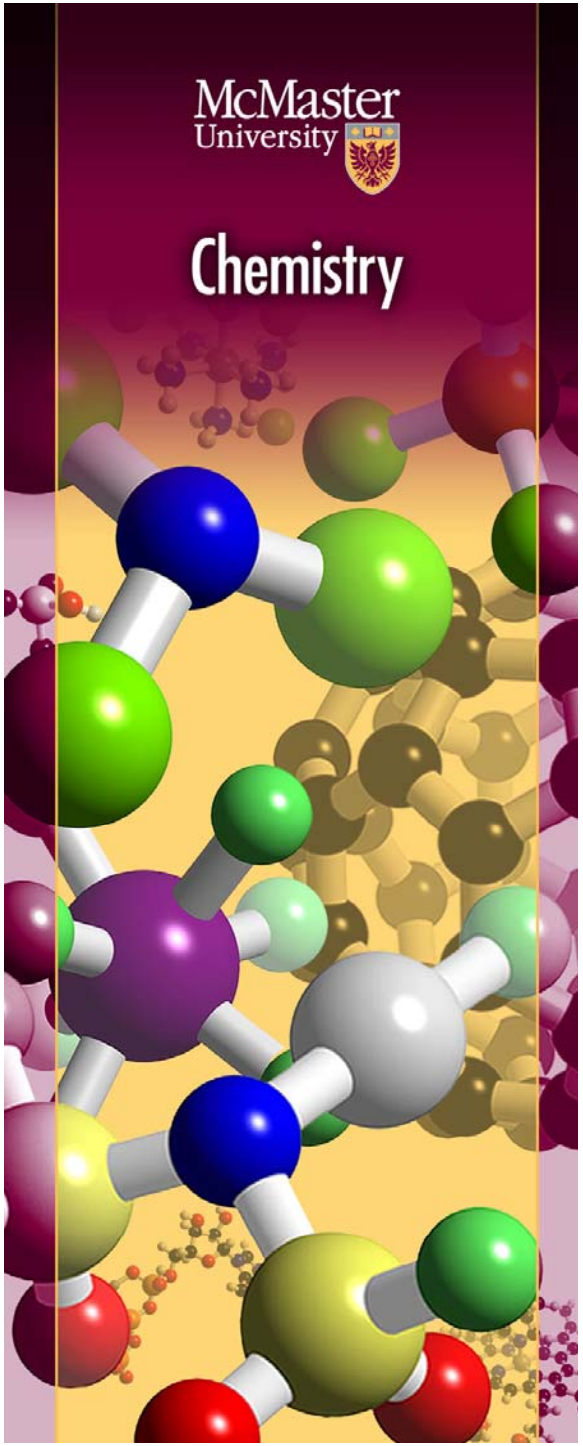
CHEM 1A03: Intro. Chemistry I

Essential Elements: Chemistry, Life & Health

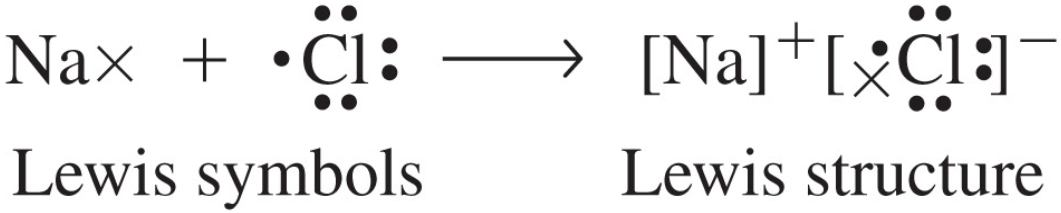
Ch.10: Chemical Bonding



Bonding

- Involves **transfer** or **sharing** of outer electrons, usually to acquire a stable configuration (Lewis)

Ionic bonding
(**transfer** of electrons)



- Usually between a metal and non-metal

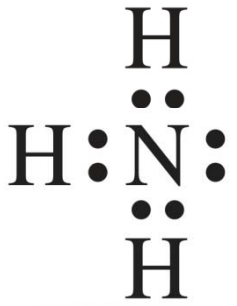
Na [Ne]$3s^1$ becomes Na^+ [Ne] and

Cl [Ne]$3s^2 3p^5$ becomes Cl^- [Ar]

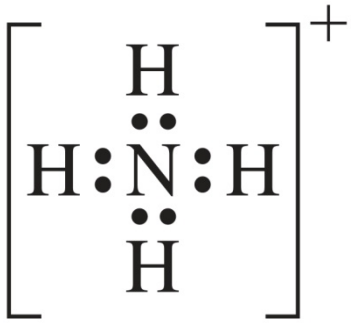
p. 396 (374, 9th ed.)

Covalent Bonding

- Covalent bonding
  - **Sharing** of electrons
  - Often to attain an octet of electrons
  - Often between 2 non-metals
  - Lewis structure shows all electrons as equivalent

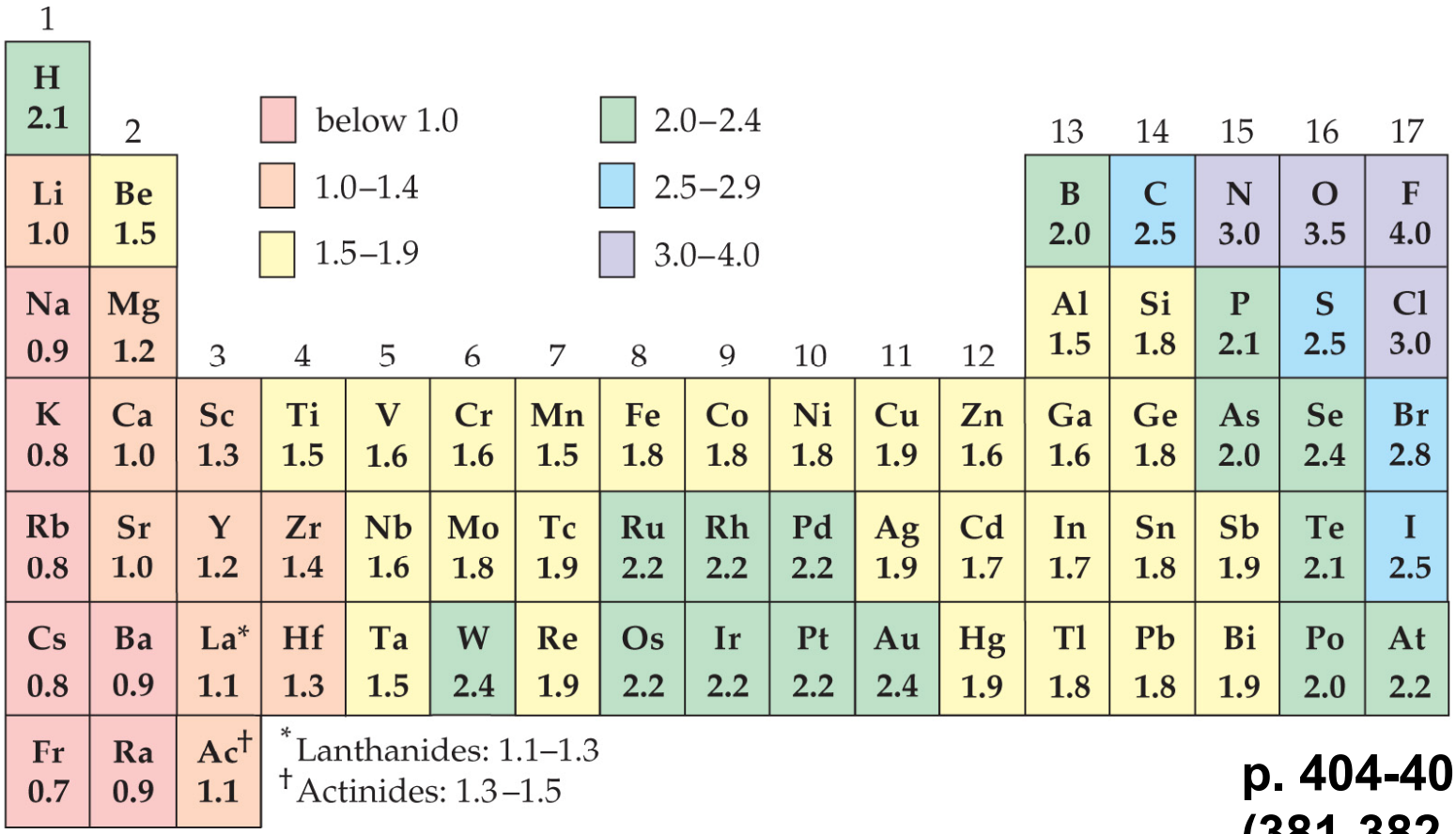


- ***Coordinate*** covalent bond
  - One atom provides both e^- for a bond
  - e.g. $NH_3 + H^+ \rightarrow NH_4^+$



p. 399-401 (375-377, 9th ed.)

