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program editor: H. A. Neidig

Balancing Oxidation–Reduction Equations Using the Ion-Electron Method

prepared by **M.L. Gillette**, Indiana University Kokomo,
and **H.A. Neidig**, Lebanon Valley College

Purpose of the Experiment

Balance equations for oxidation–reduction reactions using the ion-electron method.

Background Information

When we listen to an alkaline battery-powered CD player, the chemical reaction occurring in the battery provides the energy to power the CD player. The reaction has two parts, each called a **half-reaction**. **Oxidation**, in which a reactant loses electrons, takes place in one half-reaction; and **reduction**, in which a reactant gains electrons, takes place in the other half-reaction. We refer to the total electron transfer reaction as an **oxidation–reduction**, or **redox**, reaction. The total unbalanced redox reaction inside our alkaline CD player battery is represented by Equation 1.

$$Zn + MnO_2 \rightarrow ZnO + Mn_2O_3 \qquad \text{(Eq. 1)}$$

To balance equations for redox reactions in aqueous solution without using the oxidation numbers of the reactants and products, we employ the **ion-electron method**. The method involves eight simple steps:

1. Write the equation you wish to balance in ionic form.

2. Remove coefficients in front of any species, and remove any species that are **spectator** ions, that is, ions not involved in electron transfer.

3. Based on the resulting skeletal equation, write the two equations representing the two half-reactions: one for oxidation and one for reduction.

4. If the reaction occurs in acidic solution, add H^+ ions and H_2O molecules to balance hydrogen and oxygen atoms. We use H^+ ion rather than H_3O^+ ion, in order to simplify the process of balancing charges and atoms.

5. Balance the charges on opposite sides of each half-reaction equation by adding electrons to the appropriate side.

6. The number of electrons lost in the oxidation half-reaction must equal the number of electrons gained in the reduction half-reaction. If necessary, multiply each half-reaction equation by a **stoichiometric coefficient**, a number that will equalize the number of electrons transferred.

00 99 98 97 96 95 — 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1

7. Add the resulting half-reaction equations to obtain the balanced net ionic equation.

8. To this point, assume that any change in the presence of H^+ ion is due to the fact that the reaction takes place in an acid solution. If the reaction occurs in basic solution, now add OH^- ions and H_2O molecules to cancel any H^+ ions.

We will illustrate the use of these steps with the reaction represented by Equation 2.

$$Ce(SO_4)_2 + FeSO_4 \rightarrow Ce_2(SO_4)_3 + Fe_2(SO_4)_3 \qquad \text{(Eq. 2)}$$

We begin by writing the total ionic equation, as shown in Equation 2a.

$$Ce^{4+} + 2\ SO_4^{2-} + Fe^{2+} + SO_4^{2-} \rightarrow 2\ Ce^{3+} + 3\ SO_4^{2-} + 2\ Fe^{3+} + 3\ SO_4^{2-} \qquad \text{(Eq. 2a)}$$

Then, we eliminate all coefficients and spectator ions in Equation 2a. The result is a skeletal equation, shown in Equation 2b.

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+} \qquad \text{(Eq. 2b)}$$

In the next step we write an equation for each half-reaction. Equations 2c and 2d represent the half-reactions making up the reaction represented by Equation 2.

$$Ce^{4+} \rightarrow Ce^{3+} \qquad \text{(Eq. 2c)}$$

$$Fe^{2+} \rightarrow Fe^{3+} \qquad \text{(Eq. 2d)}$$

Note that neither Equation 2c nor 2d is balanced electrically. Our next step is to balance the charges on opposite sides of Equation 2c by adding an electron, represented by e^-, as shown in Equation 2e.

$$Ce^{4+} + e^- \rightarrow Ce^{3+} \qquad \text{(Eq. 2e)}$$

We can balance the charges in Equation 2d similarly, as shown in Equation 2f.

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad \text{(Eq. 2f)}$$

Now each of the half-reactions for Equation 2 is balanced electrically. Equation 2e involves reduction and Equation 2f involves oxidation.

The number of electrons lost in Equation 2f equals the number gained in Equation 2e, so we do not need to add a coefficient to either equation, as described in Step 6.

