the difference in *EN* between two atoms, the *more polar* their bond.

Exercise

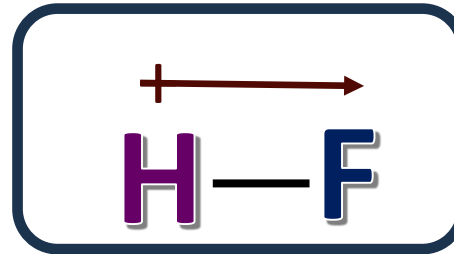
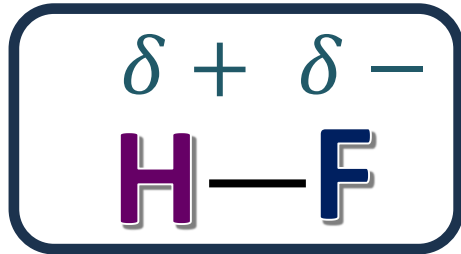
- In each case, which bond is more polar? (a) $\text{B}-\text{Cl}$ or $\text{C}-\text{Cl}$, (b) $\text{P}-\text{F}$ or $\text{P}-\text{Cl}$. Indicate in each case which atom has the partial negative charge.

Solution

- a) Because B is to the left of C in PT and Cl is common. We predict $\text{B} < \text{C}$ in EN. Also, Cl has a high EN (right side of PT). $\Rightarrow \text{B}-\text{Cl}$ is more polar & Cl of this molecule carries the partial negative charge because it has a higher electronegativity.
- b) Similarly, Cl is below F in PT and P is common, we predict $\text{Cl} < \text{F}$ in EN. $\Rightarrow \text{P}-\text{F}$ is more polar & F of this molecule carries the partial negative charge.

Polar molecules, PM

- A molecule such as HF, in which the centers of **positive** and **negative** charge do not coincide, is a polar molecule.

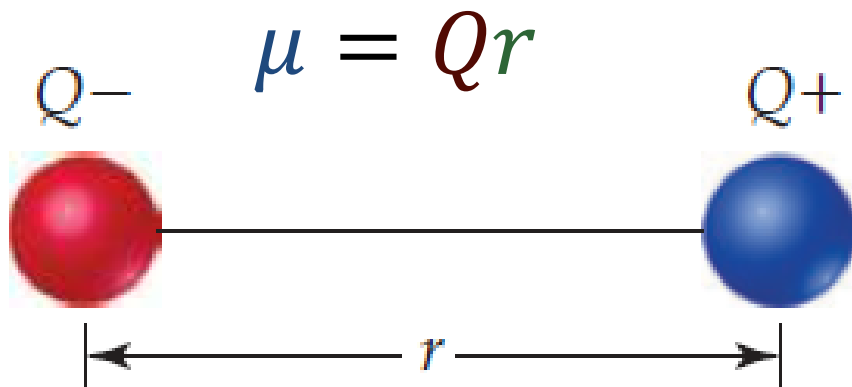


- **PM** align themselves with the negative end of one molecule and the positive end of another attracting each other.
- **PM** are attracted to ions & that accounts for many properties of liquids, solids, and solutions.

Dipole Moments, μ

- Whenever two electrical charges of equal magnitude (Q) but opposite sign are separated by a distance (r), a dipole is established.

The quantitative measure of the magnitude of a dipole is called its dipole moment (μ)



$$Q \uparrow \rightarrow \mu \uparrow$$

$$r \uparrow \rightarrow \mu \uparrow$$

The larger μ , the more polar the bond.

$$\mu \text{ of } F_2 = 0$$

Dipole Moments, μ

- μ is experimentally measurable and is usually reported in *debyes* (D), a unit that equals $3.34 \times 10^{-30} \text{ C m}$.
- For molecules, we measure charge in units of the electronic charge $e = 1.60 \times 10^{-19} \text{ C}$, and distance in *meters*.
- Suppose that two charges $1+$ and $1-$ (in units of e) are separated by 100 pm :

$$\mu = Qr = (1.60 \times 10^{-19} \text{ C})(100 \text{ pm}) \left(\frac{10^{-12} \text{ m}}{1 \text{ pm}} \right) \left(\frac{1 \text{ D}}{3.34 \times 10^{-30} \text{ C m}} \right)$$
$$\mu = 4.79 \text{ D}$$

Exercise

- The bond length in the HCl molecule is 127 pm. (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

