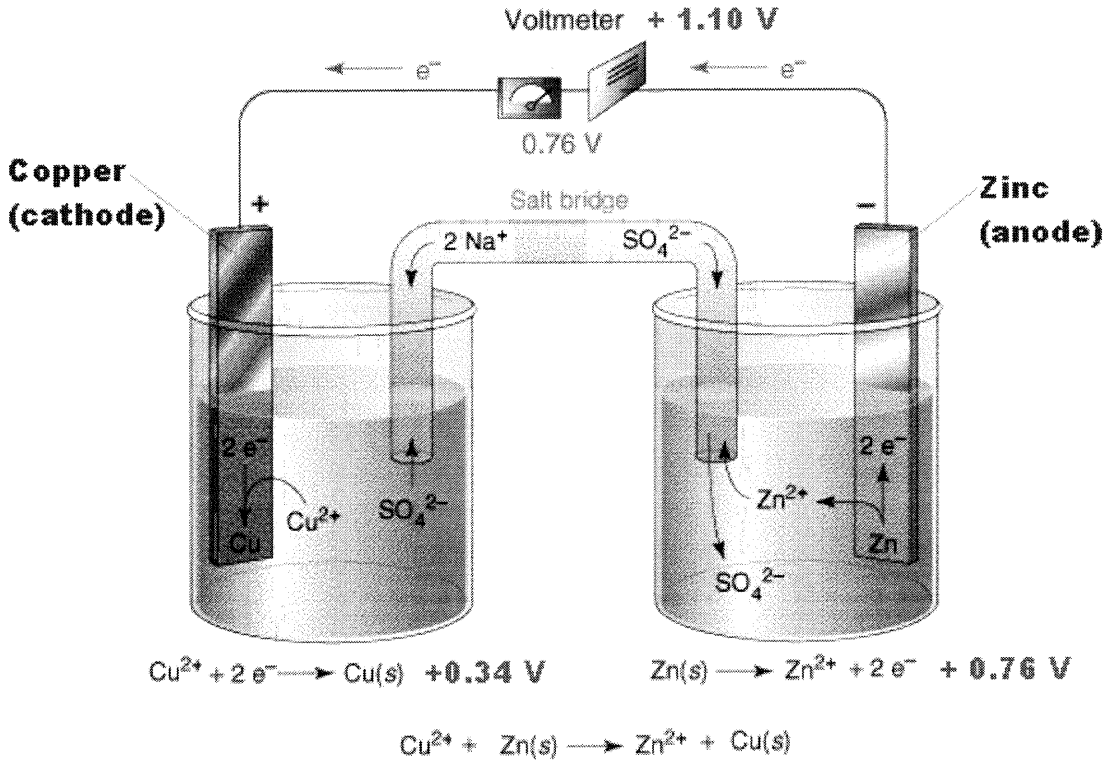
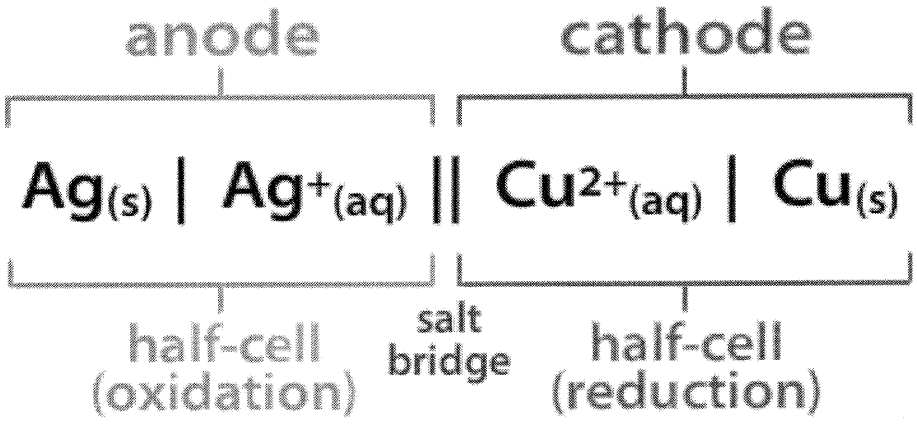
Chapter 19 and 20 Redox and Electrochemistry



Cell Diagram



Graphic by Shamsher Singh

RULES FOR ASSIGNING OXIDATION NUMBERS

RULE 1: The oxidation number of any free element is 0.

RULE 2: The oxidation number of a monatomic ion is equal to the charge on the ion.

