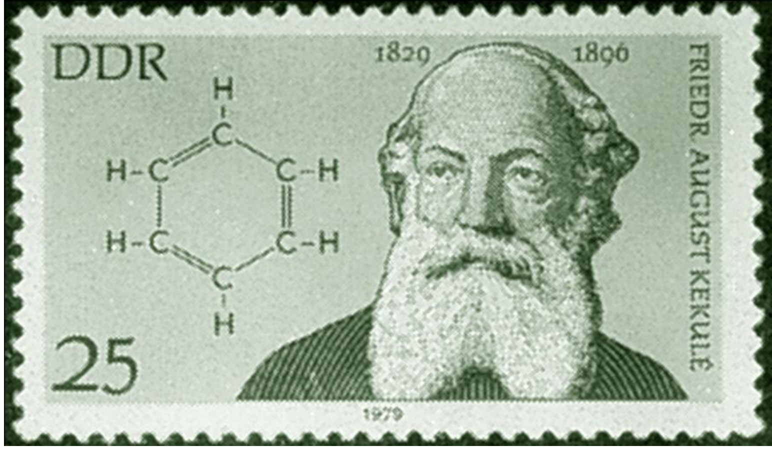
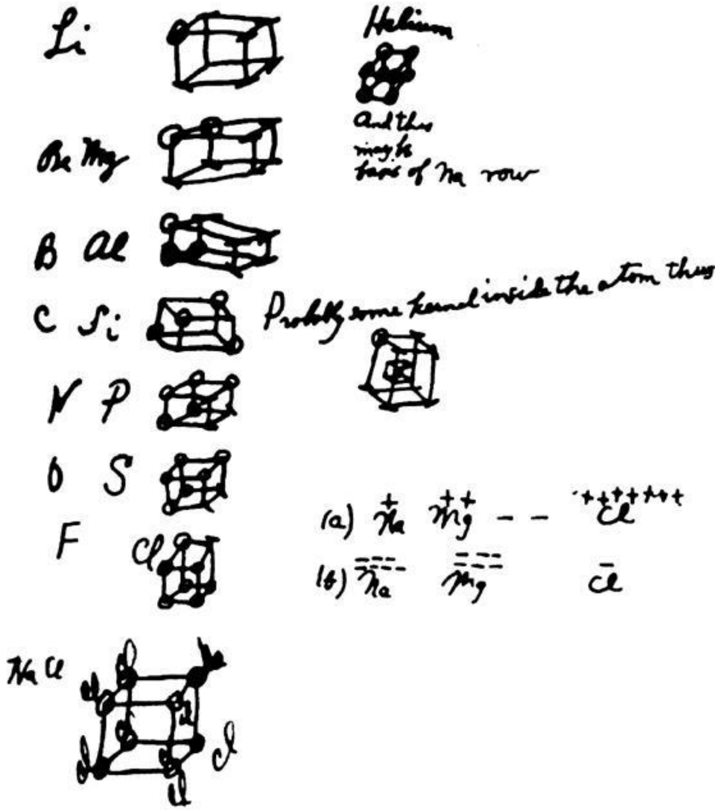


