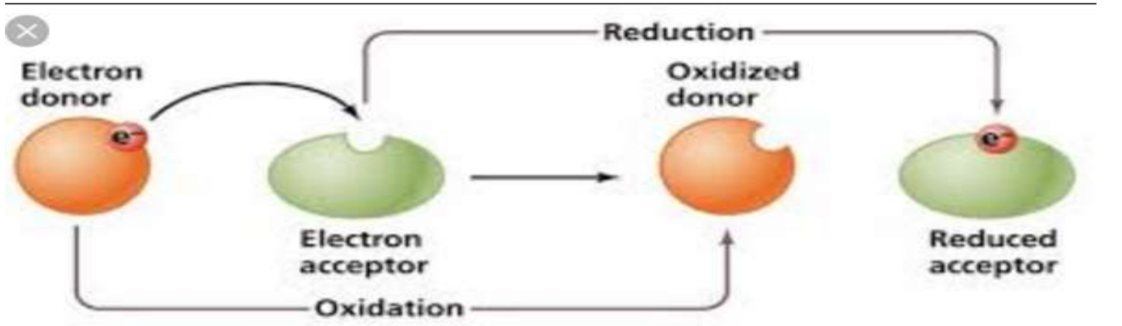
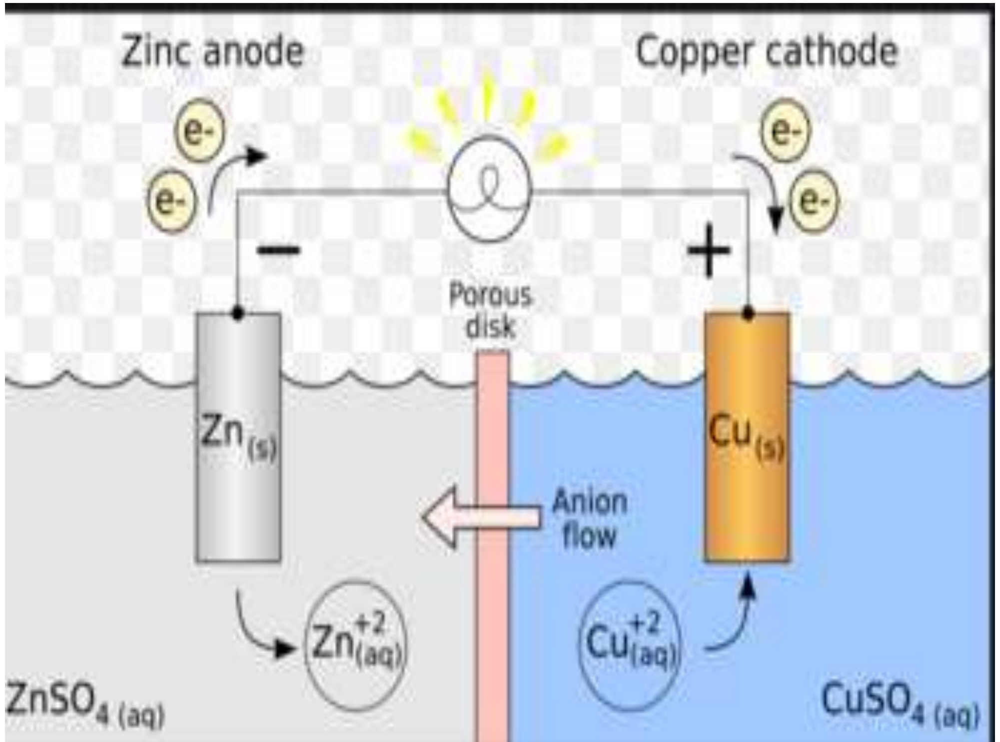
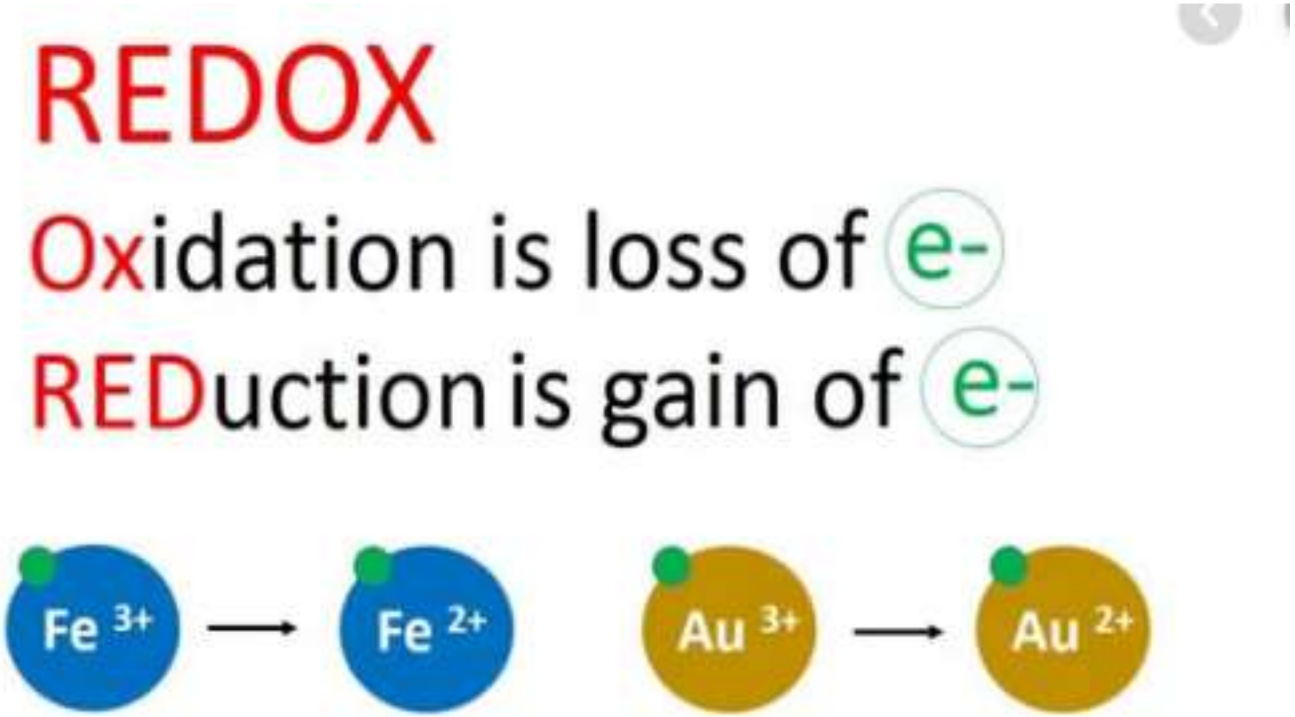