To complete the process of balancing equations by the ion-electron method we combine our half-reactions to form the balanced net equation, shown in Equation 2g. Note that the numbers of atoms are balanced.

$$\text{reduction:} \quad Ce^{4+} + e^- \rightarrow Ce^{3+} \qquad \text{(Eq. 2e)}$$

$$\text{oxidation:} \quad Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad \text{(Eq. 2f)}$$

$$Ce^{4+} + Fe^{2+} + e^- \rightarrow Ce^{3+} + Fe^{3+} + e^- \qquad \text{(Eq. 2g)}$$

Because there is an equal number of e^- on each side of the equation, they cancel, producing Equation 2h.

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+} \qquad \text{(Eq. 2h)}$$

In this example, because we were not informed otherwise, we assumed that the reaction occurs in a neutral solution. Because we did not have to use Step 4 to add H^+ and H_2O to balance H and O atoms, our assumption was correct. For similar reasons, we did not use Step 8.

Consider another example. The redox reaction represented by Equation 3 takes place when aluminum (Al) is treated with copper(II) sulfate ($CuSO_4$).

$$Al + CuSO_4 \rightarrow Al_2(SO_4)_3 + Cu \qquad \text{(Eq. 3)}$$

Again, we begin by writing the equation in ionic form, as shown in Equation 3a.

$$Al + Cu^{2+} + SO_4^{2-} \rightarrow 2\ Al^{3+} + 3\ SO_4^{2-} + Cu \qquad \text{(Eq. 3a)}$$

Next, we remove the spectator ions and coefficients in Eq. 3a, write the skeletal forms of the half-reactions, and add to each equation the number of electrons needed to balance the charge. The balanced half-reactions are shown in Equations 3b and 3c.

$$\text{oxidation:} \quad Al \rightarrow Al^{3+} + 3\ e^- \qquad \text{(Eq. 3b)}$$

$$\text{reduction:} \quad Cu^{2+} + 2\ e^- \rightarrow Cu \qquad \text{(Eq. 3c)}$$

To equalize the number of electrons gained and lost within the net redox reaction, we multiply Equation 3b by 2 and Equation 3c by 3.

$$2[Al \rightarrow Al^{3+} + 3\ e^-] \qquad \text{(Eq. 3d)}$$

$$3[Cu^{2+} + 2\ e^- \rightarrow Cu] \qquad \text{(Eq. 3e)}$$

Because the numbers of electrons involved in each half-reaction are now equal, they cancel when we add the half-reactions to get the balanced net ionic equation, Equation 3f.

$$2\ Al + 3\ Cu^{2+} \rightarrow 2\ Al^{3+} + 3\ Cu \qquad \text{(Eq. 3f)}$$

To balance the equations for redox reactions that occur in acidic solution, we need to add H^+ ions and H_2O. For example, consider the balance of atoms in Equation 4.

$$Fe + HNO_3 \rightarrow Fe(NO_3)_2 + H_2O + NO \qquad \text{(Eq. 4)}$$

To develop the skeletal ionic equation derived from Equation 4, we write the net ionic equation, as shown in Equation 4a.

$$Fe + H^+ + NO_3^- \rightarrow Fe^{2+} + 2\ NO_3^- + H^+ + OH^- + NO \qquad \text{(Eq. 4a)}$$

Because Fe is in an elemental form on the left side of Equation 4a and an ion on the right, we retain it in the skeletal ionic equation. The nitrogen and oxygen in this reaction are in the form of NO_3^- ion on the left side of the equation and in the form of NO on the right, therefore, they will remain also. However, the NO_3^- ions on the right side of the equation are no different in form than the NO_3^- ion on the left. The NO_3^- ions on the right are spectator ions, and therefore can be removed, as can H^+ and OH^-. After using Step 2, removing coefficients and spectator ions, Equation 4a becomes the skeletal equation, as shown in Equation 4b.

$$Fe + NO_3^- \rightarrow Fe^{2+} + NO \qquad \text{(Eq. 4b)}$$

The skeletal half-reactions for this reaction are shown as Equations 4c and 4d.

$$Fe \rightarrow Fe^{2+} \qquad \text{(Eq. 4c)}$$

$$NO_3^- \rightarrow NO \qquad \text{(Eq. 4d)}$$

To balance the oxidation half-reaction, Equation 4c, we add 2 e^-.