RULE 3: The oxidation number of each hydrogen atom in most compounds is 1+.

RULE 4: The oxidation number of each oxygen atom in most compounds is 2−.

RULE 5: The sum of the oxidation numbers of all the atoms in a particle must equal the apparent charge of that particle.

RULE 6: In compounds, the elements of Group IA (1) and Group IIA (2) and aluminum have positive oxidation numbers numerically equal to their group number in the periodic table.

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CHAPTER 21 REVIEW ACTIVITY Text Reference: Section 21-2

Oxidation Numbers

The *oxidation number* of an atom is the apparent charge assigned to it in a particular molecule or ion. Certain rules are followed in assigning oxidation numbers.

Use the rules at the right to assign oxidation numbers to each element in each of the given formulas.

Example

H_2O	$+1, -2$
N_2	0

Rules

The oxidation number of:

- an element in the uncombined state is 0.
- a monatomic ion equals the charge on the ion.
- hydrogen is generally +1; in hydrides, −1.
- oxygen is generally −2; in peroxides, −1.
- the more electronegative element in a binary covalent compound is negative, while that of the other element is positive.
- elements other than oxygen and hydrogen in a neutral compound is such that the sum of the oxidation numbers for all atoms in the compound is 0.
- elements other than oxygen and hydrogen in a polyatomic ion is such that the sum of the oxidation numbers for all atoms in the ion equals the charge on the ion.

1. Cl_2	1. _____
2. Cl^-	2. _____
3. Na	3. _____
4. Na^+	4. _____
5. KCl	5. _____
6. H_2S	6. _____
7. CaO	7. _____
8. H_2SO_4	8. _____
9. NO_3^-	9. _____
10. $Cr_2O_7^{2-}$	10. _____
11. NH_4Cl	11. _____
12. NH_3	12. _____
13. NO_2	13. _____
14. CaH_2 (calcium hydride)	14. _____
15. Na_2O_2 (sodium peroxide)	15. _____

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20–1 Practice Problems

1. What is the oxidation number of each element in (a) H_2SO_4 (b) $H_2S_2O_7$ (c) SO_3?

2. What is the oxidation number of each element in (a) H_3PO_4 (b) P_4O_6 (c) KH_2PO_4?

3. What is the oxidation number of each element in (a) $Ca(H_2PO_4)_2$ (b) $CaSO_4$ (c) K_2MnO_4?

4. What is the oxidation number of each element in (a) $Be(OH)_2$ (b) $B(OH)_3$ (c) $Si(OH)_4$?

5. What is the oxidation number of each element in (a) NH_3 (b) SCl_2 (c) $Sr(OH)_2$?

6. What is the oxidation number of each element in (a) Mg_3N_2 (b) $FeCl_3$ (c) $BaSO_4$?

7. What is the oxidation number of each element in (a) NaH_2PO_4 (b) Na_3PO_4 (c) H_3BO_3?

8. What is the oxidation number of each element in (a) $ZnCO_3$ (b) Ag_2CO_3 (c) BaF_2?

9. What is the oxidation number of each element in (a) $Mg(OH)_2$ (b) $MgCl_2$ (c) $CrCl_3$?

10. What is the oxidation number of each element in (a) $Co(OH)_2$ (b) $HAuCl_4$ (c) $HgSO_4$?

11. Identify the oxidizing agent and the reducing agent in the following reaction:

$C + 2Cl_2 \rightarrow CCl_4$

12. Identify the element that is oxidized and the element that is reduced in the following reaction:

$H_2 + Cl_2 \rightarrow 2HCl$

13. Identify the oxidizing agent and the reducing agent in the following reaction:

$2P + 3Cl_2 \rightarrow 2PCl_3$

14. Identify the element that is oxidized and the element that is reduced in the following reaction:

$C + H_2O \rightarrow CO + H_2$

15. Identify the oxidizing agent and the reducing agent in the following reaction:

$Fe + 3Cl_2 \rightarrow 2FeCl_3$

16. Identify the element that is oxidized and the element that is reduced in the following reaction:

$2Al + 3Br_2 \rightarrow 2AlBr_3$

17. Identify the oxidizing agent and the reducing agent in the following reaction:

$Pb + 2HCl \rightarrow PbCl_2 + H_2$

18. Identify the element that is oxidized and the element that is reduced in the following reaction:

$SiO_2 + 2C \rightarrow Si + 2CO$

19. Identify the oxidizing agent and the reducing agent in the following reaction:

$CO_2 + 2Mg \rightarrow 2MgO + C$

20. Identify the element that is oxidized and the element that is reduced in the following reaction:

$H_2SO_4 + Zn \rightarrow ZnSO_4 + H_2$

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20–4 Practice Problems

1. Balance the following equation and identify the element oxidized and the oxidizing agent.

   $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

2. Balance the following equation and identify the element oxidized and the oxidizing agent.

   $Cu + H_2SO_4 \rightarrow CuSO_4 + SO_2 + H_2O$

3. Balance the following equation and identify the element oxidized and the oxidizing agent. The reaction occurs in an acidic solution.

