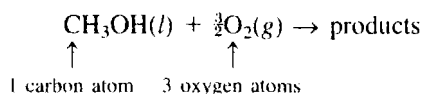
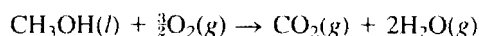


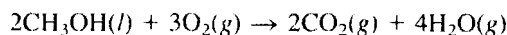
.. This means that three oxygen atoms are needed to balance the increase in the oxidation state of the single carbon atom. We can write this relationship as follows:



The rest of the equation can be balanced by inspection:



We write it in conventional format (multiply through by 2):



In using the oxidation states method to balance an oxidation-reduction equation, we find the coefficients for the reactants that will make the total increase in oxidation state balance the total decrease. The remainder of the equation is then balanced by inspection.

The procedures for balancing an oxidation-reduction reaction by the oxidation states method are summarized below.

Balancing an Oxidation-Reduction Reaction by the Oxidation States Method

Assign the oxidation states of all atoms.

Decide which element is oxidized and determine the increase in oxidation state.

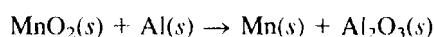
Decide which element is reduced and determine the decrease in oxidation state.

Choose coefficients for the species containing the atom oxidized and the atom reduced such that the total increase in oxidation state equals the total decrease in oxidation state.

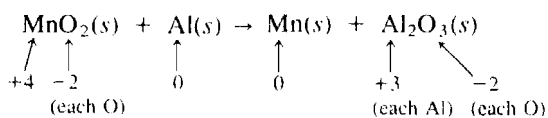
Balance the remainder of the equation by inspection.

Sample Exercise 4.22

Because metals are so reactive, very few are found in nature in pure form. Metallurgy involves reducing the metal ions in ores to the elemental form. In Sample Exercise 4.21, we considered the treatment of the lead-containing ore galena. The production of manganese from the ore pyrolusite, which contains MnO_2 , uses aluminum as the reducing agent. Using oxidation states, balance the equation for this process.

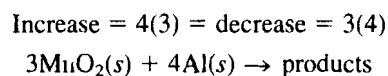


First we assign oxidation states:

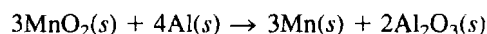


Each Mn atom undergoes a decrease in oxidation state of 4 (from +4 to 0), while each Al atom undergoes an increase of 3 (from 0 to +3).

Thus we need three Mn atoms for every four Al atoms in order to balance the increase and decrease in oxidation states:

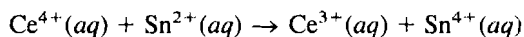


We balance the rest of the equation by inspection:

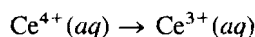


The Half-Reaction Method

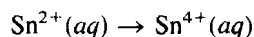
For oxidation-reduction reactions that occur in aqueous solution, it is often useful to separate the reaction into two **half-reactions**: one involving oxidation and the other involving reduction. For example, consider the unbalanced equation for the oxidation-reduction reaction between cerium(IV) ion and tin(II) ion:



This reaction can be separated into a half-reaction involving the substance being *reduced*,



and one involving the substance being *oxidized*,



The general procedure is to balance the equations for the half-reactions separately and then to add them to obtain the overall balanced equation. The half-reaction method for balancing oxidation-reduction equations differs slightly depending on whether the reaction takes place in acidic or basic solution.

The Half-Reaction Method for Balancing Equations for Oxidation-Reduction Reactions Occurring in Acidic Solution

Write the equations for the oxidation and reduction half-reactions.

For each half-reaction:

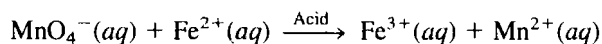
- Balance all of the elements except hydrogen and oxygen.
- Balance oxygen using H_2O .
- Balance hydrogen using H^+ .
- Balance the charge using electrons.

If necessary, multiply one or both balanced half-reactions by an integer to equalize the number of electrons transferred in the two half-reactions.

Add the half-reactions, and cancel identical species.

