Biochem 03
November 13, 2009

- Redox Review
- Effective Charge

Oxidation States

- Oxidation states only represent true charges on atoms in ionic compounds. In covalent compounds, they represent an *effective* charge.
- Assigning oxidation states allows us to keep track of electrons in chemical reactions
  - This is essential in order to ensure that the conservation of charge is maintained
- Oxidation states depends upon the electronegativity of the elements in a covalent compound
- The electronegativity of an element measures its tendency to attract electrons (pp. 581-583, Zumdahl)
  - Ranges from 0.7 (Fr and Cs with little ability to attract electrons) to 4.0 (fluorine the atom with the greatest appetite for electrons)

Common Charges of Groups

COLUMN	TENDS to......	OXIDATION	NAME
Group 1A	loose an electron	+1	Alkali Metals
Group 2A	loose two electrons	+2	Alkaline Earth
Group 3A,13	share 3 electrons	(+3)	B, Al,....…
Group 4A,14	share 4 electrons	(+4)	C, Si,....…
Group 5A,15	share 3 electrons	(-3)	N, P......…
Group 6A,16	gain two electrons	-2	O, S......…
Group 7A,17	gain one electron	-1	Halides
Group 8A,18	doesn’t react	0	Noble Gases

Rules for Assigning Oxidation States

1. The oxidation state of an atom in an element is 0.

2. The oxidation numbers of the atoms in a neutral molecule must add up to zero, and those in an ion must add up to the charge on the ion.

3. Alkali metals have an oxidation number of +1, and alkaline earth metals +2, in their compounds.

4. Fluorine always has an oxidation number of –1 in its compounds. The other halogens have –1 in their compounds *except* in compounds with oxygen and other halogens, where they can have positive oxidation #s.

5. Hydrogen has an oxidation number of +1 in its compounds *except* metal hydrides (i.e., LiH), where rule #3 takes precedence, and H has oxidation number –1

6. Oxygen is assigned an oxidation number of –2 in its compounds except when bound to fluorine (rule #4 takes precedence) and in compounds containing O–O bonds (such as Na_2O_2 and H_2O_2) where rules #3 and #5 take precedence.

Assigning Oxidation States:

What are the oxidation states of the atoms in the following compounds/ions?

CO_3^{2-}	$Fe_2(SO_4)_3$	SO_2
NH_3	ClO^-	CaH_2
$KMnO_4$	I_2	N_2O

Assigning Oxidation States:

What are the oxidation states of the atoms in the following compounds/ions?

$+4\ -2$ CO_3^{2-}	$+3\ \ +6\ -2$ $Fe_2(SO_4)_3$	$+4\ -2$ SO_2
$-3\ +1$ NH_3	$+1\ -2$ ClO^-	$+2\ -1$ CaH_2
$+1\ +7\ \ -2$ $KMnO_4$	0 I_2	$+1\ \ -2$ N_2O

Oxidation, Reduction, and Charge Balance in Chemical Equations

- If a material is oxidized, it loses electron (acts as a reducing agent).
- If a material is reduced, it gains electrons (acts as an oxidizing agent).
- **Remember LEO the GERman, Lose Electrons Oxidized, Gain Electrons Reduced**

Igniting Mg in Air

$$\_\_\_Mg(s) + \_\_\_O_2(g) \rightarrow \_\_\_MgO(s)$$

$$\boxed{Mg^0 \rightarrow Mg^{2+} + \_\,e^-}$$

$$O_2 + \_\_e^- \rightarrow 2O^{2-}$$

$$\_\_\_Mg(s) + \_\_\_O_2(g) \rightarrow \_\_\_MgO(s)$$

Mg is oxidized to Mg^{2+}

O_2 is reduced to O^{2-}

Igniting Mg in Air

$$\underline{\ \ 2\ \ }\,Mg(s) + \underline{\ \ 1\ \ }\,O_2(g) \rightarrow \underline{\ \ 2\ \ }\,MgO(s)$$

