17.4: Balancing Oxidation-reduction Reactions

Having defined oxidation states, we can now redefine an ***oxidation–reduction reaction*** as one in which at least one element undergoes a change of oxidation state. For example, in the reaction between permanganate ion and oxalate ion, the oxidation states of manganese and carbon atoms change. In the reactants, the oxidation state of manganese is 7+; in the products, it is 2+. In the reactants, the oxidation state of carbon is 3+; in the products, it is 4+.

$$\begin{matrix} 7+ & & 3+ & & 2+ & & 4+ \\ MnO_4^- & + & C_2O_4^{2-} & \rightarrow & Mn^{2+} & + & CO_2 \end{matrix}$$

These oxidation state changes determine the stoichiometry of the reaction. In terms of the oxidation state formalism, each manganese atom gains five electrons and each carbon atom loses one electron. Thus the reaction must involve five times as many carbon atoms as manganese atoms. Allowing for the presence of two carbon atoms in the oxalate ion, conservation of electrons requires that the stoichiometric coefficients be

$$2\ MnO_4^- + 5\ C_2O_4^- \rightarrow 2\ Mn^{2+} + 10\ CO_2$$

Written this way, two MnO_4^- moieties gain ten electrons, and five $C_2O_4^{2-}$ moieties lose ten electrons. When we fix the coefficients of the redox reactants, we also fix the coefficients of the redox products. However, inspection shows that both charge and the number of oxygen atoms are out of balance in this equation.

The reaction occurs in acidic aqueous solution. This means that enough water molecules must participate in the reaction to achieve oxygen-atom balance. Adding eight water molecules to the product brings oxygen into balance. Now, however, charge and hydrogen atoms

$$2\ MnO_4^- + 5\ C_2O_4^- \rightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$$

do not balance. Since the solution is acidic, we can bring hydrogen into balance by adding sixteen protons to the reactants. When we do so, we find that charge balances also.

$$2\ MnO_4^- + 5\ C_2O_4^- + 16\ H^+ \rightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$$

Evidently, this procedure achieves charge balance because the oxidation state formalism enables us to find the correct stoichiometric ratio between oxidant and reductant.

We can formalize this thought process in a series of rules for balancing oxidation–reduction reactions. In doing this, we can derive some advantage from splitting the overall chemical change into two parts, which we call half-reactions. It is certainly not necessary to introduce half-reactions just to balance equations; the real advantage is that a half-reaction describes the chemical change in an individual half-cell. The rules for balancing oxidation–reduction reactions using half-cell reactions are these:

1. Find the oxidation state of every atom in every reactant and every product.
2. Write skeletal equations showing:
   1. the oxidizing agent $\rightarrow$ its reduced product
   2. the reducing agent $\rightarrow$ its oxidized product
3. Balance the skeletal equations with respect to all elements other than oxygen and hydrogen.
4. Add electrons to each equation to balance those gained or lost by the atoms undergoing oxidation-state changes.
5. For a reaction occurring in acidic aqueous solution:
   1. balance oxygen atoms by adding water to each equation.
   2. balance hydrogen atoms by adding protons to each equation
6. For a reaction occurring in basic aqueous solution, balance oxygen and hydrogen atoms by adding water to one side of each equation and hydroxide ion to the other.
7. The net effect of adding one water and one hydroxide is to increase by one the number of hydrogen atoms on the side to which the water is added.

8. Adding two hydroxide ions to one side and a water molecule to the other increases by one the number of oxygen atoms on the side to which hydroxide is added.
   1. Multiply each half-reaction by a factor chosen to make each of the resulting half-reactions contain the same number of electrons.
   2. Add the half-reactions to get a balanced equation for the overall chemical change. The electrons cancel. Often, some of the water molecules, hydrogen atoms, or hydroxide ions cancel also.

When we apply this method to the permanganate–oxalate reaction, we have

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

reduction half-reaction

$$5\,C_2O_4^- \rightarrow 10\,CO_2 + 10\,e^-$$

oxidation half-reaction

$$2\,MnO_4^- + 5\,C_2O_4^- + 16\,H^+ \rightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$$

balanced reaction

The half-reactions sum to the previously obtained result; the electrons cancel. For an example of a reaction in basic solution, consider the disproportionation of chloride dioxide to chlorite and chlorate ions:

$$\begin{array}{ccccc} 4+ & & 3+ & & 5+ \\ ClO_2 & \rightarrow & ClO_2^- & + & ClO_3^- \end{array}$$

skeletal reaction

$$ClO_2 + e^- \rightarrow ClO_2^-$$

reduction half-reaction

$$ClO_2 + 2OH^- \rightarrow ClO_3^- + H_2O + e^-$$

oxidation half-reaction

$$2\,ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

balanced equation
