WILEY

Chapter 5
Oxidation–Reduction Reactions

Chemistry, 7th Edition
International Student Version

Brady/Jespersen/Hyslop

Chapter in Context

- Define oxidation, reduction, oxidizing agents, reducing agents, and oxidation numbers
- Balance oxidation/reduction reactions
- Explore, at the molecular level, how acids react with metals
- Use the activity series to predict products of reactions
- Learn about the reaction of oxygen with organic compounds, metals, and nonmetals
- Perform calculations using the stoichiometry of oxidation/reduction reactions

Oxidation-Reduction Reactions

Electron transfer reactions

- Electrons transferred from one substance to another
- Originally only combustion of fuels or reactions of metal with oxygen
- Important class of chemical reactions that occur in all areas of chemistry and biology
- Also called redox reactions to emphasize that reduction and oxidation must always occur together

Oxidation–Reduction Reactions

Involves 2 processes:

Oxidation = Loss of electrons

$Na \longrightarrow Na^+ + e^-$ Oxidation Half-Reaction

Reduction = Gain of electrons

$Cl_2 + 2e^- \longrightarrow 2Cl^-$ Reduction Half-Reaction

Net reaction:

$2Na + Cl_2 \longrightarrow 2Na^+ + 2Cl^-$

- Oxidation and reduction always occur together
- Can't have one without the other

Oxidation Reduction Reaction

Oxidizing Agent

- Substance that accepts electrons
  - Accepts electrons from another substance
  - Substance that is reduced
  - $Cl_2 + 2e^- \longrightarrow 2Cl^-$

Reducing Agent

- Substance that donates electrons
  - Releases electrons to another substance
  - Substance that is oxidized
  - $Na \longrightarrow Na^+ + e^-$

Redox Reactions

- Very common
  - Batteries—car, flashlight, cell phone, computer
  - Metabolism of food
  - Combustion
- Chlorine Bleach
  - Dilute NaOCl solution
  - Cleans through redox reaction
  - Oxidizing agent
  - Destroys stains by oxidizing them

Bloomberg/Getty Images, Inc.

Redox Reactions

e.g., Fireworks displays

Net: $2Mg + O_2 \longrightarrow 2MgO$

Oxidation:

$Mg \longrightarrow Mg^{2+} + 2e^-$

- Loses electrons = oxidized
- Reducing agent

Reduction:

$O_2 + 4e^- \longrightarrow 2O^{2-}$

- Gains electrons = reduced
- Oxidizing agent

Jung-Pang Wu/Getty Images

Your Turn!

Which species functions as the oxidizing agent in the following oxidation-reduction reaction?

$$Zn(s) + Pt^{2+}(aq) \longrightarrow Pt(s) + Zn^{2+}(aq)$$

A. $Pt(s)$

B. $Zn^{2+}(aq)$

C. $Pt^{2+}(aq)$

D. $Zn(s)$

E. None of these, as this is not a redox reaction.

Your Turn!

Which species gets oxidized in the following reaction?

$$2Ag^{+}(aq) + Zn(s) \longrightarrow Zn^{2+}(s) + 2Ag(s)$$

A. $Ag(s)$

B. $Ag^{+}(aq)$

C. $Zn^{2+}(aq)$

D. $Zn(s)$

E. None of these, as this is not a redox reaction

Your Turn!

In the following reaction, which species is the oxidizing agent and which gets reduced?

$$2H^+(aq) + Mn(s) \longrightarrow Mn^{2+}(aq) + H_2(g)$$

A. H^+ is the oxidizing agent and Mn gets reduced

B. H^+ is the oxidizing agent and H^+ gets reduced

C. Mn is the oxidizing agent and H^+ gets reduced

D. Mn is the oxidizing agent and Mn gets reduced

E. Mn is the oxidizing agent and Mn^{2+} gets reduced

Guidelines For Redox Reactions

- Oxidation and reduction always occur simultaneously
- Total number of electrons lost by one substance equals total number of electrons gained by second substance
- For a redox reaction to occur, something must accept electrons that are lost by another substance