2x $\boxed{Mg^0 \rightarrow Mg^{2+} + 2e^-}$

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

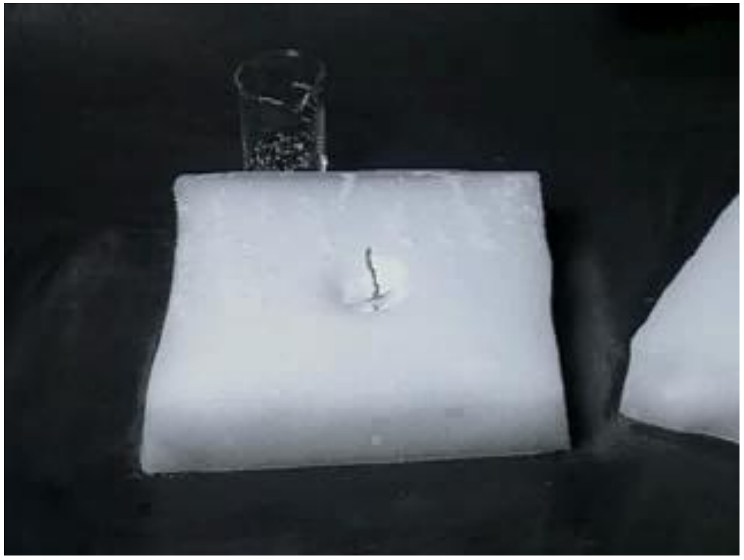
$$\underline{\ \ 2\ \ }\,Mg(s) + \underline{\ \ 1\ \ }\,O_2(g) \rightarrow \underline{\ \ 2\ \ }\,MgO(s)$$

Mg is oxidized to Mg^{2+}

O_2 is reduced to O^{2-}

Reaction of Mg with CO_2

When solid Mg is ignited in the presence of CO_2, a different reaction occurs



What is oxidized and what is reduced?

Mg is oxidized to Mg^{2+}

C is reduced from C^{4+} to C

http://www.youtube.com/watch?v=wqErrNvns4o&feature=related

$$\_\_\_Mg(s) + \_\_\_CO_2(g) \rightarrow \_\_\_C(s) + \_\_\_MgO(s)$$

$$Mg^{?} \rightarrow Mg^{?} + \_e^{-}$$

$$C^{?} + \_e^{-} \rightarrow C^{?}$$

$$\_\_\_Mg(s) + \_\_\_CO_2(g) \rightarrow \_\_\_C(s) + \_\_\_MgO(s)$$

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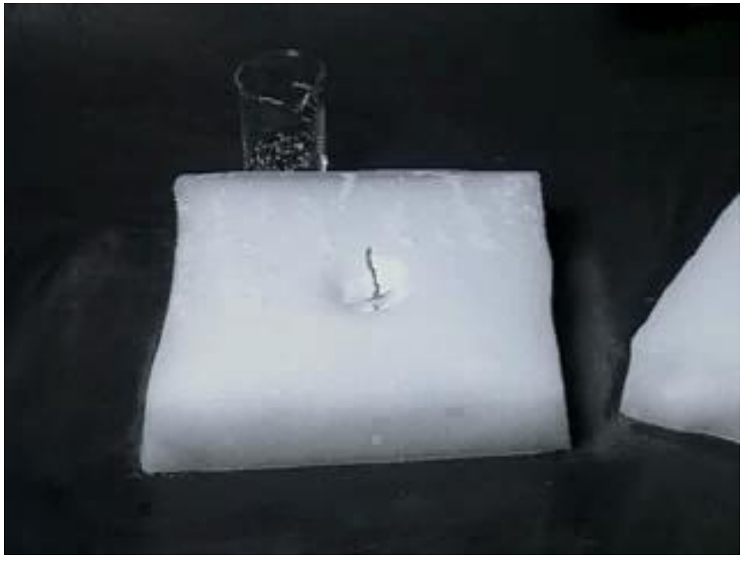

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$$\underline{\ \ 2\ \ }Mg(s) + \underline{\ \ 1\ \ }CO_2(g) \rightarrow \underline{\ \ 1\ \ }C(s) + \underline{\ \ 2\ \ }MgO(s)$$

$$Mg^0 \rightarrow Mg^{2+} + 2e^-$$

$$C^{4+} + 4e^- \rightarrow C^0$$

$$\underline{\ \ 2\ \ }Mg(s) + \underline{\ \ 1\ \ }CO_2(g) \rightarrow \underline{\ \ 1\ \ }C(s) + \underline{\ \ 2\ \ }MgO(s)$$

Effective Charges

- Effective charges are another way of keeping track of electrons
- This method is typically used for organic compounds, which contain many carbon, hydrogen, and oxygen atoms
- The advantage of the effective charge method is that you can determine which atom has been oxidized or reduced
- To determine effective charges, we will need to use some more advanced topics, such as Lewis dot structures, and an understanding of the number of valence electrons in an atom

Charge Distribution in Covalent Compounds

- Elements in groups 3A-6A, and sometimes 7A, in the periodic table will often make compounds in which they do not gain or lose electrons, but share them in a covalent bond. In these molecules, electrons may be evenly shared or unevenly shared.
  - Evenly shared: when a bond is formed between two identical atoms:
    - Examples: N_2, O_2, H_2
  - Unevenly shared: when a bond is formed between atoms with different abilities to attract electrons (i.e., different electronegativities)
    - Examples: CH_4, NH_3, NO_2, CO_2, HCl, H_2O