Electronegativity (EN) – Fig. 10-6

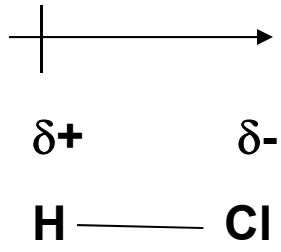


p. 404-406
(381-382, 9th ed.)

- Atom's ability to compete for e^- in a bond
- Trend: EN increases across a period and up a group
- Pauling scale: F 4.0 (highest EN)

Bond Polarity

- **Polar** covalent bonds
  - ***Unequal*** sharing of e^-
  - Indicated by polar arrow and partial charges



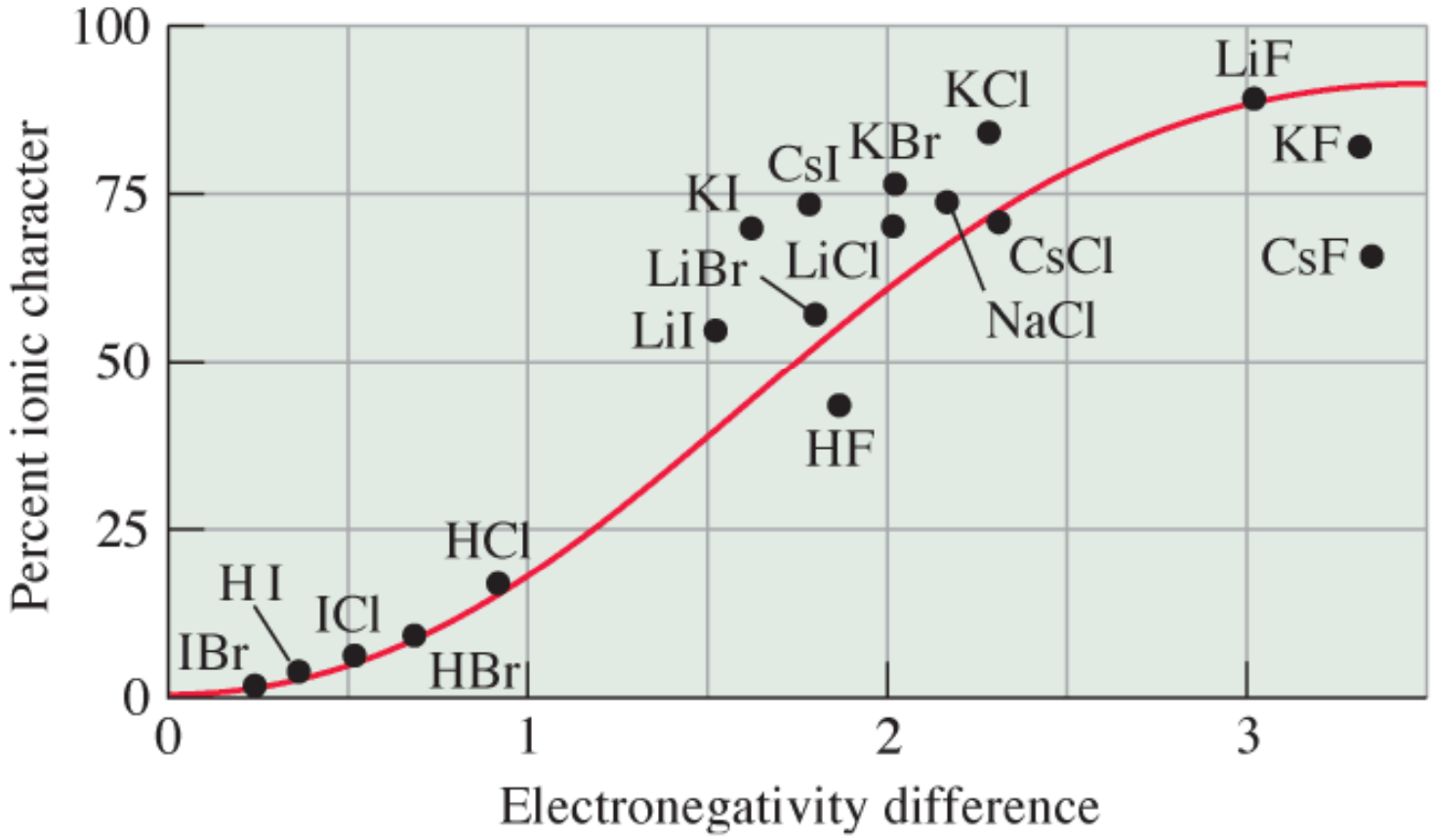
- Dictated by ΔEN between atoms

ΔEN	Bonding	Example
Large	Ionic	NaCl
Intermediate	Polar Covalent	PCl_5
Zero (Small)	Pure Covalent	Cl_2

- Percent ionic character of a bond involving a certain element (e.g. Cl) decreases across a period

p. 402-404 (378-380, 9th ed.)

Percent ionic character vs. ΔEN



Approximately:

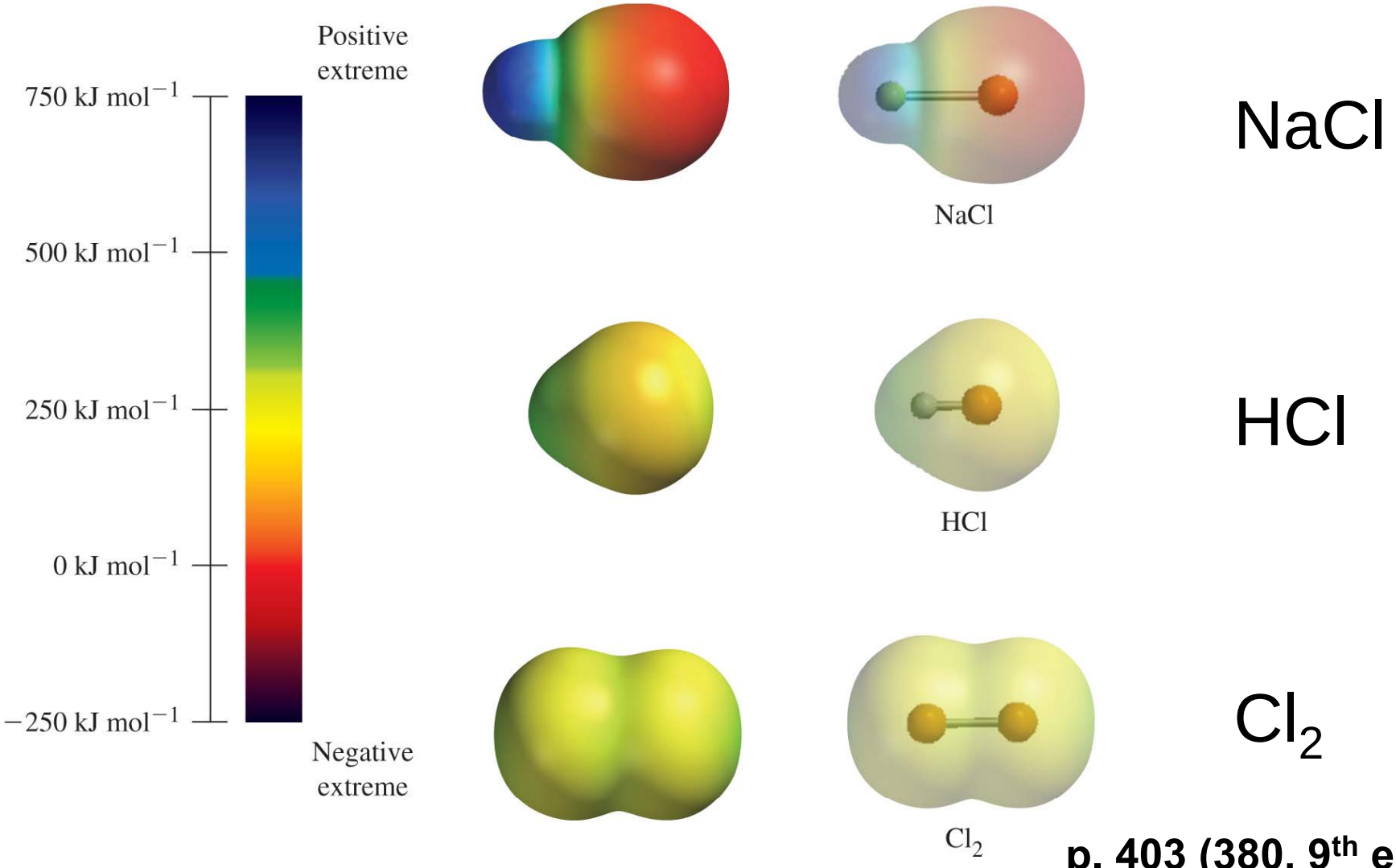
0 – 0.4 Covalent (weakly polar covalent)

0.4 – 1.9 Polar covalent; > 1.9 Ionic

Fig. 10-7

p. 406 (382, 9th ed.)

