10.1 Defining Oxidation and Reduction

Redox – oxidation Reduction reactions

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$2AgNO_{3(aq)} + Cu_{(s)} \longrightarrow Cu(NO_3)_2 + 2Ag_{(s)}$

Total ionic equation:

The nitrate ion is the spectator ion i.e. not involved in the chemical reaction
Net ionic equation:

$2Ag^{1+}_{(aq)} + Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$

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- “ copper is oxidized to copper ions and silver is reduced to silver metal from ions”

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- oxidizing agent –
- reducing agent –

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

- Reducing agent
- Donates electrons
- Undergoes oxidation

- Oxidizing agent
- Accepts electrons
- Undergoes reduction

Practice problems p. 467 # 1-4

Half-Reactions

-

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$2Ag^{1+}_{(aq)} + Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$

oxidation half reaction:

$\therefore\ Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2é$

reduction half reaction:

$\therefore\ 2Ag^{1+}_{(aq)} + 2é \longrightarrow 2Ag_{(s)}$

-
-
-

- **Disproportionation reactions –**

Eg. $2Cu^{+}_{(aq)} \longrightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$

Two half reactions:

- Oxidation -

- reduction -

practice problems p. 468 # 5-8

10.2 Oxidation Numbers

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Oxidation Numbers

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Oxidation numbers from Lewis Structures

• using E.N. we see that O= 3.44 H= 2.20

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P. 478 #9-12

Applying Oxidation Numbers to Redox Reactions

Assign O.N. $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$

$\therefore$ there are changes in O.N. in a redox reaction
Zn – O.N. increases
Cu – O.N. decreases

Examples: Determine if each of the reactions is a redox reaction

(a) $CH_{4(g)} + Cl_{2(g)} \longrightarrow CH_3Cl_{(g)} + HCl_{(g)}$

(b) $CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$

(a) Assign O.N. to each element

- the O.N. of H is +1 on both sides
-
-
-

(b) $CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$

Because the reaction involves ions, write the T.I.E. and the N.I.E.
T.I.E.

N.I.E. (chloride ion is the spectator)

Assign O.N. to each element

** No elements undergo oxidation or reduction therefore this is not redox

p. 480 #13 – 16

Oxidation Numbers are Assigned Using Several Arbitrary Rules

1. The oxidation number of an atom in its elemental state is 0. {S_8, P_4, O_2}

2. The oxidation number of an atom in a monatomic ion is equal to the charge on the ion. {Fe^{3+} = +3, O^{2-} = -2, N^{3-} = -3}

3. The oxidation number of fluorine atoms in a compound is -1. {CF_4, F = -1}

4. The oxidation number of alkali metal atoms in compounds is +1. {Na^+ = +1; K^+ = +1}

5. The oxidation number of alkaline earth metal atoms in compounds is +2. {Ca^{2+} = +2; Mg^{2+} = +2}

6. The oxidation number of aluminum in compounds is +3.

7. When halogen elements are in compounds with less electronegative elements, halogen atoms have oxidation numbers of-1.
   {Cl in NaC1 = -1; Cl in PCl_3 = -1; Cl in HCl = -1}

8. Hydrogen has an oxidation number of +l with more electronegative elements.
   {H in HI=+1}, except for metal hydrides such as NaH or LiH in which hydrogen has an oxidation number of -1

9. Oxygen usually has an oxidation number of-2 in compounds, except in peroxides it has an oxidation number of –1 and in combination with fluorine it is +2.

10. The sum of oxidation numbers of all atoms in a neutral molecule is 0. The sum of oxidation numbers of all atoms in an ion is equal to the charge of the ion.

11. In combinations of nonmetals (covalent bonds) the oxidation number of the more electronegative atom is negative. The oxidation number of the less electronegative atom is positive.

