Teacher's Tools[®] Chemistry

Chemical Reactions : Redox Reactions: Student Review Notes

I. Balancing Redox Reactions

In addition to understanding oxidation numbers to the point where they are second nature, you also have to be very good at balancing redox reactions. When you are given an oxidation-reduction reaction, assign every atom an oxidation number and determine who is oxidized (loses electrons so the oxidation number increases) and who is reduced (gains electrons so the oxidation number increases). Remember, LEO (Loss of Electrons is Oxidation) goes GER (Gain of Electrons is Reduction). Here's a pretty good (quick and painless) Redox balancing technique

Step 1. Identify who is oxidized and who is reduced and break the reaction into two half-reactions.

- One for oxidation (loss of electrons) \rightarrow The oxidation half reaction
- One for the reduction (gain of electrons) \rightarrow The reduction half-reaction

Step 2. Then do these steps

In acid solution

- 1. Balance all atoms other than H and O
- 2. Balance O with H₂O
- 3. Balance H with H^+
- 4. Balance charge (both sides have to have the same net charge) by adding electrons, e-
- 5. Add the two half-reactions so that the e-'s cancel algebraically
- 6. Cancel other species that appear on both sides of the equation
- 7. Check and make sure everybody's balanced

In basic solution

- 1. Do everything exactly the same as in acid solution (steps 1 to 3)
- 2. For each H^+ that's left, add an OH^- to both sides of the equation
- 3. On the side with H^+ , add the H^+ and the OH^- together to get H₂O
- 4. Balance charge (both sides have to have the same net charge) by adding electrons, e-
- 5. Add the two half-reactions so that the e⁻'s cancel algebraically
- 6. Cancel other species that appear on both sides of the equation
- 7. Check and make sure everybody's balanced

Example: Balance this reaction
1. Assign each atom oxidation numbers:

$$Cr^{3+} + MnO_{2} + H_{2}O \rightarrow Mn^{2+} + H_{2}CrO_{4}$$

$$3 \quad 4 \quad -2 \quad 1 \quad -2 \quad 2 \quad 1 \quad 6 \quad -2$$

$$Cr^{3+} + MnO_{2} + H_{2}O \rightarrow Mn^{2+} + H_{2}CrO_{4}$$

$$\boxed{Cr^{3+} + MnO_{2} + H_{2}O \rightarrow Mn^{2+} + H_{2}CrO_{4}}$$

2. It's in acid solution (H₂CrO₄), break up the half reactions and proceed with the steps (labeled with numbers).

Oxidation:
$$C_{1}^{3^{+}} + 4 H_{2}O \rightarrow H_{2}CrO_{4} + 6 H^{+} + 3 e^{-}$$

Reduction: $MnO_{2} + 4 H^{+} + 2 e^{-} \rightarrow Mn^{2^{+}} + 2 H_{2}O$
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I. Balancing Redox Reactions: continued

Add 2 (ox. 1/2-rxns) to 3 (red. 1/2-rxns): $2 \operatorname{Cr}^{3+} + 3 \operatorname{MnO}_2 + 2 \operatorname{H}_2 O \rightarrow 3 \operatorname{Mn}^{2+} + 2 \operatorname{H}_2 \operatorname{CrO}_4$

II. Oxidation Reduction Reactions to know

*all ions are assumed to be in the aqueous phase

Metals in H₂O

Many metals are strong enough reducing agents to reduce water.