Redox Reactions

CHM 101





Redox Reactions

- Historically, the term "oxidation" was used because the redox reactions that were first systematically investigated took place in oxygen, with oxygen being reduced and the other species being oxidized, hence the term oxidation reaction.
- However, it was later realized that this case (oxidation reactions involving oxygen) was just one possible scenario. For example consider the redox reaction shown below.

$$Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$$

- In this process the Fe^{2+} ion is oxidized, but there is no oxygen involved in this reaction.
- The Ce^{4+} ion, which is reduced acts as the oxidizing agent. So oxidation reactions need not involve oxygen.
- This redox reaction is actually the sum of two separate half-reactions (a reduction half-reaction and an oxidation half-reaction).

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \quad \text{(oxidation half - reaction)}$$

$$Ce^{4+} + e^{-} \rightarrow Ce^{3+} \quad \text{(reduction half - reaction)}$$

$$\overline{Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}}$$

Redox Reactions

- Redox reactions are reactions in which one species is reduced and another is oxidized. Therefore the oxidation state of the species involved must change. These reactions are important for a number of applications, including energy storage devices (batteries), photographic processing, and energy production and utilization in living systems including humans.

- **Reduction:** *A* process in which an atom *gains* an electron and therefore decreases (or reduces its oxidation number). Basically the positive character of the species is reduced.

- **Oxidation:** *A* process in which an atom loses an electron and therefore increases its oxidation number. In other words, the positive character of the species is increased.

oxidation

$$4HCl + O_2 \longrightarrow 2Cl_2 + 2\,H_2O$$

$$H_2 + Br_2 \longrightarrow 2\,HBr$$

reduction

Reduction

$$\text{Oxidant} + e^- \longrightarrow \text{Product}$$

(Electrons **gained**; oxidation number **decreases**)

Oxidation

$$\text{Reductant} \longrightarrow \text{Product} + e^-$$

(Electrons **lost**; oxidation number **increases**)