How to Balance Redox Equations

Using Half Reactions

To determine each half reaction

1. Assign oxidation numbers and identify LEO and GER.
2. Make sure that the amount of each atom that is oxidized or reduced is the same on each side.
3. Now work with the LEO and GER half reactions separately. For each half reaction, carry out the following steps:

M*- balance mass on each side of the half reaction - ignore O and H at this point
W - balance O by adding H_2O to the appropriate side
H - balance H by adding H^+ to the appropriate side
E - balance charge by adding electrons to the appropriate side. (N.B. the numbers of electrons added should correspond to your original analysis of ox. & red, in step 1)

4. Balance the number of electrons involved in LEO & GER by multiplying one or both half reactions by the appropriate coefficients.

5. Add half reactions to obtain the overall balanced reaction.

6. For reactions in **basic** solution, follow the steps above, but add the proper number of **OH^-** ions to neutralize the **H^+** ions added in step 5.

7. Make sure that you add the same number of OH^- ions to both sides.

8. Combine H^+ and OH^- ions to form H_2O. Cancel water molecules as appropriate so that water appears only on one side of the equation.

N.B. Be sure to do a final check for: mass/charge/LEO & GER
* My Wallaby Hates Eggs

Mirror Mirror in the Test Tube

Introduction

Everyday mirrors that we take for granted are manufactured using redox reactions in which silver compounds are reduced to silver metal. Because the silver metal becomes bonded to the glass so that tarnishing of the silver is slow, a shiny 'silver mirror' lasts for months or years, depending on methods of preservation.

PurposeAn ordinary silver mirror is produced in a test tube using typical laboratory materials.

Safety

1. Wear protective goggles throughout the laboratory activity.

2. Silver nitrate causes stains.

3. Handle these substances with caution. Wash spills immediately with large amounts of water. Hold your thumb on the stopper while shaking.

4. Always mix the solutions fresh and dispose of them immediately after use with large amounts of water. The materials may form explosive silver fulminate, $Ag_2C_2N_2O_2$, on standing. ***Never* premix the reagents**.

5. Dispose of all materials as your teacher directs.

Procedure

1. Add the following amounts of solutions in the *exact* order listed:

   32 Drops stabilized honey solution (5%). Roll the tube to wet it with this solution before adding silver nitrate.
   16 Drops 8.0% silver nitrate solution
   16 Drops 12% ammonium nitrate solution
   32 Drops 10% sodium hydroxide solution (16 drops at first then shake for 1 minute and then add the 16 other drops)

5. Quickly stopper the test-tube with a cork and shake it while holding the cork in place. The inside surface of the test-tube should be wetted for a good coating. Continue shaking the test-tube for about 3 min. Observe the changes in appearance for 5 min.

6. Wash the solution down the drain with lots of tap water. This is an important safety precaution to prevent the possible formation of an explosive mixture (after standing many hours or days). **Rinse the mirrored test-tube gently but thoroughly with distilled water**. Allow the tube to air dry.

7. Thoroughly wash your hands before leaving the laboratory.

Pre-lab Questions:

1. Why is it necessary to mix the chemicals in the exact order specified during the lab and not before?

Post Lab Questions:

1. What is the visible product of the reaction?
2. Did the silver ions gain or lose electrons in the reduction process?
3. An oxidation reaction must take place along with a reduction reaction. Honey (actually the sugars in honey) is the partner for the reaction of silver ions in this activity. What happened to the sugar molecules?

Determination of [$FeSO_4$] by Redox Microtitration

You will determine [$FeSO_4$] by titration with a potassium permanganate, $KMnO_4$, solution of known concentration. The skeleton equation is:

$$Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+} \text{ (acidic solution)}$$

You will be supplied with:

- a stock solution of 0.0100 mol/L $KMnO_4$ (10 drops)
- a solution of $FeSO_4$ of unknown concentration
- several plastic Beral micropipets
- a well plate
- 3.0 mol/L H_2SO_4 (2 drops)

Pre-lab Questions

1. a) Write a balanced chemical equation for the reaction. {5}

   b) What is the reducing agent in this titration? {1}

2. What indicator should be used? Explain why. {2}

3. Which reactant, if any, may be used in excess? Explain. {2}

4. Is it necessary to know the volume of one drop delivered by the plastic Beral pipets?
   If so, explain why we need to know the volume of one drop AND how to determine the volume of one drop from a Beral pipet.