Assuming charges of 1+ & 1−

$$\mu = Qr = (1.60 \times 10^{-19} \text{ C})(127 \text{ pm}) \left(\frac{10^{-12} \text{ m}}{1 \text{ pm}} \right) \left(\frac{1 \text{ D}}{3.34 \times 10^{-30} \text{ C m}} \right)$$

$$\mu = 6.08 \text{ D} \quad \gg \gg \text{1.08 D}$$

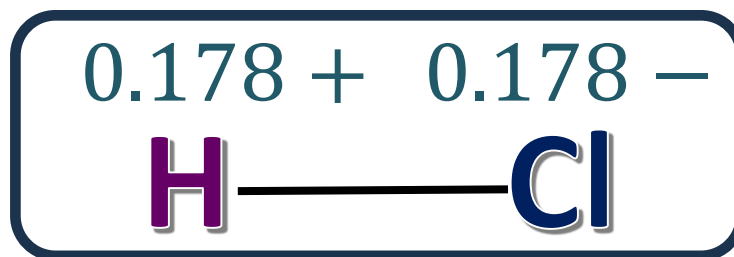
Real charges:

$$Q = \frac{\mu}{r} = \frac{1.08 \text{ D}}{127 \text{ pm}} \left(\frac{1 \text{ pm}}{10^{-12} \text{ m}} \right) \left(\frac{3.34 \times 10^{-30} \text{ C m}}{1 \text{ D}} \right) = 2.84 \times 10^{-20} \text{ C}$$

In terms of e :

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

Experimental μ



H—Cl bond is **polar** covalent rather than **ionic**

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

Compound	Bond length (pm)	ΔEN	μ (D)
HF	92	1.9	1.82
HCl	127	0.9	1.08
HBr	141	0.7	0.82
HI	161	0.4	0.44

- As we proceed from HF to HI, ΔEN decreases and the bond length increases. The decrease in ΔEN decreases the amount of charge separated and causes μ to decrease, even though the bond length is increasing.
- Charges on the atoms decrease from 0.41+ and 0.41- in HF to 0.057+ and 0.057- in HI.

LiF

- LiF exists as an **ionic** solid with an arrangement of atoms analogous to **NaCl** structure.
- However, it is possible to generate **LiF** molecules (**polar covalent**) by vaporizing the ionic solid at **high T**.
- The molecules have μ of 6.28 **D** and a bond distance of **153 pm**. From these values we can calculate the charge on **Li** and **F** to be **0.857+** and **0.857-**, respectively.
- This bond is extremely **polar**, and the presence of such large charges strongly favors the formation of an extended **ionic lattice** in which each Li ion is surrounded by F ions and vice versa.
- Experimentally determined charges on the ions are still not **1+** and **1-**, that tells that even in **ionic** compounds, there is still some **covalent** contribution to the bonding.

Comparing Ionic and Covalent Bonding

- There is a lack of a well-defined separation between them.
- When **covalent** bonding is dominant, we expect compounds to exist as **molecules**, relatively **low melting** and boiling points and nonelectrolyte behavior when dissolved in water.
- When **ionic** bonding is dominant, we expect the compounds to be **brittle**, **high-melting** solids with **extended lattice structures**, exhibiting strong **electrolyte** behavior when dissolved in water.

Approaches expecting the nature of Bonding

The interaction between a **metal** and a **nonmetal** is **ionic** and that between two **nonmetals** is **covalent**

- This classification is reasonably predictive, yet there are far too many exceptions to use it blindly.
- **Tin** is a metal, and chlorine is a nonmetal, but **SnCl_4** is a **molecular** substance that exists as a colorless liquid at **RT**. It freezes at **$-33\text{ }^\circ\text{C}$** and boils at **$114\text{ }^\circ\text{C}$** .
- The characteristics of **SnCl_4** are not those typical of an **ionic** substance.

Approaches expecting the nature of Bonding

A more sophisticated approach is to use ΔEN as the main criterion for determining whether **ionic** or **covalent** bonding will be dominant.

- This correctly predicts the bonding in SnCl_4 to be polar covalent based on ΔEN of 1.2.
- It also correctly predicts the bonding in NaCl to be predominantly ionic based on ΔEN of 2.1.
- A shortcoming of this approach appears as the **electronegativity** values do not take into account changes in bonding that accompany changes in the **oxidation state** of the metal.

- ΔEN between manganese and oxygen is $3.5 - 1.5 = 2.0$, which falls in the range where the bonding is normally considered ionic (the electronegativity difference for NaCl is $3.0 - 0.9 = 2.1$). Therefore, it is not surprising to learn that manganese (II) oxide, MnO , is a green solid that melts at $1842\text{ }^{\circ}C$ and has the same crystal structure as NaCl.
- However, the bonding between Mn and O is not always ionic. Manganese (VII) oxide, Mn_2O_7 , is a green liquid that freezes at $5.9\text{ }^{\circ}C$, an indication that covalent rather than ionic bonding dominates.