Electrostatic potential maps: Fig. 10-5



p. 403 (380, 9th ed.)

Effect of EN on charge distribution

Lewis Structures

- Show bonding (b) and non-bonding (nb) e^-, and formal charges

- Octet* can be achieved by combination of bonding and nonbonding e^-

  ***(not all atoms will have an octet)**

- Bonding e^- can be single, double, triple bonds

p. 408 (384, 9th ed.)

Drawing Lewis Structures

1. Count total # of e^- (include charge)
   - Add e^- for negative charge, subtract e^- for positive charge
2. Draw skeletal structure (central & terminal atoms)
   - The least electronegative atom is generally the central atom
   - H and F are always terminal
3. Deduct 2 e^- for each single bond of skeleton
4. Use remaining e^- to complete octet of terminal atoms
   - Only 2 e^- for H
5. Subtract e^- used for terminal octets
6. If e^- remain, place on central atom

p. 409-411
(385-388, 9th ed.)

Drawing Lewis Structures…continued

7. Do all atoms have octet (2 for H)?
   - If not: use lone pairs to form multiple bonds
   - But note: Often Group 2, 3 elements have < 8 e^-

8. Calculate formal charges on each atom
   FC = (Group A # – # non-bonding e^- – # bonds)
   All formal charges must add up to total charge

9. Minimize formal charges to zero, where possible*, by creating multiple bonds (*more notes on this later)

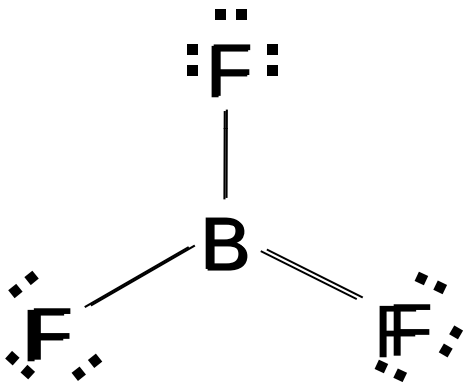
   Steps 8 and 9: may be new to you!

Examples: Draw BF_3, NO_3^-, $BrOF_2^+$

Also p. 412-413 (392-395, 9th ed.)

BF_3

B: 1x3= 3
F: 3x7= 21
Total e^-= 24

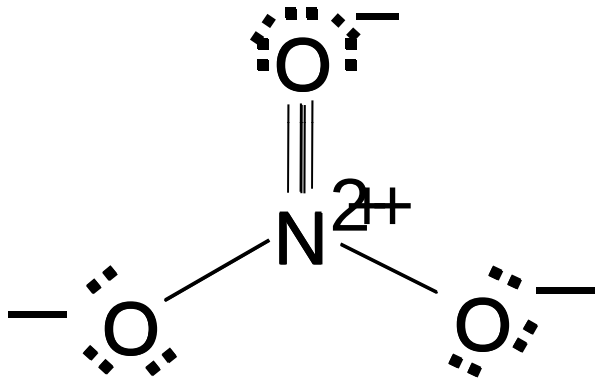


Formal Charge:
F: 7−1−6= 0
B: 3−3−0= 0

Initial e^-: 24
Bonds: −6
18
Outer e^-: −18
0

NO_3^-

N: 1x5= 5
O: 3x6= 18
charge= 1
Total e⁻= 24



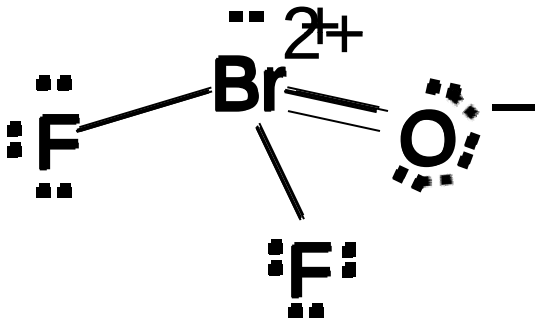
Formal Charge:
O: 6−1−6= −1
N: 5−3−0= +2

Initial e⁻: 24
Bonds: −6
18
Outer e⁻: −18
0

Formal Charge:
O: 6−1−6= −1
O: 6−2−4= 0
N: 5−4−0= +1

$BrOF_2^+$

Br: 1x7= 7
O: 1x6= 6
F: 2x7= 14
charge= −1
Total e⁻= 26



Formal Charge:
F: 7−1−6= 0
O: 6−1−6= −1
Br: 7−3−2= +2

Initial e⁻: 26
Bonds: −6
20
Outer e⁻: −18
2
Center e⁻: −2
0

Formal Charge:
F: 7−1−6= 0
O: 6−2−4= 0
Br: 7−4−2= +1

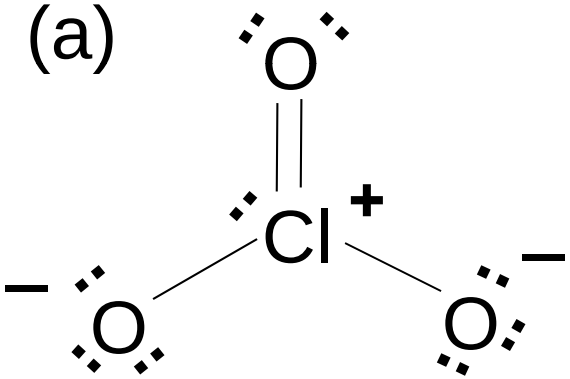
Notes about Lewis structures

- Octet is not exceeded in Period 2 **p. 413, 418-421**
  - C N O F can not over fill **(389, 9th ed.)**
  - cannot exceed the "octet rule" even if there are adjacent formal charges that could be minimized
- For elements in Periods 3, 4, etc., minimizing formals charges is the priority, even if it means breaking the "octet rule".
- Usually don't have adjacent atoms with same formal charge
- Negative formal charges ***usually*** appear on the most electronegative atoms, positive charges on the most electropositive atoms

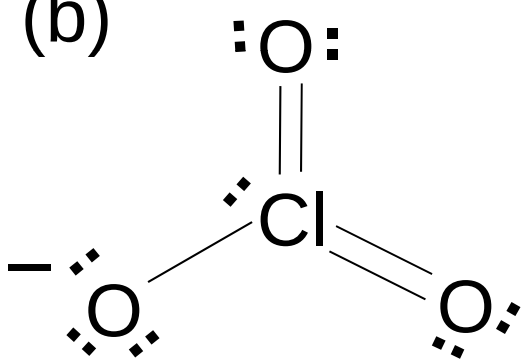
i-Clicker Question #1

1. Select the **most** appropriate Lewis structure for chlorate anion: ClO_3^-.

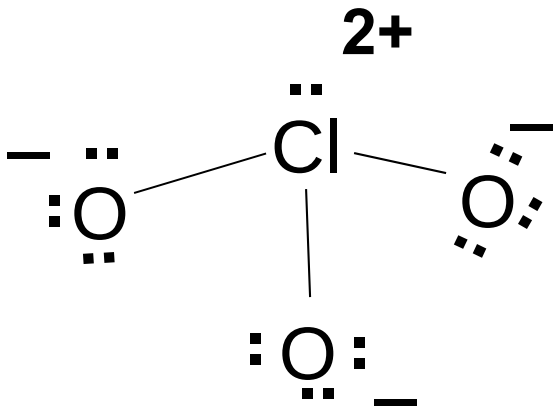
(a)



(b)



(c)