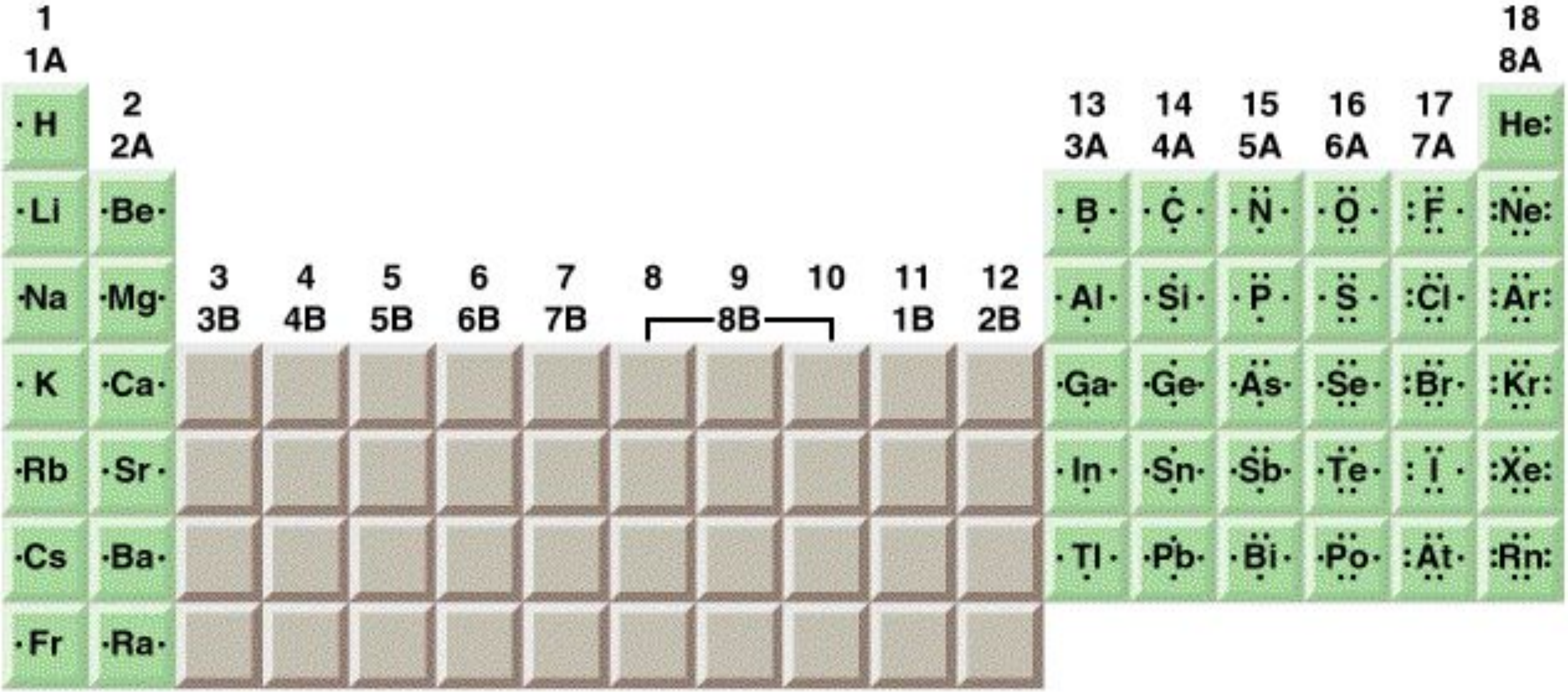
Chemical Bonding I: Basic Concepts



Valence electrons are the outer shell electrons of an atom. The valence electrons are the electrons that particpate in chemical bonding.

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

Lewis Dot Symbols



The Ionic Bond

$$\cdot\mathrm{Li} + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}\cdot \longrightarrow \mathrm{Li}^{+}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:^{-}$$

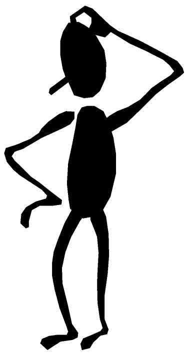
1s^{2}2s^1 1s^{2}2s^{2}2p^5 [He] 1s^2 [Ne] 1s^{2}2s^{2}2p^6

$$\cdot\mathrm{Li} \longrightarrow \mathrm{Li}^{+} + e^{-}$$

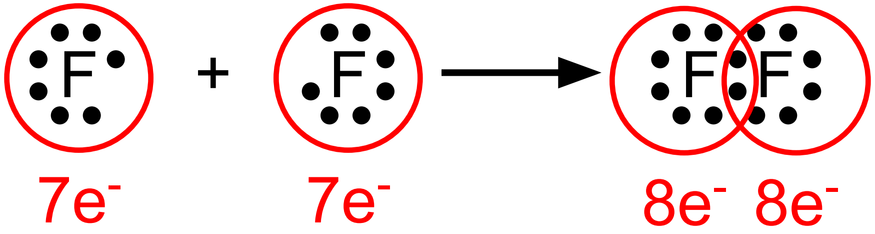
$$e^{-} + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}\cdot \longrightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:^{-}$$

$$\mathrm{Li}^{+} + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:^{-} \longrightarrow \mathrm{Li}^{+}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:^{-}$$

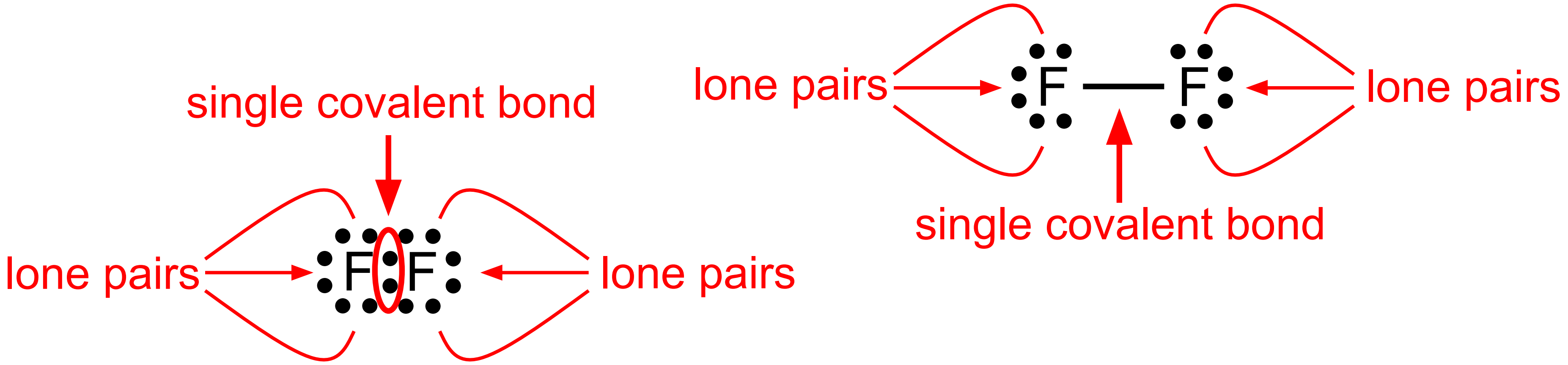
A ***covalent bond*** is a chemical bond in which two or more electrons are shared by two atoms.



