## Balancing Redox Equations

## Strategy for redox equations in acidic solutions

Problem: When dilute nitric acid is poured on a piece of copper metal, copper(II) ions and the gas nitric oxide, NO, are formed. Write the balanced equation for the reaction.

Step 0: Write the "skeleton equation"

$$
\mathrm{Cu}(\mathrm{~s})+\mathrm{H}^{+}(\mathrm{aq})+\mathrm{NO}_{3}^{-}(\mathrm{aq}) \longrightarrow \mathrm{Cu}^{2+}(\mathrm{aq})+\mathrm{NO}(\mathrm{~g})
$$

and determine the oxidation state (the oxidation state is per atom!)

$$
\stackrel{+}{\mathrm{Cu}(\mathrm{~s})+\stackrel{+1}{\mathrm{H}^{+}}(\mathrm{aq})+\stackrel{+5-2}{\mathrm{NO}_{3}^{-}}(\mathrm{aq}) \longrightarrow \stackrel{+2}{\mathrm{Cu}^{2+}}(\mathrm{aq})+\stackrel{+2-2}{\mathrm{NO}}(\mathrm{~g})}
$$

So we have

$$
\begin{array}{cc}
\mathrm{Cu}: 0 \rightarrow+2 & \text { ox } \\
\mathrm{N}:+5 \rightarrow+2 & \text { red }
\end{array}
$$

Step 1: Write the "skeleton" half-reactions

$$
\begin{aligned}
\text { ox: } & \mathrm{Cu} \longrightarrow \mathrm{Cu}^{2+} \\
\text { red: } & \mathrm{NO}_{3}{ }^{-} \longrightarrow \mathrm{NO}
\end{aligned}
$$

Step 2: Balance each half-reaction "atomically"

- all atoms other than H and O (You can use any of the species that appear in the skeleton equation-Step 0-for this purpose.)
- balance O atoms by adding $\mathrm{H}_{2} \mathrm{O}$
- balance H atoms by adding $\mathrm{H}^{+}$

$$
\text { ox: } \mathrm{Cu} \longrightarrow \mathrm{Cu}^{2+}
$$

$$
\begin{gathered}
\text { red: } \quad \mathrm{NO}_{3}{ }^{-} \longrightarrow \mathrm{NO}+2 \mathrm{H}_{2} \mathrm{O} \\
\text { red: } \mathrm{NO}_{3}^{-}+4 \mathrm{H}^{+} \longrightarrow \mathrm{NO}+2 \mathrm{H}_{2} \mathrm{O}
\end{gathered}
$$

Step 3: Balance the electric charges by adding electrons

$$
\begin{gathered}
\text { ox: } \mathrm{Cu} \longrightarrow \mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \\
\text {red: } \mathrm{NO}_{3}^{--}+4 \mathrm{H}^{+}+3 \mathrm{e}^{-} \longrightarrow \mathrm{NO}+2 \mathrm{H}_{2} \mathrm{O}
\end{gathered}
$$

The electrons have to appear on the right hand side for the oxidation half-reaction, and on the left hand side for the reduction half-reaction.

Step 4: Prepare the two half-equations for summation by making the number of electrons the same in both, i.e, find the least common multiple

$$
\begin{gathered}
3 \times \text { ox: } \quad 3 \mathrm{Cu} \longrightarrow 3 \mathrm{Cu}^{2+}+6 \mathrm{e}^{-} \\
2 \times \text { red: } \quad 2 \mathrm{NO}_{3}^{-}+8 \mathrm{H}^{+}+6 \mathrm{e}^{-} \longrightarrow 2 \mathrm{NO}+4 \mathrm{H}_{2} \mathrm{O}
\end{gathered}
$$

Step 5: Combine the two half-reactions

$$
3 \mathrm{Cu}+2 \mathrm{NO}_{3}^{-}+8 \mathrm{H}^{+}+6 \mathrm{e}^{-} \longrightarrow 3 \mathrm{Cu}^{2+}+6 \mathrm{e}^{-}+2 \mathrm{NO}+4 \mathrm{H}_{2} \mathrm{O}
$$

Step 6: Simplify

$$
3 \mathrm{Cu}+2 \mathrm{NO}_{3}^{-}+8 \mathrm{H}^{+} \longrightarrow 3 \mathrm{Cu}^{2+}+2 \mathrm{NO}+4 \mathrm{H}_{2} \mathrm{O}
$$

Step 7: Indicate the state of each species

$$
3 \mathrm{Cu}(\mathrm{~s})+2 \mathrm{NO}_{3}^{-}(\mathrm{aq})+8 \mathrm{H}^{+}(\mathrm{aq}) \longrightarrow 3 \mathrm{Cu}^{2+}(\mathrm{aq})+2 \mathrm{NO}(\mathrm{~g})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

This is the fully balanced net ionic equation.
Check by writing a table:

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| species | left | right |
| :---: | :---: | :---: |
| Cu | 3 | 3 |
| N | 2 | 2 |
| O | 6 | 6 |
| H | 8 | 8 |
| charge | +6 | +6 |

## Strategy for redox equations in basic solutions

In basic solutions, no $\mathrm{H}^{+}$are available to balance H !
Strategy: Pretend the solution is acidic and carry out a "neutralization reaction" at the end.

Problem: The reaction of permanganate ions with bromide ions in basic solution yields solid manganese(IV) oxide and bromate ions. Write the fully balanced net equation.

