

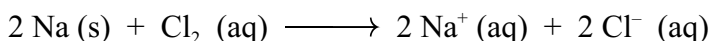
### Oxidation / Reduction Reactions (Method III):

All oxidation/reduction reactions involve the transfer of one or more electrons ( $e^-$ ) from one solution component to another component. The overall reaction can be thought of as a combination of two separate processes: the loss of electrons from one component and the gain of electrons by another component. Under this system,

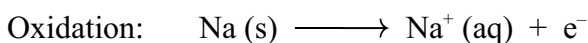
**Oxidation:** the loss of one or more electrons

**Reduction:** the gain of one or more electrons

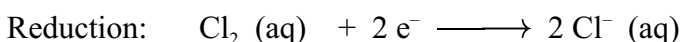
The previously mentioned redox reaction:



can be separated into two processes.



and



These equations are referred to as “half-reaction” as each constitutes half of the entire process occurring: oxidation **and** reduction.

The direction of the transfer can then be used as a means of classifying the two reacting components.

**Oxidizer:** the component that **causes** the other component to undergo oxidation (the loss of  $e^-$ )  
I.e., the oxidizer gains  $e^-$ 's from the other component.

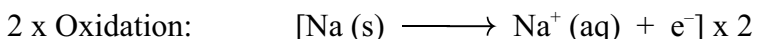
**Reducer:** the component that **causes** the other component to undergo reduction (the gain of  $e^-$ )  
I.e., the reducer loses  $e^-$ 's to the other component.

In the above processes, Na is the reducer because it causes the other component,  $\text{Cl}_2$ , to undergo reduction (gain  $e^-$ 's). Conversely,  $\text{Cl}_2$  is the oxidizer because it causes the other component, Na, to undergo oxidation (loss  $e^-$ 's).

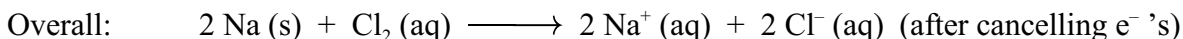
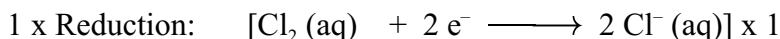
Question: How can  $\text{Cl}_2$  gain 2 electrons if Na gives up only one?

Answer: It can't!

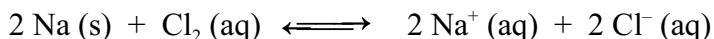
Thus, the oxidation process  $[\text{Na (s)} \longrightarrow \text{Na}^+ \text{ (aq)} + e^-]$  MUST occur twice every time the reduction process  $[\text{Cl}_2 \text{ (aq)} + 2 e^- \longrightarrow 2 \text{Cl}^- \text{ (aq)}]$  occurs once ( stoichiometry of 2:1).



and



As with acid/base reactions, redox reactions never reach 100% and thus a dynamic equilibrium is ultimately achieved.

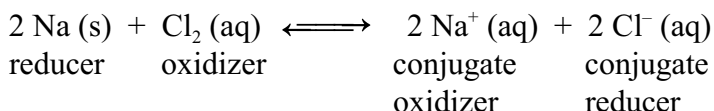


In the reverse direction, the  $\text{Cl}^-$  donates  $e^-$ 's to the  $\text{Na}^+$  and therefore  $\text{Cl}^-$  is a reducer and  $\text{Na}^+$  is an oxidizer. The product oxidizer ( $\text{Na}^+$  is derived from the reactant reducer,  $\text{Na}$ ) and the product reducer ( $\text{Cl}^-$  is derived from the reactant oxidizer,  $\text{Cl}_2$ ). This relationship is a conjugate relationship.

Conjugate Reducer: A reducer **created** when an oxidizer accepts one or more  $e^-$ 's.

Conjugate Oxidizer: An oxidizer **created** when a reducer donates one or more  $e^-$ 's.

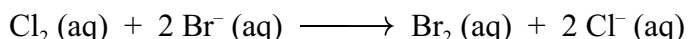
Thus, the reactants and products can be labeled as:



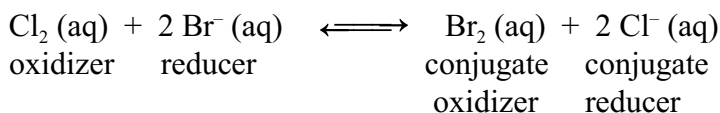
### Relative Strengths of Oxidizers and Reducers:

As with the classification of acids, a useful classification can be achieved by allowing the reducers (and oxidizers) to “compete” against one another to produce an absolute ranking of the reducers (and oxidizers). Let's look at a couple of examples of such “competitions”.