   $Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$

4. Balance the following equation and identify the element oxidized and the oxidizing agent. The reaction occurs in an acidic solution.

   $SO_3^{2-} + MnO_4^- \rightarrow SO_4^{2-} + Mn^{2+}$

5. Balance the following equation and identify the element oxidized and the oxidizing agent. The reaction occurs in an acidic solution.

   $Zn + NO_3^{-1} \rightarrow Zn^{+2} + N_2O$

6. Balance the following equation and identify the element oxidized and the oxidizing agent. The reaction occurs in an acidic solution.

   $MnO_4^- + I^- \rightarrow MnO_2 + IO^-$

7. Balance the following equation and identify the element oxidized and the oxidizing agent. The reaction occurs in an acidic solution.

   $P + NO_3^- \rightarrow H_2PO_4^- + NO$

8. Balance the following equation and identify the element oxidized and the oxidizing agent. The reaction occurs in an acidic solution.

   $NO_3^- + I_2 \rightarrow IO_3^- + NO_2$

9. Balance the following equation and identify the element oxidized and the oxidizing agent. The reaction occurs in an acidic solution.

   $I^- + ClO^- \rightarrow IO_3^- + Cl^-$

10. Balance the following equation and identify the element oxidized and the oxidizing agent. The reaction occurs in an acidic solution.

    $SO_3^{2-} + MnO_4^- \rightarrow SO_4^{2-} + MnO_2$

Balancing Equations for Reactions Occurring in Basic Solutions

A redox reaction occurring in a basic solution must be completed by using OH-ions and H_2O, rather than H^+ and H_2O.
Here are the steps:

1. Balance each side of your half reaction using water and H^+ just like before.
2. Add a quantity of OH- to each side of your half reaction equal to the amount of H^+ you added.
3. On the side that has H^+ and OH^-, these make water. Cancel the resulting water molecules as needed.

1. $CN^- + MnO_4^- \rightarrow CNO^- + MnO_2$ (basic solution)

2. $CrO_4^{2-} + S^{2-} \rightarrow Cr(OH)_3 + S$ (basic solution)

3. $Cr(OH)_3 + ClO_3^- \rightarrow CrO_4^{2-} + Cl^-$ (basic solution)