Oxidation Numbers

Bookkeeping Method

- Way to keep track of electrons
  - Not all redox reactions contain O_2 or ions
  - Covalent molecules and ions often involved

    e.g., CH_4, SO_2, MnO_4^-, etc.
- Defined by set of rules
  - How to divide up shared electrons in compounds with covalent bonds
  - Often whole numbers but can be fractions
- Change in oxidation number of element during reaction indicates redox reaction has occurred

Hierarchy of Rules for Assigning Oxidation Numbers

1. Oxidation numbers must add up to charge on molecule, formula unit or ion
2. Atoms of free elements have oxidation numbers of zero
3. Metals in Groups 1A, 2A, and Al have +1, +2, and +3 oxidation numbers, respectively
4. H and F in compounds have +1 and –1 oxidation numbers, respectively
5. Oxygen has –2 oxidation number
6. Group 7A elements have –1 oxidation number

Hierarchy of Rules for Assigning Oxidation Numbers

7. Group 6A elements have –2 oxidation number
8. Group 5A elements have –3 oxidation number
9. When there is a conflict between two of these rules or ambiguity in assigning an oxidation number, apply rule with lower oxidation number and ignore conflicting rule

Oxidation State

- Used interchangeably with oxidation number
- Indicates charge on monatomic ions
- Iron(III) means +3 oxidation state of Fe or Fe^{3+}

Ex. 1 Assigning Oxidation Number

1. Li_2O

Li (2 atoms) × (+1) = +2 (Rule 3)

O (1 atom) × (–2) = –2 (Rule 5)

sum = 0 (Rule 1)

+2 –2 = 0 so the charges are balanced to zero

2. CO_2

C (1 atom) × (x) = x

O (2 atoms) × (–2) = –4 (Rule 5)

sum = 0 (Rule 1)

$x - 4 = 0$ or $x = +4$

C is in +4 oxidation state

Learning Check

Assign oxidation numbers to all atoms:

Example 1: ClO_4^-

O (4 atoms) × (–2) = –8

Cl (1 atom) × (–1) = –1

(molecular ion) sum ≠ –1 (violates Rule 1)

Rule 5 for oxygen comes before Rule 6 for halogens

O (4 atoms) × (–2) = –8

Cl (1 atom) × (x) = x

sum = –1 (Rule 1)

$-8 + x = -1$ or $x = 8 - 1$

So $x = +7$; Cl is oxidation state +7

Learning Check

Assign oxidation states to all atoms:

- $MgCr_2O_7$

  Mg =+2; O = –2; and Cr = x (unknown)

  $[+2] + [2x] + [7 \times (-2)] = 0$

  $2x - 12 = 0 \qquad x = +3$

  Cr is oxidation number of +3

- $KMnO_4$

  K =+1; O = – 2; so Mn = x

  $[+1] + [x] + [4 \times (-2)] = 0$

  $x - 7 = 0 \qquad x = +7$

  Mn is oxidation number of +7

Your Turn!

What is the oxidation number of each atom in H_3PO_4?

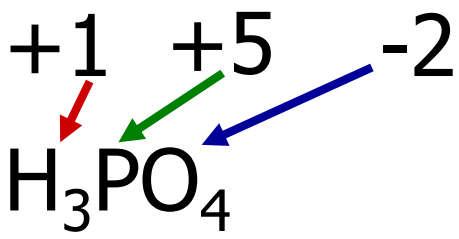
A. H = –1; P = +5; O = –2

B. H = 0; P = +3; O = –2

C. H = +1; P = +7; O = –2

D. H = +1; P = +1; O = –1

E. H = +1; P = +5; O = –2



Your Turn!

What is the oxidation number of each atom in sodium chlorate?