Consider the following redox reaction between aqueous  $\text{Cl}_2$  and aqueous  $\text{NaBr}$  solutions:

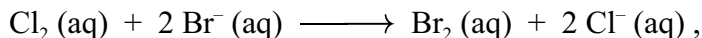


When equilibrium is reached, there are two different competitions taking place. The two reducers,  $\text{Br}^-$  and  $\text{Cl}^-$ , are each trying to donate an electron ( $e^-$ ) while the two oxidizers,  $\text{Cl}_2$  and  $\text{Br}_2$  are each trying to accept electrons (again, the  $\text{Na}^+$  is a “spectator ion”).



Knowledge of the position of the equilibrium (and thus the extent of the original reaction) allows one to deduce which of the two reducers is the stronger and which of the two oxidizers is stronger.

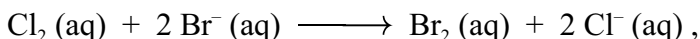
IF at equilibrium, there is more  $\text{Br}_2$  than  $\text{Cl}_2$  and more  $\text{Cl}^-$  than  $\text{Br}^-$ , THEN, the original reaction:



must have gone to a LARGE EXTENT (>50%).

IF it went to >50%,  $\text{Br}^-$  must have donated more electrons ( $e^-$ 's) than  $\text{Cl}^-$  donated and thus  $\text{Br}^-$  must be a stronger reducer than  $\text{Cl}^-$ . In addition,  $\text{Cl}_2$  must have accepted more electrons than did  $\text{Br}_2$  and thus  $\text{Cl}_2$  must be a stronger oxidizer than  $\text{Br}_2$ .

Conversely, IF at equilibrium, there is more  $\text{Cl}_2$  than  $\text{Br}_2$  and more  $\text{Br}^-$  than  $\text{Cl}^-$ , THEN, the reaction:



must have gone to a SMALL EXTENT (<50%).

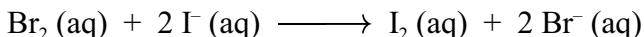
IF it went to <50%,  $\text{Cl}^-$  must have donated more electrons ( $e^-$ 's) than  $\text{Br}^-$  donated and thus  $\text{Cl}^-$  must be a **stronger** reducer than  $\text{Br}^-$ . In addition,  $\text{Br}_2$  must have accepted more electrons than did  $\text{Cl}_2$  and thus  $\text{Br}_2$  must be a **stronger** oxidizer than  $\text{Cl}_2$ .

Question: How can the extent of this reaction be determined?

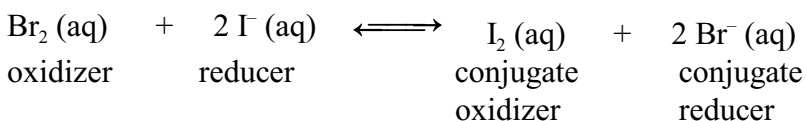
Conductivity measurements are not useful in this reaction as both products and reactants conduct. However, an examination of the physical properties of the reactants and products allows the equilibrium position to be determined easily. Both,  $\text{NaCl}$  and  $\text{NaBr}$ , are white solids which produces colorless solutions. Thus,  $\text{Na}^+ (\text{aq})$ ,  $\text{Cl}^- (\text{aq})$ , and  $\text{Br}^- (\text{aq})$  are colorless. The element chlorine,  $\text{Cl}_2$ , has a faint yellow-green color (the color of household bleach solutions is due to the presence of  $\text{Cl}_2$ ). The element bromine,  $\text{Br}_2$ , has a orange-brown color similar to "rust".

When, solutions of  $\text{Cl}_2$  and  $\text{NaBr}$  are combined an intense orange-brown colored mixture is produced. Therefore, we can now definitively state that on an absolute basis that  $\text{Br}^-$  is a **stronger** reducer than  $\text{Cl}^-$  ..... and  $\text{Cl}_2$  is a **stronger** oxidizer than  $\text{Br}_2$ .

In a reaction similar to the previous reaction, let's look at the redox reaction between aqueous  $\text{Br}_2$  and aqueous  $\text{NaI}$  solutions:

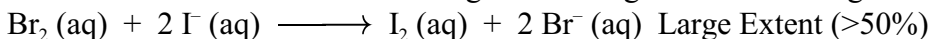


As before, there are two different competitions taking place at equilibrium. The two reducers,  $\text{I}^-$  and  $\text{Br}^-$ , are each trying to donate an electron ( $e^-$ ) while the two oxidizers,  $\text{Br}_2$  and  $\text{I}_2$  are each trying to accept electrons (again, the  $\text{Na}^+$  is a "spectator ion").



