

OXIDATION - REDUCTION REACTIONS

[MH5; 4.4]

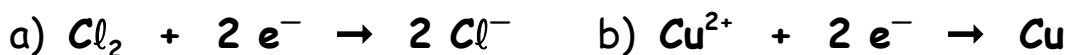
- Commonly called Redox reactions, these reactions involve a transfer of electrons - one species gives them up, another receives them.
- They are easiest to deal with if we divide the overall reaction into two half - reactions.
- In one half-reaction, electrons are **LOST**; this is called the **OXIDATION** half - reaction.

EXAMPLES:



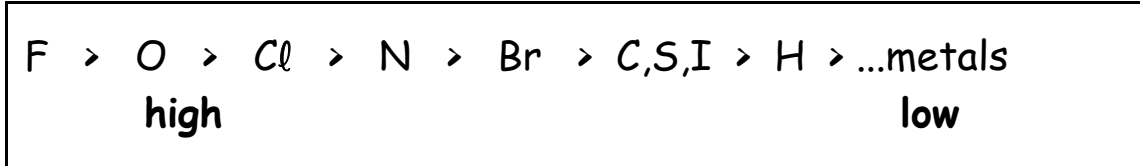
- In each case, the reactant is **losing** electrons.
- In the other half-reaction, electrons are **GAINED**; this is called the **REDUCTION** half-reaction.

EXAMPLES:



- In each case, the reactant is **gaining** electrons.
- It may help to remember that " **LEO says GER** "
Loss of Electrons is Oxidation and Gain of Electrons is Reduction
OIL RIG \Rightarrow Oxidation is Loss, Reduction is Gain
- The reactant taking part in the **oxidation** half - reaction is called the **REDUCING AGENT** because it is reducing the other reactant.
- In doing so, it is **OXIDIZED** !
- The reactant taking part in the **reduction** half -reaction is called the **OXIDIZING AGENT** because it is oxidizing the other reactant.
- In doing so, it is **REDUCED** !

- Recall the order of **electronegativity** of the elements.....



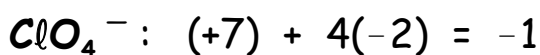
Values are given in **Table 6.5; MH5, p154**

RULES FOR ASSIGNING OXIDATION NUMBERS [MH5; page 88]

- Oxidation Number is always zero in the pure element:
($H_2(g)$, $Cl_2(g)$, $Na(s)$ etc)
- Oxidation Number is always equal to the charge on a monatomic ion:

 Na^+ is +1 Ba^{2+} is +2 Cl^- is -1 etc.
- In a neutral molecule, the total charge on the molecule must be equal to 0.

 $H - Br: (+1) + (-1) = 0$ $PBr_5: (+5) + 5(-1) = 0$
- In a complex ion, the total charge must be equal to the charge on the ion.



5) Priority Rules (Memorize these!!!)

These rules, based on the electronegativity scale are useful in assigning Oxidation Numbers in a compound:

- Fluorine** is always -1
- Group I** metals (Na, K, etc.) always $+1$
- Group II** metals (Ca, Mg, etc.) always $+2$
- H** is always $+1$ except when combined with a metal to form a hydride
EXAMPLE: LiH is $[\text{Li}^+][\text{H}^-]$; therefore H is -1
- Oxygen** is always -2 except when combined with fluorine

EXAMPLES: OF_2 : O is $+2$ (because F is -1)

In Peroxides, which contain the O - O bond;
such as H - O - O - H (Hydrogen Peroxide), where O is -1

Na_2O_2 : is $2 \text{Na}^+ [\text{O} - \text{O}]^{2-}$, therefore O is -1

f) Other Halogens (**Group VII**) are always -1 , except when combined with fluorine or oxygen.....



$$\begin{array}{r} 4\text{O} @ -2 = -8 \\ 1\text{Mn} @ ? = \textcircled{+7} \\ \hline \text{Overall} = -1 \end{array}$$

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BALANCING REDOX EQUATIONS BY HALF REACTIONS

EXAMPLE 1:

Permanganate ion oxidizes oxalate ions in **ACIDIC** solution.....

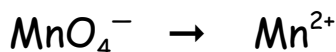


Separate the reaction into two half-reactions:

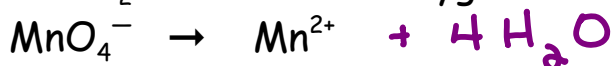


Now, deal with each half reaction individually:

- 1) Balance non-O and non-H atoms as usual



- 2) Add H₂O to balance oxygen



- 3) Add H⁺ to balance H atoms (regardless of acidic or basic)



→ to the more positive side

- 4) Add electrons to balance the charge



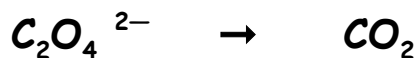
- 5) We are told the solution is acidic, so we may use H⁺ ions to balance H.

