CHEM 205 section 03

LECTURE #21 Thurs. March 20, 2008

ASSIGNED READINGS:

TODAY'S CLASS: Ch.9: 9.1-9.6…

NEXT CLASS: continue Ch.9

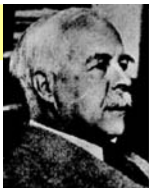
Chapter 9: Bonding & Molecular Structure – Fundamental Concepts

9.1 Valence Electrons
9.2 Chemical Bond Formation
9.3 Bonding in Ionic Compounds
9.4 Covalent Bonding & Lewis Structures
9.5 Resonance
9.6 Exceptions to the Octet Rule
9.7 Charge Distribution in Covalent Bonds & Molecules
9.8 Bond Properties
9.9 Molecular Shapes
9.10 Molecular Polarity
9.11 The DNA Story…

Chapter Goals:

- **Understand the difference between ionic & covalent bonds**
- **Draw Lewis electron dot structures for small molecules and ions**
- **Use electronegativity to predict the polarity of bonds and molecules**
- **Understand the properties of covalent bonds & their influence on molecular properties**
- **Use VSEPR theory to predict the shapes of simple molecules and ions & to understand the structures of more complex molecules**

9.1 Valence electrons… and Gilbert Lewis



G. N. Lewis
1875 - 1946

Valence e^-s: highest E, farthest from nucleus…
→ determine chemical properties

Main group elements: s & p e^-s of outermost shell
Transition series elements: in s & partly-filled d shell
OR s & partly-filled f shell

Representing valence electrons: Lewis dot structures

- use element's symbol to represent NUCLEUS + CORE e^-s
- use dots to represent VALENCE e^-s that element has…
  - place one dot per each side of symbol
  - if more left…begin to pair them up (<u>sort of</u> like $2e^-$ per orbital)
  - "full octet" = 4 pairs of e^-s = noble gas configuration
  - "full duet" = 2 pairs of e^-s, for He…and H in compounds…

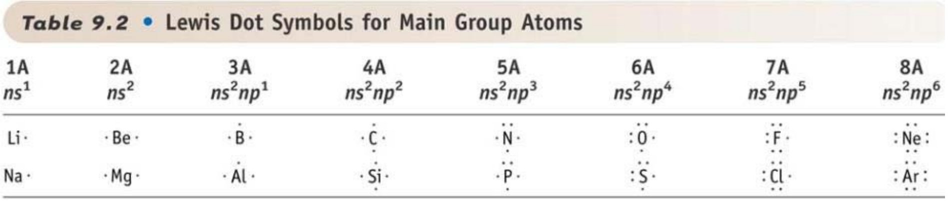


Table 9.2 • Lewis Dot Symbols for Main Group Atoms

1A ns^1	2A ns^2	3A ns^2np^1	4A ns^2np^2	5A ns^2np^3	6A ns^2np^4	7A ns^2np^5	8A ns^2np^6
$\mathrm{Li}\cdot$	$\cdot\mathrm{Be}\cdot$	$\cdot\overset{\cdot}{\mathrm{B}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}\cdot$	$\cdot\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{N}}}\cdot$	$:\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{O}}}\cdot$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\cdot$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Ne}}}:$
$\mathrm{Na}\cdot$	$\cdot\mathrm{Mg}\cdot$	$\cdot\overset{\cdot}{\mathrm{Al}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{Si}}}\cdot$	$\cdot\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{P}}}\cdot$	$:\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{S}}}\cdot$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Ar}}}:$

9.2 Chemical bond formation

- **Bonds** = forces that hold groups of atoms together and make them function as a unit

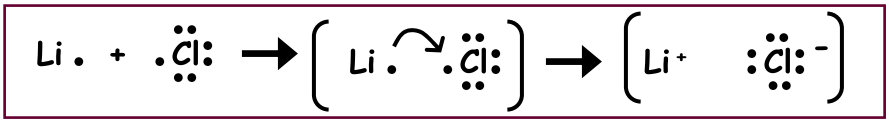
CONTINUUM:

COVALENT BONDING

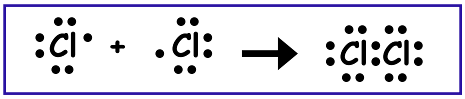
IONIC BONDING

Equal sharing
(no charge separation)

No sharing
(separate ions)



e^- transferred into valence of Cl
Li's valence shell emptied (now like He)



