Balancing an electrochemical reaction in acidic aqueous solution is performed in the presence of $H_2O(\ell)$ and $H^+(aq)$. In this case, any of these two species can be added if necessary to balance the reaction.

Steps for balancing a redox reaction (in an acidic solution)

- 1. Separate the reactions in two half-reactions that will both be balanced individually.
- 2. Balance the elements other than "O" and "H"
- 3. Balance "O" by adding $H_2O(\ell)$
- 4. Balance "H" by adding H⁺(aq)
- 5. Balance the charges by adding the appropriate number of electrons (e⁻)
- 6. Make sure that the number of electrons is the same in both half reactions
- 7. Add the two half reactions together and cancel-out the electrons

Example: Balance the following reaction using the half reaction method

$$Fe^{3+} + Mn_2O_3 \longrightarrow MnO_2 + Fe^{2+}$$

$$Step 1 \qquad Mn_2O_3 \longrightarrow MnO_2 \qquad Fe^{3+} \longrightarrow Fe^{2+}$$

$$Step 2 \qquad Mn_2O_3 \longrightarrow 2MnO_2$$

$$Step 3 \qquad H_2O + Mn_2O_3 \longrightarrow 2MnO_2$$

$$Step 4 \qquad H_2O + Mn_2O_3 \longrightarrow 2MnO_2 + 2H^+$$

$$Step 5 \qquad H_2O + Mn_2O_3 \longrightarrow 2MnO_2 + 2H^+ + 2e^- \qquad e^- + Fe^{3+} \longrightarrow Fe^{2+}$$

$$Step 6 \qquad H_2O + Mn_2O_3 \longrightarrow 2MnO_2 + 2H^+ + 2e^- \qquad 2e^- + 2Fe^{3+} \longrightarrow 2Fe^{2+}$$

$$Step 7 \qquad 2e^- + 2Fe^{3+} + H_2O + Mn_2O_3 \longrightarrow 2MnO_2 + 2Fe^{2+} + 2H^+ + 2e^-$$

$$2Fe^{3+} + H_2O + Mn_2O_3 \longrightarrow 2MnO_2 + 2Fe^{2+} + 2H^+$$

IMPORTANT

Electrons are negative particles that carry electrical charge. Since it is an actual physical entity, it cannot be "mathematically" subtracted in a chemical reaction.

$$X + e^{-} \longrightarrow X^{-}$$
 YES
 $M \longrightarrow M^{+} + e^{-}$ YES
 $M - e^{-} \longrightarrow M^{+}$ NO, NEVER!

Steps to balance a redox reaction in a basic aqueous solution

To balance the reaction in a basic solution, the initial steps are the same as those for an acidic solution. However, an additional step is added at the end to neutralize the acid.

Example: Balance the following reaction in a basic solution using the half reaction method.

Step 1 Al
$$\rightarrow$$
 AlO₂⁻ + Fe₂O₃
Step 2 Al \rightarrow AlO₂⁻ \qquad FeO₄²⁻ \rightarrow Fe₂O₃
Step 3 $2H_2O + Al \rightarrow AlO_2^ \qquad$ $2FeO_4^{2-} \rightarrow Fe_2O_3$
Step 4 $2H_2O + Al \rightarrow AlO_2^ \qquad$ $2FeO_4^{2-} \rightarrow Fe_2O_3 + 5H_2O$
Step 5 $2H_2O + Al \rightarrow AlO_2^- + 4H^+$ \qquad $10H^+ + 2FeO_4^{2-} \rightarrow Fe_2O_3 + 5H_2O$
Step 6 $4H_2O + 2Al \rightarrow AlO_2^- + 4H^+ + 3e^ 6e^- + 10H^+ + 2FeO_4^{2-} \rightarrow Fe_2O_3 + 5H_2O$
Step 7 $4H_2O + 2Al \rightarrow 2AlO_2^- + 8H^+ + 6e^ 6e^- + 10H^+ + 2FeO_4^{2-} \rightarrow Fe_2O_3 + 5H_2O$
Step 7 $4H_2O + 2Al + 2FeO_4^{2-} + 10H^+ + 6e^- \rightarrow Fe_2O_3 + 2AlO_2^- + 5H_2O + 8H^+ + 6e^-$
Final: $2Al + 2FeO_4^{2-} + 2H^+ \rightarrow Fe_2O_3 + 2AlO_2^- + H_2O$

In an **alkaline solution**, there must be no $H^+(aq)$ present anywhere. If there is, it is neutralized by an acid-base neutralization with the addition of OH^- .