- 6) Since e⁻ appear on the left, this is **REDUCTION** (gain of electrons).

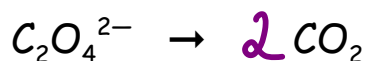
- 7) Mn goes from Oxidation Number +7 to Oxidation Number +2 ;

→ it has gained 5 e⁻

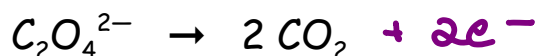
Now deal with the other half reaction:



- 1) Balance non-O and non-H atoms as usual; in this case we must balance the C:



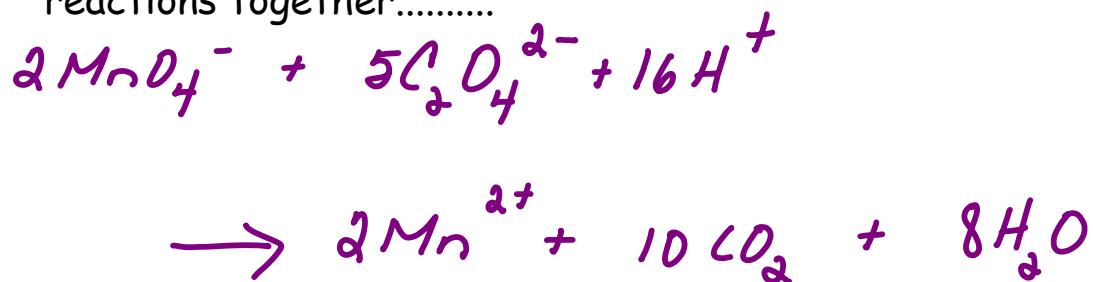
- 2) Add H_2O to balance oxygen; oxygen is already balanced!!
- 3) Add H^+ to balance H atoms (regardless of acidic or basic); there are no H's!!
- 4) Add electrons to balance the charge:



- Since e^- appear on the right, this is **OXIDATION** (loss of electrons)
- Each Carbon has gone from Oxidation Number **+3** to Oxidation Number **+4**; \Rightarrow each C has lost one e^-
- In a balanced redox equation, there are no electrons; we must make the number of electrons in the two half reactions equal (then they can be cancelled)
- So.....multiply each half -reaction by the number of e^- in the other half reaction!



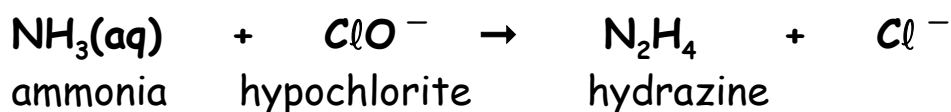
- The $10 e^-$ on each side may be cancelled; then add the two half reactions together.....



- Always check that the equation is balanced for both atoms and charge

EXAMPLE 2:

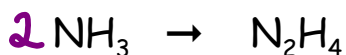
The following reaction occurs in **BASIC** solution.....



Separate the reaction into two half reactions:

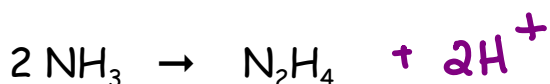


- Balance all non-O and non-H atoms; in this case balance N:

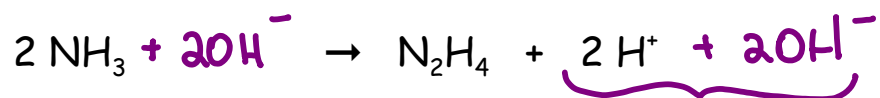


- Add H_2O to balance oxygen; no need - as there is no oxygen present.

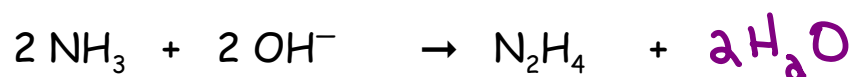
- Add H^+ to balance H atoms; although there is no appreciable H^+ concentration in basic solution, we (temporarily) use H^+ to balance H.....