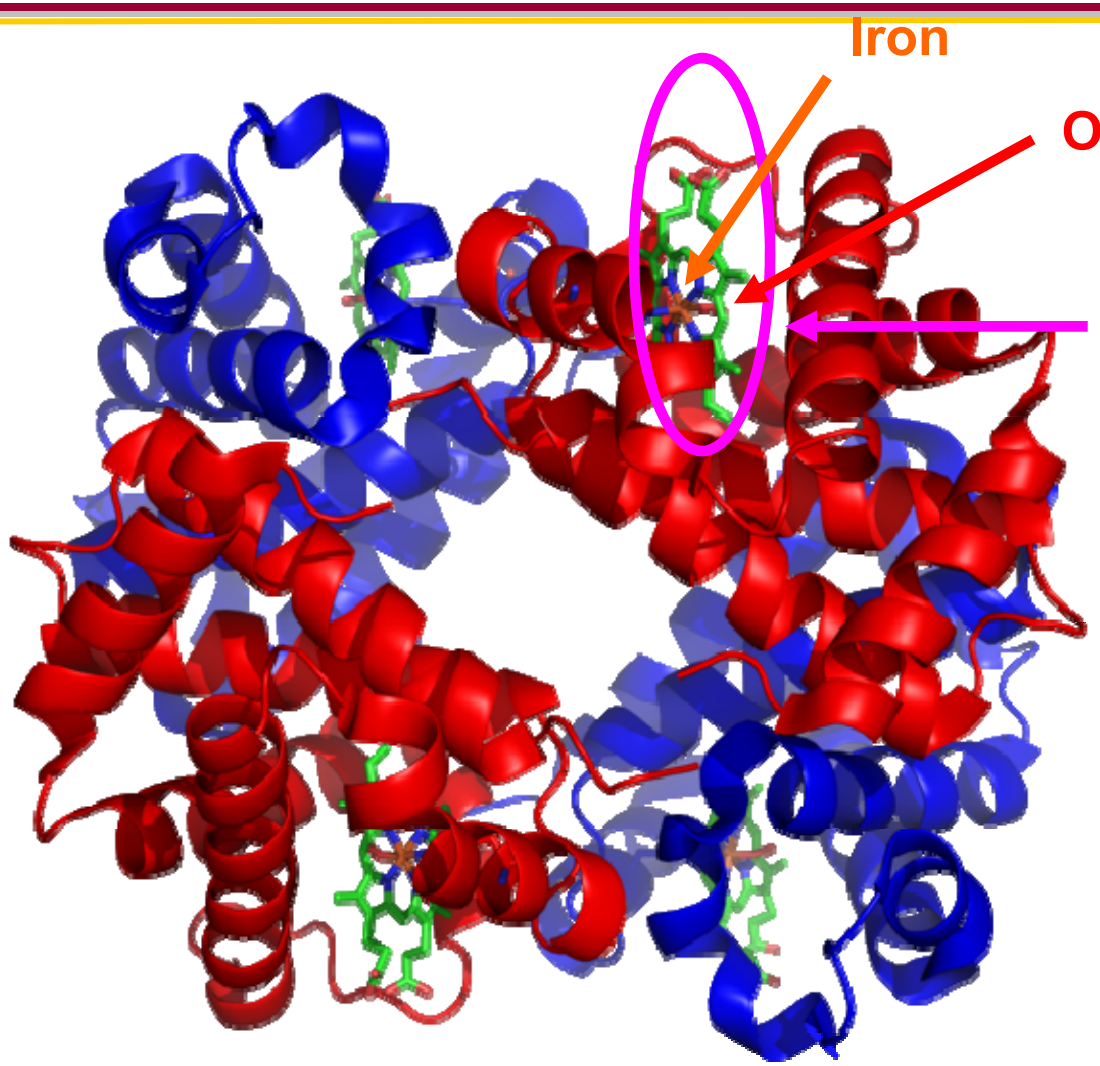


©Chemistry

ClO_3^-

- Cl is in period 3 and can accommodate more than an octet of electrons.
- A charge-minimized Lewis structure shows that formal charges have been made as close to zero as possible; for elements in periods 3, 4, 5, … this can often be achieved by creating multiple bonds in order to minimize formal charges towards zero.
- Structure (b) on the previous page shows this.

Hemoglobin



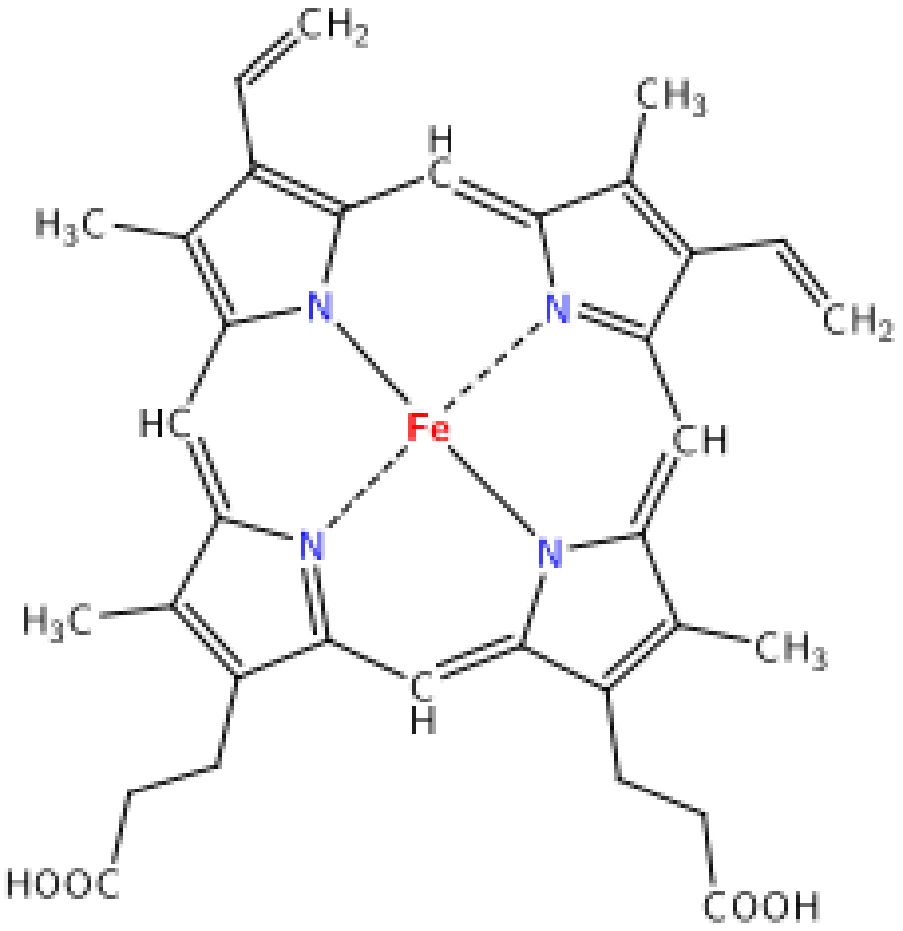
http://en.wikipedia.org/wiki/Image:1GZX_Haemoglobin.png

$C_{738}H_{1166}N_{812}O_{203}S_2Fe$ - human

Heme structure

- Structure details:

http://www.umass.edu/molvis/tutorials/hemoglobin/heme.htm



Animation of O_2 binding to Hb

- http://www.chemistry.wustl.edu/~edudev/LabTutorials/Hemoglobin/changemovie.html

O_2 molecule binds to iron of the heme unit

Note how the geometry around iron changes as O_2 is bound vs. free

What do we know about hemoglobin?

Carboxyhemoglobin: The Silent Killer

CO binds competitively to the heme unit and displaces O_2

CO poisoning can result!

< 50 ppm: Upper safety limit

50-200ppm: Headache/nausea

> 200 ppm: Dizziness/convulsions

Treatment?

Saturation with O_2 can reverse the process (the binding is an equilibrium process – Ch 15)

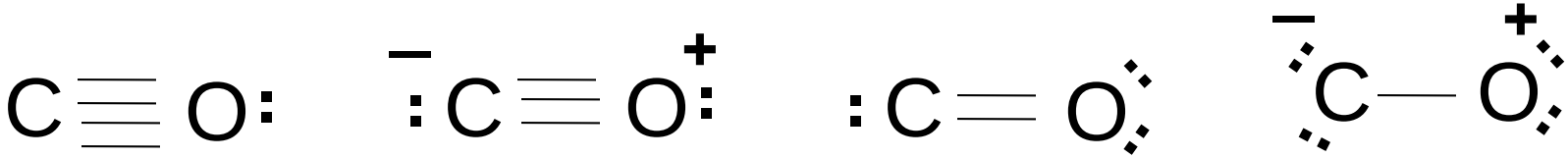
FOCUS:

Why does CO bind so well to the heme unit?

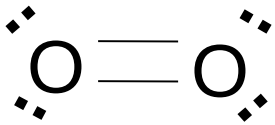
i-Clicker Question #2

Select from the following Lewis structures the one that is the most appropriate for CO?