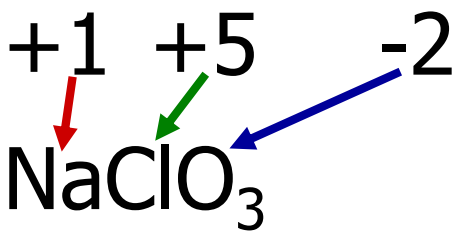
A. Na = +1; Cl = +5; O = –2

B. Na = +1; Cl = +7; O = –4

C. Na = +1; Cl = +7; O = –2

D. Na = +1; Cl = +3; O = –1

E. Na = -1; Cl = +5; O = –2



Your Turn!

What are the oxidation numbers of sodium and iodine in potassium triiodide, KI_3?

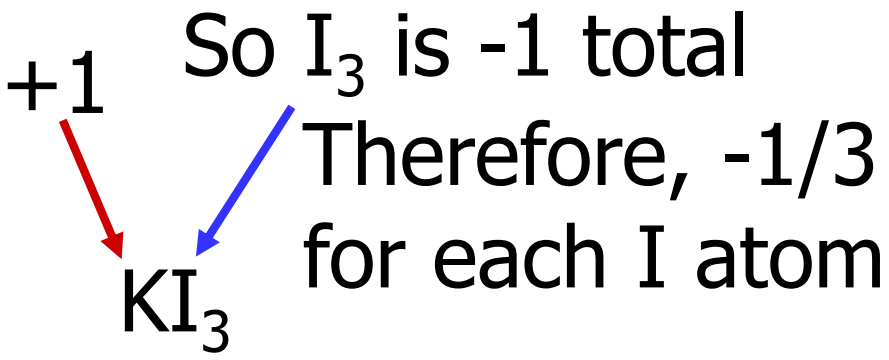
A. K = +1; I = 0

B. K = +1; I = -1

C. K = -1; I = -3

D. K = +1; I = –1/3

E. K = +1; I = –2/3



Oxidation numbers can be fractions because they represent an average number of 'excess' electrons (or lack thereof) on the atoms – in this case, one extra electron on the three iodide atoms

Redefine Oxidation-Reduction in Terms of Oxidation Number

- A redox reaction occurs when there is a change in oxidation number

Oxidation

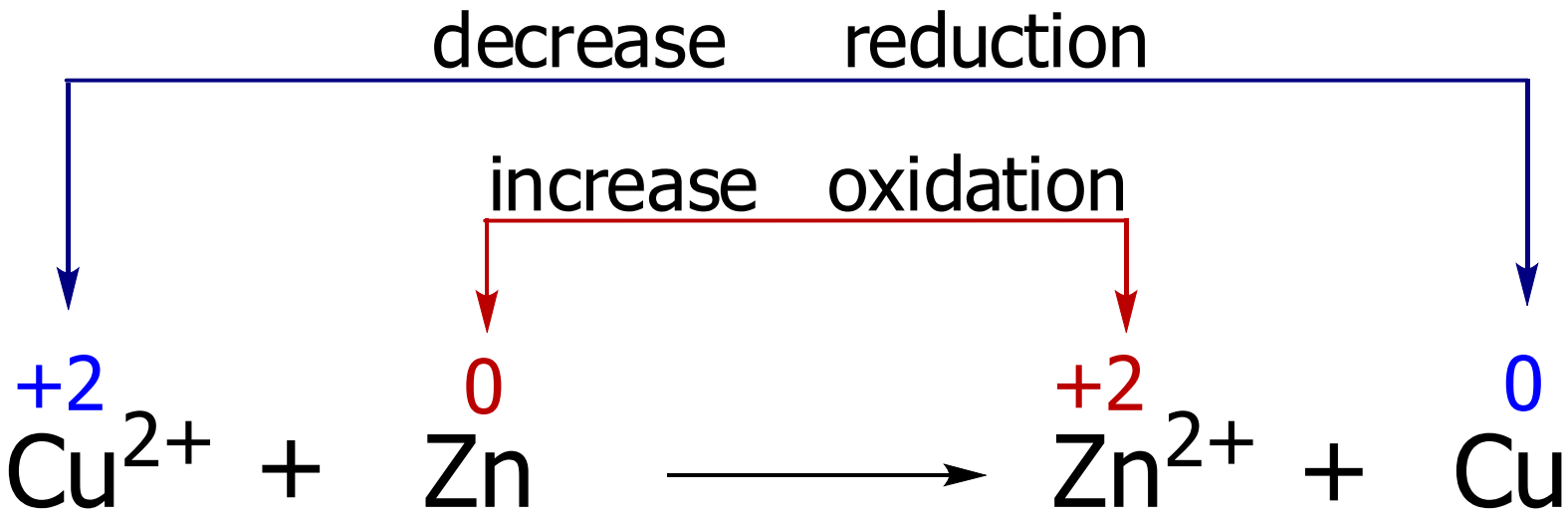
- Increase in oxidation number
- Electron loss