Redox Reactions

+ 8 electrons

- 8 electrons

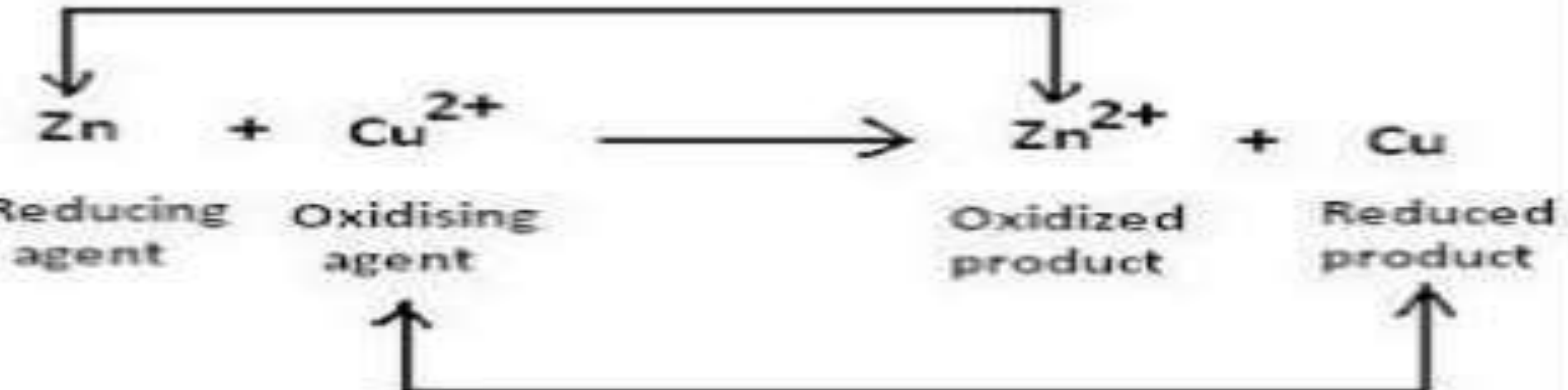
$$\underset{(-4)}{CH_4} + 2\,\underset{(0)}{O_2} \longrightarrow \underset{(+4)}{C}\underset{(-2)}{O_2} + 2\,H_2\underset{(-2)}{O}$$

- 1 C atom is oxidized from -4 to +4
- 4 O atoms are reduced from 0 to -2
- 4 H atoms remain unchanged at +1