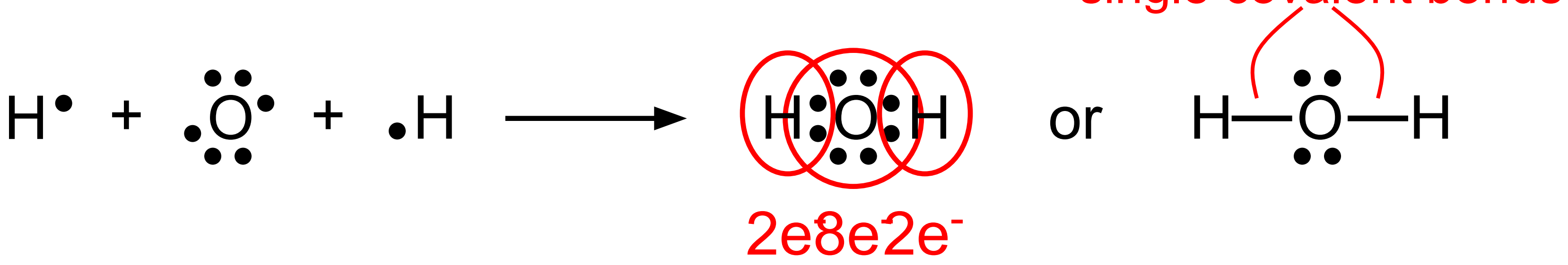
Why should two atoms share electrons?