Electronegativities of Commonly Encountered Elements

Element	Electronegativity
H	2.2
P	2.2
C	2.6
S	2.6
N	3.0
Br	3.0
Cl	3.2
O	3.4
F	4.0

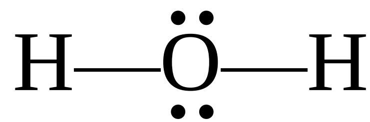
These electronegativity values are based on a scale that varies from 0.7 (Fr) to 4.0 (F)

Data from Zumdahl, 5th Edition, p. 588

Calculating Effective Charge in Covalent Compounds

- Effective charge on an atom in a covalent molecule is calculated by subtracting the total number of electrons surrounding the atom (lone pair electrons plus the number of bonding pair electrons that the atom "owns") from the number of electrons in the valence shell of the element
- When two bonded atoms have equivalent electronegativities (i.e., C bonded to C), they each get one of the two electrons from the bond
- **Effective Charge = # of Valence Electrons − (lone pair electrons + bonding electrons from less electronegative elements + ½ bonding pair electrons from equally electronegative elements)**

Calculating Effective Charge in Covalent Compounds

- Example: Water, H_2O
- Lewis structure: 
  - Electronegativies: H (2.2), O (3.4),
    - so O "owns" the e^- in the two O–H bonds

–Effective charge of O

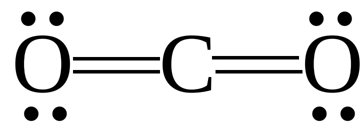
6 valence electrons – (4 lone pair electrons + 4 bonding pair electrons) = –2

– Effective charge of H is 1 – (0) = +1

– Overall charge in water is –2 + [2(+1)] = 0 so water is net neutral as expected

Calculating Effective Charge in Covalent Compounds

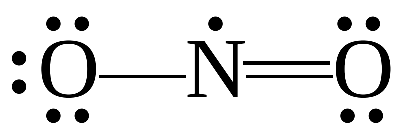
- **What are the effective charges of the atoms in carbon dioxide?**



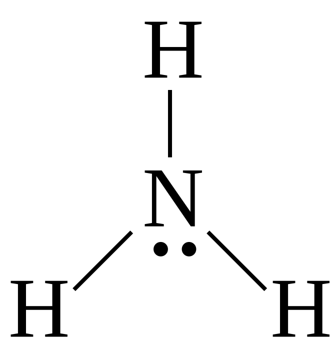
  - Electronegativies *C*: (2.6), *O*: (3.4), so O would "take" electrons away from *C*
  - Oxygen has a valence of six, but "owns" eight electrons so it has an effective charge of –2 (true for each oxygen)
  - Carbon has a valence of four, but here "owns" zero electrons, so it has an effective charge of +4
  - Overall, the compound is net neutral $(2 \times (-2)) + 4 = 0$

Effective Charges: a few more examples

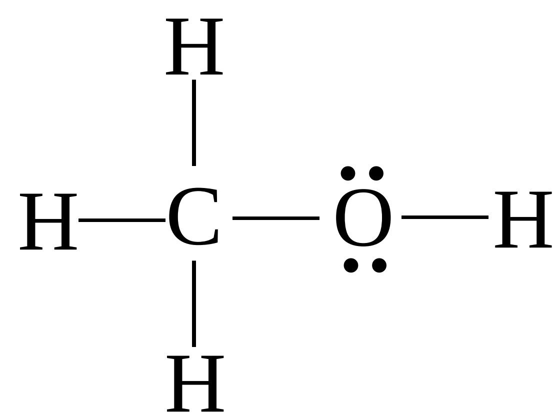
- Given the following Lewis structures, determine the effective charges of all atoms in the compounds shown:



Nitrogen dioxide

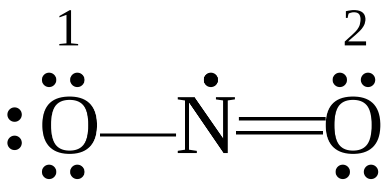


Ammonia



Methanol

Effective Charges: a few more examples



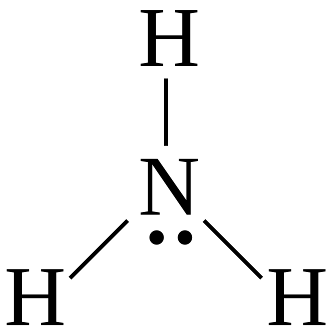
N: 5 - 1 = +4,

O(1): 6 - (4+4) = -2

O(2): 6 - (6+2) = -2

Net neutral?