Shared valence, but each is "full"

9.3 Bonding in ionic compounds

IONIC BONDS = electrostatic attractions of closely packed, oppositely charged ions

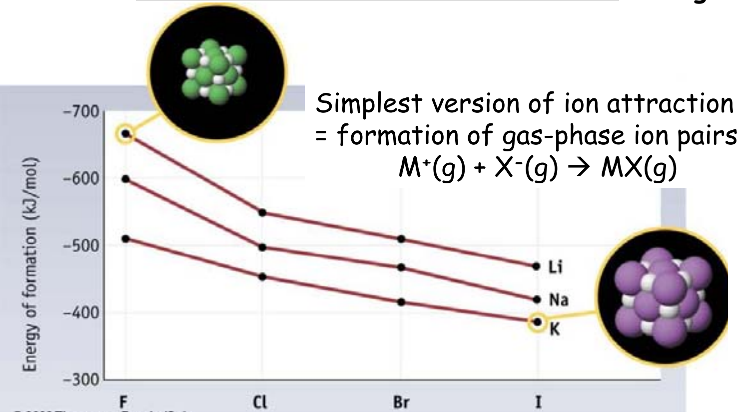
Coulomb's law $E = (2.31\times10^{-19}\ J\cdot nm)(Q_1Q_2/r)$

+/+ *or* -/- ⇨ E = +ve ⇨ repulsion

+/- ⇨ E = -ve ⇨ attraction

ion charges

distance between ion centres (nm)



Simplest version of ion attraction = formation of gas-phase ion pairs:

$M^+(g) + X^-(g) \rightarrow MX(g)$

Can quantify ion attractions this way… …but crystals provide further stabilization!

How strongly do the ions attract each other in a crystal?

- Electrostatic attraction brings ion together (↑ stability…)
  ⇨ E released as heat: "exothermic" process
- Energy released as heat: called "enthalpy", "H"
  - Note: this is from Ch.6, which we cover in Chem 206 (ignore here!)
  - Summary: $\Delta H < 0$ (negative) means system loses E as heat…

"LATTICE ENERGY" = energy released when separated, gas-phase ions are packed together into a crystal lattice

$$M^+(g) + X^-(g) \rightarrow MX(s)$$

$$\text{Lattice Energy} = k\,\frac{Q_1Q_2}{r}$$

- same form as Coulomb's law
- Q_1, Q_2 = charges on the ions
- r = shortest distance between centres of cations & anions
- k = constant for any compound… related to ion packing in 3D & e^- configuration of ions

Magnitude of LE depends on ions

- Higher charge ⇨ larger LE
- Larger ions ⇨ smaller LE

Formation of an Ionic Solid: broken down into hypothetical steps…

ENERGY INPUT/OUTPUT ?

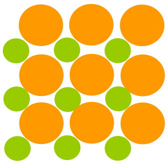
1. **Sublimation of the solid metal**
   $Li(s) \rightarrow Li(g)$ [endothermic]
2. **Ionization of the metal atoms**
   $Li^{+}(g)$: $Li(g) \rightarrow Li^{+}(g) + e^{-}$ [**I.E.**= endothermic]
3. **Dissociation of the nonmetal into atoms**
   $\frac{1}{2} F_2(g) \rightarrow F(g)$ [endothermic]
4. **Formation of X^{-} ions in the gas phase:**
   $F(g) + e^{-} \rightarrow F^{-}(g)$ [**E.A.**= exothermic]
5. **Formation of the solid MX**
   $Li^{+}(g) + F^{-}(g) \rightarrow LiF(s)$ [very exothermic]

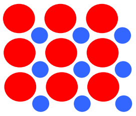
NET: $Li(s) + \frac{1}{2} F_2(g) \rightarrow LiF(s)$ **[exothermic overall…]**
FORMATION OF SALT **HEAT EVOLVED BY RXN**

Useful: if measure heat evolved by net reaction *("heat of formation")*
& subtract energies associated with steps 1-4 *(all measurable…)*
= **way to determine LATTICE ENERGY (step 5…)**

Example: predict relative lattice energy of…

One of the following pictures represents part of a KBr crystal and one represents part of a CaO crystal





Which spheres represent the anions? …the cations?
Which crystal is which?
Which crystal would have the larger lattice energy?