(a) (b) (c) (d)

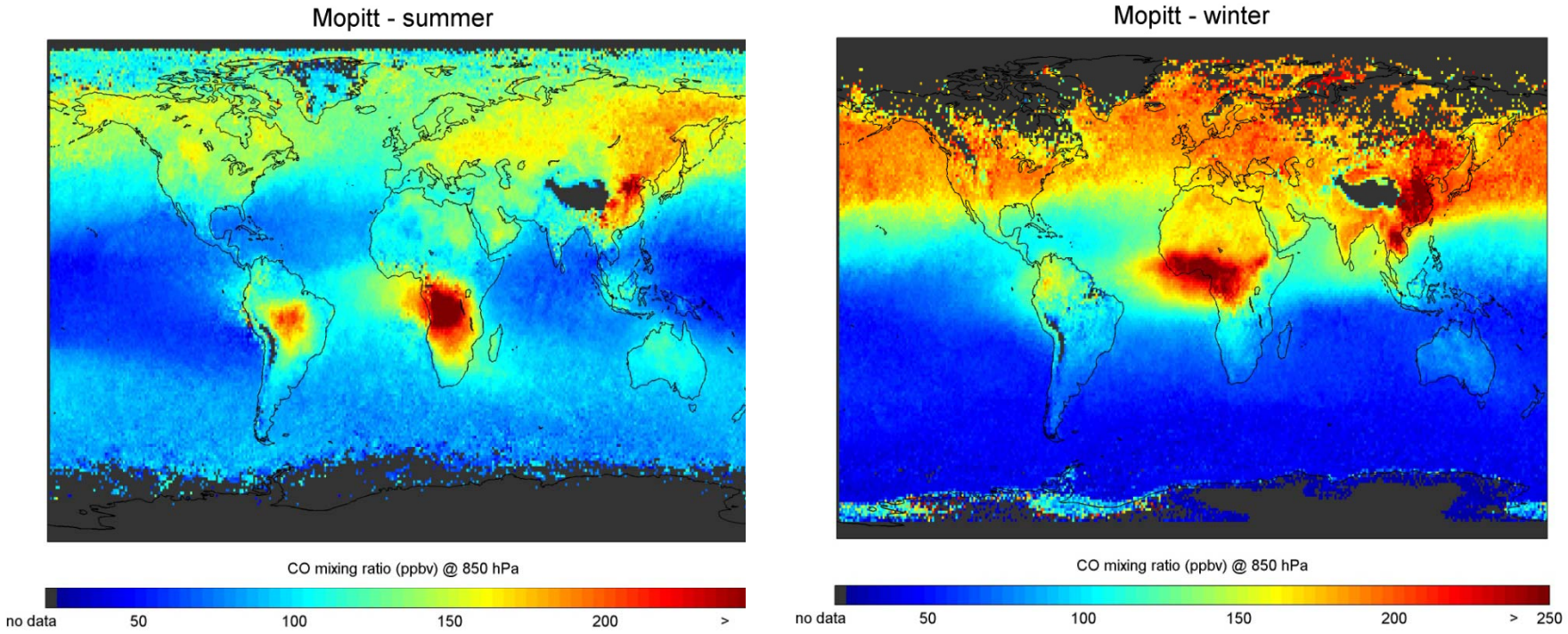


The Lewis structure of O_2 is:



Earth CO Atmospheric Concentrations

Identify patterns and sources of CO emissions in summer/winter world maps (2000-2004) below:

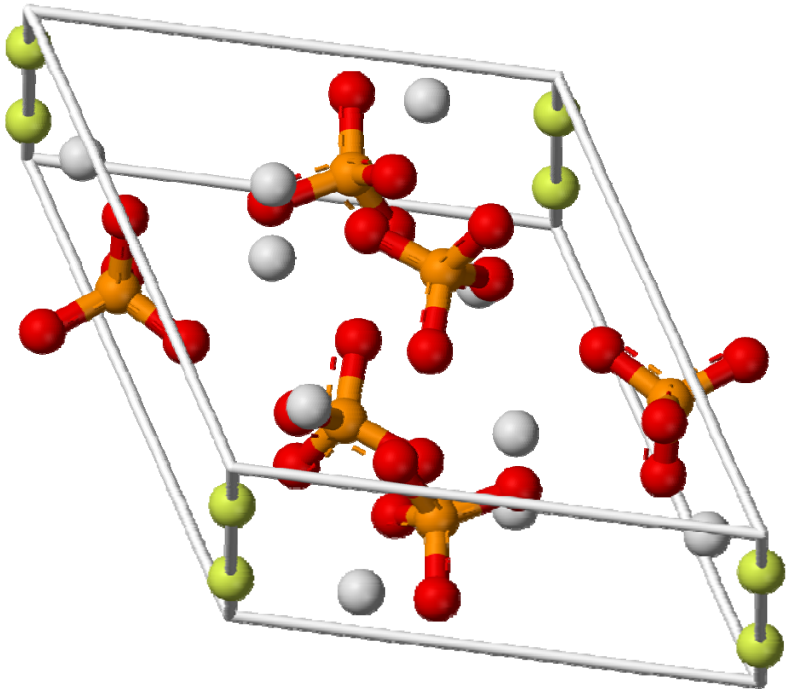


http://earthobservatory.nasa.gov/Newsroom/NewImages/images.php3?img_id=16550

Resonance structures

- Average formal charge
- Average bond order

- Recall: Teeth!
  - Fluorapatite
  - $Ca_5(PO_4)_3F$
  - Look at PO_4^{3-} ions

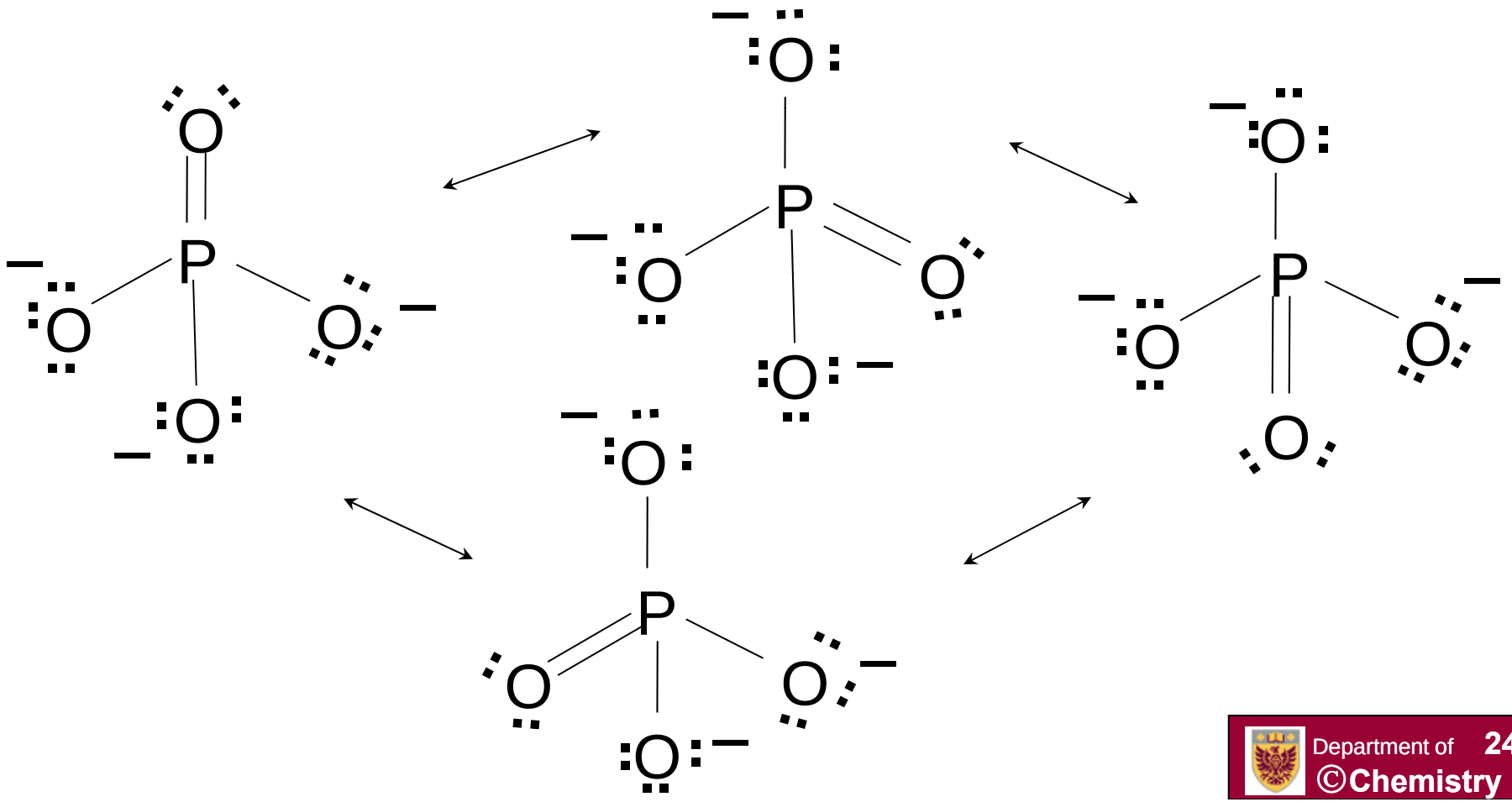


Draw

p. 416-417 (391- 392, 9th ed.)