The Relative Strengths of Common Oxidizing Agents and Reducing Agents

	$K^+ + e^- \rightleftharpoons K$	Best
	$Ba^{2+} + 2\ e^- \rightleftharpoons Ba$	reducing
	$Ca^{2+} + 2\ e^- \rightleftharpoons Ca$	agents
	$Na^+ + e^- \rightleftharpoons Na$	
	$Mg^{2+} + 2\ e^- \rightleftharpoons Mg$	
	$H_2 + 2\ e^- \rightleftharpoons 2\ H^-$	
	$Al^{3+} + 3\ e^- \rightleftharpoons Al$	
	$Mn^{2+} + 2\ e^- \rightleftharpoons Mn$	
	$Zn^{2+} + 2\ e^- \rightleftharpoons Zn$	
	$Cr^{3+} + 3\ e^- \rightleftharpoons Cr$	
	$S + 2\ e^- \rightleftharpoons S^{2-}$	
	$2\ CO_2 + 2\ H^+ + 2\ e^- \rightleftharpoons H_2C_2O_4$	
	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	
	$Fe^{2+} + 2\ e^- \rightleftharpoons Fe$	
	$Co^{2+} + 2\ e^- \rightleftharpoons Co$	
	$Ni^{2+} + 2\ e^- \rightleftharpoons Ni$	
	$Sn^{2+} + 2\ e^- \rightleftharpoons Sn$	
	$Pb^{2+} + 2\ e^- \rightleftharpoons Pb$	
	$Fe^{3+} + 3\ e^- \rightleftharpoons Fe$	
	$2\ H^+ + 2\ e^- \rightleftharpoons H_2$	
	$S_4O_6^{2-} + 2\ e^- \rightleftharpoons 2\ S_2O_3^{2-}$	
	$Sn^{4+} + 2\ e^- \rightleftharpoons Sn^{2+}$	
	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	
	$O_2 + 2\ H_2O + 4\ e^- \rightleftharpoons 4\ OH^-$	
	$Cu^+ + e^- \rightleftharpoons Cu$	
	$I_2 + 2\ e^- \rightleftharpoons 2\ I^-$	
oxidizing	$MnO_4^- + 2\ H_2O + 3\ e^- \rightleftharpoons MnO_2 + 4\ OH^-$	
power	$O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons H_2O_2$	Reducing
increases	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	power
	$Hg_2^{2+} + 2\ e^- \rightleftharpoons 2\ Hg$	increases
	$Ag^+ + e^- \rightleftharpoons Ag$	
	$Hg^{2+} + 2\ e^- \rightleftharpoons Hg$	
	$H_2O_2 + 2\ e^- \rightleftharpoons 2\ OH^-$	
	$HNO_3 + 3\ H^+ + 3\ e^- \rightleftharpoons NO + 2\ H_2O$	
	$Br_2(aq) + 2\ e^- \rightleftharpoons 2\ Br^-$	
	$2\ IO_3^- + 12\ H^+ + 10\ e^- \rightleftharpoons I_2 + 6\ H_2O$	
	$CrO_4^{2-} + 8\ H^+ + 3\ e^- \rightleftharpoons Cr^{3+} + 4\ H_2O$	
	$Pt^{2+} + 2\ e^- \rightleftharpoons Pt$	
	$MnO_2 + 4\ H^+ + 2\ e^- \rightleftharpoons Mn^{2+} + 2\ H_2O$	
	$O_2 + 4\ H^+ + 4\ e^- \rightleftharpoons 2\ H_2O$	
	$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightleftharpoons 2\ Cr^{3+} + 7\ H_2O$	
	$Cl_2(g) + 2\ e^- \rightleftharpoons 2\ Cl^-$	
	$PbO_2 + 4\ H^+ + 2\ e^- \rightleftharpoons Pb^{2+} + 2\ H_2O$	
	$MnO_4^- + 8\ H^+ + 5\ e^- \rightleftharpoons Mn^{2+} + 4\ H_2O$	
	$Au^+ + e^- \rightleftharpoons Au$	
	$H_2O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ H_2O$	
	$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	
Best	$S_2O_8^{2-} + 2\ e^- \rightleftharpoons 2\ SO_4^{2-}$	
oxidizing	$O_3(g) + 2\ H^+ + 2\ e^- \rightleftharpoons O_2(g) + H_2O$	
agents	$F_2(g) + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ HF(aq)$	

Commonly Observed Oxidation Numbers of the Representative Elements

1A	2A	2B	3A	4A	5A	6A	7A	8A
H +1 -1							**H** +1 -1	**He**
Li +1	**Be** +2		**B** +3	**C** +4 to -4	**N** +5 to -3	**O** -1 -2	**F** -1	**Ne**
Na +1	**Mg** +2		**Al** +3	**Si** +4	**P** +5 +3 -3	**S** +6 +4 -2	**Cl** +7 +5 +3 +1 -1	**Ar**
K +1	**Ca** +2	**Zn** +2	**Ga** +3	**Ge** +4	**As** +5 +3 -3	**Se** +6 +4 -2	**Br** +7 +5 +3 +1 -1	**Kr** +4 +2
Rb +1	**Sr** +2	**Cd** +2	**In** +3	**Sn** +4 +2	**Sb** +5 +3 -3	**Te** +6 +4 -2	**I** +7 +5 +3 +1 -1	**Xe** +8 +6 +4 +2
Cs +1	**Ba** +2	**Hg** +2 +1	**Tl** +3 +1	**Pb** +4 +2	**Bi** +5 +3	**Po** +2	**At** -1	**Rn**
Fr +1	**Ra** +2							

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Activity 8-2
Oxidation and Reduction

Definitions

Define each of the following terms.