To confirm your predictions:
Ionic radii (pm): K^{+} 133 pm Br^{-} 196 pm
Ca^{2+} 106 pm O^{2-} 140 pm

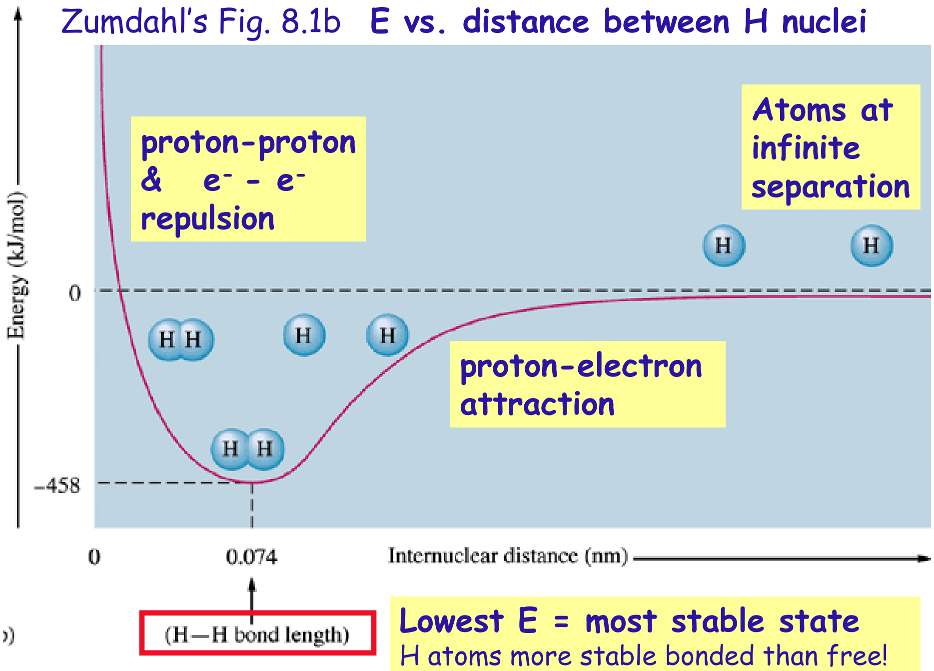
9.4-5 Covalent Bonding and Lewis Structures

- Goal: to learn to draw structures that show how electrons are shared between atoms inside molecules

- Why?
  - Can predict # bonds between atoms
  - Can predict shapes & polarities of molecules
  - Can predict properties of substances!

- First: understand covalent bonding…

Zumdahl’s Fig. 8.1b **E vs. distance between H nuclei**



proton-proton & e⁻ - e⁻ repulsion

Atoms at infinite separation

proton-electron attraction

Lowest E = most stable state

H atoms more stable bonded than free!

9.4-9.5 Covalent Bonding and Lewis Structures

- Goal: to learn to draw structures that show how electrons are shared between atoms inside molecules

- In Lewis electron dot structures **(or just "Lewis structures")**:
  - shared e^- pairs = "bonding pairs" → shown as lines
  - unshared e^- pairs = "lone pairs" → shown as two dots
    (nonbonding e^-s)
  - atoms form as many bonds as necessary to fill up their valence shell (*i.e.,* to achieve full octet…duet for H…)
  - **"octet rule"** : molecules & polyatomic ions <u>tend</u> to have structures in which each atom has 8 valence e^-s
    (but it is only a "rule" for C, N, O, F)

Drawing Lewis Structures <u>requires</u> a plan

NOTE: **Lewis structures do not require identifying which atomic orbitals are involved…**

- when atoms react: orbitals overlap (waves interfere)…Es/shapes <u>change</u>
- we will come back to orbitals at the end of Ch.9

Simplest plan of attack **(to start with…add more soon…)**

1. Decide on the central atom (never H)
2. Count total # valence e^-s (total from all atoms involved)
3. Make single covalent bonds (indicate bond using a line) to connect atoms to the central atom
4. To use remaining e^-s:
   add lone pairs (**:** 's) to achieve full octets (duet for H)
5. If central atom has <8 e^-s now:
   move a lone pair to become a bonding pair instead
   (*i.e.,* form multiple bonds)

Try: PCl_3 CO_2 HCN

Lewis structures–final steps: Exactly where is the charge?

