ChemActivity 48

Redox Reactions

(Where Have All the Electrons Gone?)

Model 1: The Chemical Reaction of Zn(s) and Cu $^{2+}$(aq).

When a bar of zinc is placed in a 1.0 M copper(II) nitrate solution and left to stand for a while, solid copper is seen to deposit on the zinc bar, and some Zn^{2+} ions are found in solution. When equilibrium is reached in this system, essentially all of the copper ions have been plated out as solid copper (assuming that Cu^{2+} is the limiting reagent). Reactions such as this involve an explicit transfer of electrons between chemical species and are known as **oxidation-reduction**, or **redox**, reactions.

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s) \qquad (1)$$

Critical Thinking Questions

1. Identify the reactant in equation (1) that:

   a) loses electrons

   b) gains electrons

2. How many electrons are transferred when:

   a) one Zn atom reacts with one Cu^{2+} ion?

   b) one mole of Zn reacts with one mole of Cu^{2+}?

3. a) Write the equilibrium expression, K, for reaction (1).

   b) Estimate $[Zn^{2+}]$ and $[Cu^{2+}]$ at equilibrium (according to the information given in Model 1).

   c) Which of the following best describes K for this reaction? $K << 1$, $K < 1$, $K = 1$, $K > 1$, $K >> 1$

Information

In oxidation-reduction reactions the species that loses electrons is said to be **oxidized**, and the species that gains electrons is said to be **reduced**. The oxidized species is often referred to as the **reducing agent**. The substance that is reduced is referred to as the **oxidizing agent**.

Critical Thinking Questions

4. a) Which species is oxidized in equation (1)?

   b) Which species is reduced in equation (1)?

5. a) Which species is the oxidizing agent in equation (1)?

   b) Which species is the reducing agent in equation (1)?

Model 2: Results of Placing Metal Bars in a Variety of Solutions at 25 °C.

Metal Bar	Ion Solution (1.0 M)	Concentration of Metal Ions at Equilibrium, M		*K*
Zn	Cu^{2+}	$[Cu^{2+}] \approx 0$	$[Zn^{2+}] \approx 1.0$	
Zn	K^{+}	$[K^{+}] \approx 1.0$	$[Zn^{2+}] \approx 0$	
Co	Ni^{2+}	$[Ni^{2+}] \approx 0.1$	$[Co^{2+}] \approx 0.9$	
Co	Cu^{2+}	$[Cu^{2+}] \approx 0$	$[Co^{2+}] \approx 1.0$	
Co	Cr^{3+}	$[Cr^{3+}] \approx 1.0$	$[Co^{2+}] \approx 0$	

The results were obtained with metal bars large enough so that the limiting reagent in any redox reaction with the solution was the ion in solution.

Critical Thinking Questions

6. For each of the five experiments described in Model 3, write the balanced chemical equation (no "e^-" appears in the balanced chemical equation) for the redox reaction that *could* occur between the metal bar and the ion in solution. Note that the same number of electrons must be lost and gained in the transfer process. In each case indicate the oxidizing agent and the reducing agent.

7. Fill in the "K" column in Model 2 by indicating whether K is >1, <1, or impossible to deduce from the data given.

8. Based on the data in the first two rows of Model 2, which do you think would be considered a stronger oxidizing agent, Cu^{2+} or K^+?

9. Based on the data in the last three rows of Model 2, rank the strength as oxidizing agents of the metal ions Ni^{2+}, Cu^{2+}, and Cr^{3+}.

10. If possible, rank the metal ions Ni^{2+}, Cu^{2+}, Cr^{3+}, and K^+ in terms of their strength as oxidizing agents. If this is not possible, rank as many as you can and propose an experiment (or series of experiments) that would enable you to complete the rankings.

Exercises

1. Identify the reducing agent and the oxidizing agent in each of the following reactions. All of these reactions have $K > 1$.

   a) $Br_2(aq) + Hg(s) \rightleftharpoons 2\,Br^-(aq) + Hg^{2+}(aq)$
   b) $2\,Co^{3+}(aq) + 2\,Br^-(aq) \rightleftharpoons Br_2(aq) + 2\,Co^{2+}(aq)$
   c) $Cl_2(aq) + 2\,Br^-(aq) \rightleftharpoons 2\,Cl^-(aq) + Br_2(aq)$
   d) $2\,H^+(aq) + Zn(s) \rightleftharpoons H_2(aq) + Zn^{2+}(aq)$
   e) $S_2O_8^{2-}(aq) + Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2\,SO_4^{2-}(aq)$
   f) $Au^{3+}(aq) + Fe(s) \rightleftharpoons Au(s) + Fe^{3+}(aq)$

2. Assume that all of the stoichiometric coefficients for the reactions in Ex. 1 represent molar quantities. How many electrons are transferred when each reaction takes place?

3. Indicate whether the following statement is true or false and explain your reasoning.

   Based on the data in Model 2, $Cu^{2+}(aq)$ is a stronger oxidizing agent than $Cr^{3+}(aq)$.A

Problem

1. Describe an experiment that would allow you to determine the relative strengths of zinc and nickel metals as reducing agents. Provide enough detail so that another student in your class could understand what to do, and also indicate what the observed results of the experiment would be. Make sure that you also indicate which of the two metals *is* the stronger reducing agent.