Reduction

- Decrease in oxidation number
- Electron gain

Using Oxidation Numbers to Recognize Redox Reactions

- Sometimes literal electron transfer:

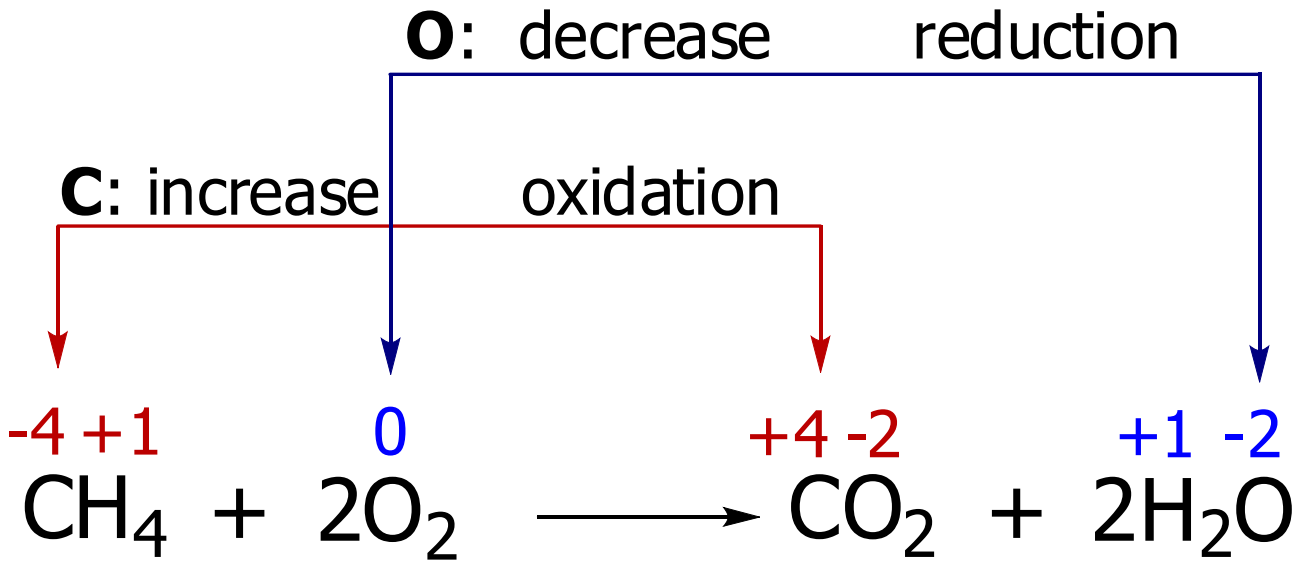


Cu: oxidation number decreases by 2
⇨ reduction

Zn: oxidation number increases by 2
⇨ oxidation

Using Oxidation Numbers to Recognize Redox Reactions

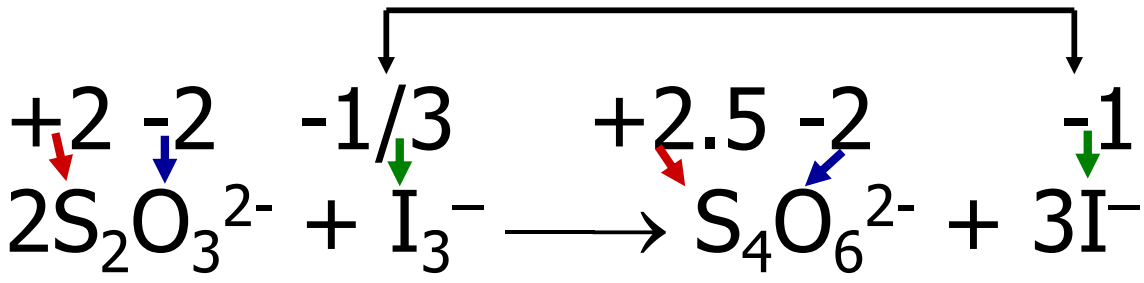
- Reduction and oxidation can be deduced from changes in oxidation numbers



- **O:** oxidation number decreases by 2 ⇨ reduction
- **C:** oxidation number increases by 8 ⇨ oxidation

Your Turn!

Assign oxidation numbers to all atoms in the following reaction and use them to determine which species gets reduced.



A. I_3^-

B. I^-

C. $S_4O_6^{2-}$

D. $S_2O_3^{2-}$

I is reduced from -1/3 to -1

Ion Electron Method

- Way to balance redox equations
- Must balance both mass and charge
- Write *skeleton equation*
  - Only ions and molecules involved in reaction
- Break into two half-reactions
  - Oxidation
  - Reduction
- Balance each half-reaction separately
- Recombine to get balanced net ionic equation

Balancing Redox Reactions

Some redox reactions are simple:

e.g., $Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$

Break into half-reactions

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ **oxidation**