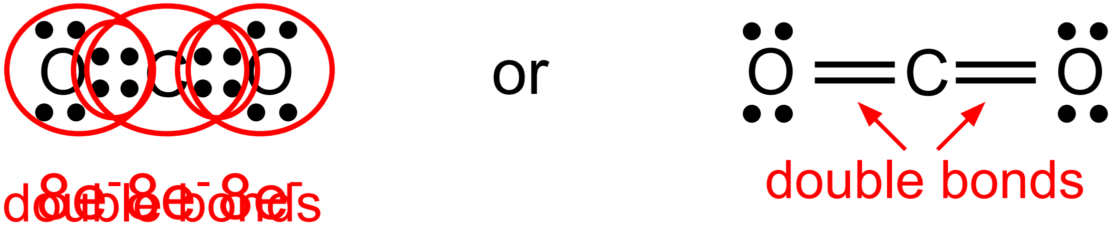
Lewis structure of F_2



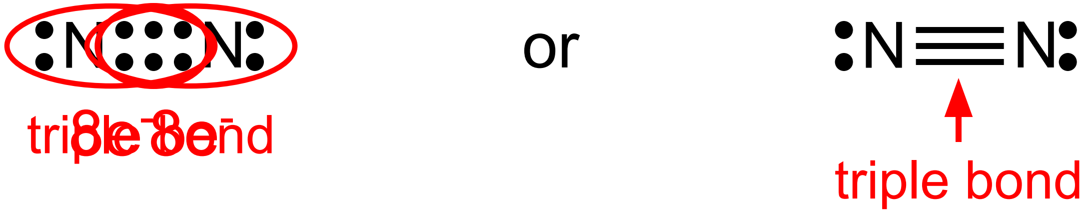
Lewis structure of water



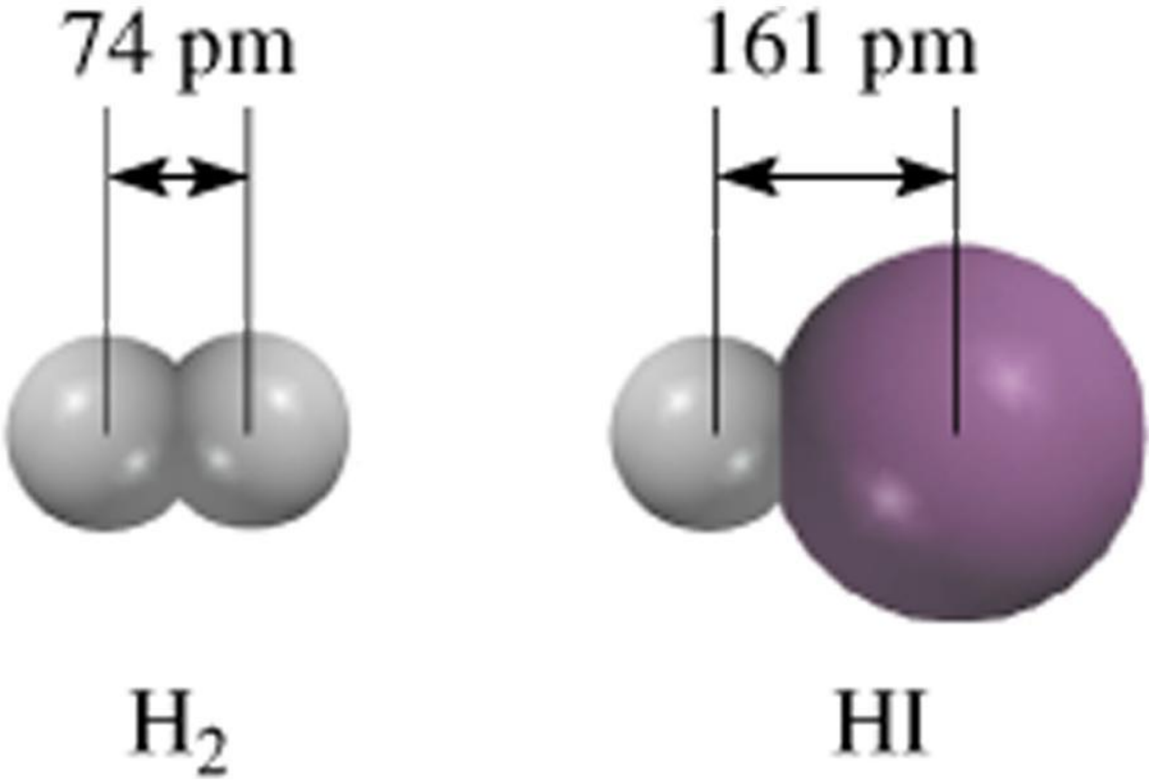
Double bond – two atoms share two pairs of electrons



Triple bond – two atoms share three pairs of electrons



Lengths of Covalent Bonds



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

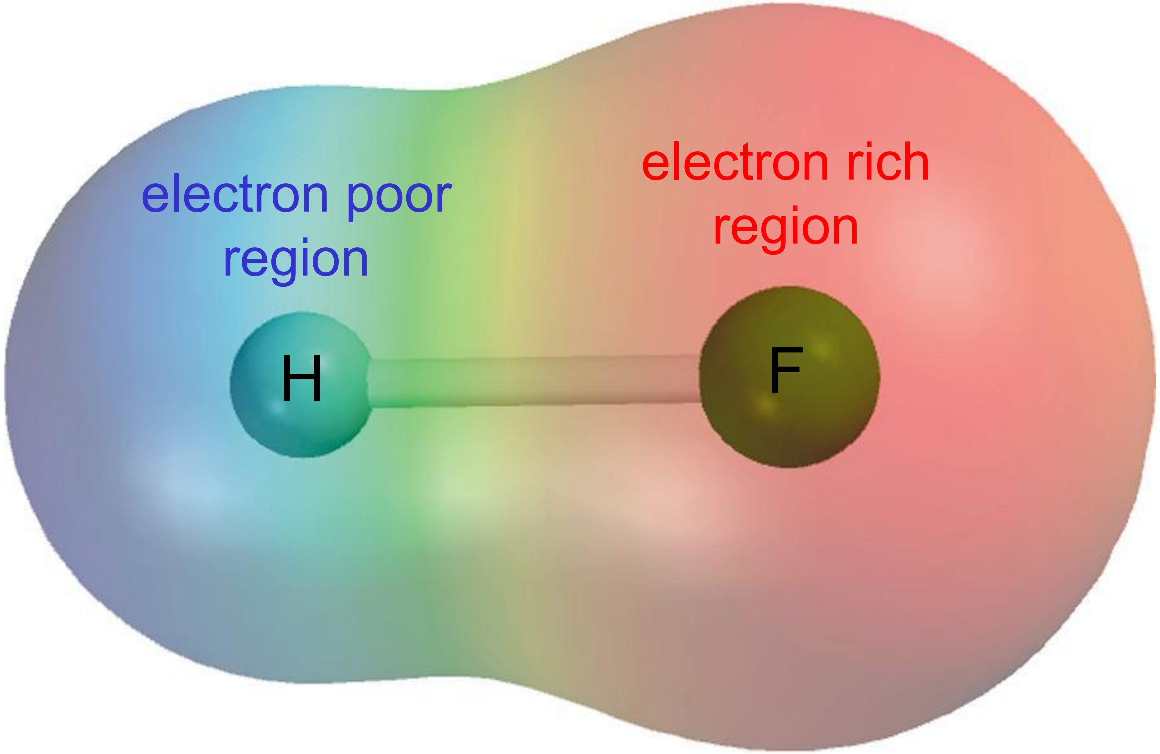
TABLE 9.3

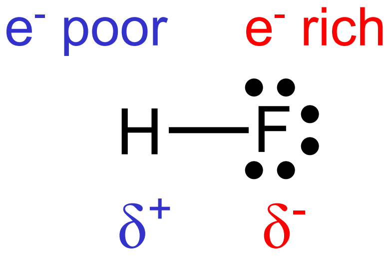
Comparison of Some General Properties of an Ionic Compound and a Covalent Compound