Step 0: Write the "skeleton equation" and determine the oxidation state (the oxidation state is per atom!)

$$
\stackrel{+7-2}{\mathrm{MnO}_{4}^{-}}{ }^{-}(\mathrm{aq})+\stackrel{-1}{\mathrm{Br}^{-}}(\mathrm{aq})+\stackrel{-2+1}{\mathrm{OH}^{-}} \longrightarrow \stackrel{+4-2}{\mathrm{MnO}_{2}(\mathrm{~s})}+\stackrel{+5-2}{\mathrm{BrO}_{3}^{-}}(\mathrm{aq})
$$

So we have

$$
\begin{array}{rll}
\mathrm{Br}:-1 & \rightarrow+5 & \text { ox } \\
\mathrm{Mn}:+7 & \rightarrow+4 & \\
\text { red }
\end{array}
$$

Step 1: Write the "skeleton" half-reactions

$$
\text { ox: } \mathrm{Br}^{-} \longrightarrow \mathrm{BrO}_{3}^{-}
$$

red: $\mathrm{MnO}_{4}{ }^{-} \longrightarrow \mathrm{MnO}_{2}$
Step 2: Balance each half-reaction "atomically"

- all atoms other than H and O (You can use any of the species that appear in the skeleton equation-Step 0-for this purpose.)
- balance O atoms by adding $\mathrm{H}_{2} \mathrm{O}$
- balance H atoms by adding $\mathrm{H}^{+}$

$$
\begin{gathered}
\text { ox: } \quad \mathrm{Br}^{-}+3 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{BrO}_{3}^{-} \\
\text {ox: } \quad \mathrm{Br}^{-}+3 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{BrO}_{3}^{-}+6 \mathrm{H}^{+}
\end{gathered}
$$

$$
\text { red: } \mathrm{MnO}_{4}^{-} \longrightarrow \mathrm{MnO}_{2}+2 \mathrm{H}_{2} \mathrm{O}
$$

$$
\text { red: } \mathrm{MnO}_{4}^{-}+4 \mathrm{H}^{+} \longrightarrow \mathrm{MnO}_{2}+2 \mathrm{H}_{2} \mathrm{O}
$$

Step 3: Balance the electric charges by adding electrons

$$
\begin{aligned}
& \text { ox: } \quad \mathrm{Br}^{-}+3 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{BrO}_{3}^{-}+6 \mathrm{H}^{+}+6 \mathrm{e}^{-} \\
& \text {red: } \mathrm{MnO}_{4}^{-}+4 \mathrm{H}^{+}+3 \mathrm{e}^{-} \longrightarrow \mathrm{MnO}_{2}+2 \mathrm{H}_{2} \mathrm{O}
\end{aligned}
$$

The electrons have to appear on the right hand side for the oxidation half-reaction, and on the left hand side for the reduction half-reaction.

Step 4: Prepare the two half-equations for summation by making the number of electrons the same in both, i.e, find the least common multiple

$$
\begin{aligned}
\text { ox: } & \mathrm{Br}^{-}+3 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{BrO}_{3}^{-}+6 \mathrm{H}^{+}+6 \mathrm{e}^{-} \\
2 \times \text { red: } & 2 \mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+}+6 \mathrm{e}^{-} \longrightarrow 2 \mathrm{MnO}_{2}+4 \mathrm{H}_{2} \mathrm{O}
\end{aligned}
$$

Step 5: Combine the two half-reactions

$$
\mathrm{Br}^{-}+3 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+}+6 \mathrm{e}^{-} \longrightarrow \mathrm{BrO}_{3}^{-}+6 \mathrm{H}^{+}+6 \mathrm{e}^{-}+2 \mathrm{MnO}_{2}+4 \mathrm{H}_{2} \mathrm{O}
$$

Step 6: Simplify

$$
\mathrm{Br}^{-}+2 \mathrm{MnO}_{4}^{-}+2 \mathrm{H}^{+} \longrightarrow \mathrm{BrO}_{3}^{-}++2 \mathrm{MnO}_{2}+\mathrm{H}_{2} \mathrm{O}
$$

Step 6a: Change to basic solution by adding as many $\mathrm{OH}^{-}$to both sides as there are $\mathrm{H}^{+}$

$$
\mathrm{Br}^{-}+2 \mathrm{MnO}_{4}^{-}+2 \mathrm{H}^{+}+2 \mathrm{OH}^{-} \longrightarrow \mathrm{BrO}_{3}^{-}++2 \mathrm{MnO}_{2}+\mathrm{H}_{2} \mathrm{O}+2 \mathrm{OH}^{-}
$$

"neutralization": Combine the $\mathrm{H}^{+}$and the $\mathrm{OH}^{-}$to form $\mathrm{H}_{2} \mathrm{O}$

$$
\mathrm{Br}^{-}+2 \mathrm{MnO}_{4}^{-}+2 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{BrO}_{3}^{-}++2 \mathrm{MnO}_{2}+\mathrm{H}_{2} \mathrm{O}+2 \mathrm{OH}^{-}
$$

simplify

$$
\mathrm{Br}^{-}+2 \mathrm{MnO}_{4}^{-}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{BrO}_{3}^{-}++2 \mathrm{MnO}_{2}+2 \mathrm{OH}^{-}
$$

Step 7: Indicate the state of each species

$$
\mathrm{Br}^{-}(\mathrm{aq})+2 \mathrm{MnO}_{4}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longrightarrow \mathrm{BrO}_{3}^{-}(\mathrm{aq})++2 \mathrm{MnO}_{2}(\mathrm{~s})+2 \mathrm{OH}^{-}(\mathrm{aq})
$$

This is the fully balanced net ionic equation.
Check by writing a table:

| species | left | right |
| :---: | :---: | :---: |
| Br | 1 | 1 |
| Mn | 2 | 2 |
| O | 9 | 9 |
| H | 2 | 2 |
| charge | -3 | -3 |