The reduction of water is $2 H_2O \rightarrow H_2 + OH^-$ with $E_{red} = -.828 V$. Any metal with an oxidation potential larger than .828 V will reduce H₂O. For example, take a look at these reactions:

- 1. Alkali metals: $2 \operatorname{Na}_{(s)} + 2 \operatorname{H}_2 O \rightarrow 2 \operatorname{Na}^+ + 2 \operatorname{OH}^- + \operatorname{H}_2(g)$
- 2. Alkaline earth metals: $Mg_{(s)} + 2 H_2O \rightarrow Mg^{2+} + 2 OH^- + H_2(g)$
- 3. Aluminum: $2 \operatorname{Al}_{(s)} + 6 \operatorname{H}_2 O \rightarrow 2 \operatorname{Al}^{3+} + 6 \operatorname{OH}^- + 3 \operatorname{H}_2(g)$

A metal in a solution containing a metal ion

If you put a metal into a solution containing a metal ion, go to the table of standard reduction potentials to see if your solid metal will be oxidized and the metal ion reduced. Just look up E_{OX} (the negative of E_{red}) for the metal and E_{red} for the metal ion. If $E_{total} > 0$, the redox reaction will spontaneously occur. Here are some examples:

1. Solid Aluminum/silver ion solution: $Al_{(s)} + Ag^+ \rightarrow Al^{3+} + Ag_{(s)}$ 2. Daniel Cell rxn: $Zn_{(s)} + Cu^{2+} \rightarrow Zn^{2+} + Cu_{(s)}$ 3. Solid iron/iron (III) ion solution: $Fe^{3+} + Fe(s) \rightarrow 2Fe^{2+}$

A metal ion solution mixed with a different metal ion solution

Metals can have more than one oxidation state so if you mix solutions containing metal ions, a redox reaction may occur. Go to the table of standard reduction potentials and look at oxidation and reduction half-reactions. If they yield a positive E_{total} , the reaction shall spontaneously occur. Essentially this is as if one metal ion can take electrons from the other metal ion. Here is an example:

1. Solutions of tin(II) chloride and iron(III) chloride are mixed: $Sn^{2+} + Fe^{3+} \rightarrow Sn^{4+} + Fe^{2+}$

Metals in acidic solutions

Most metals have **positive oxidation potentials**. They can be oxidized while H^+ ($E_{red} = 0.00 V$) is reduced in an acid solution. Here are some examples:

- 1. A strip of zinc is added to a solution of 6.0-molar hydrobromic acid.: $Zn_{(s)} + H^+ \rightarrow Zn^{2+} + H_{2(g)}$
- 2. A piece of nickel is added to concentrated hydrochloric acid: $Ni_{(s)} + H^+ \rightarrow Ni^{2+} + H_{2(g)}$

If you look at the table of standard reduction potentials, **Ag and Cu are exceptions**. They have **negative oxidation potentials**. Here you have to use a nitric acid solution commonly referred to as *aqua regia*, which is three parts HCl and one part HNO₃ (4 H⁺ to each NO₃⁻) or heated sulfuric acid (the heating increases its oxidizing strength. Here are examples and remember its not the hydrogen ion that is getting reduced:

1. A strip of silver is added to a concentrated solution of nitric acid:

$$3 \operatorname{Ag}_{(s)} + \operatorname{NO}_{3}^{-} + 4 \operatorname{H}^{+} \rightarrow \operatorname{NO}_{(g)} + 3 \operatorname{Ag}^{+} + 2 \operatorname{H}_{2}\operatorname{O}_{(l)}$$

2. A strip of copper metal is added to a concentrated heated solution of sulfuric acid:

$$\operatorname{Cu}_{(s)} + \operatorname{H}^{+} + \operatorname{SO}_{4}^{2-} \rightarrow \operatorname{Cu}^{2+} + \operatorname{H}_{2}\operatorname{O}_{(l)} + \operatorname{SO}_{2(g)}$$

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II. Oxidation Reduction Reactions to know: continued

Oxidizing Agents: Know these common ones and their associated reduction half reactions.