Property	NaCl	CCl_4
Appearance	White solid	Colorless liquid
Melting point (°C)	801	−23
Molar heat of fusion* (kJ/mol)	30.2	2.5
Boiling point (°C)	1413	76.5
Molar heat of vaporization* (kJ/mol)	600	30
Density (g/cm^3)	2.17	1.59
Solubility in water	High	Very low
Electrical conductivity		
Solid	Poor	Poor
Liquid	Good	Poor

* Molar heat of fusion and molar heat of vaporization are the amounts of heat needed to melt 1 mole of the solid and to vaporize 1 mole of the liquid, respectively.

Polar covalent bond or ***polar bond*** is a covalent bond with greater electron density around one of the two atoms



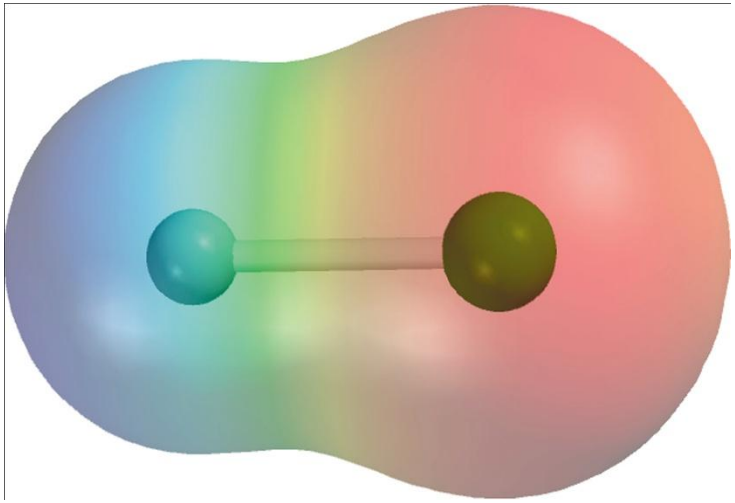


Electronegativity is the ability of an atom to attract toward itself the electrons in a chemical bond.

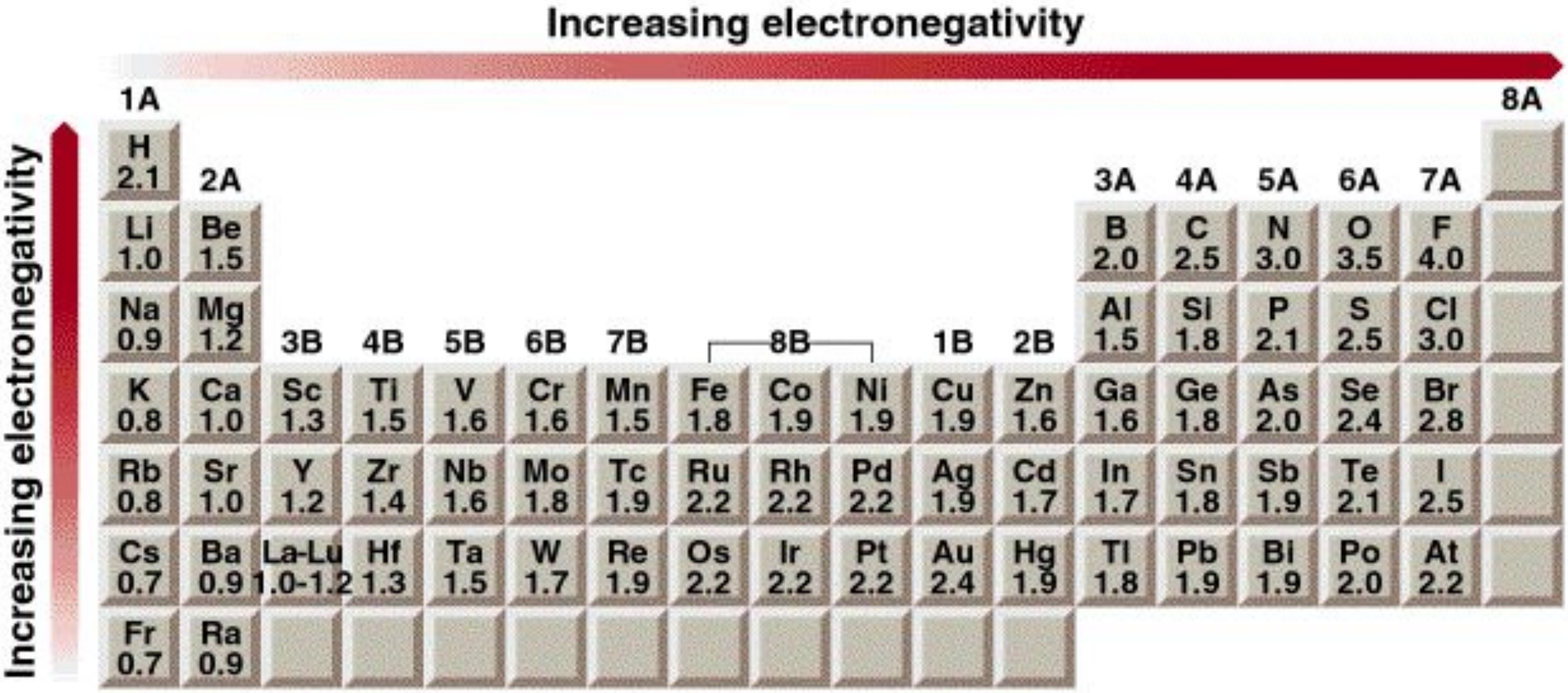
Electron Affinity - measurable, Cl is highest