6. Assign **formal charges** to atoms in molecule: **(section 9.7)**

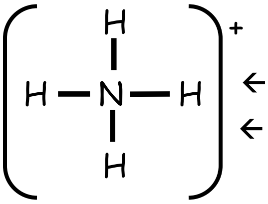
FORMAL CHARGE: how bonded atom looks relative to a free atom

= **(nuclear charge – # core e$^-$) – (# valence e$^-$s atom "owns")**

= **(# valence e$^-$s on free atom) – (# nonbonding e$^-$s + ½# bonding e$^-$s)**

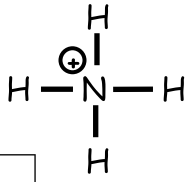
= **(# valence e$^-$s on free atom) – (# nonbonding e$^-$s + # bonds)**

Ammonium ion: NH_4^+ …the +ve charge lies on the N atom… why can we say that?



← **F.C. on N: 5 – (0+4) = +1**

← **F.C. on H: 1 – (0+1) = 0**



NOTE: formal charges usually written inside little circles ⊕ ⊖

When more than one Lewis structure can be drawn:
STRUCTURES IN WHICH FORMAL CHARGES ARE MINIMIZED ARE MORE LIKELY TO REPRESENT REALITY: more stable → preferred

Lewis structures: there is one final step, but for now…

Practise drawing Lewis structures, following the plan…
…including assigning formal charges where needed

Tetrafluoroborate anion: BF_4^-	Ozone: O_3	Carbonate anion: CO_3^{2-}

Note: sometimes there is more than one correct way to draw the same structure -- details soon ("resonance")

⇨ come back later to COMPLETE your O_3 & CO_3^{2-} structures

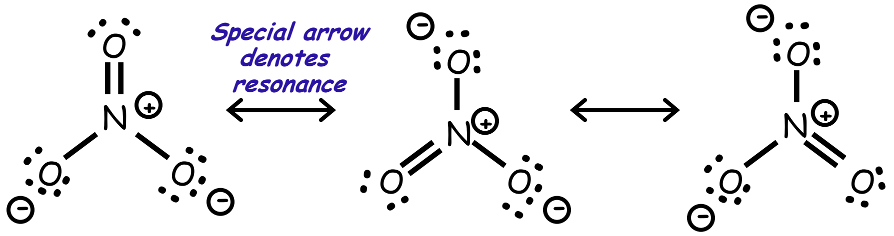
Lewis structures–final steps: Is there >1 option?

7. If more than one equivalent structure can be drawn for the same molecule: draw them all…
…the molecule's real structure is an average of them.

" resonance structures " (section 9.5)

Nitrate ion: NO_3^-

3 structures: same bonding, thus same E

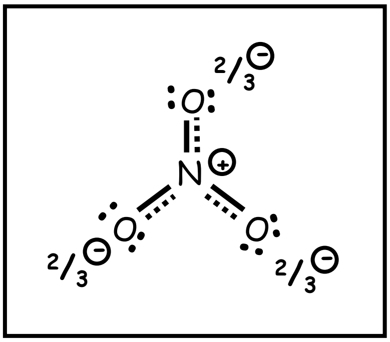


Reality: "resonance hybrid" with 3 equivalent NO bonds & 3 identical O's
→ 3 NO bonds are same length, with strength between a single & double bond
→ each O atom carries a charge of $-{}^{2}/_{3}$

The real structure:

symmetric
a resonance hybrid

= average of the most stable resonance structures (resonance contributors)



3 equivalent NO bonds & 3 identical O's
→ 3 NO bonds are same length, with strength between a single & double bond
→ each O atom carries a charge of $-{}^{2}/_{3}$ because each has ${}^{2}/_{3}$ of an extra lone pair (not shown)

9.6 Exceptions to the Octet "Rule"

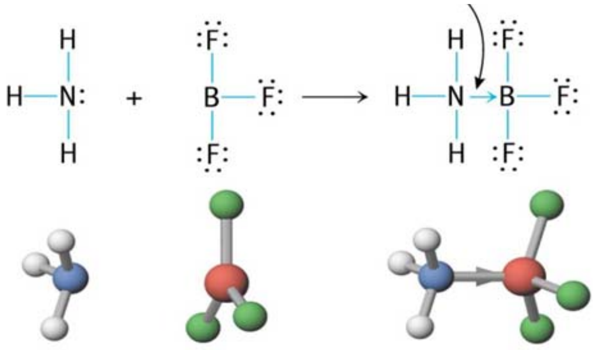
1) 2nd row elements C, N, O, F <u>always follow the octet rule</u>