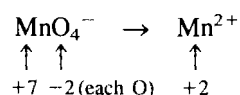
Check that the elements and charges balance.

We will illustrate this method by balancing the equation for the reaction between permanganate and iron(II) ions in acidic solution:

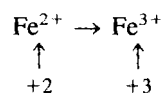


This reaction is used to analyze iron ore for its iron content.

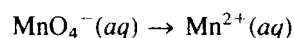
Step 1: Identify and write equations for the half-reactions. The oxidation states for the half-reaction involving the permanganate ion show that manganese is reduced:



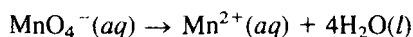
This is the *reduction half-reaction*. The other half-reaction involves the oxidation of iron(II) to iron(III) ion and is the *oxidation half-reaction*:



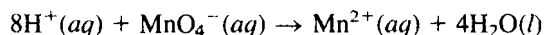
Step 2: Balance each half-reaction. For the reduction reaction, we have



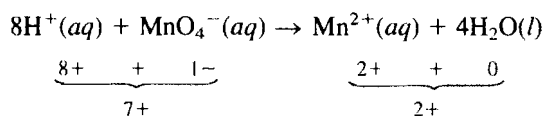
- The manganese is balanced.
- We balance oxygen by adding $4\text{H}_2\text{O}$ to the right side of the equation:



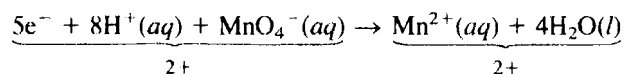
- Next we balance hydrogen by adding 8H^+ to the left side:



- All of the elements have been balanced, but we need to balance the charge using electrons. At this point we have the following charges for reactants and products in the reduction half-reaction:



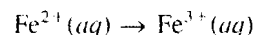
We can equalize the charges by adding five electrons to the left side:



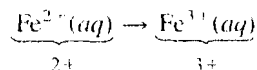
Both the *elements* and the *charges* are now balanced, so this represents the balanced reduction half-reaction. The fact that five electrons appear on the reactant side of the equation makes sense since five electrons are required to

reduce MnO_4^- (Mn has an oxidation state of +7) to Mn^{2+} (Mn has an oxidation state of +2).

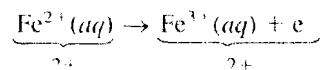
For the oxidation reaction,



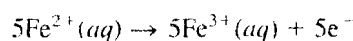
the elements are balanced, and we must simply balance the charge.



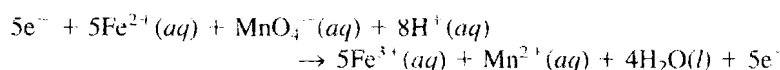
One electron is needed on the right side to give a net 2+ charge on both sides:



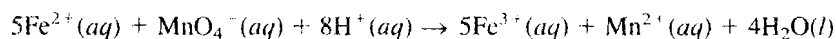
Step 3: Equalize the electron transfer in the two half-reactions. Since the reduction half-reaction involves a transfer of five electrons and the oxidation half-reaction involves a transfer of only one electron, the oxidation half-reaction must be multiplied by 5:



Step 4: Add the half-reactions. The half-reactions are added to give



Note that the electrons cancel out (as they must) to give the final balanced equation:



Step 5: Check that elements and charges balance.

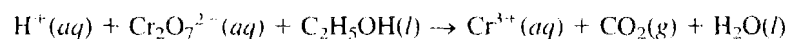
Elements balance: 5 Fe, 1 Mn, 4 O, 8 H \rightarrow 5 Fe, 1 Mn, 4 O, 8 H

Charges balance: $5(2+) + (1-) + 8(1+) = 17+ \rightarrow 5(3+) + (2+) + 0 = 17+$

The equation is balanced.

Sample Exercise 4.23

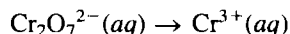
Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is a bright orange compound that can be reduced to a green solution of Cr^{3+} ions. This color change can be used to test a person's breath for alcohol ($\text{C}_2\text{H}_5\text{OH}$) content.* The reactants and products of the oxidation-reduction reaction are



Balance this equation using the half-reaction method.