1. Oxidation number. _____

2. Oxidation. _____

3. Reduction. _____

4. Oxidizing agent. _____

5. Reducing agent. _____

Redox in direct combination (synthesis) reactions

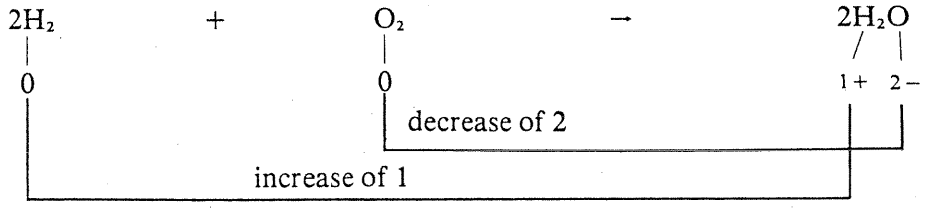
6. What is a direct combination, or synthesis, reaction?
   (See Activity 4-6.) _____

Questions 7-9. Apply steps *a, b,* and *c* below to each of the reactions in questions 7 to 9.

a. Below each equation, write the oxidation number of each element. As an example, we apply this step to the reaction for producing water from hydrogen and oxygen:

$$\underset{0}{2H_2} + \underset{0}{O_2} \rightarrow \underset{1+\ 2-}{2H_2O}$$

b. Show the change in oxidation number for one atom of each element in the equation. For example:



c. Indicate which element is oxidized and which is reduced. For example, for the reaction above, H_2 is oxidized since its atoms increase in oxidation number, while O_2 is reduced since its atoms decrease in oxidation number.

For questions 7, 8, and 9, carry out steps *a, b,* and *c* above. Then balance each equation by inspection, and write the correct coeffecient in front of each substance of the equation.

7. _____H_2 + _____Br_2 → _____HBr

substance oxidized _____

substance reduced _____

8. _____Al + _____ Cl_2 → _____$AlCl_3$

substance oxidized _____

substance reduced _____

9. _____ Mg + _____ N_2 → _____ Mg_3N_2

substance oxidized _____

substance reduced _____

Redox in decomposition (analysis) reactions

10. What is a decomposition, or analysis, reaction?

(See Activity 3-10.) _____

_____

_____

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Questions 11, 12, and 13. Carry out steps *a*, *b*, and *c* on page 272 for each of the following decomposition reactions. Balance each equation by inspection, and write the correct coefficient in front of each substance in the equation. Note that when atoms of one element in a substance are oxidized and atoms of another element *in the same substance* are reduced, the substance is said to undergo auto-oxidation. Auto-oxidation takes place in the following reactions.

11. _____ $HI \rightarrow$ _____ H_2 + _____ I_2 substance oxidized _____

substance reduced _____

12. _____ $Al_2O_3 \rightarrow$ _____ Al _____ O_2 substance oxidized _____

substance reduced _____

13. _____ $2H_2O_2 \rightarrow$ _____ $2H_2O$ + _____ O_2 substance oxidized _____

substance reduced _____

Redox in single replacement reactions

14. What is a single replacement reaction?

(See Activity 3-10). _____

_____

_____

Questions 15, 16, 17. Carry out steps *a*, *b*, and *c* on page 272 for each of the following single replacement reactions. Balance each equation by inspection and write the correct coefficient in front of each substance in the equation.

15. _____ Zn + _____ $HCl \rightarrow$ _____ $ZnCl_2$ + _____ H_2 substance oxidized _____

substance reduced _____

16. _____ $FeBr_3$ + _____ $Cl_2 \rightarrow$ _____ $FeCl_3$ + _____ Br_2 substance oxidized _____

substance reduced _____

17. _____ Al + _____ $H_2SO_4 \rightarrow$ _____ $Al_2(SO_4)_3$ + _____ H_2

substance oxidized _____

substance reduced _____

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Activity 8-3

Balancing Redox Equations by Oxidation Numbers

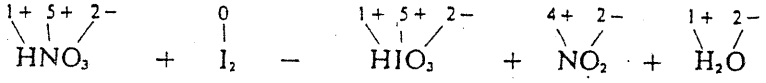
Redox equations of the types studied in Activity 8-2 can easily be balanced by inspection. Equations for more complicated redox reactions are often not easy to balance by inspection. However, the total increase of oxidation numbers equals the total decrease of oxidation numbers in a correctly balanced equation. This fact is the basis for a method of balancing redox equations.