- valence e^{-}s can only access 2s & 2p orbitals… 3s too high in E…

2) 2nd row elements B and Be often have < 8 e^{-}s

- B only has 3 valence e^{-}s to share: "trivalent"
- not strong enough pull on e^{-}s to make highly electronegative partners share lone pairs to fill valence via multiple bonds…
  - ⇨ "open valence" <u>very reactive towards species with lone pairs</u>

Note:
aluminum also
behaves this way…



Exceptions to the Octet Rule *continued…*

3) 3rd row and heavier elements CAN violate octet rule

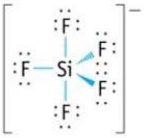
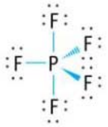
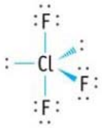
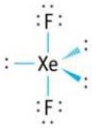
WHY?

- Valence e^{-}s in higher E orbitals ⇨ E required to access the even-higher E orbitals is LESS than for light elements…
- Thus: if necessary, can put e^{-}s into, say, the 3d orbitals…

e.g.: P, S, Cl… commonly have >8 valence e^{-}s <u>in molecules</u>

<u>THUS</u>: When writing Lewis structures, satisfy octets first, then place "extra" electrons around heavy elements

Table 9.7 • Lewis Structures in Which the Central Atom Exceeds an Octet

Group 4A	Group 5A	Group 6A	Group 7A	Group 8
SiF_5^-	PF_5	SF_4	ClF_3	XeF_2
				

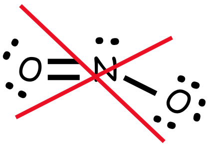
Exceptions to the Octet Rule *continued…*

4) **Molecules with odd numbers of electrons**

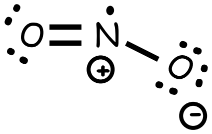
- Rare cases when C,N,O,F simply CAN'T obey octet rule… since not enough e^-s available
- Result: molecule ends up containing <u>an unpaired e^-</u>

"free radical"   *yes - paramagnetic!*

e.g., NO_2 **Total # valence electrons: 5 + 2(6) = 17 e^-**



Adds up to 18 e^-!
Must remove one from our structure…



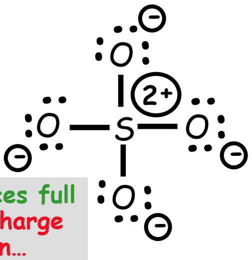
N ends up one e^- short
i.e., valence not full: "open shell" (reactive!)

Why not the oxygen instead?
→ Because O has stronger pull on e^-s than N…

Finally: the most realistic possible Lewis structure HAS…

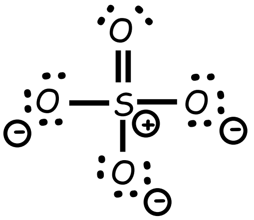
1. All atoms with full valence shell, if possible (except Be,B,Al…).
2. Minimum charge separation (reduce F.C.'s using multiple bonds…).
3. Formal charges agreeing with atoms' electronegativity (if possible).

Sulfate ion: SO_4^{2-}
6 + 4(6) + 2 = 32 e^-s
& S can exceed octet…



☑ All valences full
☒ Lots of charge separation…

↔



☑ All valences full
☒ Charge separation could still be less…

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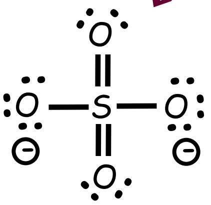
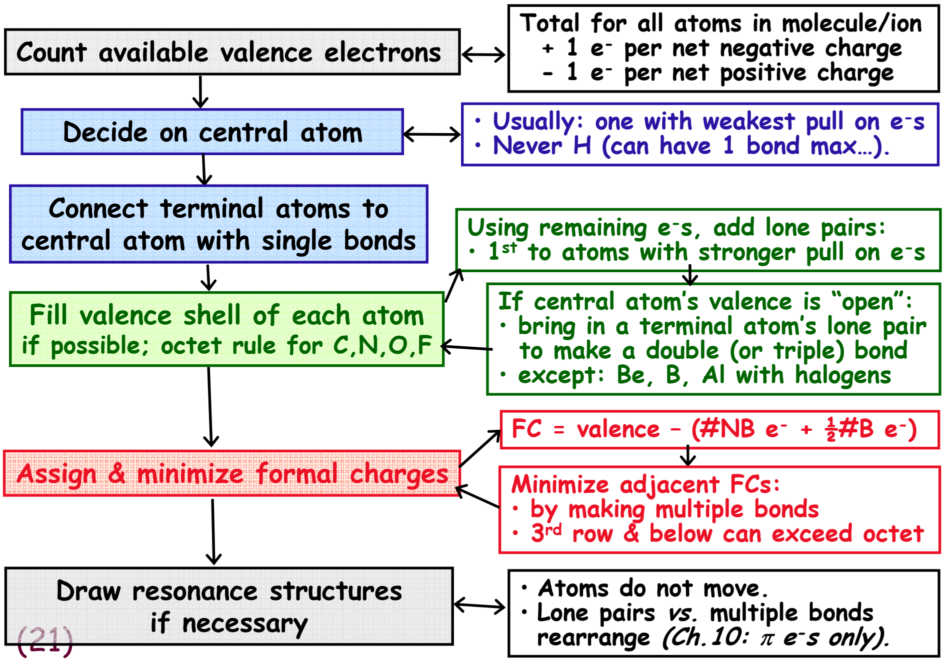