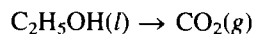
*For an experiment based on the breathalyzer see William C. Timmer, An Experiment in Forensic Chemistry, *J. Chem. Ed.* **63** (1986): 897.

The reduction half-reaction is



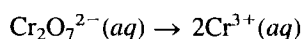
Chromium is reduced from an oxidation state of +6 in $\text{Cr}_2\text{O}_7^{2-}$ to one of +3 in Cr^{3+} .

The oxidation half-reaction is

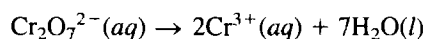


Carbon is oxidized from an oxidation state of -2 in $\text{C}_2\text{H}_5\text{OH}$ to +4 in CO_2 .

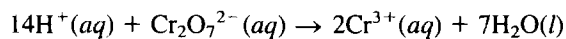
Balancing all elements except hydrogen and oxygen in the first half-reaction, we have



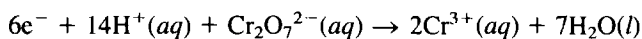
Balancing oxygen using H_2O , we have



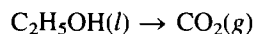
Balancing hydrogen using H^+ , we have



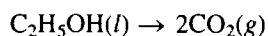
Balancing the charge using electrons, we have



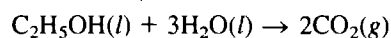
Next, we turn to the oxidation half-reaction



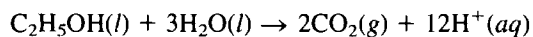
Balancing carbon, we have



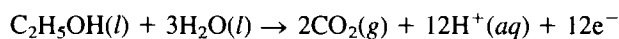
Balancing oxygen using H_2O , we have



Balancing hydrogen using H^+ , we have

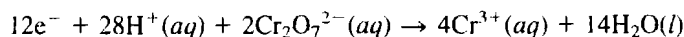


Balancing the charge using electrons, we have



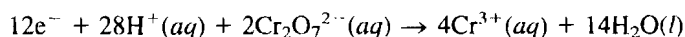
In the reduction half-reaction there are 6 electrons on the left-hand side, and there are 12 electrons on the right-hand side of the oxidation half-reaction.

Thus we multiply the reduction half-reaction by 2 to give

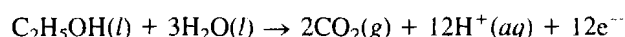


Adding the half-reactions, and canceling identical species, we have

Reduction half-reaction:



Oxidation half-reaction:



Check that elements and charges balance.

Elements balance: 22 H, 4 Cr, 15 O, 2 C \rightarrow 22 H, 4 Cr, 15 O, 2 C

Charges balance: $+16 + 2(-2) + 0 = +12 \rightarrow 4(+3) + 0 + 0 = +12$

Oxidation-reduction reactions can occur in basic as well as in acidic solutions. The half-reaction method for balancing equations is slightly different in such cases.

The Half-Reaction Method for Balancing Equations for Oxidation-Reduction Reactions Occurring in Basic Solution

Use the half-reaction method as specified for acidic solutions to obtain the final balanced equation *as if H^+ ions were present*.

To both sides of the equation obtained above, add a number of OH^- ions that is equal to the number of H^+ ions. (We want to eliminate H^+ by forming H_2O .)

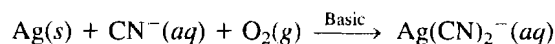
Form H_2O on the side containing both H^+ and OH^- ions, and eliminate the number of H_2O molecules that appear on both sides of the equation.

Check that elements and charges balance.

We will illustrate how the rules are applied in Sample Exercise 4.24.

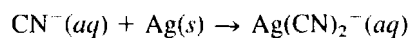
Sample Exercise 4.24

Silver is sometimes found in nature as large nuggets; more often it is found mixed with other metals and their ores. Cyanide ion is often used to extract the silver by the following reaction that occurs in basic solution:

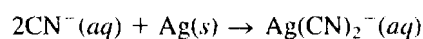


Balance this equation using the half-reaction method.