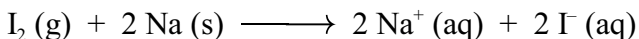
Ascertaining the position of the equilibrium (and thus the extent of the original reaction) allows one to deduce which of the two reducers is the stronger and which of the two oxidizers is stronger. Again, knowledge of the physical properties of the reactants and products allows us to determine the position of the equilibrium. Iodine is a purple/black solid which is only very slightly soluble in water. The small amount of dissolved iodine imparts a (it is only slightly soluble) is a straw yellow color to the water. Both  $\text{NaI}$  and  $\text{NaBr}$  are white solids which dissolve to give colorless solutions.

When, solutions of  $\text{Br}_2$  and  $\text{NaI}$  are combined an murky black heterogeneous mixture is produced. This means that the reaction must have gone to a large extent to the right. I.e.,

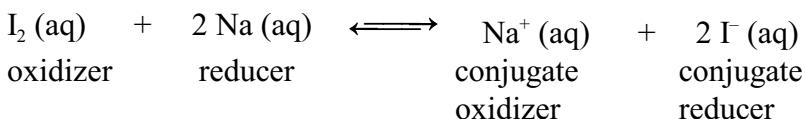


Therefore, we can now definitively state that on an absolute basis that  $\text{I}^-$  is a **stronger** reducer than  $\text{Br}^-$  ..... and  $\text{Br}_2$  is a **stronger** oxidizer than  $\text{I}_2$ .

Lastly, let's take an interesting reaction which is actually easier to carry out if the solvent is added after the reaction! Sodium metal reacts vigorously with iodine vapors (the iodine solid actually sublimates at room temperature to give a beautiful purple vapor). After reaction water can be added to establish the equilibrium in water. This can be summarized as

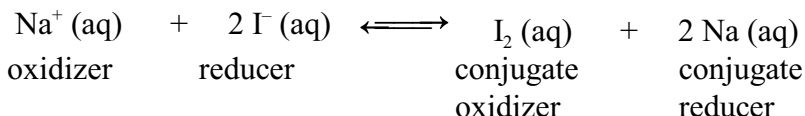


Thus at equilibrium in water we have



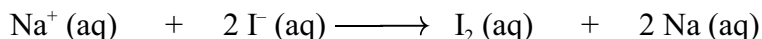
When this reaction is performed and the water is added the result is the formation of a clear colorless solution with no signs of metal, purple solid or yellow tint to the water. Clearly the reaction went to a large extent (~100% based on observations!).

Of course we should have anticipated this! Previously we used a NaI solution. When NaI is added to water it dissolves to  $\text{Na}^+$  and  $\text{I}^-$  ions. This combination is the reverse of the above equilibrium.



The fact that the resultant is a colorless solution means that the above equilibrium lies FAR to the left and thus the reaction

Thus, based on **either** reaction, we can now definitively state that on an absolute basis that Na metal is a stronger reducer than  $\text{I}^-$  ..... and  $\text{I}_2$  is a stronger oxidizer than  $\text{Na}^+$ .



goes to the right to a VERY small (imperceptible) extent!

Combining the oxidizer comparisons gives:  $\text{Cl}_2 > \text{Br}_2 > \text{I}_2 > \text{Na}^+$   
while combining the reducer comparisons gives:  $\text{Na} > \text{I}^- > \text{Br}^- > \text{Cl}^-$

We can place the oxidizers and reducers into a table form similar to the acid/base table discussed earlier.

Placing the conjugate reducers next to their respective oxidizers gives ,

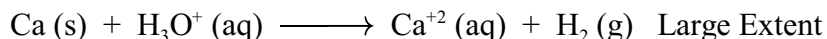
| Oxidizers |   | Reducers      |               |
|-----------|---|---------------|---------------|
| Stronger  | ↑ | $\text{Cl}_2$ | $\text{Cl}^-$ |
|           |   | $\text{Br}_2$ | $\text{Br}^-$ |
|           |   | $\text{I}_2$  | $\text{I}^-$  |
| Weaker    | ↓ | $\text{Na}^+$ | $\text{Na}$   |
|           |   |               | Stronger      |