↑

Reducing agent

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ **reduction**

↑

Oxidizing agent

Balancing Redox Reactions

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ **oxidation**

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ **reduction**

- Each half-reaction is balanced for atoms
  - Same number of atoms of each type on each side
- Each half-reaction is balanced for charge
  - Same sum of charges on each side
- Add both equations algebraically, canceling electrons
- NEVER have electrons in net ionic equation

$$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

Balancing Redox Equations in Aqueous Solutions

- Many redox reactions in aqueous solution involve H_2O and H^+ or OH^-
- Balancing the equation cannot be done by inspection
- Need method to balance equation correctly
- Start with acidic solution then work to basic conditions

Ion-Electron Method – Acidic Solution

1. Divide equation into two half-reactions

2. Balance atoms other than H and O

3. Balance O by adding H_2O to side that needs O

4. Balance H by adding H^+ to side that needs H

5. Balance net charge by adding e^-

6. Make electron gain equal electron loss; then add half-reactions

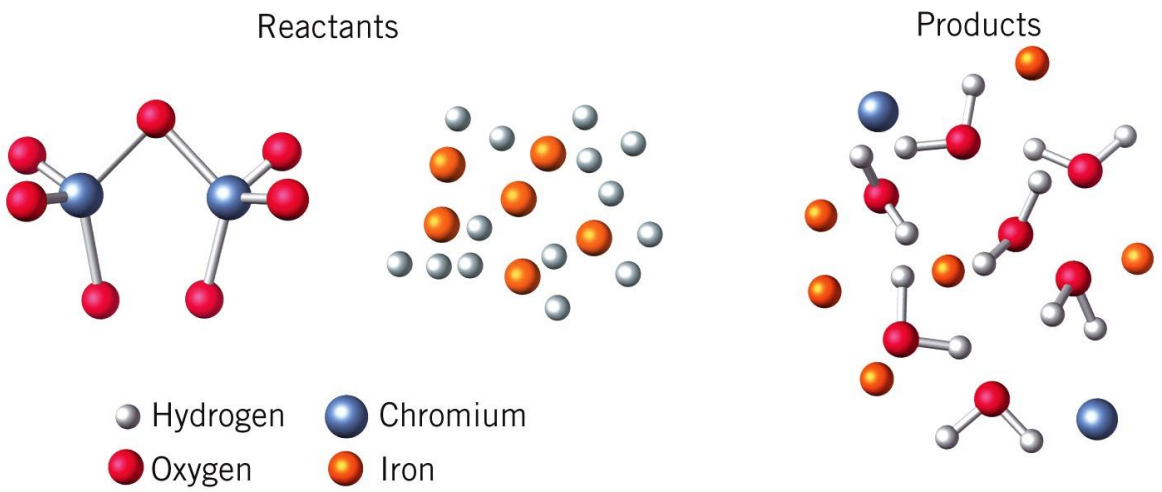
7. Cancel electrons and anything that is the same on both sides