$$Fe \rightarrow Fe^{2+} + 2\ e^- \qquad \text{(Eq. 4e)}$$

In order to balance the reduction half-reaction, Equation 4d, we must first balance the atoms and then balance the charge by adding electrons. Because there are more oxygen atoms on the left side of Equation 4d than on the right, we add 2 H_2O to the right side. To balance the addition of hydrogen atoms to the right side, we add 4 H^+ ions to the left side. The result is Equation 4f.

$$NO_3^- + 4\ H^+ \rightarrow NO + 2\ H_2O \qquad \text{(Eq. 4f)}$$

Next, we balance the charges. We do this by adding 3 e^- to the left side.

$$NO_3^- + 4\ H^+ + 3\ e^- \rightarrow NO + 2\ H_2O \qquad \text{(Eq. 4g)}$$

Before we add the half-reactions, we must multiply each half-reaction by the appropriate stoichiometric coefficient, a factor that makes the number of electrons lost equal to the number of electrons gained. In this example, we multiply Equation 4e by 3 (Equation 4h) and Equation 4g by 2 (Equation 4i). When we add the resulting half-reactions, the 6 e^- cancel. The result is the balanced net ionic equation, Equation 4j.

$$3[Fe] \rightarrow 3[Fe^{2+} + 2\ e^-\ ] \qquad \text{(Eq. 4h)}$$

$$2[NO_3^- + 4\ H^+ + 3\ e^-] \rightarrow 2[NO + 2\ H_2O] \qquad \text{(Eq. 4i)}$$

$$3\ Fe + 2\ NO_3^- + 8\ H^+ \rightarrow 3\ Fe^{2+} + 2\ NO + 4\ H_2O \qquad \text{(Eq. 4j)}$$

If a redox reaction occurs in basic solution and we want to balance the equation, we add OH^- ions to eliminate H^+ ions (Step 8). We do this manipulation after adding the two half reactions to get the net ionic equation. Consider Equation 5, which represents a reaction that occurs in basic solution.

$$CrO_4^{2-} + Br_2 \rightarrow Cr^{3+} + BrO_3^- \qquad \text{(Eq. 5)}$$

We proceed as we did with the other two examples. The skeletal half-reactions for this reaction are shown in Equations 5a and 5b.

$$Br_2 \rightarrow BrO_3^- \qquad \text{(Eq. 5a)}$$

$$CrO_4^{2-} \rightarrow Cr^{3+} \qquad \text{(Eq. 5b)}$$

We balance the atoms in Equation 5a by multiplying BrO_3^- ion by 2, then adding 6 H_2O to the left side to balance the additional oxygen atoms. We add 12 H^+ ions to the right side to balance the added hydrogen atoms. The result is Equation 5c.

$$Br_2 + 6\ H_2O \rightarrow 2\ BrO_3^- + 12\ H^+ \qquad \text{(Eq. 5c)}$$

Finally, we add electrons to balance the charge (Eq. 5d).

$$Br_2 + 6\ H_2O \rightarrow 2\ BrO_3^- + 12\ H^+ + 10\ e^- \qquad \text{(Eq. 5d)}$$

We balance the atoms in the other skeletal half-reaction equation, Equation 5b, by adding H_2O and H^+ ions. The result is Equation 5e.

$$CrO_4^{2-} + 8\ H^+ \rightarrow Cr^{3+} + 4\ H_2O \qquad \text{(Eq. 5e)}$$

We balance the charge by adding 3 e^- to the left side.

$$CrO_4^{2-} + 8\ H^+ + 3\ e^- \rightarrow Cr^{3+} + 4\ H_2O \qquad \text{(Eq. 5f)}$$

Next, we multiply each half-reaction by the appropriate stoichiometric coefficient to equalize the number of electrons lost and gained, as shown in Equations 5g and 5h.

$$3[Br_2 + 6\ H_2O \rightarrow 2\ BrO_3^- + 12\ H^+ + 10\ e^-] = 3\ Br_2 + 18\ H_2O \rightarrow 6\ BrO_3^- + 36\ H^+ + 30\ e^- \qquad \text{(Eq. 5g)}$$

$$10[CrO_4^{2-} \rightarrow 8\ H^+ + 3\ e^- \rightarrow Cr^{3+} + 4\ H_2O] =$$
$$10\ CrO_4^{2-} + 80\ H^+ + 30\ e^- \rightarrow 10\ Cr^{3+} + 40\ H_2O \qquad \text{(Eq. 5h)}$$