   OR

   If not, explain why it is not necessary to know the volume of one drop. {2}

Post-lab Questions

1. Write a suitable abstract for this experiment below. {3}

2. From the results of your titrations, calculate [$FeSO_4$]. {5}

3. Why would hydrogen peroxide not have been a practical substitute for $KMnO_4$ in this titration? {1}

Chapter 10
Oxidation–Reduction Reactions

Practice Problems

Problem 1
Compare the oxidation number of sulfur in the following molecules and ions.
(a) $S_2O_7^{2-}$
(b) $S_2O_5Cl_2$
(c) S_2OCl_4
(d) $S_2O_5^{2-}$
(e) S_4N_2Cl
(f) SO_2Cl_2
(g) HSO_3^-

Problem 2
Determine whether each of the following reactions is a redox reaction. If so, identify the oxidizing agent and the reducing agent.
(a) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$
(b) $CaH_2 + 2H_2O \longrightarrow 2H_2 + Ca(OH)_2$
(c) $2NF_3 + 3H_2 \longrightarrow N_2 + 6HF$
(d) $2KNO_3 \longrightarrow 2KNO_2 + O_2$

Problem 3
(a) For the reaction $4NH_{3(g)} + O_{2(g)} \longrightarrow 2N_2H_{4(g)} + 2H_2O_{(g)}$, identify the oxidation half-reaction, the reduction half-reaction, the oxidizing agent, and the reducing agent.
(b) Given the experimental evidence that $Au^{3+}_{(aq)}$ will react with $Sn_{(s)}$, and that $Ag^+_{(aq)}$ will react with $Sn_{(s)}$ but not with $Au_{(s)}$, arrange the ions $Ag^+_{(aq)}$, $Au^{3+}_{(aq)}$, and $Sn^{2+}_{(aq)}$ in increasing order of their tendency to gain electrons.

Problem 4
Draw a Lewis diagram for carbon monoxide and, from the diagram, determine the oxidation number of carbon in this compound.

Problem 5
Balance each of the following half-reactions under acidic conditions.
(a) $NO_3^-{}_{(aq)} \longrightarrow NO_{2(g)}$
(b) $C_2O_4^{2-}{}_{(aq)} \longrightarrow CO_{2(g)}$
(c) $NO_3^-{}_{(aq)} \longrightarrow NH_4^+{}_{(aq)}$

Problem 6
Balance each of the following half-reactions under basic conditions.
(a) $Cr^{3+}_{(aq)} \longrightarrow CrO_4^{2-}{}_{(aq)}$
(b) $HSnO_2^-{}_{(aq)} \longrightarrow HSnO_3^-{}_{(aq)}$

Problem 7
Write a balanced equation for the following reaction that occurs in a basic solution by the half-reaction method.
$CrO_2^-{}_{(aq)} + ClO^-{}_{(aq)} \longrightarrow CrO_4^{2-}{}_{(aq)} + Cl^-{}_{(aq)}$

Problem 8

Balance the following equation for acid conditions. Identify the oxidizing agent and the reducing agent.

$SO_3^{2-}{}_{(aq)} + MnO_4^-{}_{(aq)} \longrightarrow SO_4^{2-}{}_{(aq)} + Mn^{2+}{}_{(aq)}$

Problem 9

Use the oxidation number method to balance the following equation.

$Cr_2O_7^{2-}{}_{(aq)} + C_2H_5OH_{(l)} \longrightarrow Cr^{3+}{}_{(aq)} + C_2H_4O_{(l)}$ (in acid solution)

Problem 10

Balance the following redox reaction equations.