## USING AN OXIDIZER/REDUCER TABLE

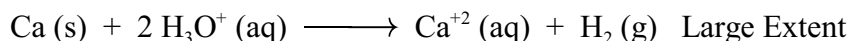
Below is an expanded table with 8 oxidizers and 8 conjugate reducers.

|          | Oxidizers | Reducers                      |                 |
|----------|-----------|-------------------------------|-----------------|
| Stronger | ↑         | F <sub>2</sub>                | F <sup>-</sup>  |
|          |           | Cl <sub>2</sub>               | Cl <sup>-</sup> |
|          |           | Br <sub>2</sub>               | Br <sup>-</sup> |
|          |           | I <sub>2</sub>                | I <sup>-</sup>  |
|          |           | H <sub>3</sub> O <sup>+</sup> | H <sub>2</sub>  |
|          |           | Ca <sup>+2</sup>              | Ca              |
|          |           | Na <sup>+</sup>               | Na              |
| Weaker   | ↓         | Li <sup>+</sup>               | Li              |
|          |           |                               | Stronger        |

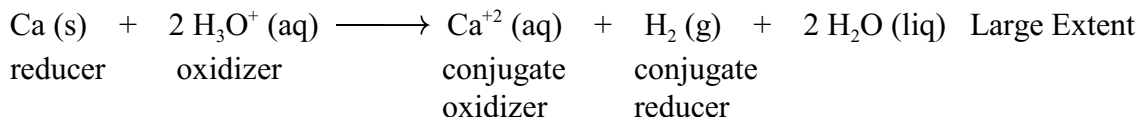
Consider a mixture of 0.1 M HCl and Ca metal. Recall that the inventory of 0.1 M HCl is actually  $[H_3O^+] = [Cl^-] = 0.1$  M. The expanded oxidizer/reducer table shows that a reaction will occur between the  $H_3O^+$  and Ca metal with  $H_3O^+$  acting as the oxidizer and Ca functioning as the reducer. It also shows that when these two react they will produce their respective conjugates,  $H_2$  and  $Ca^{+2}$ . The extent of reaction can also be gleaned from the table by comparing the strengths of the two oxidizers (or the strengths of the two reducers). The table indicates that the reactant oxidizer,  $H_3O^+$  is a stronger oxidizer than the product oxidizer,  $Ca^{+2}$  and thus the reaction will go to a large extent (>50%) before equilibrium is reached. However, there is a problem. We know that the products will be  $H_2$  gas and  $Ca^{+2}$  and we know the extent but its not balanced and there is at least one product missing. So far we know:



To balance the charge 2  $H_3O^+$  are needed which gives



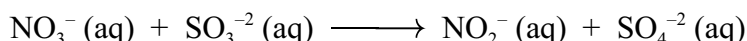
There are four hydrogen atoms and two oxygen atoms on the reactant side that are missing on the product side. Clearly that means two waters are needed.



The waters are a “by-product” of the reaction. Recall, that the  $H_3O^+$  was formed when an “H<sup>+</sup>” from the HCl was accepted by water. Thus, when the “H<sup>+</sup>” accepts the electron to form half a molecule of  $H_2$ , the water molecule is released once again!

The basics of oxidation/reduction reactions including how to use the corresponding table is quite similar to acid/base reactions. Unfortunately, there is more to redox reactions than the basics.

Consider this oxidation/reduction.



This sure doesn't look like a redox reaction! There is no change in charge so how can this be an oxidation/ reduction reaction? Well, we need help!

Recall we needed help with Lewis structures so a "tool" called "the formal charge concept" was invented. Well, a tool called "oxidation states" or sometimes called "oxidation numbers" was invented to help with redox reactions. Similarly, these "oxidation states" or "oxidation numbers" **do not exist**.

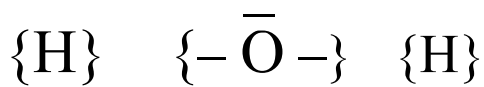
How do we calculate oxidation states and how do we use them?

There are two steps to calculating oxidation states.

- #1) Divide all bonds in the Lewis structure so that the more electronegative atoms receives **all** of the electron in the bond. This will produce a set of "fragments" of the former molecule.
- #2) Calculate the oxidation state for each fragment by comparing the number of electrons in each fragment to the original number of valence electron in the Lewis symbol.

Let start with water. The Lewis structure for water is  $\text{H} - \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} - \text{H}$

Since oxygen is more electronegative than hydrogen the bonds are divided so that the oxygen receives all of the electrons in the bonds.