+ 5 other structures with 2 S=O & 2 S–O bonds
Same stability as one shown!
Resonance hybrid (reality)
= average of those 6 resonance contributors.

↔

The most stable!
☑ All valences full
☑ Charge separation minimized!

Summary: strategy for drawing Lewis structures



Count available valence electrons

Total for all atoms in molecule/ion
+ 1 e^- per net negative charge
- 1 e^- per net positive charge

Decide on central atom

- Usually: one with weakest pull on e^-s
- Never H (can have 1 bond max…).

Connect terminal atoms to central atom with single bonds

Fill valence shell of each atom if possible; octet rule for C,N,O,F

Using remaining e^-s, add lone pairs:
- 1st to atoms with stronger pull on e^-s

If central atom's valence is "open":
- bring in a terminal atom's lone pair to make a double (or triple) bond
- except: Be, B, Al with halogens

Assign & minimize formal charges

FC = valence – (#NB e^- + $\frac{1}{2}$#B e^-)

Minimize adjacent FCs:
- by making multiple bonds
- 3rd row & below can exceed octet

Draw resonance structures if necessary

- Atoms do not move.
- Lone pairs *vs.* multiple bonds rearrange *(Ch. 10: π e^-s only).*

Draw the best possible Lewis structures…
& then identify if all atoms obey octet rule.

(remember: C,N,O,F CANNOT exceed)

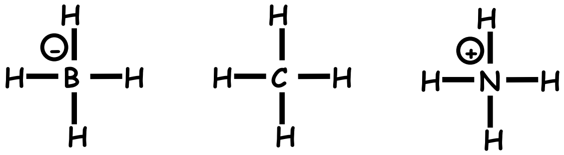
SO_2

ClO_4^-

Isoelectronic and Isostructural species

- Molecules/ions with same number of valence electrons in same bonding/nonbonding arrangement
  - *i.e.,* same Lewis structure
    but some atoms & formal charges will differ…

Table 9.6 • Some Common Isoelectronic Molecules and Ions

Formulas	Lewis Structure
BH_4^-, CH_4, NH_4^+	

ASSIGNED READINGS

BEFORE NEXT CLASS:

read up to 9.6…

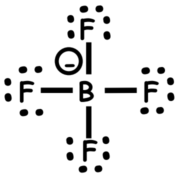
practice Lewis structures
(with formal charges…)

ESSENTIAL FOR NEXT TOPIC!

Practise drawing Lewis structures, following the plan...
…including assigning formal charges where needed

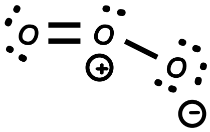
Tetrafluoroborate anion: BF_4^-

1 B: 1(3) = 3 valence e^-s
4 F: 4(7) = 28
1 – charge = 1
Total = 32 valence e^-s



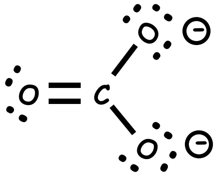
Ozone: O_3

3 O: 3(6) = 18 val. e^-s
0 charge = 0
Total = 18 val. e^-s



Carbonate anion: CO_3^{2-}

1 C: 1(4) = 4 val. e^-s
3 O: 3(6) = 18
2 - charge = 2
Total = 24 val. e^-s



Note: sometimes there is more than one correct way to draw the same structure –- “resonance” structures

⇨ include equivalent resonance structures for O_3 & CO_3^{2-}