When we add Equations 5g and 5h, the electrons on each side of the net equation cancel (see Equation 5i). Because this reaction takes place in basic solution, we must cancel the 80 H^+ ions on the left side of the net ionic equation by adding 80 OH^- ions to each side of the net equation.

$$3\ Br_2 + 18\ H_2O \rightarrow 6\ BrO_3^- + 36\ H^+ + 30\ e^- \qquad \text{(Eq. 5g)}$$

$$10\ CrO_4^{2-} + 80\ H^+ + 30\ e^- \rightarrow 10\ Cr^{3+} + 40\ H_2O \qquad \text{(Eq. 5h)}$$

$$3\ Br_2 + 18\ H_2O + 10\ CrO_4^{2-} + 80\ H^+ + 80\ OH^- + \cancel{30\ e^-} \rightarrow$$
$$6\ BrO_3^- + 36\ H^+ + \cancel{30\ e^-} + 10\ Cr^{3+} + 40\ H_2O + 80\ OH^- \qquad \text{(Eq. 5i)}$$

The OH^- and H^+ ions combine to form water molecules, which we can balance by subtraction to obtain the balanced net ionic equation, Equation 5j.

$$22\ H_2O + 3\ Br_2 + 10\ CrO_4^{2-} \rightarrow$$
$$6\ BrO_3^- + 10\ Cr^{3+} + 44\ OH^- \qquad \text{(Eq. 5j)}$$

To check the accuracy of our work, we determine the net charges of the reactant and product sides of the final balanced equation. These net charges should be equal. In Equation 5j, the net charges of the reactant and product sides are each –20. We conclude, therefore, that our net ionic equation is balanced.

Another check is to make sure that the atoms in the final equation are balanced. In the case of Equation 5j:

	Br	*Cr*	*O*	*H*
left	6	10	62	44
right	6	10	62	44

This confirms that Equation 5j is balanced.

name section date

Problem Set

On separate sheets of paper, balance the following redox equations using the ion-electron method. Write and balance the oxidation half-reaction first, then do the reduction half-reaction. Balance the atoms, the charges, and the numbers of electrons lost and gained. After adding the half reactions to determine the net ionic equation, cancel all electrons and extra H^+ ions, OH^- ions, and H_2O molecules. Check your work by comparing the net charges on the left and right sides of the net equation. Also check that the atoms are balanced.

1. $Fe + S \rightarrow Fe^{2+} + S^{2-}$

2. $Cl_2 + Br^- \rightarrow Br_2 + Cl^-$

3. $Cu^{2+} + I^- \rightarrow CuI + I_2$

4. $Cu + NO_3^- \rightarrow Cu^{2+} + NO$ (acidic solution)

5. $Al + NO_3^- \rightarrow Al(OH)_4^- + NH_3$ (basic solution)

6. $NaI + H_2SO_4 \rightarrow Na_2SO_4 + H_2S + I_2$ (acidic solution)

7. $ClO^- + As \rightarrow AsO_4^{3-} + Cl^-$ (basic solution)

8. $S^{2-} + I_2 \rightarrow SO_4^{2-} + I^-$ (basic solution)

9. $CH_3OH + MnO_4^- \rightarrow CO_2 + MnO_2$ (acidic solution) name section date

10. $CH_3OH + MnO_4^- \rightarrow CO_2 + MnO_2$ (basic solution)

11. $I_2 + Cl_2 \rightarrow H_3IO_6^{2-} + Cl^-$ (basic solution)

12. $NO_3^- + As_2S_3 \rightarrow AsO_4^{3-} + SO_4^{2-} + NO$ (acidic solution)

13. $C_6H_5CH_3 + Cr_2O_7^{2-} \rightarrow Cr^{3+} + C_6H_5COOH$ (acidic solution)

14. $Cr_2O_7^{2-} + C_8H_{10} \rightarrow C_7H_6O_2 + CO_2 + Cr^{3+}$ (acidic solution)

15. $Fe_3O_4 + MnO_4^{-} \rightarrow Fe_2O_3 + MnO_2$ (basic solution)

16. $MnO_4^{-} + ClO_2^{-} \rightarrow MnO_2 + OH^{-} + ClO_4^{-}$ (basic solution)

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