Resonance structures for PO_4^{3-}

- For each PO_4^{3-} there are 4 equivalent charge-minimized structures (resonances structures)



Resonance structures for PO_4^{3-}

- Average formal charge for an atom = $\frac{\text{total charges on atom}}{\text{total \# of that atom}}$

  Average formal charge on O: = $\frac{0 + (-1) + (-1) + (-1)}{4} = -3/4$

- Average bond order = $\frac{\text{total number of 1 type of bond}}{\text{\# of places where the bond is found}}$

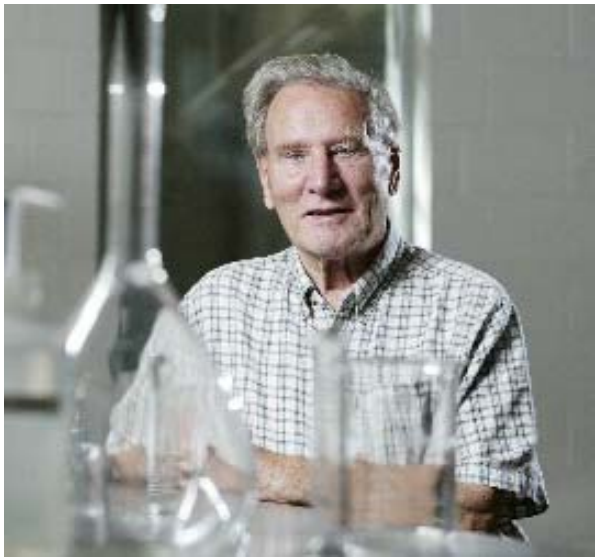
  Average P-O bond order = $\frac{1 + 1 + 1 + 2}{4} = 5/4$ or 1.25

Molecular Shape

- VSEPR* (valence shell electron pair repulsion) Theory *[Ron Gillespie, McMaster Chemistry!]*

  *50+ Years of VSEPR!

http://www.chemistry.mcmaster.ca/extracts/extracts99/ronald_gillespie/



- Electron pairs repel one another
- Repulsion decreases:

  lone pair/lone pair >

  bonded pair/lone pair >

  bonded pair – bonded pair

  – Note: double bonds occupy slightly ***more*** space than a lone pair

p. 421-424 (395-398, 9th ed.)

VSEPR classes

- AX_nE_m

  A = central atom

  X = atoms bonded to central atom

  E = lone electron pairs

- Electron pair geometry dictates the observed molecular shape (watch where they are different!)

- Table 10.1 – know the shapes!

  Note: Table 10.1 gives only ideal angles; know which ones are non-ideal also! (class notes)

p. 424-428 (398–402, 9th ed.)

2 electron pairs

- AX_2 linear 180°

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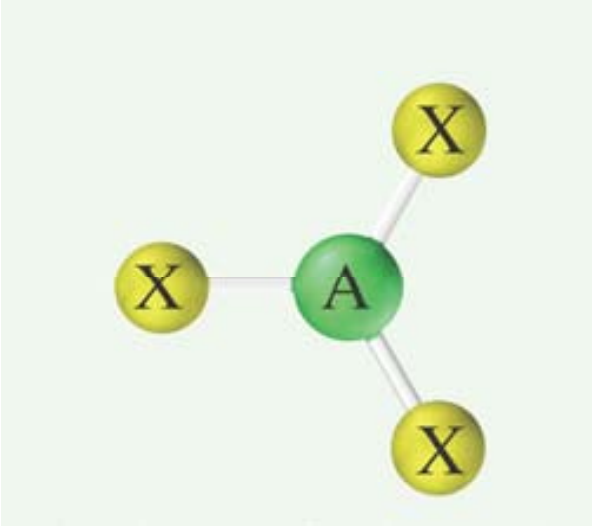
3 electron pairs

AX_3

Trigonal planar

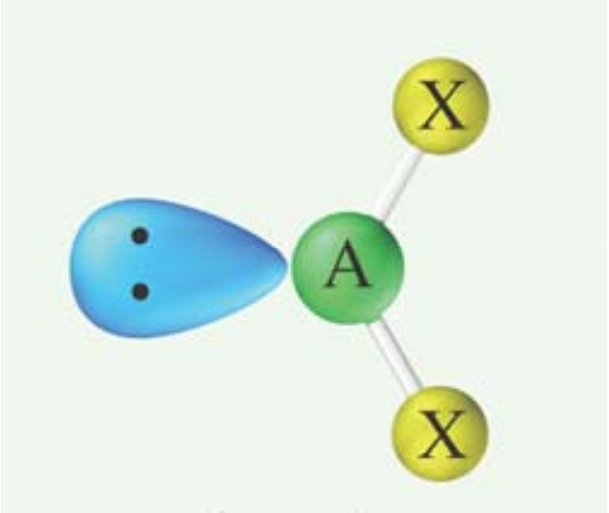
120°



AX_2E

Bent

< 120° (non-ideal)

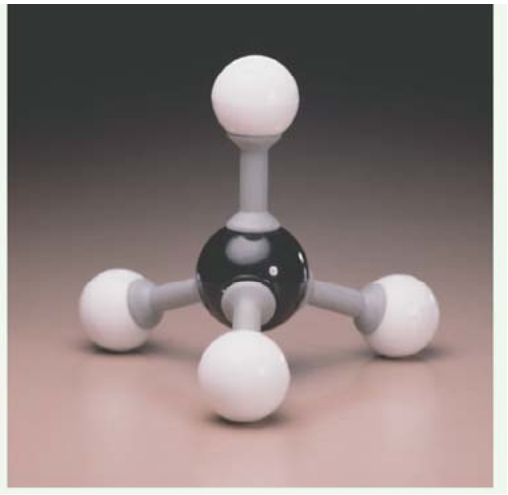


4 electron pairs

AX_4

Tetrahedron

109.5°

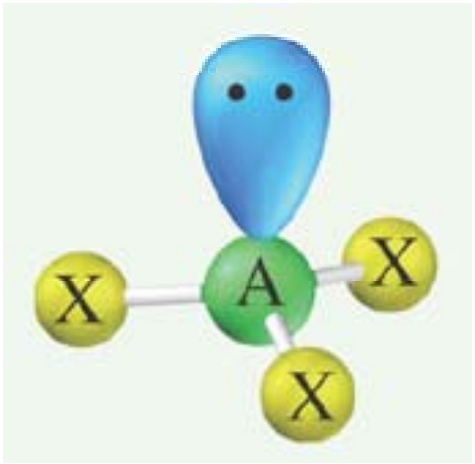


AX_3E

Trigonal pyramidal

< 109.5° (non-ideal)

NH_3: 107°

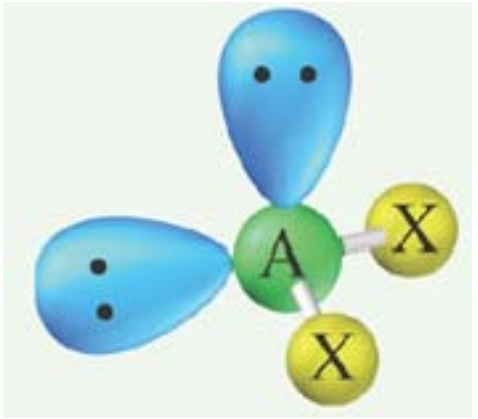


AX_2E_2

Bent

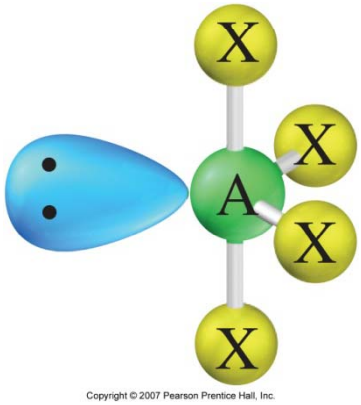
< 109.5°

H_2O: 104.5°



5 electron pairs

AX_5	AX_4E	AX_3E_2	AX_2E_3
Trigonal bipyramidal	Seesaw	T-shape	linear
90°, 120°	non-ideal	non-ideal	180°