- a. Use the equation from "Step 7" and add the equivalent number of moles of OH⁻(aq) to that of H⁺ ON BOTH SIDES of the reaction to maintain equilibrium.
- b. H^+ is consumed and $H_2O(\ell)$ is produced (acid-base reaction).
- c. any excess H₂O, present on both side of the reaction is removed.

Step 8 (Neutralize H⁺ with OH⁻)

a.
$$\mathbf{2OH^-} + \mathbf{2H^+} + 2AI + 2FeO_4^{2^-} \longrightarrow Fe_2O_3 + 2AIO_2^- + H_2O + \mathbf{2OH^-}$$

b. $\mathbf{2H_2O} + 2AI + 2FeO_4^{2^-} \longrightarrow Fe_2O_3 + 2AIO_2^- + \mathbf{H_2O} + 2OH^-$

c. $\mathbf{H_2O} + 2AI + 2FeO_4^{2^-} \longrightarrow Fe_2O_3 + 2AIO_2^- + 2OH^-$

The reaction is now balanced in alkaline solution.

1. Balance each of the the following half-reactions in acidic aqueous solution.

Tell whether it is a reduction or an oxidation reaction.

- a. $SiO_2 \longrightarrow SiO_4$
- d. $HN_3 \longrightarrow H_3N$
- b. $CO_2 \longrightarrow CO$
- e. $HNO_2 \longrightarrow NO_3^-$
- c. $Cr^{3+} \longrightarrow Cr_2O_7^{2-}$
- 2. Balance the following redox reactions in acidic (H^+) aqueous solution.

Identify the reducing agent.

- a. $Cl^- + Sn + NO_3^- \longrightarrow SnCl_6^{2-} + NO_2$
- b. $Fe^{2+} + NO_2 \longrightarrow NH_3 + Fe^{3+}$
- c. $MnO_4^- + Sn^{2+} \longrightarrow Sn^{4+} + Mn^{2+}$
- d. $N_2O_4 \longrightarrow NO_3^- + NO_2^-$ (hint : The two half-reactions use the same reactant.)
- 3. Balance the following redox reactions in basic (OH⁻) aqueous solution. Identify the oxidizing agent.
 - a. Ag + CN⁻ + O₂ \longrightarrow Ag(CN)₂⁻
 - b. $NO_2^- + AI \longrightarrow NH_3 + AIO_2^-$

Answer

- 1. a. $2H_2O + SiO_2 \longrightarrow SiO_4 + 4H^+ + 4e^-$ (oxidation)
 - b. $2e^- + 2H^+ + CO_2 \longrightarrow CO + H_2O$ (reduction)
 - c. $7H_2O + 2Cr^{3+} \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$ (oxidation)
 - d. $8e^- + 8H^+ + HN_3 \longrightarrow 3H_3N$ (reduction)
 - e. $H_2O + HNO_2 \longrightarrow NO_3^- + 3H^+ + 2e^-$ (oxidation)
- 2. a. $8H^+ + 6CI^- + Sn + 4NO_3^- \longrightarrow SnCl_6^{2-} + 4NO_2 + 4H_2O$ red. agent: Sn
 - b. $7Fe^{2+} + NO_2 + 7H^+ \longrightarrow NH_3 + 7Fe^{3+} + 2H_2O$ red. agent: Fe^{2+}
 - c. $2MnO_4^- + 5Sn^{2+} + 16H^+ \longrightarrow 5Sn^{4+} + 2Mn^{2+} + 8H_2O$ red. agent: Sn^{2+}
 - d. $2N_2O_4 + 2H_2O \longrightarrow 2NO_3^- + 2NO_2^- + 4H^+$ red. agent: N_2O_4
- 3. a. $2H_2O + 4Ag + 8CN^- + O_2 \longrightarrow 4Ag(CN)_2^- + 4OH^-$ ox. agent: O_2
 - b. $NO_2^- + 2AI + OH^- + H_2O \longrightarrow NH_3 + 2AIO_2^-$ ox. Agent: NO_2^-