- The change in the oxidation state of **Mn** is responsible for the change in bonding.
- In general, as the oxidation state of a metal **increases**, so **does** the degree of covalent bonding.
- When the **oxidation state** of the metal is highly **positive** (*roughly speaking, +4 or larger*), we can expect significant **covalency** in the bonds it forms with nonmetals. Thus, metals in high oxidation states form molecular substances, such as **Mn₂O₇**, or polyatomic ions, such as **MnO₄⁻** and **CrO₄²⁻**, rather than ionic compounds.

Drawing Lewis Structures

Lewis structures can help us understand properties of molecules and the bonding in many compounds.

How to Draw Lewis Structures

- 1) Sum **Ves** from all atoms, considering overall charge.
- 2) Write the **symbols** for the atoms, show which atoms are attached to which, and connect them with a **single** bond (a line, representing **2 es**).
- 3) Complete the **octets** around all the atoms bonded to the central atom.
- 4) Place any remaining **es** on the central atom.
- 5) If there are not enough **es** to give the central atom an octet, try **multiple** bonds.

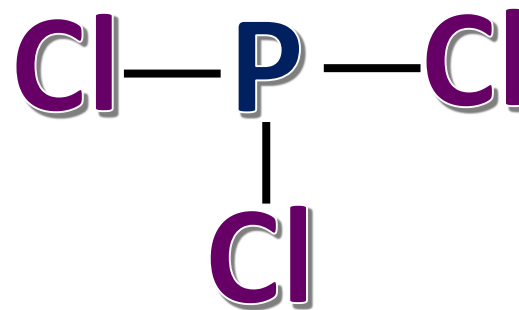
Exercise

- Draw the Lewis structure for phosphorus trichloride, PCl_3 .

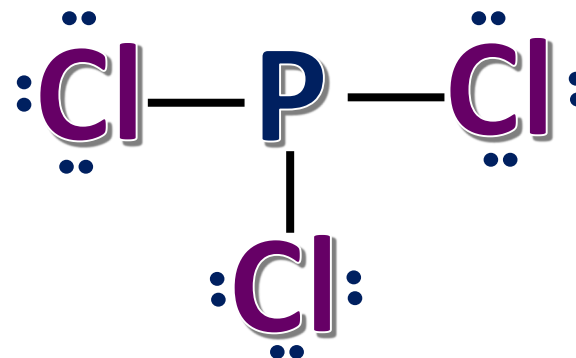
Solution

$$\sum \text{Ves} = 5 + 3(7) = 26$$

Arrange the atoms in connection
(bonded)



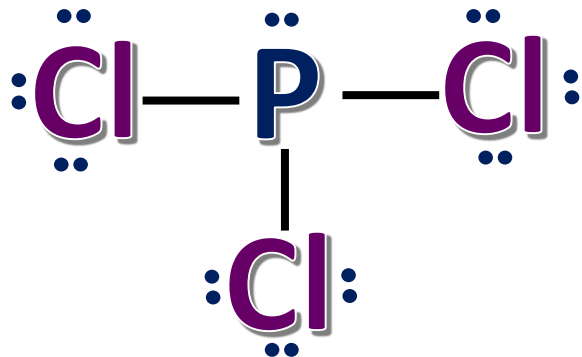
Add **Lewis electron** dots to complete the octets on the atoms bonded to the central atom



Remaining **Ves** after consuming **6 es** in bonding and placing ($3 \times 6 = 18$ **es**) to complete octets around Cl atoms:

$$\text{Remaining } \mathbf{Ves} = 26 - 24 = 2$$

Place remaining **Ves** on the central atom, P



This structure gives each atom an octet, so we stop at this point.

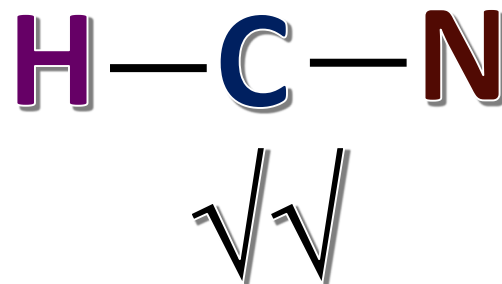
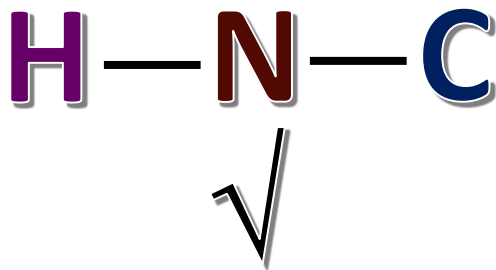
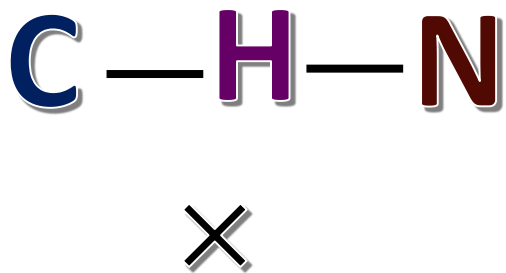
Exercise

○ Draw the Lewis structure for HCN.