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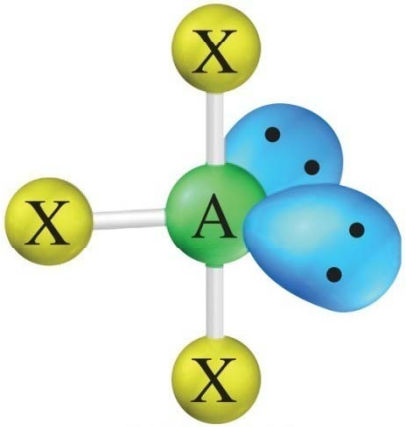

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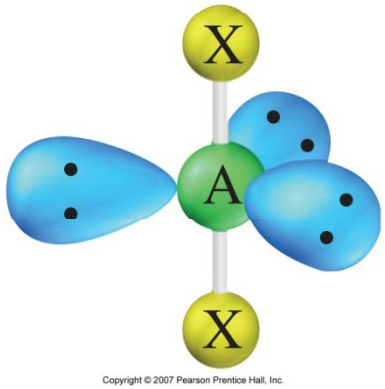

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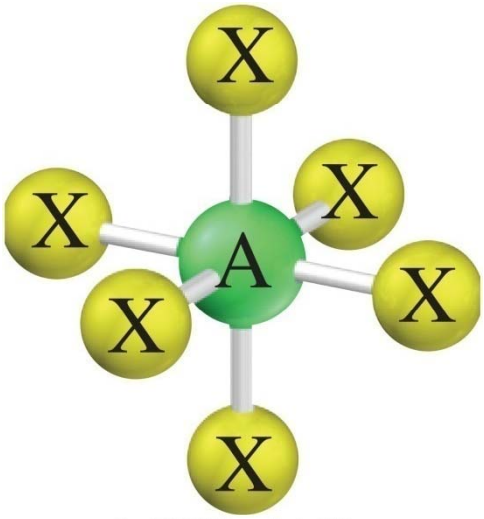
6 electron pairs

AX_6
Octahedral
90°



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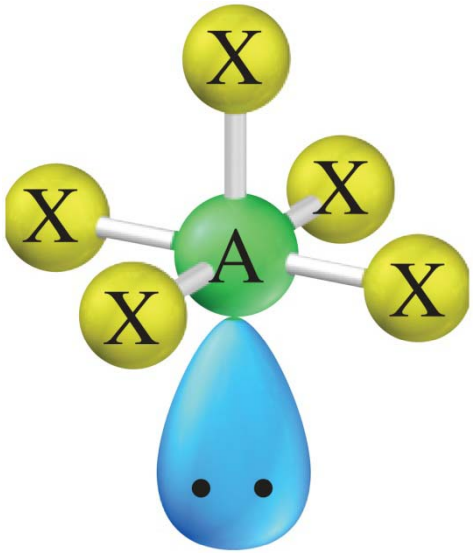
AX_5E
Square pyramidal
not ideal (< 90°)



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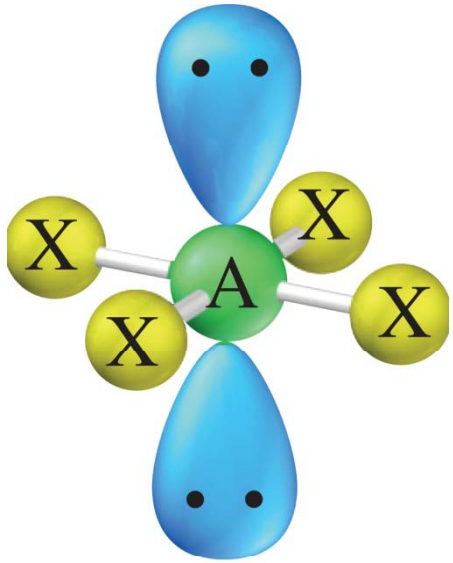
AX_4E_2
Square planar
90° (or 180 °)



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i-Clicker Question # 3

Which statement is true regarding the shape/symmetry of formaldehyde (H_2CO)?

(a) Trigonal Planar,
Ideal H-C-H angle

(b) Trigonal Pyramidal
Non-ideal H-C-H angle

(c) T-shape
Ideal H-C-H angle

(d) See-saw
Non-ideal H-C-H angle

(e) Trigonal Planar,
Non-ideal H-C-H angle

Dipole moments

- A molecule with polar bonds can, as an entity, be polar or non-polar!

- Polar molecules have a permanent dipole (polarization of charge): $\mu = \delta \times d$

  μ = dipole moment (Debye, D)

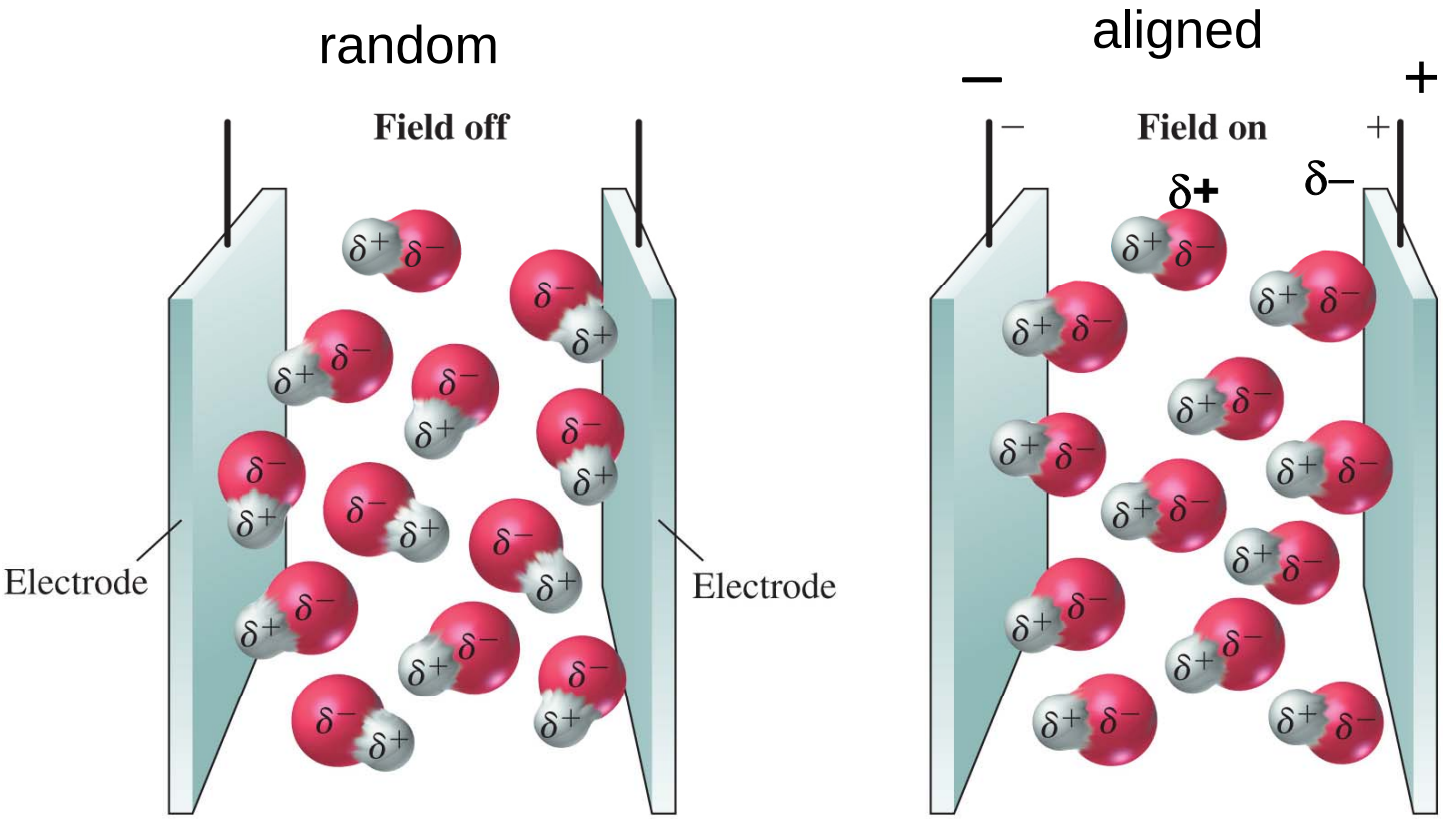
  δ = partial charge (Coulomb, C)

  d = distance (m)

p. 430-432 (403-405, 9th ed.)