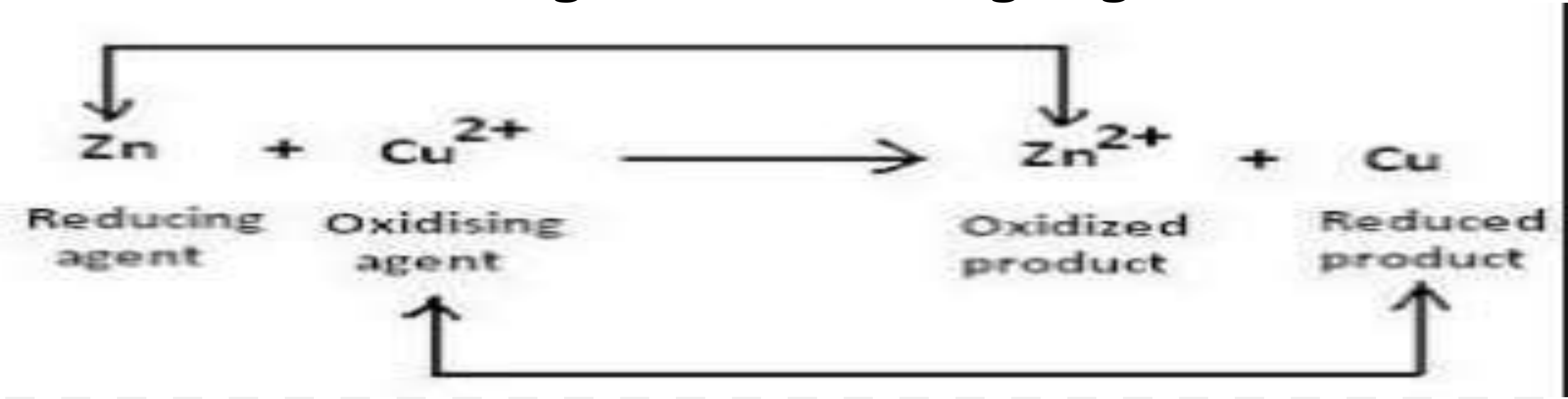
Oxidizing and Reducing Agents

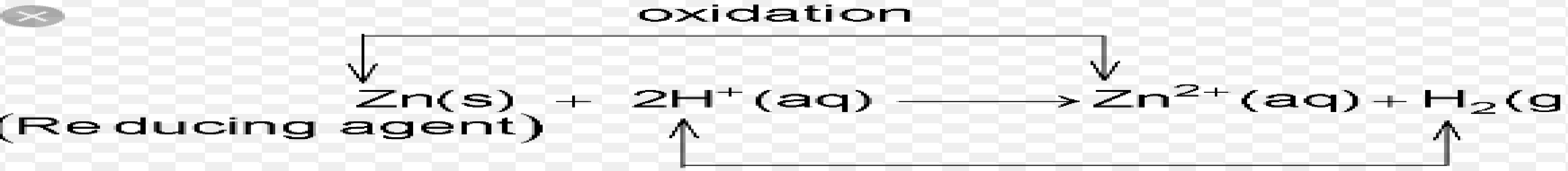
- An **oxidizing agent**, or **oxidant**, *gains* electrons and is reduced in a chemical reaction. Also known as the electron acceptor, the oxidizing agent is normally in one of its higher possible oxidation states because it will gain electrons and be reduced. Examples of oxidizing agents include halogens, potassium nitrate, and nitric acid.
- A **reducing agent,** or **reductant**, *loses* electrons and is oxidized in a chemical reaction. A reducing agent is typically in one of its lower possible oxidation states, and is known as the electron donor. A reducing agent is oxidized, because it loses electrons in the redox reaction.
- Examples of reducing agents include the earth metals, formic acid, and sulfite compounds.

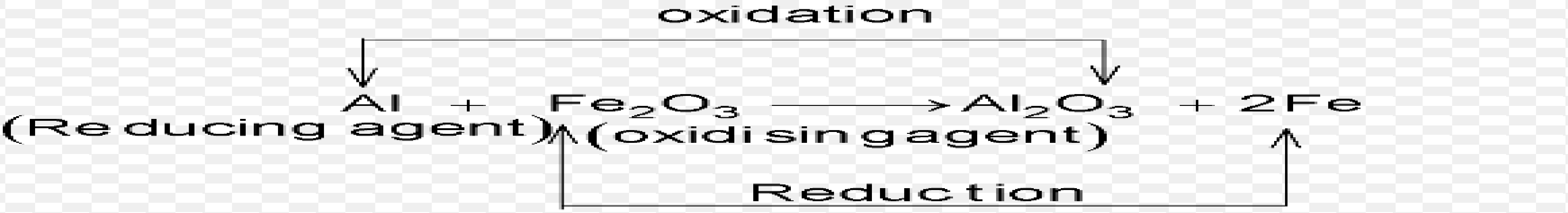
- The key idea is the net movement of electrons from one reactant to the other:
- Oxidation is the loss of electrons
- Reduction is the gain of electrons
- Oxidizing agent is the species doing the oxidizing
- Reducing agent is the species doing the reducing



Oxidizing and Reducing Agents







Oxidizing and Reducing Agents

Removal of oxygen [Reduction]