Redox in Aqueous Solution

Example 2: Mix solutions of $K_2Cr_2O_7$ and $FeSO_4$

- Dichromate ion, $Cr_2O_7^{2-}$, oxidizes Fe^{2+} to Fe^{3+}
- $Cr_2O_7^{2-}$ is reduced to form Cr^{3+}
- Acidity of mixture decreases as H^+ reacts with oxygen to form water

Skeletal Eqn. $Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$



Ex. 2 Ion Electron Method

Balance in Acidic Solution

$$Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+}$$

1. Break into half-reactions

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

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

2. Balance atoms other than H and O

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

Put in 2 coefficient to balance Cr

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

Fe already balanced

Ex. 2 Ion-Electron Method in Acid

3. Balance O by adding H_2O to the side that needs O

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

Left side has seven O atoms

Right side has none

Add seven H_2O to right side

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

No O to balance

Ex. 2 Ion-Electron Method in Acid

4. Balance H by adding H^+ to side that needs H

$$14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

Right side has fourteen H atoms

Left side has none

Add fourteen H^+ to left side

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

No H to balance

Ex. 2 Ion-Electron Method in Acid

5. Balance net charge by adding electrons.

$$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

Net Charge = $14(+1) + (-2) = 12$

Net Charge = $2(+3) + 7(0) = 6$

6 electrons must be added to reactant side

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

1 electron must be added to product side

Now both half-reactions balanced for mass and charge

Ex. 2 Ion-Electron Method in Acid

6. Make electron gain equal electron loss; then add half-reactions

$$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6\times[\ Fe^{2+} \longrightarrow Fe^{3+} + e^-\ ]$$

$$\cancel{6e^-} + 6Fe^{2+} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O + \cancel{6e^-}$$

7. Cancel anything that's the same on both sides

$$6Fe^{2+} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Ion-Electron in Basic Solution

- The simplest way to balance an equation in basic solution

Use steps 1 – 7 above, then

8. Add the same number of OH^- to both sides of the equation as there are H^+

9. Combine H^+ and OH^- to form H_2O

10. Cancel any H_2O that you can from both sides

Ex. 2 Ion-Electron Method in Base

Returning to our example of $Cr_2O_7^{2-}$ and Fe^{2+}

8. Add to ***both*** sides of equation the same number of OH^- as there are H^+.

$$6Fe^{2+} + 14H^+ + Cr_2O_7^{2-} + 14\,OH^- \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O + 14\,OH^-$$

9. Combine H^+ and OH^- to form H_2O.

$$6Fe^{2+} + \cancel{14}\,7H_2O + Cr_2O_7^{2-} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + \cancel{7H_2O} + 14OH^-$$

10. Cancel any H_2O that you can

$$6Fe^{2+} + 7H_2O + Cr_2O_7^{2-} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 14OH^-$$

Your Turn!

Which of the following is a correctly balanced reduction half-reaction?

A. $Fe^{3+} + e^- \longrightarrow Fe$

B. $2Fe + 6HNO_3 \longrightarrow 2Fe(NO_3)_3 + 3H_2$

C. $Mn^{2+} + 4H_2O \longrightarrow MnO_4^- + 8H^+ + 5e^-$

D. $2O^{2-} \longrightarrow O_2 + 4e^-$

E. $Mg^{2+} + 2e^- \longrightarrow Mg$

Your Turn!