(a) $S^{2-}{}_{(aq)} + ClO_3^- \longrightarrow Cl^-{}_{(aq)} + S_{(s)}$ (in basic solution)

(b) $CN^-{}_{(aq)} + IO_3^-{}_{(aq)} \longrightarrow I^-{}_{(aq)} + CNO^-{}_{(aq)}$ (in basic solution)

(c) $Mn^{2+}{}_{(aq)} + HBiO_{3(aq)} \longrightarrow Bi^{3+}{}_{(aq)} + MnO_4^-{}_{(aq)}$

(d) $SO_{2(aq)} + Cl_{2(aq)} \longrightarrow Cl^-{}_{(aq)} + SO_4^{2-}{}_{(aq)}$

Answers

1. Let x be the oxidation number of S.

(a) $2x + 7(-2) = -2 \quad x = +6$

(b) $2x + 5(-2) + 2(-1) = 0 \quad x = +6$

(c) $2x + 1(-2) + 4(-1) = 0 \quad x = +3$

(d) $2x + 5(-2) = -2 \quad x = +4$

(e) $4x + 2(-3) + 1(-1) = 0 \quad x = +\frac{7}{4}$

(f) $x + 2(-2) + 2(-1) = 0 \quad x = +6$

(g) $1(+1) + x + 3(-2) = -1 \quad x = +4$

2. OA = oxidizing agent RA = reducing agent

(a) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

+6 –1 +1 –2 +6 –2 +1–1

No elements undergo changes in oxidation numbers, so the reaction is not a redox reaction.

(b) $CaH_2 + 2H_2O \longrightarrow 2H_2 + Ca(OH)_2$

+2 –1 +1 –2 0 +2 –2 +1

(RA) (OA)

(c) $2NF_3 + 3H_2 \longrightarrow N_2 + 6HF$

+3–1 0 0 +1–1

(OA) (RA)

(d) $2KNO_3 \longrightarrow 2KNO_2 + O_2$

+1+5–2 +1+3–2 0

(OA/RA)

3.(a) $4NH_{3(g)} + O_{2(g)} \longrightarrow 2N_2H_{4(g)} + 2H_2O_{(g)}$

–3+1 0 –2 +1 +1 –2

Oxidation half-reaction: $NH_{3(g)} \longrightarrow N_2H_{4(g)}$

Reduction half-reaction: $O_{2(g)} \longrightarrow H_2O_{(g)}$

O_2 is the oxidizing agent.

NH_3 is the reducing agent.

(b) $Sn^{2+}_{(aq)} < Ag^{+}_{(aq)} < Au^{3+}_{(aq)}$

4.

:C _ O:

The oxygen atom has a higher electronegativity and, therefore, the shared pairs of electrons belong to the oxygen atom. Carbon is considered to have two valence electrons and, thus, is assigned the oxidation number of +2.

5.

(a) $NO_3^-{}_{(aq)} \longrightarrow NO_{2(g)}$ $\quad NO_3^-{}_{(aq)} + 2H^+_{(aq)} + 1e^- \longrightarrow NO_{2(g)} + H_2O_{(l)}$

(b) $C_2O_4^{2-}{}_{(aq)} \longrightarrow CO_{2(g)}$ $\quad C_2O_4^{2-}{}_{(aq)} \longrightarrow 2CO_{2(g)} + 2e^-$

(c) $NO_3^-{}_{(aq)} \longrightarrow NH_4^+{}_{(aq)}$ $\quad NO_3^-{}_{(aq)} + 10H^+_{(aq)} + 8e^- \longrightarrow NH_4^+{}_{(aq)} + 3H_2O_{(l)}$

6.

(a) $Cr^{3+}_{(aq)} \longrightarrow CrO_4^{2-}{}_{(aq)}$ $\quad Cr^{3+}_{(aq)} + 8OH^-_{(aq)} \longrightarrow CrO_4^{2-}{}_{(aq)} + 4H_2O_{(l)} + 3e^-$

(b) $HSnO_2^-{}_{(aq)} \longrightarrow HSnO_3^-{}_{(aq)}$ $\quad HSnO_2^-{}_{(aq)} + 2OH^-_{(aq)} \longrightarrow HSnO_3^-{}_{(aq)} + H_2O_{(l)} + 2e^-$

7.