Manganese

| 1. Permanganate in water: | $2 \operatorname{MnO_4^-} + 4 \operatorname{H_2O} + 3 e^- \rightarrow \operatorname{MnO_2}(s) + 4 \operatorname{OH^-}$ | $E_{red} = 0.59 V$ | |
|---|--|--------------------|--|
| 2. Permanganate in acid: | $MnO_4^- + 8 H^+ + 5 e^- \rightarrow Mn^{2+} + 4 H_2O$ | $E_{red} = 1.51 V$ | |
| 3. MnO_2 in acid: | $MnO_2(s) + 4 H^+ + 2 e^- \rightarrow Mn^{2+} + 2 H_2O$ | $E_{red} = 1.23 V$ | |
| | | | |
| Chromium | | | |
| 1. Dichromate in acid: | $Cr_2O_7^{2-} + 14 H^+ + 6 e^- \rightarrow 2 Cr^{3+} + 7 H_2O$ | $E_{red} = 1.33 V$ | |
| Hydrogen Peroxide | | | |
| 1. H_2O_2 in acid: | $H_2O_2 + 2 H^+ + 2 e^- \rightarrow 2 H_2O$ | $E_{red} = 1.77 V$ | |
| Here are some examples: | | | |
| A concentrated solution of hydrochloric acid is added to powdered manganese dioxide and gently heated | | | |

Ac

$$MnO_{2(s)} + H^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + H_2O_{(l)} + Cl_{2(g)}$$

A concentrated solution of hydrochloric acid is added to solid potassium permanganate

$$KMnO_{4(s)} + H_{(aq)} + Cl_{(aq)} \rightarrow Cl_2 + Mn^2_{(aq)} + H_2O_{(l)} + K_{(aq)}$$

A solution of potassium dichromate is added to an acidified solution of iron(II) chloride

$$Cr_2O_7^{2-}(aq) + H^+(aq) + Fe^{2+}(aq) \rightarrow Cr^{3+}(aq) + H_2O_{(1)} + Fe^{3+}(aq)$$

Halogens

The halogens can oxidize/reduce each other. Remember that electronegativity/electron affinity increases as you go up the group. The more electronegative halogen in its diatomic form will oxidize the less electronegative halogen from its ionic form. You can verify this by looking at the half-reaction potentials. For example:

1. chlorine gas is bubbled into a solution of sodium bromide: $Cl_{2(g)} + Br_{(aq)} \rightarrow Cl_{(aq)} + Br_{2(g)}$

Disproportionation Reactions

These are redox reactions in which a species undergoes oxidation and reduction simultaneously. For example in the following reaction, bromine is both oxidized and reduced.:

 $Br_{(aq)} + H^{+}_{(aq)} + BrO_{3(aq)} \rightarrow Br_{2(l)} + H_2O_{(l)}$

III. Common Electrolysis Reactions

Remember that in an electrolytic cell, water is often the molecule that completes the redox couple. You have to memorize the reduction and oxidation reactions for water and know that for oxidation water has an overvoltage that makes the potential more like 2 V than 1.23 V.

| Reduction of water: | $2 H_2O_{(1)} + 2 e^- \rightarrow H_{2(g)} + 2 OH_{(aq)}$ | $E_{red} = -0.83 V$ |
|---------------------|--|-------------------------------------|
| Oxidation of water: | $2 H_2O_{(1)} \rightarrow O_{2(g)} + 4 H^+_{(aq)} + 4 e^-$ | $E_{red} = -1.23 V (really -2.0 V)$ |

Typical examples are:

- 1. A solution of potassium iodide is electrolyzed: $I_{(aq)} + H_2O_{(l)} \rightarrow I_{2(s)} + H_{2(g)} + OH_{(aq)}$
- 2. A dilute solution of sulfuric acid is electrolyzed with Pt electrodes: $2 H_2O_{(1)} \rightarrow 2 H_{2(g)} + O_{2(g)}$
- 3. Electrolysis using a silver electrode and platinum electrode: $2 \operatorname{Ag}_{(s)} + 2 \operatorname{H}_2 O_{(1)} \rightarrow 2 \operatorname{Ag}_{(aq)}^+ + 2 \operatorname{OH}_{(aq)}^- + \operatorname{H}_{2(g)}^-$

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