Balance the following reaction in acidic solution

$I^- + HNO_2 \longrightarrow NO + I_2$

A. $H^+ + HNO_2 + I^- \longrightarrow NO + I_2 + H_2O$

B. $2H^+ + 2HNO_2 + I^- \longrightarrow 2NO + I_2 + 2H_2O$

C. $2H^+ + 2HNO_2 + 2I^- \longrightarrow 2NO + I_2 + 2H_2O$

D. $H^+ + HNO_2 + 2I^- \longrightarrow 2NO + I_2 + 2H_2O$

E. $H^+ + HNO_2 + 2I^- \longrightarrow NO + I_2 + H_2O + e^-$

Example 3: Ion-Electron Method

Balance the following equation in basic solution:

$MnO_4^- + HSO_3^- \longrightarrow Mn^{2+} + SO_4^{2-}$

1. Break it into half-reactions

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

$HSO_3^- \longrightarrow SO_4^{2-}$

2. Balance atoms other than H and O

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

Balanced for Mn

$HSO_3^- \longrightarrow SO_4^{2-}$

Balanced for S

Example 3: Ion-Electron Method

3. Add H_2O to balance O

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

$$H_2O + HSO_3^- \longrightarrow SO_4^{2-}$$

4. Add H^+ to balance H

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

$$H_2O + HSO_3^- \longrightarrow SO_4^{2-} + 3H^+$$

Example 3: Ion-Electron Method

5. Balance net charge by adding electrons.

$5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$

$8 \times (+1) + (-1) = +7$ $\qquad$ $+2 + 0 = +2$

Add 5 e^- to reactant side

$H_2O + HSO_3^- \longrightarrow SO_4^{2-} + 3H^+ + 2e^-$

$0 + (-1) = -1$ $\qquad$ $-2 + 3(+1) = +1$

Add 2 electrons to product side

Example 3: Ion-Electron Method

6. Make electron gain equal electron loss

$2\times[\ 5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O\ ]$

$5\times[\ H_2O + HSO_3^- \longrightarrow SO_4^{2-} + 3H^+ + 2e^-\ ]$

- Must multiply Mn half-reaction by 2
- Must multiply S half-reaction by 5
- Now have 10 electrons on each side

Example 3: Ion-Electron Method

6. Then add the two half-reactions

$$10e^- + 16H^+ + 2MnO_4^- \longrightarrow 2Mn^{2+} + 8H_2O$$

$$5H_2O + 5HSO_3^- \longrightarrow 5SO_4^{2-} + 15H^+ + 10e^-$$

$$10e^- + 16H^+ + 2MnO_4^- + 5H_2O + 5HSO_3^- \longrightarrow 2Mn^{2+} + 8H_2O + 5SO_4^{2-} + 15H^+ + 10e^-$$

(1 and 3 mark the coefficients 16 and 8)

7. Cancel anything that is the same on both sides.

$$H^+ + 2MnO_4 + 5HSO_3^- \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$$

Balanced in acid

Ex. 3 Ion-Electron Method in Base

8. Add same number of OH^- to both sides of equation as there are H^+

$$H^+ + 2MnO_4^- + OH^- + 5HSO_3^- \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-} + OH^-$$

9. Combine H^+ and OH^- to form H_2O

$$H_2O + 2MnO_4^- + 5HSO_3^- \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-} + OH^-$$

(2)

10. Cancel any H_2O that you can

$$2MnO_4^- + 5HSO_3^- \rightarrow 2Mn^{2+} + 2H_2O + OH^- + 5SO_4^{2-}$$

Your Turn!

Balance each equation in the solution indicated by the skeletal reaction using the ion electron method.

$MnO_4^- + C_2O_4^{2-} \longrightarrow MnO_2 + CO_3^{2-} + H^+$ **in acid**

$2MnO_4^- + 3C_2O_4^{2-} + 2H_2O \rightarrow 2MnO_2 + 4H^+ + 6CO_3^{2-}$

$ClO^- + VO_3^- \longrightarrow ClO_3^- + V(OH)_3 + OH^-$ **in base**

$ClO^- + 4H_2O + 2VO_3^- \rightarrow ClO_3^- + 2V(OH)_3 + 2OH^-$