Sample Problem 1 Balance the following equation for a redox reaction between nitric acid and iodine:

$$HNO_3 + I_2 - HIO_3 + NO_2 + H_2O$$

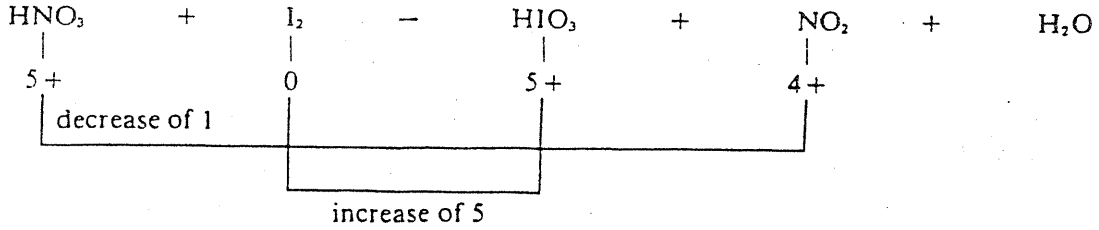
Solution There are five steps, *a-e* below, in the solution.

a. Assign oxidation numbers to each atom in the equation, and determine which atoms are changing oxidation numbers.

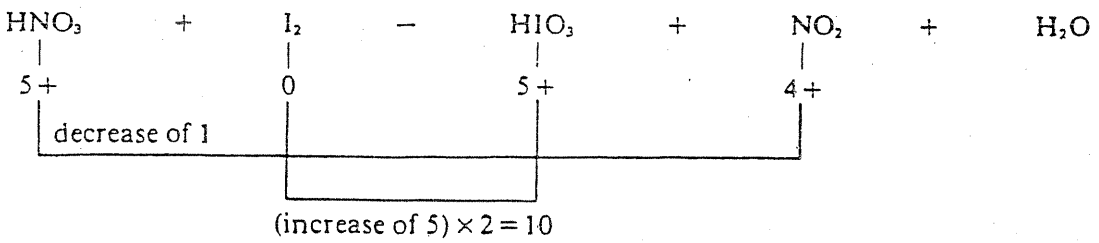


We see that the atoms changing oxidation numbers are nitrogen (N) and iodine (I).

b. Indicate the changes of oxidation number below the equation.



c. Multiply the increase and decrease by the subscripts of the atoms undergoing changes in oxidation number. Only those subscripts—and, therefore, multipliers—that are greater than 1 need be written.



d. Pick coefficients that make the total increase and total decrease of oxidation number the same. If 10 atoms of N decrease by 1, the total decrease will be 10, the same as the total increase already determined for I. Therefore, we use 10 as the coefficient for both HNO_3 and NO_2. And we use 2 for HIO_3 since there are 2 atoms of I in I_2 that must be balanced.

$$10HNO_3 + I_2 - 2HIO_3 + 10NO_2 + H_2O$$

e. By inspection, adjust the coefficients for the rest of the substances, leaving oxygen for the last. Here, we see that since we have 10 hydrogen atoms on the left side, we need $5H_2O$ to ma 10 hydrogen atoms on the right side. Finally, check the result by finding the total number oxygen atoms on each side of the equation. If the total on the left equals the total on the right, the equation is correctly balanced. Thus, the count of oxygen atoms serves as a check on the balancing of the equation.

	$10HNO_3$	+ I_2	– $2HIO_3$	+	$10NO_2$	+	$4H_2O$
oxygen atoms	$10 \times 3 = 30$		$2 \times 3 = 6$	+	$10 \times 2 = 20$	+	4
					total = 30		

Use steps *a-e* as in Sample Problem 1 to balance the following equations. In the final balanced equation, draw a circle around the formula of the oxidizing agent.

1. ____$CrCl_3$ + ____MnO_2 + ____H_2O – ____$MnCl_2$ + ____H_2CrO_4

2. ____H_2S + ____HNO_3 – ____NO_2 + ____S + ____H_2O

3. ____HNO_3 + ____S – ____NO + ____H_2SO_4

4. ____$KMnO_4$ + ____Na_2SnO_2 + ____H_2O – ____MnO_2 + ____Na_2SnO_3 + ____KOH

5. ____PbO_2 + ____H_2MnO_3 + ____HNO_3 – ____$Pb(NO_3)_2$ + ____$HMnO_4$ + ____H_2O

6. ____HNO_3 + ____P – ____H_3PO_4 + ____NO_2 + ____H_2O.

Sample Problem 2 Balance the following equation for a redox reaction between copper and nitric acid:

$$Cu + HNO_3 - Cu(NO_3)_2 + NO + H_2O$$

Solution Carry out steps *a-d* as in Sample Problem 1. As the result of step *d*, we have the following:

$$3Cu + 2HNO_3 - 3Cu(NO_3)_2 + 2NO + H_2O \qquad \text{(not balanced yet)}$$