Web Supplement 7.2

7.2.W1 **Oxidation Numbers**

In the preceding equations, the dissolved copper and zinc species are shown as ions having a +2 charge, i.e., $Cu^{2+}(aq)$ and $Zn^{2+}(aq)$. Chemists have extended this concept of charge to chemically bound atoms by assigning its atom an *oxidation number*. The rules for determining the oxidation number of an atom are briefly described next, with a fuller list provided in Appendix 11.

1. The oxidation number of a monoatomic ion is equivalent to its charge, e.g., the oxidation number of $Cu^{2+}(aq)$ is II.
2. The oxidation number of an atom in its elemental state is 0, e.g., the oxidation number of atomic oxygen in O_2 is 0, as is the oxidation number of atomic copper in Cu(s).
3. The oxidation number of oxygen in most molecules is −II. Notable exceptions are peroxides (R−OOH), in which oxygen's oxidation number is −I and O_2, in which oxygen's oxidation number is 0.
4. The oxidation number of atomic hydrogen is I, except when it is in hydrides; then it is −I.

With these rules, the oxidation number of an atom in a molecule can be calculated by constructing a charge-balance equation as shown below for chromium in the dichromate ion, $Cr_2O_7^{2-}$:

$$\text{Total charge on } Cr_2O_7^{2-} = (\text{number of Cr atoms})(\text{oxidation number of Cr}) + (\text{number of O atoms})(\text{oxidation number of O}) \quad (7.W1)$$

$$-2 = (2)(Cr) + (7)(-2) \quad (7.W2)$$

$$Cr = VI \quad (7.W3)$$

Oxidation numbers are commonly written as Roman numerals, often in parentheses, e.g., Cu(II)O. Redox reactions cause the oxidation number of elements to change. If an atom is being oxidized, its oxidation number will increase. If it is being reduced, its oxidation number will decrease. In the case of the spontaneous reaction written in

Eq. 7.1, the oxidation number of Zn increases from 0 to II, so it is being oxidized. The oxidation number of Cu decreases from II to 0, so it is being reduced.

7.2.W2 Balancing Redox Reactions

Redox reactions can be constructed by combining half-cell reactions. The following strategies are used to generate balanced redox reactions from half-cell reactions.

Balancing by Inspection

Some redox reactions can be balanced by inspection, that is by the standard technique for balancing nonredox equations. Equation 7.1 is a good example; you can easily see that the molar masses have been conserved between the products and reactions, so that the reaction is balanced with respect to molar mass. Note that for redox reactions, you must also ensure that the net charge is the same on both sides of the equation.

Equation 7.1 can also be constructed by adding the two half-cell reactions (Eqs. 7.2 and 7.3) as if they were mathematical equations, i.e.,

$$Zn(s) + Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) + Zn^{2+}(aq) + 2e^- \qquad (7.W4)$$

Since $2e^-$ appears as both a product and reactant, it can be eliminated to generate a presentation of the reaction stoichiometry as shown in Eq. 7.1.

Balancing by the Method of Half-Reactions

Acidic Solutions

The following steps can used to construct a balanced redox reaction that proceeds under acidic conditions, where $H_2O(l)$ and $H^+(aq)$ are added to achieve mass and charge balance. To illustrate, we use the following example: dichromate ions, $Cr_2O_7^{2-}(aq)$ reacting with nitrous acid molecules, $HNO_2(aq)$ under acidic conditions to form chromium ions, $Cr^{3+}(aq)$, and nitrate ions, $NO_3^-(aq)$.

Step 1: Write the skeleton redox reaction, in which you identify the products and reactants. [Don't worry about balancing charge or mass and ignore $H_2O(l)$ and $H^+(aq)$]. Decide which reactant is getting oxidized and which is getting reduced.

$$Cr_2O_7^{2-}(aq) + HNO_2(aq) \rightarrow Cr^{3+}(aq) + NO_3^-(aq) \qquad (7.W5)$$

In this case, the oxidation number of Cr is being reduced from VI to III and the oxidation number of N is increasing from III to V. This means that this reaction is causing Cr to be reduced and N to be oxidized.

Step 2: Write the skeletons of the oxidation and reduction half-reactions. [Once again, don't worry about balancing charge or mass and ignore $H_2O(l)$ and $H^+(aq)$].

$$\text{Reduction:} \quad Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq) \qquad (7.W6)$$

$$\text{Oxidation:} \quad HNO_2(aq) \rightarrow NO_3^-(aq) \qquad (7.W7)$$

Step 3: Balance all elements other than H and O by inserting stoichiometric coefficients.

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) \quad (7.W8)$$

$$HNO_2(aq) \rightarrow NO_3^-(aq) \quad (7.W9)$$

Step 4: Balance the oxygen atoms by adding H_2O molecules where needed.