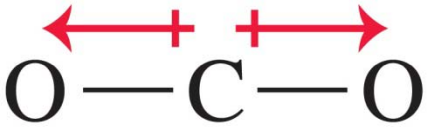
Identifying polar molecules (Fig. 10-14)

- **When an electric field is applied, polar molecules will orient such that opposite charges attract**



Guidelines for nonpolar molecules

- Symmetrical molecules are nonpolar because dipole moments cancel out
  - AX_n molecules where all X are the same
  - AX_2E_3 and AX_4E_2 also



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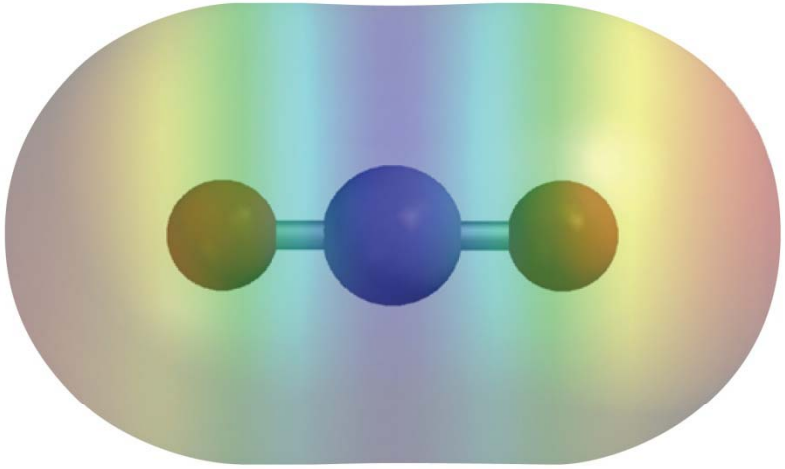
$\mu = 0$



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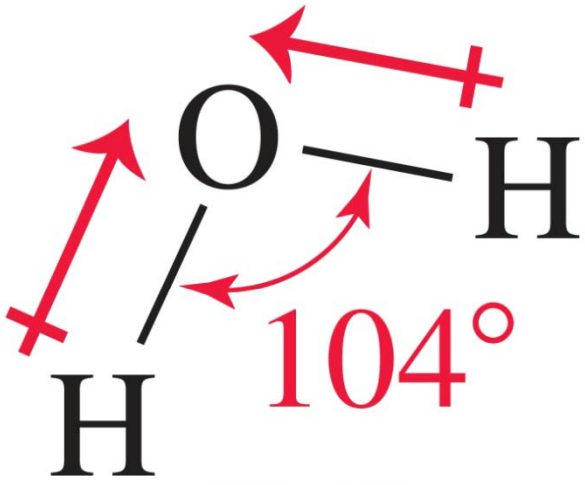
Guidelines for polar molecules

- Asymmetric molecules are Polar
  - All other AX_nE_m
  - Any AX_n where X groups differ, as long as there is an electronegativity difference



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Bond order, length & energy

- Bond order: single (1), double (2), triple (3)
- Covalent bond length (Table 10.2)
  - Approximately the sum of covalent radii
  - Diatomic molecules allow precise values; other values are averages
    - e.g. H – H 74.14 pm
      H – C 110 pm
- Bond dissociation energy, *D*
  - Energy required to break 1 mol of bonds in gas phase
  - Diatomic molecules allow precise values; other values are averages

p. 433-437 (406-409, 9th ed.)

Bond energy - Fig. 11-2 (11-1 9th ed.)

Energy is absorbed in order to break bonds:

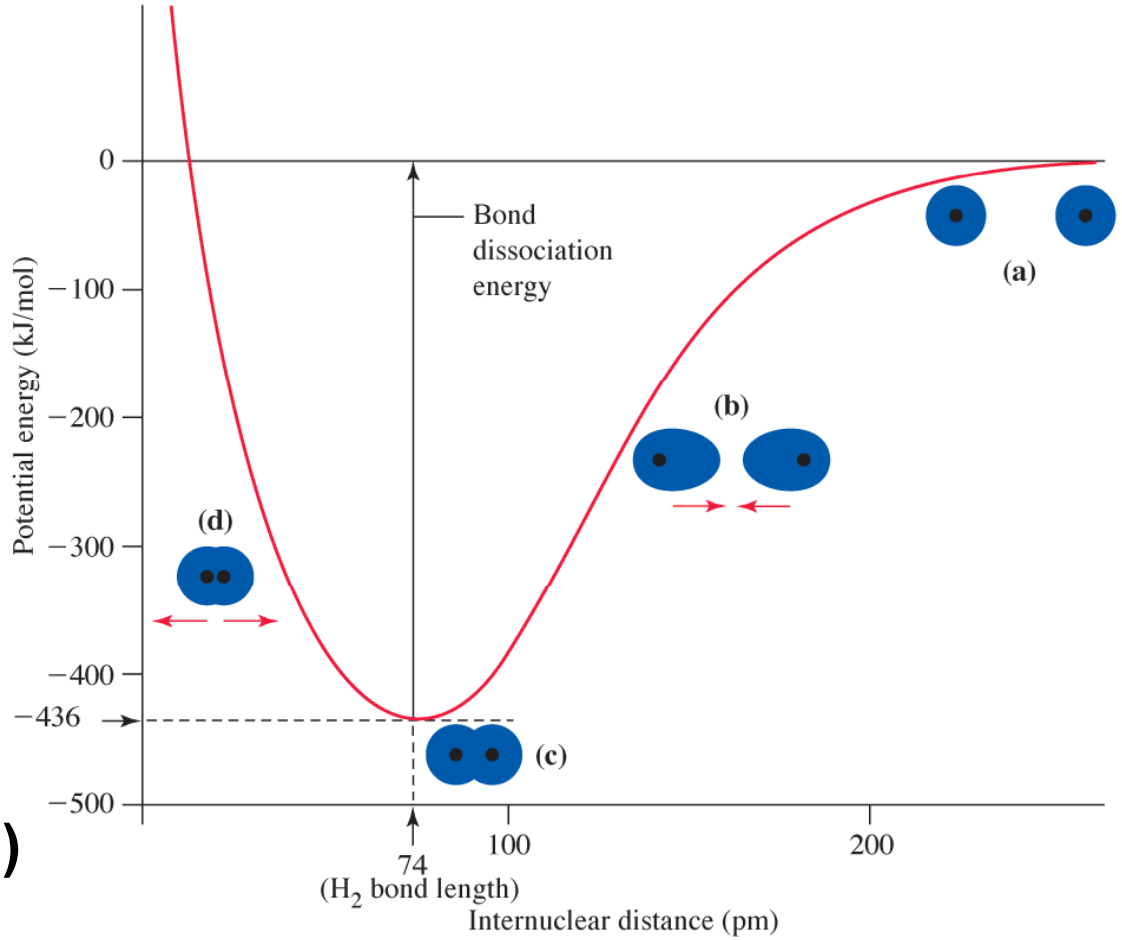
$H_2(g) \rightarrow 2H(g)$

$\Delta H = D(H\text{-}H)$ or $BE(H\text{-}H)$

Energy is released when bonds form:

$2H(g) \rightarrow H2(g)$

$\Delta H = -D(H\text{-}H)$ or $-BE(H\text{-}H)$



$\Delta Hrxn = \Sigma BE\ (reactants) - \Sigma BE\ (products)$

or

$\Delta Hrxn = \Delta H(bonds\ broken) + \Delta H(bonds\ formed)$

Bond energies to estimate $\Delta Hrxn$

Bond order, length & energy

- Direct and inverse relationships:

Bond	Order	Length, pm	Energy, kJ mol^{-1}
C-C	1	154	347
C=C	2	134	611
C≡C	3	120	837
N≡N	3	109.8	946

Note: Bond energy calculations (p. 434-437 or 409- 412 9th ed.) will be included with Ch 7

Practice – Lewis, shape, polarity

For the following molecules

- Draw Lewis structures and correct shapes
- Name the shapes
- Give approximate bond angles
- Indicate if polar or non-polar

1. PF_5, BrF_5, SF_6
2. CF_4, XeF_4, SF_4
3. CO_2, H_2O, SO_2
4. BF_3, PF_3, SO_3, $BrCl_3$

Solutions to these questions have been posted in a separate file in Avenue.

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