$$CuO + H_2 \rightarrow Cu + H_2O$$

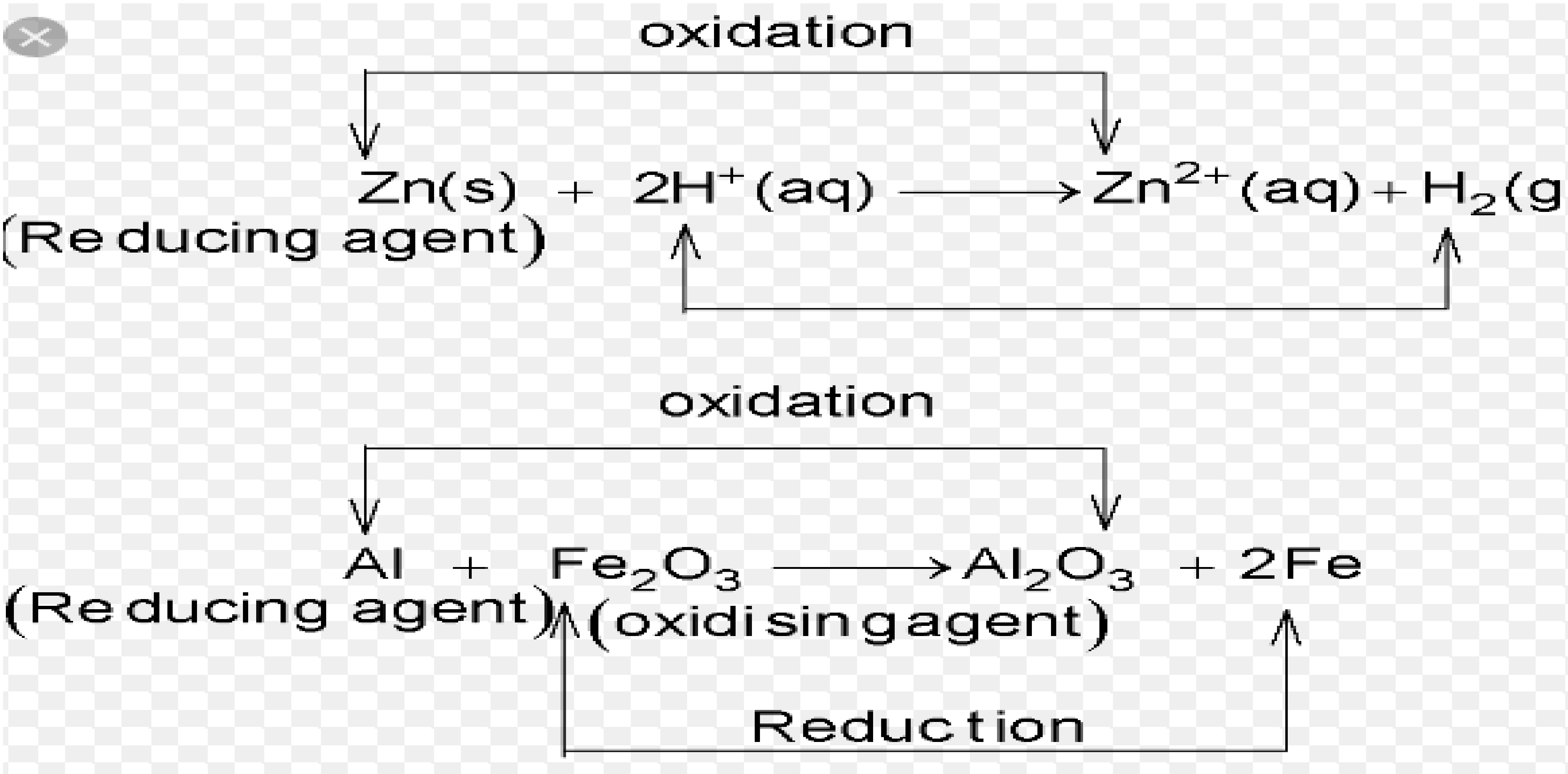
Addition of oxygen [Oxidation]

Removal of oxygen [Reduction]

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$$

Addition of oxygen [Oxidation]

Oxidizing and Reducing Agents



Oxidation State and Oxidation Number

- **Oxidation State:** The condition of a species with a specified oxidation number. An element with a given oxidation number exists in the corresponding oxidation state.
- **Assigning Oxidation Numbers**
- The following rules for assignment of oxidation numbers are listed in hierarchical order.

1. Pure elements (in their natural, standard state): ox. # = 0.
2. Monatomic ions: ox. # = ionic charge.
3. F is always F (-I) in compounds.
4. Alkali metals (those in the 1st column of the periodic table): ox. # = I.
5. Alkaline-earth metals (those in the 2nd column of the periodic table): ox # = II.
6. Hydrogen is almost always H (I). The exception is in metal hydrides (MH_x).
7. Oxygen is almost always O (-II) in compounds. Exceptions are O-O and O-F.
8. The sum of all oxidation numbers in the species will equal the total charge of that species.

Oxidation Number

- Oxidation number (O.N.) is also known as oxidation state.
- It is defined as the charge the atom would have if electrons were not shared but were transferred completely
- For a binary ionic compound, the O.N. is equivalent to the ionic charge
- For covalent compounds or polyatomic ions, the O.N. is less obvious and can be determined by a given set of rules

Rules for Assigning an Oxidation Number

- General Rules

1. For an atom in its elemental form (Na, O2): O.N. = 0
2. For a monatomic ion: O.N. = ion charge
3. The sum of O.N. values for the atoms in a molecule or formula unit of a compound equals to zero. (equals to the ion's charge if it is a polyatomic ion)

Rules for Specific Atoms or Periodic Table Groups

1. For Group 1A(1): O.N. = +1 in all compounds
2. For Group 2A(2): O.N. = +2 in all compounds
3. For hydrogen: O.N. = +1 in combination with nonmetals O.N. = -1 in combination with metals and boron
4. For fluorine: O.N. = -1 in all compounds
5. For oxygen: O.N. = -1 in peroxides O.N. = -2 in all other compounds (except with F)
6. For Group 7A(17): O.N. = -1 in combination with metals, nonmetals (except O), and other halogens lower in the group

Balancing Redox Equations

- When balancing redox reactions, make sure that the number of electrons lost by the reducing agent equals the number of electrons gained by the oxidizing agent .