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \quad (7.W10)$$

$$HNO_2(aq) + H_2O(l) \rightarrow NO_3^-(aq) \quad (7.W11)$$

Step 5: Balance the hydrogen atoms by adding H^+ ions where needed.

$$14H^+ + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \quad (7.W12)$$

$$HNO_2(aq) + H_2O(l) \rightarrow NO_3^-(aq) + 3H^+(aq) \quad (7.W13)$$

Step 6: Balance the charge by adding electrons, e^-.

$$6e^- + 14H^+ + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \quad (7.W14)$$

$$HNO_2(aq) + H_2O(l) \rightarrow NO_3^-(aq) + 3H^+(aq) + 2e^- \quad (7.W15)$$

Step 7: If the number of electrons lost in the oxidation half-reaction is not equal to the number of electrons gained in the reduction half-reaction, multiply one or both of the half-cell reactions by the lowest number that will make the number of electrons gained equal to the number of electrons lost.

$$6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \quad (7.W16)$$

$$3HNO_2(aq) + 3H_2O(l) \rightarrow 3NO_3^-(aq) + 9H^+(aq) + 6e^- \quad (7.W17)$$

Step 8: Add the two half-cell reactions as if they were mathematical equations. The electrons will always cancel. If the same molecules or ions occur on the product side, combine them. Do the same for the reactant side. If any molecules or ions occur on both the product and reactant sides, cancel them such that you have eliminated the molecule or ion from the side with the least amount.

$$6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) + 3HNO_2(aq) + 3H_2O(l) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3NO_3^-(aq) + 9H^+(aq) + 6e^- \quad (7.W18)$$

$$5H^+(aq) + Cr_2O_7^{2-}(aq) + 3HNO_2(aq) \rightarrow 2Cr^{3+}(aq) + 4H_2O(l) + 3NO_3^-(aq) \quad (7.W19)$$

Step 9: Check to make sure that the atoms and the charges in the reactants balance those in the products.

Basic Solutions

Because of the high pH of seawater, many redox reactions can be considered to proceed in the presence of a base. In this case, the steps used to balance the half-cell reactions would include $H_2O(l)$ and $OH^-(aq)$ rather than $H_2O(l)$ and $H^+(aq)$.

Balancing by Change in Oxidation Number

If the redox reaction is too complicated to be balanced by the inspection method just outlined, the following stepwise approach can be used. To illustrate, we return to the chromate example in which you are given the identities of the reactants and products and are told that the reaction proceeds under acidic conditions. Start with the skeleton reaction given in Eq. 7.W5.

Step 1: Determine the oxidation numbers for each atom. Use them to identify the oxidation and reduction half-cell reactions. Note that the oxidation number of O is −II in each of the oxygen-containing molecules, so O does not undergo any change in oxidation state during this reaction. In this example, Cr is being reduced and N oxidized.

$$\text{Reduction:} \quad Cr_2(VI)O_7^{2-}(aq) \rightarrow Cr^{3+}(III)(aq) \tag{7.W20}$$

$$\text{Oxidation:} \quad HN(III)O_2(aq) \rightarrow N(V)O_3^-(aq) \tag{7.W21}$$

Step 2: Determine the net increase in oxidation number for the element being oxidized and the net decrease in oxidation number for the element undergoing reduction.

$$Cr_2(VI)O_7^{2-}(aq) \rightarrow Cr^{3+}(III)(aq) \quad \text{Net decrease} = 6 - 3 = +3 \tag{7.W22}$$

$$HN(III)O_2(aq) \rightarrow N(V)O_3^-(aq) \quad \text{Net increase} = 3 - 5 = -2 \tag{7.W23}$$

Step 3: Determine the ratio of reductant to oxidant atoms that will make the number of electrons lost equal to the number of electrons gained. (This ratio will determine the stoichiometric coefficient to be applied to the reactant atoms.) In this example, N is the reductant and its oxidation produces 2 electrons because only 1 N atom is present in each molecule of nitrous oxide gas. Cr is the oxidant and its reduction requires a gain of 6 electrons because 2 Cr atoms are present in each molecule of chromate ion. Thus, the stoichiometric ratio of reductant to oxidant that should be applied to the reactant atoms is $6:2 = 3:1$.

Step 4: Apply the stoichiometric ratio to the reactants that contain the atoms undergoing changes in their oxidation number. Then balance the products.

$$1Cr_2O_7^{2-}(aq) + 3HNO_2(aq) \rightarrow 2Cr^{3+}(aq) + 3NO_3^-(aq) \tag{7.W24}$$

Step 5: Add $H_2O(l)$ to balance the O atoms and then $H^+(aq)$ to balance the H atoms.

$$5H^+(aq) + Cr_2O_7^{2-}(aq) + 3HNO_2(aq) \rightarrow 2Cr^{3+}(aq) + 4H_2O(l) + 3NO_3^-(aq) \tag{7.W25}$$

Step 6: Check to make sure that the atoms and the charges in the reactants balance those in the products.

Sometimes you are presented with a group of chemicals for which you wish to write a full-balanced redox reaction that proceeds spontaneously. To determine which of the chemicals are the reactants and which are products requires an assessment of their relative electron affinities. The procedure for doing this is presented next.