Now the H fragments have zero electron and the O fragment has eight electron. Applying step two, we see that the oxidation state of the H fragments in water are +1 (each lost their only electron) and the oxidation state of the oxygen in water is -2 (it gained two electrons).

Now consider these two Lewis structures. a)  $|\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} - \text{C} - \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}|$  B)  $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} = \text{C} = \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}$

For comparison, lets calculate the formal charges AND the oxidation states for all of the atoms in these two structures.

First FC's

In "A" each oxygen fragment has seven electrons and the carbon has two. Thus, each oxygen has a - FC and the carbon has +2 FC.

In "B" each oxygen fragment has six electrons and the carbon has four. Thus, all atoms have zero FC.

Thus, "B" is the correct Lewis structure for CO<sub>2</sub>

Now oxidation states.

In “A” each oxygen fragment has eight electrons and the carbon has zero. Thus, each oxygen has a  $-2$  FC and the carbon has  $+4$  FC.

In “B” each oxygen fragment has eight electrons and the carbon has zero. Thus, each oxygen has a  $-2$  FC and the carbon has  $+4$  FC.

Notice, the oxidation states on each atom is the same in both structures. So, don’t calculate oxidation states IF you are trying to decide which structure is more plausible, use FC!

The fact that the oxidation states remain the same despite differences in the two Lewis structures should prompt the question, “If the oxidation states are the same for different Lewis structures, is drawing a Lewis structure really necessary to determine oxidation states?” The answer is that while drawing a Lewis structure will always give the correct assignment of oxidation states, **under certain conditions and using specific logic** the oxidation states can be determined without a Lewis structure.

### The Logic of Oxidation States/Numbers

#1) In order for fluorine to have a formal charge of zero it must have 3 lone pairs and one bond.

I.e.,  $X : \ddot{F} :$  Since fluorine is the most electronegative element known, the F fragment will end up with eight electrons assigned to it when X is **any** element **except** another fluorine (where the electrons will be split between the two F’s). Thus, F will have an oxidation state of  $-1$  in all structure except when F is bonded to another F (where the oxidation state will be zero).

#2) In order for oxygen to have a formal charge of zero it must have 2 lone pairs and two bonds.

I.e.,  $H : \ddot{O} : H$  Since oxygen is the second most electronegative element known, the O fragment will end up with eight electrons assigned to it when X is **any** element **except** a fluorine (where the electrons will be assigned to F) or another O (where the electrons will be split between the two O’s). Thus, O will have an oxidation state of  $-2$  in all structure except when O is bonded to F or O.

#3) In order for chlorine, bromine or iodine to have a formal charge of zero they must have 3 lone pairs and one bond.

I.e.,  $X : \ddot{I} :$  Since these three elements are the next most electronegative elements known, these fragments will end up with eight electrons assigned to it when X is **any** element **except** an oxygen or to a family member higher in the periodic table (where the electrons will be assigned to the other atom) or to an atom identical to itself (where the electrons will be split). Thus, each will have an oxidation state of  $-1$  in all structure except when each is bonded to an O, a higher family member or to itself.

#4) In order for hydrogen to have a formal charge of zero it must have one bond.

I.e.,  $X : H$  Since H is less electronegative than the other nonmetals it will lose its electron to all nonmetals and thus be assigned an oxidation state of  $+1$ . Since H is more electronegative than all metals it will gain one electron from metals and thus is assigned an oxidation state of  $-1$  with metals.

## Summary of Oxidation State Rules

- 1) F will always be  $-1$ .
- 2) O will always be  $-2$  unless bonded to F or itself.
- 3) Cl, Br, and I will be  $-1$  unless bonded to O or a higher family member.
- 4) H will be  $+1$  when bonded to non-metals or  $-1$  when bonded to metals.

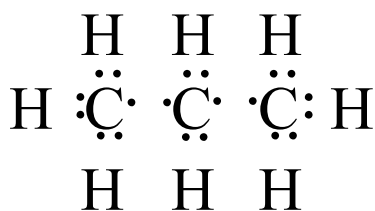
Examples of how to use the oxidation state rules.