$$X_{(g)} + e^{-} \longrightarrow X^{-}_{(g)}$$

Electronegativity - relative, F is highest

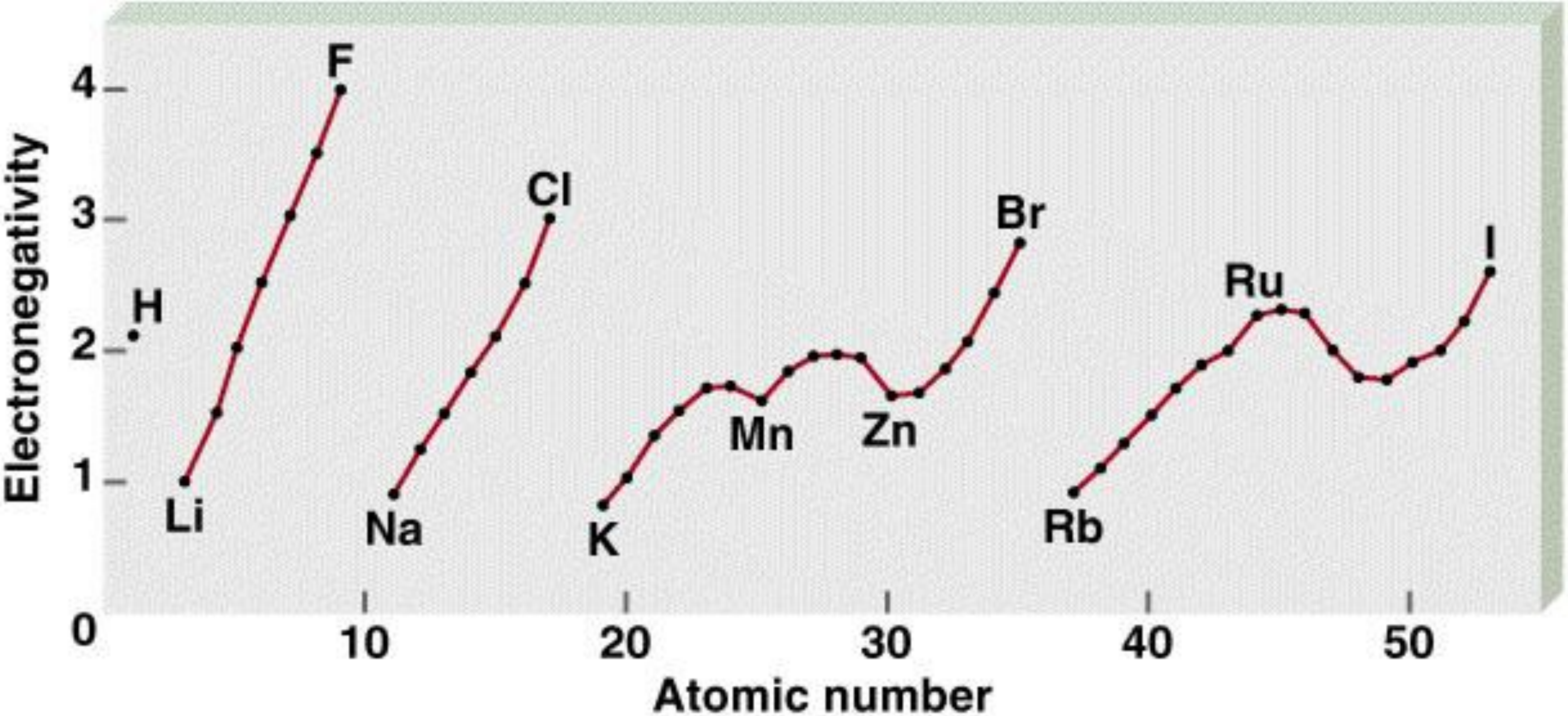


Electronegativities of Common Elements



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

Variation of Electronegativity with Atomic Number



Classification of bonds by difference in electronegativity

Difference	Bond Type
0	Covalent
≥ 2	Ionic
0 < and <2	Polar Covalent

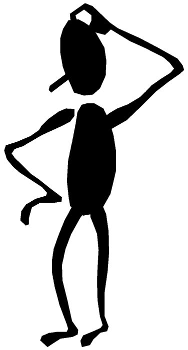
Increasing difference in electronegativity →

