SCIENCE 1110 CHEMISTRY REVIEW

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Harrisonburg, Virginia 22802 Tel. 1-540-434-0768 Redox equilibriums. A typical oxidation-reduction can be represented in symbol form:

$$Zn_{(s)} + Cu^{+2} + SO_4^{-2}$$
. $\Longrightarrow Zn^{+2} + Cu_{(s)} + SO_4^{-2}$

What is the net ionic equation?

$$(Zn + Cu^{+2} \Longrightarrow Zn^{+2} + Cu)$$

Any change in ion charge depends upon the transfer of electrons. For example, sodium is readily changed to form positive sodium ions. Na \longrightarrow Na $^+$ + e. We can generalize this equation for any metal by writing: $M \longrightarrow M^+$ + Ne; N represents the number of electrons lost by each metal atom. This type of electron change is called *oxidation*. In an *oxidation system* the atoms show an algebraic increase in ion charge

(becomes more positive). Oxidation causes a loss of these electrons.

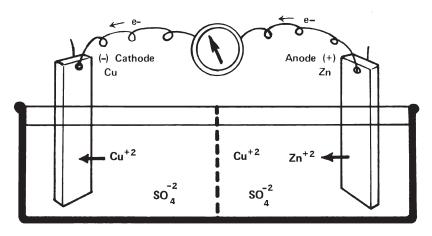
Look closely at the Zn as a reactant and then as a product. It follows a reaction that can be represented as $Zn^0_{(s)} \longrightarrow Zn^{*2} + 2e^-$. For the zinc atom to take on a +2 charge, two electrons must have been removed.

The opposite process of electron transfer is called *reduction*. Some examples of reduction are shown by the following reactions:

$$S + 2 \xrightarrow{e} \longrightarrow S^{-2}$$
; $2 \xrightarrow{H^+} + 2 \xrightarrow{e} \longrightarrow H_2$.

A reduction system requires that atoms show an algebraic decrease in ion charge. This decrease results in a gain of electrons.

Look closely at the reaction $Cu^{-2} \longrightarrow Cu_{(s)}$. For this charge to occur, two electrons must have been added to the Cu^{-2} ion: $Cu^{-2} + 2e^{-} \longrightarrow Cu^{0}_{(s)}$.



Take a close look at what happens in an electrochemical cell. The term electrochemical implies that we are converting chemical energy into electrical energy. Look again at the Zn-Cu⁺² system. At the zinc electrode, electrons are released; and oxidation occurs. The electrode, where oxidation occurs is called the anode. Electrons are gained at the copper electrode and reduction occurs. The electrode at which reduction occurs is called the cathode. As electrons leave the cell from the anode, positively charged Zn⁻² ions are produced. Negative charge is leaving and positive charge is being produced. Electrical neutrality is maintained. Because negative ions always drift toward the anode, they are called anions. Since positive ions drift away from the anode toward the cathode, they are called cations. The Zn-2 ion drifts away into solution but electrons remain in the zinc electrode. They move up the zinc electrode through the wire and enter the

copper cathode. At the surface of the rod, the electrons encounter Cu^{*2} ions in solution. The electrons react with the Cu^{*2} to give neutral copper atoms, which remain on the rod as copper metal. To write separate "half-reaction" equations for the two separate processes is often convenient: (1) $Zn^0 \longrightarrow Zn^{*2} + 2$ e-(oxidation); (2) $Cu^{*2} + 2$ e- $\longrightarrow Cu^0$ (reduction). The net reaction (3) is found by adding the two half-reactants.

(1)
$$Zn^0 \longrightarrow Zn^{*2} + 2 e^-$$

(2) $Cu^{*2} + 2 e^- \longrightarrow Cu^0$

(1) + (2) = (3)
$$Zn^0 + Cu^{+2} \longrightarrow Zn^{-2} + Cu^0$$

Notice that the electrons on each side of the equation cancel. If they do not cancel in the half-reactions, as in the Cu⁰-Ag⁺ reaction, we must first balance the electrons and then add the half-reactions:

$$Cu^0 \longrightarrow Cu^{\cdot 2} + 2 e^{-}$$

 $Ag^{\cdot} + e^{-} \longrightarrow Ag^{0}$ (INCORRECT)

$$Cu^{0} \longrightarrow Cu^{+2} + 2 e^{-}$$

$$2 Ag^{+} + 2 e^{-} \longrightarrow 2 Ag^{0} \qquad (CORRECT)$$

Later in the section you will review how the balancing of electrons will enable you to write balanced equations for more difficult reactions.

To have a table in which the reactants are arranged in the order of their tendency to undergo oxidation (or reduction) would be convenient so that we might predict whether a reaction will actually occur if the two substances are placed together. Such a table is known as an oxidation-reduction potential series. It is a series of half-reactions written so that the reaction to the right is an oxidation and the reaction to the left is a reduction. A reaction occurs spontaneously if the oxidation half-

reaction is higher on the series than the reduction half-reaction.