- a)  $\text{CO}_2$  O will be  $-2$ . How can we deduce the oxidation state of carbon? Well,  $\text{CO}_2$  has zero charge but each O is a  $-2$ . Thus in order to maintain zero net charge the carbon must have a  $+4$  oxidation state.
- b)  $\text{SO}_4^{-2}$  O will be  $-2$ . How can we deduce the oxidation state of sulfur? In this case this ion has a  $-2$  so the oxidation state of sulfur **plus**  $4 \times (-2)$  must equal  $-2$ . Thus the oxidation state of sulfur must be  $+6$ . [ $6 + 4 \times (-2) = -2$ ].
- c)  $\text{H}_2\text{O}_2$   $\text{H}_2\text{O}_2$  has zero charge. With two O's with  $-2$  oxidation states and zero overall charge, the two H's would be assigned a  $+2$  oxidation states. That's impossible as H has only one electron and thus can only lose one electron for a  $+1$ . Let's try stating with H. Assigning an oxidation state of  $+1$  to each H would mean each O would be  $-1$ . This is possible, but why doesn't O has an oxidation state of  $-2$ ? Recall, O will be  $-2$  when bonded to any atom except F or **another O**. In  $\text{H}_2\text{O}_2$  the O must be bonded together since H's must be on the outside!
- d)  $\text{HCN}$  H is assigned  $+1$  as it is bonded to a non-metal. To maintain a net charge of zero the sum of C plus N must be  $-1$ . There are no more rule to further narrow the choices so we cannot deduce the oxidation states of C and N. We need to draw the Lewis structure for HCN.



Dividing the electron so that the more electronegative atoms gets the electrons in each bond results in eight electrons on the N fragment, two electrons on the C fragment and zero electrons on the H fragment. Thus, N is assigned an oxidation state of  $-3$ , C is assigned an oxidation state of  $+2$ , and H is assigned an oxidation state of  $+1$ .

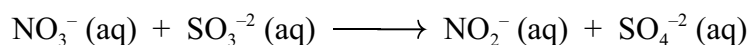
- e)  $\text{C}_3\text{H}_8$



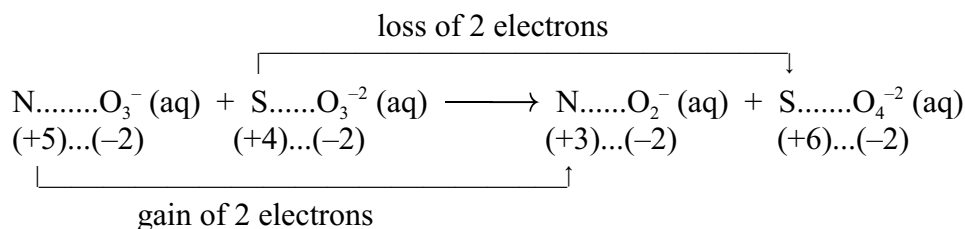
Each H is assigned  $+1$  as it is bonded to a non-metal for a total of  $+8$ . To maintain a net charge of zero the sum of the oxidation states of the three C's must be  $-8$ . This works out to  $-8/3$  for each C! This show that the rules produce only an **average** oxidation state assignment which sometimes doesn't match the actual oxidation state on each atom. To find the **actual** oxidation states in  $\text{C}_3\text{H}_8$  we must once again draw the Lewis structure.



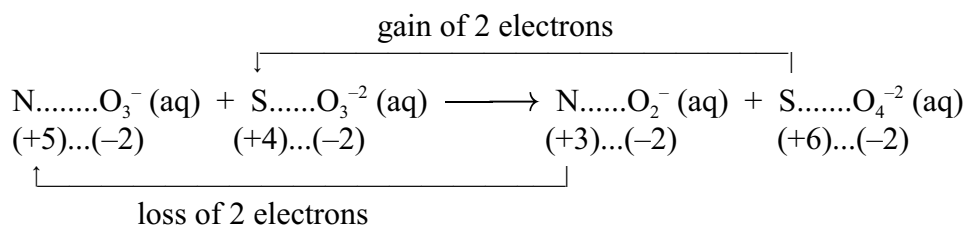
What about that “redox” reaction that didn’t look like one?



What are the oxidation states of each atom in the above reaction?



In the forward direction the oxidation state of N changes from +5 to +3 which is the gain of 2 electrons and the oxidation state of S changes from +4 to +6 which is the loss of 2 electrons. Thus,  $\text{NO}_3^-$  is the oxidizer and  $\text{SO}_3^{-2}$  is the reducer.



In the reverse direction the oxidation state of N changes from +3 to +5 which is the loss of 2 electrons and the oxidation state of S changes from +6 to +4 which is the gain of 2 electrons. Thus,  $\text{NO}_2^-$  is the reducer and  $\text{SO}_4^{-2}$  is the oxidizer.

By using oxidation states it is easy to see this is a redox reaction.