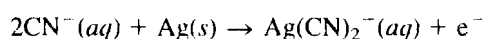
Balance the equation as if H^+ ions were present. Balance the oxidation half-reaction:



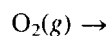
Balance carbon and nitrogen:



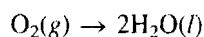
Balance the charge:



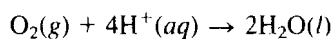
Balance the reduction half-reaction:



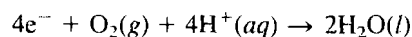
Balance oxygen:



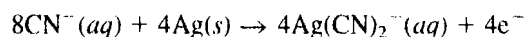
Balance hydrogen:



Balance the charge:

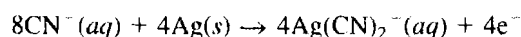


Multiply the balanced oxidation half-reaction by 4:

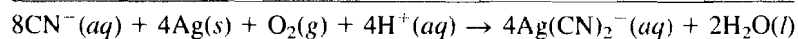
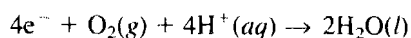


Add the half-reactions, and cancel identical species:

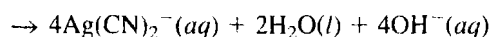
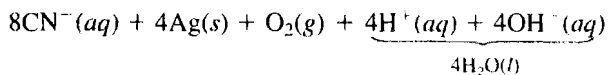
Oxidation half-reaction:



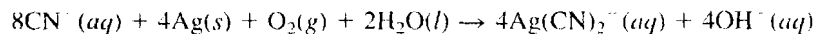
Reduction half-reaction:



Add OH^- ions to both sides of balanced equation. We need to add 4OH^- to each side:



Eliminate as many H₂O molecules as possible.



Check that elements and charges balance.

Elements balance: 8 C, 8 N, 4 Ag, 4 O, 4 H \rightarrow 8 C, 8 N, 4 Ag, 4 O, 4 H

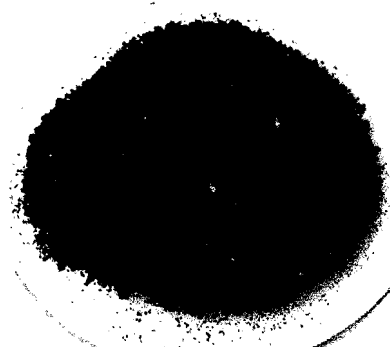
Charges balance: $8(1^-) + 0 + 0 + 0 = 8^- \rightarrow 4(1^-) + 4(1^-) = 8^-$

4.12 Simple Oxidation-Reduction Titrations

Purpose

To learn to do the calculations associated with oxidation-reduction titrations.

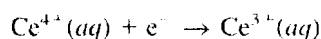
Oxidation-reduction reactions are commonly used as the basis for volumetric analytical procedures. For example, a reducing substance can be titrated with a solution of a strong oxidizing agent, or vice versa. Three of the most frequently used oxidizing agents are aqueous solutions of *potassium permanganate* (KMnO₄), *potassium dichromate* (K₂Cr₂O₇), and *cerium hydrogen sulfate* [Ce(HSO₄)₄].



Solid potassium permanganate.

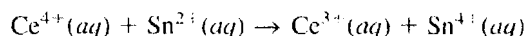
Sample Exercise 4.25

Cerium(IV) ion is a strong oxidizing agent that accepts one electron to produce cerium(III) ion:



A solution containing an unknown concentration of Sn²⁺ ions was titrated with a solution containing Ce⁴⁺ ions, which oxidize the Sn²⁺ ions to Sn⁴⁺ ions. In one titration, 1.00 L of the unknown solution required 46.45 mL of a 0.1050 M Ce⁴⁺ solution to reach the stoichiometric point. Calculate the concentration of Sn²⁺ ions in the unknown solution.

The unbalanced equation for the titration reaction is



The balanced equation is