Since we are comparing the half-reactions, we must have a reference. Therefore, chemists have assigned the half-reaction, $H_{2(g)} \longrightarrow 2 H^+ + 2 e^-$, an E^0 value of 0.00 volts. All other half-reactions are then measured against the standard hydrogen half-reaction.

Referring to the half-reaction pairs, the half-reactions (one as an oxidation, one as the reduction) and the equations for the net reactions can be determined. Be sure to balance electrons. List the E⁰ value at the end of the half-reaction. When you reverse the half-reaction as written, you reverse the sign of the E⁰ value listed. For example, let us consider a Cu⁰-Ag cell. The half-reactions would be

$$Cu^0 \longrightarrow Cu^{+2} + 2 e^ E^0 = -.34 \text{ volts}$$

 $Ag^{+1} + e^- \longrightarrow Ag^0$ $E^0 = +.80 \text{ volts}$

Balance the electrons (this half-reaction does not affect E⁰).

$$E_{3} = E_{1} + E_{2}$$

$$E_{3} = Cu^{0} + 2 Ag^{+} + 2 e^{-} + 2 Ag^{0}$$

$$E_{3} = Cu^{0} + 2 Ag^{+} + 2 Ag^{0}$$

$$E_{4} = Cu^{0} + 2 Ag^{+} + 2 Ag^{0}$$

$$E_{5} = -.34 \text{ volts}$$

$$E_{6} = -.34 \text{ volts}$$

$$E_{7} = +.80 \text{ volts}$$

$$E_{8} = -.34 \text{ volts}$$

The sign (+ or -) implies the direction the reaction proceeds.

We are now ready to turn our attention away from oxidation potentials and to take a look at the bookkeeping of electrochemical reactions. Oxidation numbers are arbitrary numbers assigned to an atom within a molecule. These numbers are useful in balancing complex equations.

Just as rules are needed in bookkeeping for procedures to follow, a chemist needs a few rules to assist him in his accounting of electron charge. The following rules will assist you in assigning oxidation numbers to various atoms.

- 1. The oxidation number of a monatomic ion is equal to the charge on the ion: for example. Na+ (Group 1), Mg⁺² (Group 2), and so on.
- 2. The oxidation number of any substance in its atomic state is zero.
- 3. The oxidation number of hydrogen in a compound is +1.
- 4. The oxidation number of oxygen in a compound is -2 (except in O2, O3, and in peroxides).
- 5. Other oxidation numbers are assigned so that the sum of charges is zero.
- 6. The Laws of Conservation of Charge and Atoms must be followed.
- 7. The halogens (F, CI, Br, I) are assigned an oxidation number of -1.

Example:
$$K_3PO_4$$
 $K = +1$ (Rule 1) 3 $K^{+1} = +3$ Therefore, $O = -2$ (Rule 4) $O^{-2} = -8$ $P = +5$ (Rule 6)

We can apply oxidation numbers to balancing equations. For example, in the following equation we can assign oxidation numbers:

$$+1-2$$
 0 $+4-2 + 1-2$
 $H_2S + O_2 \longrightarrow SO_2 + H_2O$

We see that S⁻² goes to S⁺⁴ (oxidation) and that O₂ goes to 2 O-2 (reduction). Six electrons are involved in the oxidation; and four electrons, in reduction. The half-reactions for the oxidation and reduction can be written:

oxidation:
$$S^{-2} \longrightarrow S^{+4} + 6e^{-}$$

reduction: $O_2^0 + 4 e^{-} \longrightarrow 2 O^{-2}$

The oxidizing agent is the compound that accepts electrons. A reducing agent is any compound or ion that donates electrons.

The electrons are balanced; and the halfreactions are rewritten showing the proper mole ratios:

oxidation:

$$2(S^{-2} \longrightarrow S^{-4} + 6 e^{-}) = 2 S^{-2} \longrightarrow 2 S^{+4} + 12 e^{-}$$
 reduction:

$$3(O_2 + 4 e^- \longrightarrow 2 O^{-2}) = 3 O_2 + 12 e^- \longrightarrow 6 O^{-2}.$$

The final step is to transfer these mole ratios to the original equation and to make any necessary adjustments in order to conserve the atoms. The completed balanced equation is written:

$$2 H_2S + 3 O_2 \longrightarrow 2 SO_2 + 2H_2O.$$

Complete these activities.

- 2.71 Test your understanding by assigning oxidation numbers to each element in these compounds. Write the oxidation number for each atom.
 - a. N₂O
- ____ d. CO
- ____ g. N₂O₅
- _____ i. CO₂

____ k. C(diamond)

- b. H₂SO₄
- ____ e. NO
- _____ h. KMnO₄ _____ j. N₂O₄
- ____ f. MnO₂

- c. KCI

Complete these activities.

2.72 Balance the following redox equations by the use of oxidation numbers.

a.
$$KmnO_4 + H_2S + HCI \Longrightarrow KCI + MnCl_2 + H_2O + S$$

b. $HBr + H_2SO_4 \Longrightarrow SO_2 + Br_2 + H_2O$