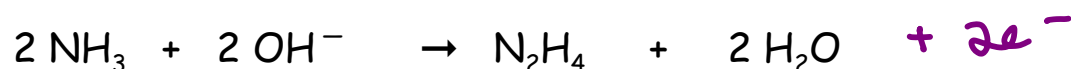
- 4) We are told the solution is basic, so use of H^+ is NOT really allowed.....
- 5) We must neutralize the H^+ by adding equal amounts of OH^- to each side; converting all H^+ to H_2O and retaining the balance:



- 6) Now combine the H^+ and OH^- on the right hand side to produce H_2O :



- 7) Add electrons to balance the charge:



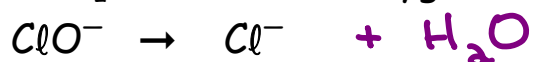
- 8) This is the **OXIDATION** half-reaction; electrons appear on the right.
- 9) Each Nitrogen has gone from **-3** to **-2**;
 \Rightarrow each Nitrogen has lost one electron

Now for the other half reaction:

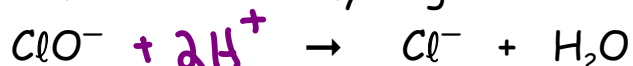


- 1) Balance all non-O and non-H atoms; the Cl is already balanced.

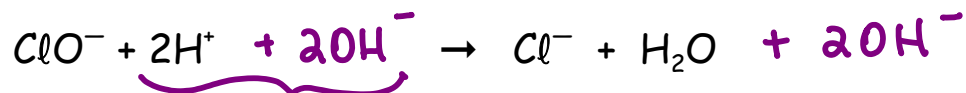
- 2) Add H_2O to balance oxygen:



- 3) Add H^+ to balance hydrogen:



4) Add OH^- to remove H^+ :



5) Combine the H^+ and OH^- on the left hand side to produce H_2O :



6) Add electrons to balance the charge:



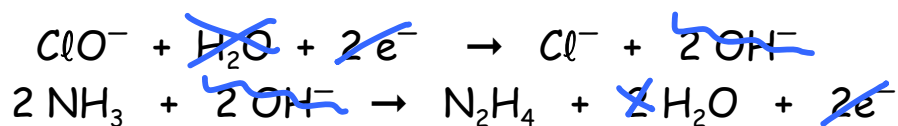
7) This is the **REDUCTION** half-reaction; electrons appear on the left.

8) Cl has gone from +1 to -1;

⇒ each Cl has gained 2 electrons

9) As we have 2 electrons in each half reaction; add the two half reactions together, cancelling the electrons.

10) Also cancel any H_2O or OH^- possible.....



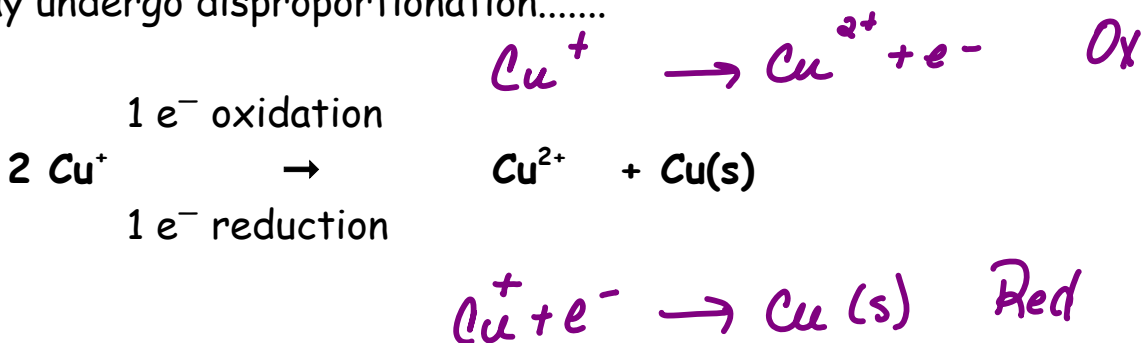
• Check the final equation for balance in both atoms and charge.

- A **DISPROPORTIONATION** reaction is a redox reaction in which a substance in an intermediate oxidation state goes to both a higher and a lower state by e^- transfer.

EXAMPLE:

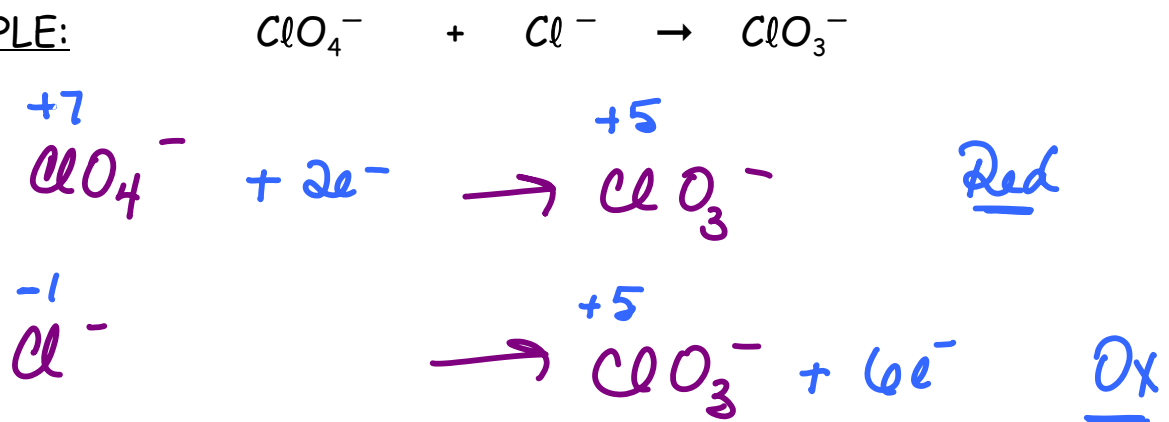
Copper, Cu, may exist in the +1 oxidation state, which is less stable than either +2 or 0.