Covalent → Polar Covalent → Ionic

share e^-

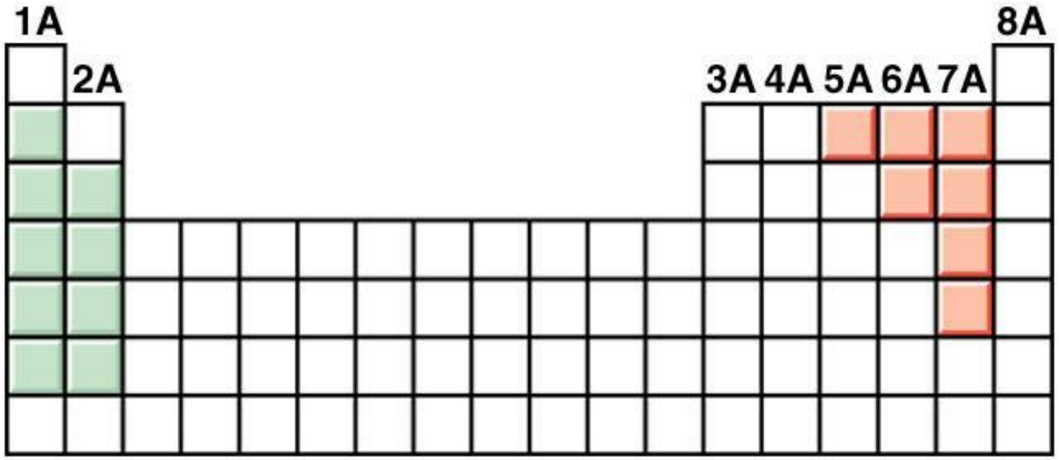
partial transfer of e^-

transfer e^-



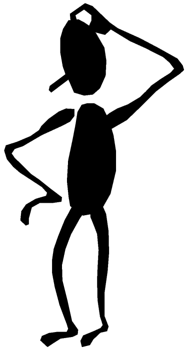
Classify the following bonds as ionic, polar covalent, or covalent: The bond in CsCl; the bond in H_2S; and the NN bond in H_2NNH_2.

Cs – 0.7	Cl – 3.0	3.0 – 0.7 = 2.3	Ionic
H – 2.1	S – 2.5	2.5 – 2.1 = 0.4	Polar Covalent
N – 3.0	N – 3.0	3.0 – 3.0 = 0	Covalent



Writing Lewis Structures

1. Draw skeletal structure of compound showing what atoms are bonded to each other. Put least electronegative element in the center.
2. Count total number of valence e^-. Add 1 for each negative charge. Subtract 1 for each positive charge.
3. Complete an octet for all atoms ***except*** hydrogen
4. If structure contains too many electrons, form double and triple bonds on central atom as needed.



Write the Lewis structure of nitrogen trifluoride (NF_3).

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

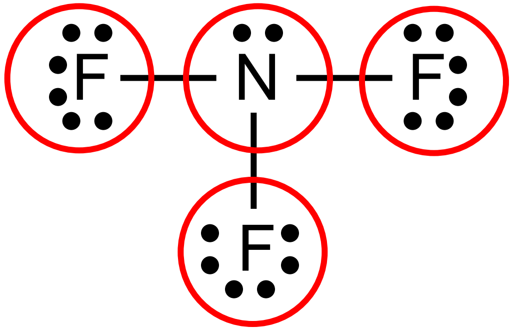
Step 2 – Count valence electrons N - 5 ($2s^22p^3$) and F - 7 ($2s^22p^5$)

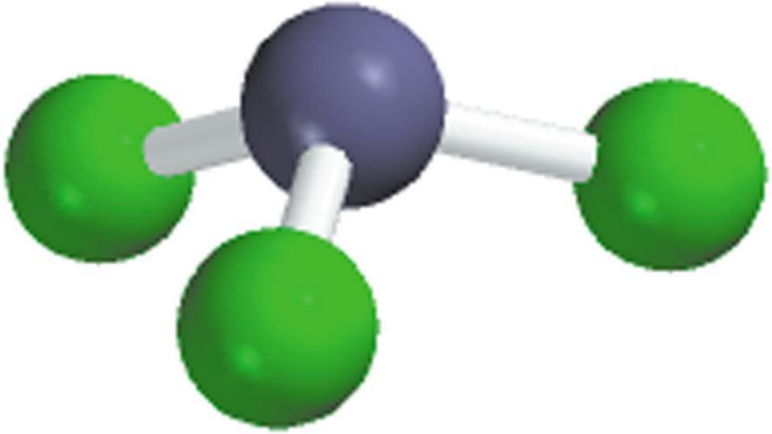
5 + (3 x 7) = 26 valence electrons

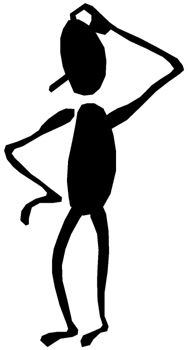
Step 3 – Draw single bonds between N and F atoms and complete octets on N and F atoms.