$CrO_2^-{}_{(aq)} + ClO^-_{(aq)} \longrightarrow CrO_4^{2-}{}_{(aq)} + Cl^-_{(aq)}$

$2CrO_2^-{}_{(aq)} + 3ClO^-_{(aq)} + 2OH^-_{(aq)} \longrightarrow 2CrO_4^{2-}{}_{(aq)} + 3Cl^-_{(aq)} + H_2O_{(l)}$

8.

$SO_3^{2-}{}_{(aq)} + MnO_4^-{}_{(aq)} \longrightarrow SO_4^{2-}{}_{(aq)} + Mn^{2+}_{(aq)}$

$2MnO_4^-{}_{(aq)} + 5SO_3^{2-}{}_{(aq)} + 6H^+_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 5SO_4^{2-}{}_{(aq)} + 3H_2O_{(l)}$

9.

$Cr_2O_7^{2-}{}_{(aq)} + C_2H_5OH_{(l)} \longrightarrow Cr^{3+}_{(aq)} + C_2H_4O_{(l)}$ (in acid solution)

+6 –2 +3 –1

$Cr_2O_7^{2-}{}_{(aq)} + 3C_2H_5OH_{(l)} + 8H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 3C_2H_4O_{(l)} + 7H_2O_{(l)}$

10.

(a) $S^{2-}_{(aq)} + ClO_3^- \longrightarrow Cl^-_{(aq)} + S_{(s)}$ (in basic solution)

$3S^{2-}_{(aq)} + ClO_3^-{}_{(aq)} + 3H_2O_{(l)} \longrightarrow Cl^-_{(aq)} + 3S_{(s)} + 6OH^-_{(aq)}$

(b) $CN^-_{(aq)} + IO_3^-{}_{(aq)} \longrightarrow I^-_{(aq)} + CNO^-_{(aq)}$ (in basic solution)

$3CN^-_{(aq)} + IO_3^-{}_{(aq)} \longrightarrow I^-_{(aq)} + 3CNO^-_{(aq)}$

(c) $Mn^{2+}_{(aq)} + HBiO_{3(aq)} \longrightarrow Bi^{3+}_{(aq)} + MnO_4^-{}_{(aq)}$

$2Mn^{2+}_{(aq)} + 5HBiO_{3(aq)} + 9H^+_{(aq)} \longrightarrow 2MnO_4^-{}_{(aq)} + 5Bi^{3+}_{(aq)} + 7H_2O_{(l)}$

(d) $SO_{2(aq)} + Cl_{2(aq)} \longrightarrow Cl^-_{(aq)} + SO_4^{2-}{}_{(aq)}$

$SO_{2(aq)} + Cl_{2(aq)} + 2H_2O_{(l)} \longrightarrow SO_4^{2-}{}_{(aq)} + 2Cl^-_{(aq)} + 4H^+_{(aq)}$

Redox Assignment

Balance the following Redox equations using the half-reaction method. Submit your solutions before the unit test.

1. $H_2O_{2(aq)} + Cr_2O_7^{2-}{}_{(aq)} \longrightarrow Cr^{3+}{}_{(aq)} + O_{2(g)} + H_2O_{(l)}$ (acidic solution)

2. $Na_2HAsO_{3(aq)} + KBrO_{3(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + Kbr_{(aq)} + H_3AsO_{4(aq)}$

3. $Al_{(s)} + MnO_4^-{}_{(aq)} \longrightarrow MnO_{2(s)} + Al(OH)_4^-{}_{(aq)}$ (basic solution)

4. $V_{(s)} + ClO_3^-{}_{(aq)} \longrightarrow HV_2O_7^{3-}{}_{(aq)} + Cl^-{}_{(aq)}$ (basic solution)

5. $Hg_{(l)} + NO_3^-{}_{(aq)} + Cl^-{}_{(aq)} \longrightarrow HgCl_4^{2-}{}_{(aq)} + NO_{2(g)}$ (acidic solution)

6. $Pb_{(s)} + PbO_{2(s)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)}$ (acidic solution)

7. $Sb_2O_{3(s)} + KIO_{3(aq)} + HCl_{(aq)} + H_2O_{(l)} \longrightarrow HSb(OH)_{6(aq)} + KCl_{(aq)} + ICl_{(aq)}$