It may undergo disproportionation.....

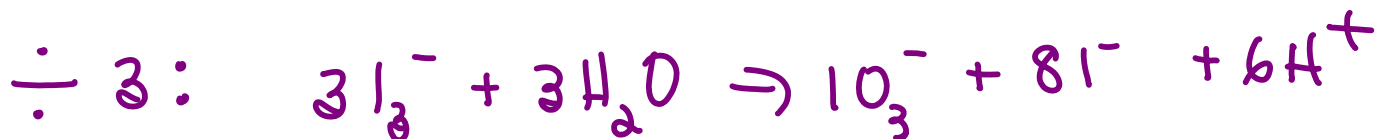
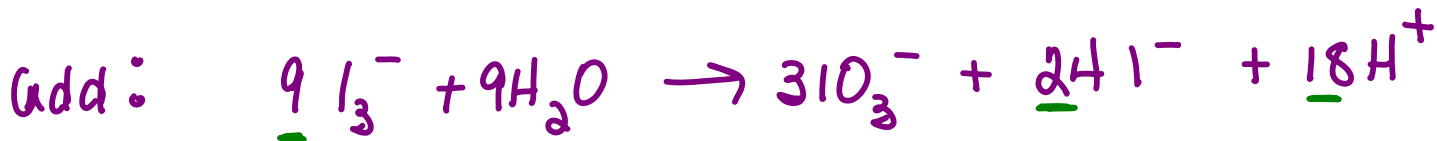
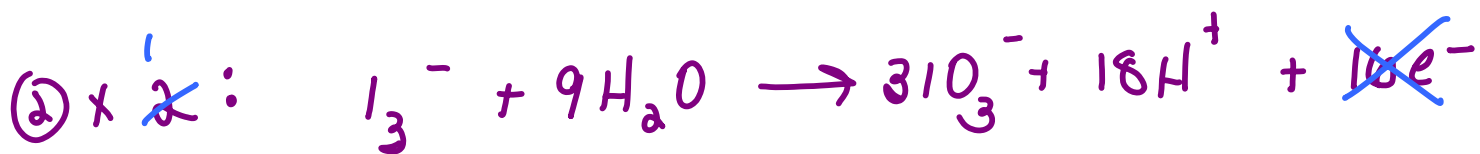
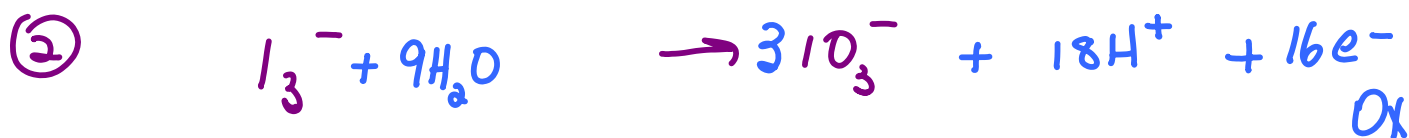


- The opposite of disproportionation is **CONPROPORTIONATION**.
- There are two reactants; one is oxidized and one is reduced.....but there is only one product.
- The oxidation state of the product is an intermediate state to those of the reactants.

EXAMPLE:

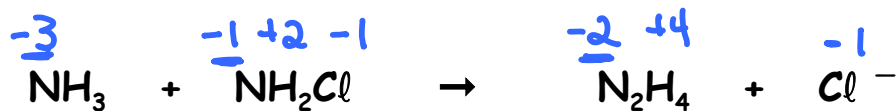


EXAMPLE 1: Balance the following reaction which occurs in acidic solution. **DISPROPORTIONATION**



EXAMPLE 2:

Hydrazine, N_2H_4 , is prepared by reaction of ammonia with chloramine in basic solution, according to :



CONPROPORTIONATION

Balance this equation.