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

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







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

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

Step 2 – Count valence electrons C - 4 ($2s^22p^2$) and O - 6 ($2s^22p^4$)

-2 charge – $2e^-$

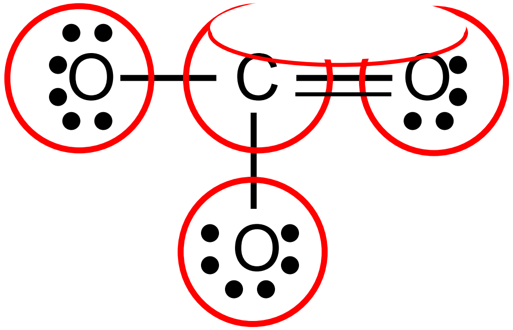
4 + (3 x 6) + 2 = 24 valence electrons

Step 3 – Draw single bonds between C and O atoms and complete octet on C and O atoms.

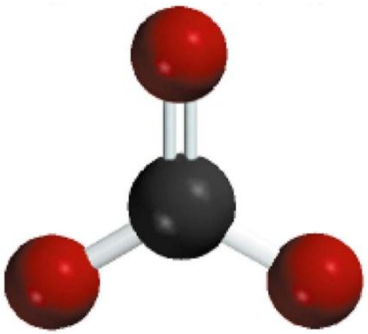
Step 4 - Check, are # of e^- in structure equal to number of valence e^-?

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

Step 5 - Too many electrons, form double bond and re-check # of e^-



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

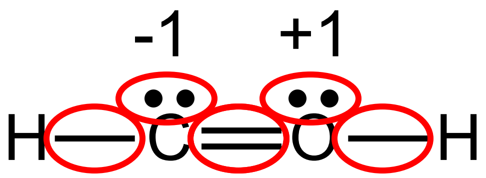


Two possible skeletal structures of formaldehyde (CH_2O)

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

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

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



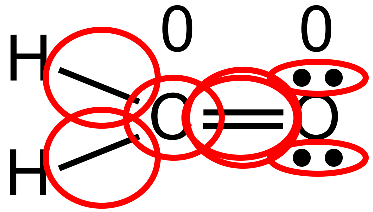
C – 4 e^-
O – 6 e^-
2H – 2x1 e^-
12 e^-

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

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

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

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



C – 4 e^-
O – 6 e^-
2H – 2x1 e^-

12 e^-

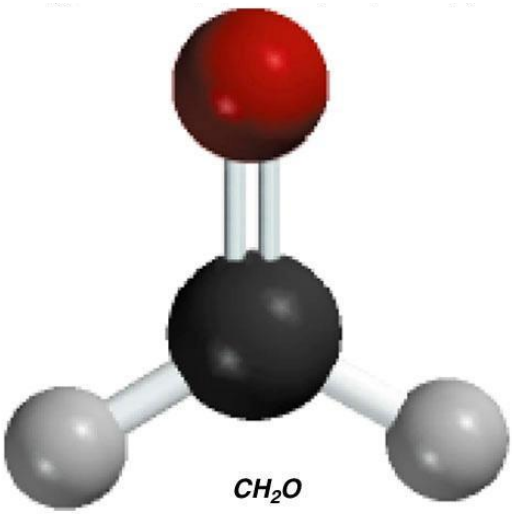
2 single bonds (2x2) = 4
1 double bond = 4
2 lone pairs (2x2) = 4

Total = 12

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

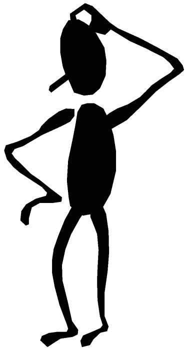
formal charge on C $= 4 - 0 - \tfrac{1}{2} \times 8 = 0$

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

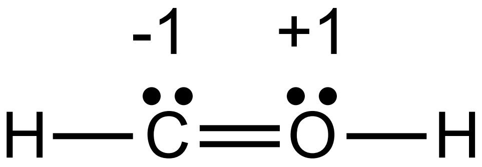


Formal Charge and Lewis Structures

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



Which is the most likely Lewis structure for CH_2O?



$$\overset{-1}{\ddot{C}}$$