Two methods can be used:

1. Oxidation number method
2. Half-reaction method

Balancing Redox Equations

Method 1: Oxidation number method

1. Assign oxidation numbers to all elements in the reaction
2. From the changes in O.N., identify the oxidized and reduced species
3. Compute the number of electrons lost in the oxidation and gained in the reduction from the O.N. changes
4. Multiply one or both of these numbers by appropriate factors to make the electrons lost equal the electrons gained, and use the factors as balancing coefficients
5. Complete the balancing by inspection, adding states of matter

Example 1

- Determine the oxidation number (O.N.) of each element in these compounds:
  a) CaO (s)
  b) KNO_3 (s)
  c) $NaHSO_4$ (aq)
  d) $CaCO_3$ (s)
  e) N_2 (g)
  f) H_2O (l)

Solution to Example 1

Simply apply the rules for assigning an oxidation number as described earlier

a) $\overset{+2}{Ca}\overset{-2}{O}$ (s)

b) $\overset{+1}{K}\overset{+5}{N}\overset{-2}{O}_3$ (s)

$N = 0-(+1)-3(-2) = +5$

c) $\overset{+1}{Na}\overset{+1}{H}\overset{+6}{S}\overset{-2}{O}_4$ (aq)

$S = 0-(+1)-(+1)-4(-2) = +5$

d) $\overset{+2}{Ca}\overset{+4}{C}\overset{-2}{O}_3$ (s)

$C = 0-(+2)-3(-2) = +4$

e) $\overset{0}{N}_2$ (g)

f) $\overset{+1}{H}_2\overset{-2}{O}$ (l)

Example 2

- Identify the oxidizing agent and reducing agent in each of the following:

a) $2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (g)$

b) $Cu\ (s) + 4HNO_3\ (aq) \longrightarrow Cu(NO_3)_2\ (aq) + 2NO_2\ (g) + 2H_2O\ (l)$

Balancing Redox Equations

Method 2: Half-reaction method

1. Divide the skeleton reaction into two half-reactions, each of which contains the oxidized and reduced forms of one of the species
2. Balance the atoms and charges in each half-reaction
   - Atoms are balanced in order: atoms other than O and H, then O, then H
   - Charge is balanced by adding electrons
     - To the left in reduction half-reactions
     - To the right in oxidation half-reactions
3. If necessary, multiply one or both half-reactions by an integer to make the number of e^- gained equal to the number of e^- lost
4. Add the balanced half-reactions, and include states of matter
5. Check that the atoms and charges are balanced

Guidelines for Balancing Redox Equations

1) Determine the oxidation states of each species.

2a)Write each half reaction and for each:

2b)Balance atoms that change oxidation state.

3)Determine number of electrons gained or lost

4)Balance charges by using H^+ (in acidic solution) or OH^- (in basic solution).

5)Balance the rest of the atoms (H's and O's) using H_2O.

6)Balance the number of electrons transferred for each half reaction using the appropriate factor so that the electrons cancel.

7)Add the two half-reactions together and simplify if necessary.

BALANCING REDOX REACTIONS

- STEP 1. Split Reaction into 2 Half-Reactions
- STEP 2. Balance Elements Other than H & O
- STEP 3. Balance O by Inserting H_2O into eqns. as necessary
- STEP 4. Balance H with H^+ or H_2O (see 4a, 4b)
- STEP 5. Balance Charge by Inserting Electrons as needed
- STEP 6. Multiply Each 1/2 Reaction by Factor needed to make no. of Electrons in each 1/2 Reaction Equal
- STEP 7. Add Eqns. & Cancel Out Duplicate terms, where possible