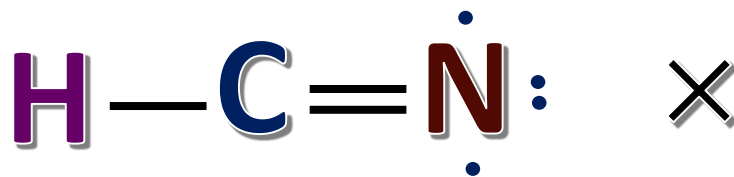
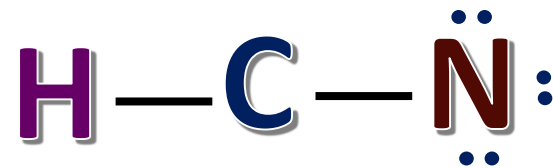
Solution

$$\sum \text{Ves} = 1 + 4 + 5 = 10$$

Arrange the atoms in connection (**bonded**)



H atom is satisfied. We have 4 **bonding es**. Add **Lewis electron dots** to N.



We did not achieve an octet on C. Try **multiple bonds**



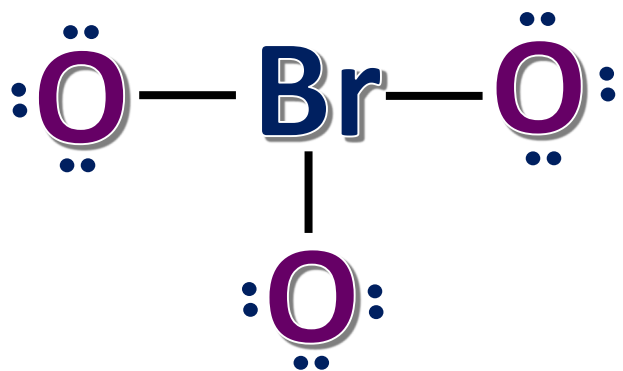
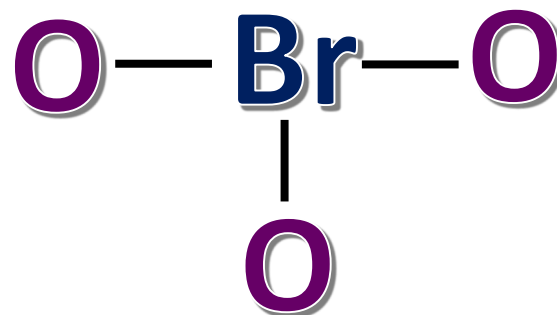
Exercise

○ Draw Lewis structure for BrO_3^- ion.

Solution

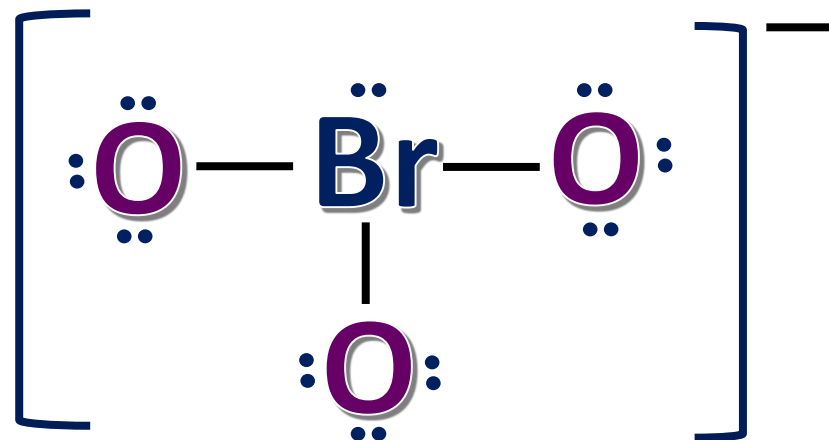
$$\sum \text{Ves} = 7 + 3(6) + 1 = 26$$

Arrange the atoms in connection (**bonded**)



Add **Lewis electron dots** to O

Place remaining **Ves** ($26 - 6 - (3 \times 6) = 2$) on the central atom, Br





Thank You