✓

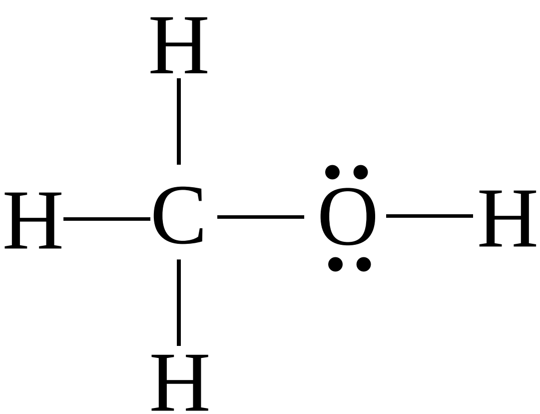


N: 5 – (2+6) = –3

H: 1 – 0 = +1

Net neutral?

✓



C: 4 – 6 = –2

H: 1 – 0 = +1

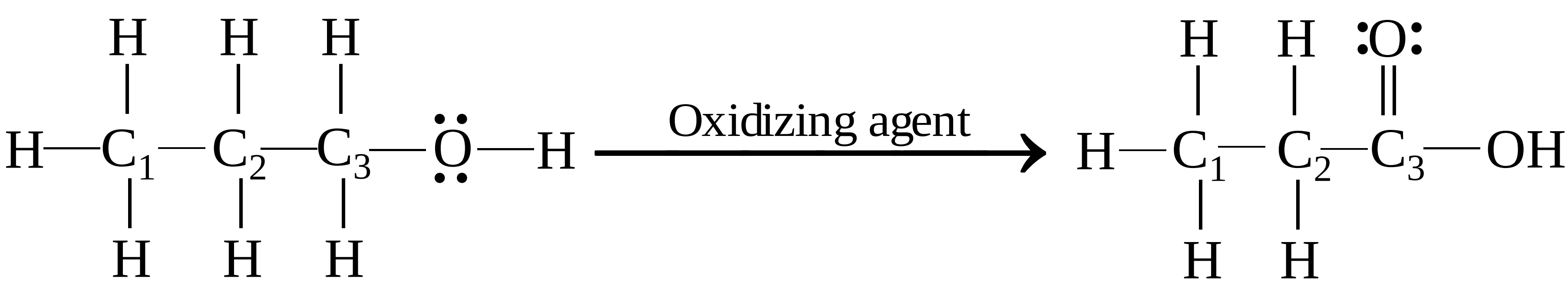
O: 6 – (4+4) = –2

Net neutral?

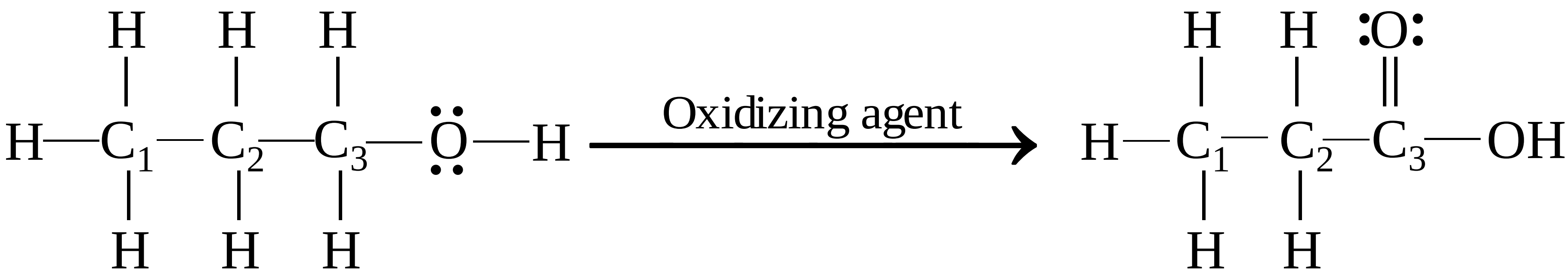
✓

Example Problem

- An area in which effective charges is particularly useful is in understanding the oxidation-reduction reactions of organic compounds
- In the following reaction, an oxidizing agent is added to a solution of n-propanol, producing propanoic acid. Determine the effective charges of the C atoms in n-propanol and propanoic acid and, from these values, determine which atom of n-propanol has been oxidized



Example Problem



- For n-propanol:
  - The effective charge of C_1 is: 4 – 7 = –3
  - The effective charge of C_2 is: 4 – 6 = –2
  - The effective charge of C_3 is: 4 – 5 = –1
- For propanoic acid:
  - The effective charge of C_1 is: 4 – 7 = –3
  - The effective charge of C_2 is: 4 – 6 = –2
  - The effective charge of C_3 is: 4 – 1 = +3
- C_3 has been oxidized, more bonds to O = oxidized