Balancing Redox Reactions

1) assign oxidation states and determine element oxidized and element reduced

$$Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$$

+2 +7 -2 +3 +2

oxid

red

2) separate into oxidation & reduction half-reactions

$Fe^{2+} \rightarrow Fe^{3+}$

$MnO_4^- \rightarrow Mn^{2+}$

3) balance half-reactions by mass

$Fe^{2+} \rightarrow Fe^{3+}$

a) first balance atoms other than O and H

$MnO_4^- \rightarrow Mn^{2+}$

b) then balance O by adding H_2O to side that lacks O

$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

c) finally balance H by adding H^+ to side that lacks H

$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$

Balancing Redox Reactions

- Now all charges and number of atoms balance. Finally, two terms you may run across in the future are
- **oxidizing agent** (or oxidant) and a **reducing agent** (reductant).
- An oxidizing agent causes oxidation and is reduced in the reaction.
- A reducing agent causes the reduction in the redox reaction. The reducing agent is oxidized in the reaction.
- In Example 4 above, MnO_4^- is the oxidizing agent and Cl^- is the reducing agent.

Solution to Example 2

Assign oxidation numbers and compare.

Oxidation is represented by an increase in oxidation number

Reduction is represented by a decrease in oxidation number

a) $2\overset{0}{H}_2\,(g) + \overset{0}{O}_2\,(g) \longrightarrow 2\overset{+1}{H}_2\overset{-2}{O}\,(g)$

- O_2 was reduced (O.N. of O: 0 -> -2); O_2 is the oxidizing agent
- H_2 was oxidized (O.N. of H: 0 -> +1); H_2 is the reducing agent

b) $\overset{0}{Cu} + 4\overset{+1}{H}\overset{+5}{N}\overset{-2}{O}_3 \longrightarrow \overset{+2}{Cu}(\overset{+5}{N}\overset{-2}{O}_3)_2 + 2\overset{+4}{N}\overset{-2}{O}_2 + 2\overset{+1}{H}_2\overset{-2}{O}$

- Cu was oxidized (O.N. of Cu: 0 -> +2); Cu is the reducing agent
- HNO_3 was reduced (O.N. of N: +5 -> +4); HNO_3 is the oxidizing agent

Example 3. Balance the following redox reaction.

$$Al(s) + 2H^+(aq) + 2Cl^- \rightarrow Al^{3+}(aq) + H_2(g) + 2Cl^-(aq)$$

Step 1. Determine the oxidation states of the species involved.

$$\underset{0}{Al}(s) + 2\underset{I}{H^+}(aq) + 2\underset{-I}{Cl^-} \longrightarrow \underset{III}{Al^{3+}}(aq) + \underset{0}{H_2}(g) + 2\underset{-I}{Cl^-}(aq)$$

The charges don't match yet so this is not a balanced equation. We can use each half-reaction to balance the charges. Notice that the Cl^- ions drop out, as they are spectator ions and do not participate in the actual redox reaction.

Step 2. Write the half reactions.

$$Al(s) \longrightarrow Al^{3+}(aq)$$

$$H^+(aq) \longrightarrow H_2(g)$$

Step 2a. Balance the atoms that change their oxidation states.

$$Al(s) \longrightarrow Al^{3+}(aq)$$

$$2H^+(aq) \longrightarrow H_2(g)$$

Step 2b. Determine the number of electrons gained or lost.

$$Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$$

$$2e^- + 2H^+(aq) \longrightarrow H_2(g)$$

- Aluminum changes from 0 to III, so three electrons are lost. For hydrogen, the case is a little different. Hydrogen is going from I to 0. This means that for each H^+ ion that reacts, one electron is needed. Since there are two H^+ ions that react, two electrons are needed.

Steps 2c and 2d are not needed in this case as the equations are balanced.

Step 3. Balance the number of electrons transferred.

$$\left(Al(s) \longrightarrow Al^{3+}(aq) + 3e^-\right)2$$

$$\left(2e^- + 2H^+(aq) \longrightarrow H_2(g)\right)3$$

The common factor for the electrons transferred is 6, so the above multiplication is performed.

Step 4. Now the charges and atoms are balanced. To verify this add all of the charges and atoms on each side. Both the charges and number of atoms must balance. Note that this reaction is not neutral. Remember that the spectator ions, Cl^-, neutralize the solution.

$$2\,Al(s) \rightarrow 2\,Al^{3+}(aq) + 6\,e^-$$

$$6\,e^- + 6\,H^+(aq) \rightarrow 3\,H_2(g)$$

$$\overline{2\,Al(s) + 6\,H^+(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,H_2(g)}$$

Acidic Conditions

- Acidic conditions usually implies a solution with an excess of H^+ concentration, hence making the solution acidic.
- The balancing starts by separating the reaction into half-reactions.
- However, instead of immediately balancing the electrons, balance all the elements in the half-reactions that are not hydrogen and oxygen. Then, add H_2O molecules to balance any oxygen atoms.
- Next, balance the hydrogen atoms by adding protons (H^+). Now, balance the *charge* by adding electrons and scale the electrons (multiply by the lowest common multiple) so that they will cancel out when added together.
- Finally, add the two half-reactions and cancel out common terms.

Example 4. Balance the following reaction, which occurs in acidic solution

$$MnO_4^- (aq) + Cl^- (aq) \rightarrow Mn^{2+} (aq) + HClO (aq)$$

Step 1. Determine the oxidation states of the species involved.
To determine the oxidation state of Mn in MnO_4^-, apply Equation 1 (see Equation 1 above): $x + 4(-2) = -1$.

$$\underset{\mathrm{VII}\ \ -\mathrm{II}}{MnO_4^-} (aq) + \underset{-\mathrm{I}}{Cl^-} (aq) \rightarrow \underset{\mathrm{II}}{Mn^{2+}} (aq) + \underset{\mathrm{I}\ \ \mathrm{I}\ -\mathrm{II}}{HClO} (aq)$$

Step 2. Write the half reactions.

$$MnO_4^- (aq) \rightarrow Mn^{2+} (aq)$$

$$Cl^- (aq) \rightarrow HClO (aq)$$

Step 2a. Mn and Cl are balanced.

Step 2b. Mn changes from VII to II, so five electrons are needed. Cl^- loses two electrons as it goes from I to -I.

$$5\,e^- + MnO_4^- \,(aq) \longrightarrow Mn^{2+}\,(aq)$$
$$Cl^-\,(aq) \longrightarrow HClO\,(aq) + 2\,e^-$$

Step 2c. The charges are not balanced on this example. Since this is in acidic solution, use H^+ to balance these charges.

$$8\,H^+\,(aq) + 5\,e^- + MnO_4^-\,(aq) \longrightarrow Mn^{2+}\,(aq)$$
$$Cl^-\,(aq) \longrightarrow HClO\,(aq) + 2\,e^- + H^+\,(aq)$$

Remember that the electrons carry a negative charge and must be considered whenever balancing the charges. Verify that the charges are balanced on each side of the equation.

Step 2d. Now the oxygen and hydrogen atoms need to be balanced.

$$8\,H^+\,(aq) + 5\,e^- + MnO_4^-\,(aq) \rightarrow Mn^{2+}\,(aq) + 4\,H_2O$$

$$H_2O + Cl^-\,(aq) \rightarrow HClO + 2\,e^- + H^+\,(aq)$$

Step 3. Balance the number of electrons transferred.

$$\left(8\,H^+\,(aq) + 5\,e^- + MnO_4^-\,(aq) \rightarrow Mn^{2+}\,(aq) + 4\,H_2O\right)2$$

$$\left(H_2O + Cl^-\,(aq) \rightarrow HClO + 2\,e^- + H^+\,(aq)\right)5$$

Step 4. Write the net reaction.

$$16\,H^+\,(aq) + 10\,e^- + 2\,MnO_4^-\,(aq) \rightarrow 2\,Mn^{2+}\,(aq) + 8\,H_2O$$

$$5\,H_2O + 5\,Cl^-\,(aq) \rightarrow 5\,HClO + 10\,e^- + 5\,H^+\,(aq)$$

$$11H^+\,(aq) + 2\,MnO_4^-\,(aq) + 5\,Cl^-\,(aq) \rightarrow 2\,Mn^{2+}\,(aq) + 5\,HClO\,(aq) + 3\,H_2O$$

EXAMPLE 5: BALANCING IN A ACID SOLUTION

Balance the following redox reaction in acidic conditions.

$$Cr_2O_7^{2-}(aq) + HNO_2(aq) \rightarrow Cr^{3+}(aq) + NO_3{-}(aq)$$

Step 1: Separate the half-reactions. The table provided does not have acidic or basic half-reactions, so just write out what is known.

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$

$$HNO_2(aq) \rightarrow NO_3{-}(aq)$$

- **Solution**
- **Step 1:** Separate the half-reactions. The table provided does not have acidic or basic half-reactions, so just write out what is known.

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$

$$HNO_2(aq) \rightarrow NO_3^-(aq)$$

Step 2: Balance elements other than O and H. In this example, only chromium needs to be balanced. This gives:

$$Cr_2O_7^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq)$$

$$HNO_2(aq) \rightarrow NO_3^-(aq)$$