ChemActivity 49

Oxidation Numbers

Information

Oxidation numbers are an accounting system for electrons (Lewis structures and formal charge are also accounting systems for electrons). One of the main uses of oxidation numbers (but not the only use) is to locate the oxidized and reduced species in redox reactions. For example, the oxidized and reduced species are not obvious in the following reactions:

$$5\ Cr^{3+}(aq) + 3\ MnO_4^-(aq) + 8\ H_2O \rightleftharpoons 5\ CrO_4^{2-}(aq) + 3Mn^{2+}(aq) + 16\ H^+(aq) \quad (1)$$

$$2\ CuI(s) \rightleftharpoons Cu(s) + Cu^{2+}(aq) + 2\ I^-(aq) \quad (2)$$

In an oxidation-reduction reaction, the species that is oxidized undergoes an increase in oxidation number, and the species that is reduced undergoes a decrease in oxidation number.

For pure ionic substances, the oxidation number and the charge on the ion are often the same. In NaCl, for example, the oxidation number and the charge on the sodium is +1, and the oxidation number and the charge on the chlorine is –1. It is important to realize, however, that for covalent polar and nonpolar molecules, oxidation numbers have little relationship to the actual charges on the atoms within the molecule. In CH_4, for example, the oxidation number on the carbon is –4 and the oxidation number of each hydrogen is +1. We know, however, that the partial charge on the carbon atom is much closer to zero than it is to –4 because the difference in the electronegativities of carbon and hydrogen is small. (A MOPAC calculation yields: $\delta_C = -0.266$; $\delta_H = +0.066$.)

Model: Oxidation Number Conventions.

Oxidation numbers are often written above the atomic symbol.

$$\overset{+1}{H}\overset{+7}{Cl}\overset{-2}{O_4} \qquad \overset{0}{O_2} \qquad \overset{-4}{C}\overset{+1}{H_4}$$

Oxidation Numbers

- The oxidation number is 0 in any neutral substance that contains atoms of only one element. Aluminum foil, iron metal, and the H_2, O_2, O_3, P_4, and S_8 molecules all contain atoms that have an oxidation number of 0.
- The oxidation number is equal to the charge on the ion for ions that contain only a single atom. The oxidation number of the Na^{+1} ion, for example, is +1, whereas the oxidation number of Cl^- is –1.
- The oxidation number of hydrogen is +1 when it is combined with a *more electronegative element.* The oxidation number of hydrogen is +1 in the CH_4, NH_3, H_2O, and HCl molecules.

- The oxidation number of hydrogen is –1 when it is combined with a *less electronegative element*. The oxidation number of hydrogen is –1 in the LiH, NaH, CaH_2, and $LiAlH_4$ molecules.
- The elements of Groups IA and IIA form compounds in which the metal atoms have oxidation numbers of +1 and +2, respectively.
- Oxygen usually has an oxidation number of –2. Exceptions include molecules and polyatomic ions that contain O–O bonds: O_2, O_3, H_2O_2, and the O_2^{2-} ion.
- Elements in Group VIIA have an oxidation number of –1 when the atom is bonded to a less electronegative element. The oxidation number of each chlorine atom in CCl_4 is –1.
- The sum of the oxidation numbers of the atoms in a neutral substance is zero.
  H_2O (2 hydrogen)(+1) + (1 oxygen)(–2) = 0
- The sum of the oxidation numbers of the atoms in a polyatomic ion is equal to the charge on the ion.
  OH^- (1 hydrogen)(+1) + (1 oxygen)(–2) = –1
- The least electronegative element is assigned a positive oxidation state. Sulfur is assigned a positive oxidation state in SO_2 because it is less electronegative than oxygen.
  SO_2 (1 sulfur)(+4) + (2 oxygen)(–2) = 0

Oxidation Numbers for Organic Molecules

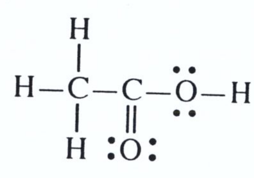
To assign oxidation numbers to atoms in organic molecules, we *treat* each bond as if it were an ionic bond and the electrons belonged to the more electronegative element. Then,

$$OX_a = G_a - V_a$$

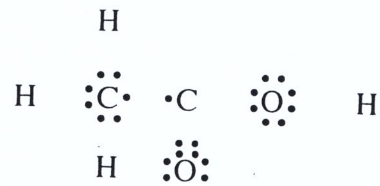
where OX_a is the oxidation number of atom "a", G_a is the group number of the atom, and V_a is the number of valence electrons assigned to the atom in the Lewis structure of the molecule.

Acetic acid is shown as an example:

Write Lewis structure



Assign electrons ionically



Calculate oxidation numbers

methyl C atom	OX = 4 – 7 = –3
carbonyl C atom	OX = 4 – 1 = +3
each H atom	OX = 1 – 0 = +1
each oxygen atom	OX = 6 – 8 = –2

Critical Thinking Questions

1. Which is the better representation of the actual charge on an atom in a molecule—the formal charge; the partial charge; the oxidation state? Why?

2. In which of the following are the oxidation number and the partial charge the same number? MgO ; CO_2 ; NaF ; H_2O ; CCl_4 ; $NiCl_2$.

3. Find the oxidation numbers of all atoms in equation (1)—on the left-hand side and on the right-hand side of the equation. Does any atom increase its oxidation number?

4. Is a species that has an atom for which there is an increase in oxidation number oxidized or reduced? Is that species the oxidizing agent or the reducing agent?

5. Which species in equation (1) is oxidized? Which species is reduced?

6. Which species in equation (2) is oxidized? Which species is reduced?

7. Describe, in grammatically correct English sentences, how one can determine whether or not a reaction is an oxidation-reduction reaction.

Exercises

1. Give the oxidation number for each atom in the following molecules: Br_2 ; $NaCl$; $CuCl_2$; CH_4 ; CO_2 ; $SiCl_4$; CCl_4 ; SCl_2 ; Br_2O.

2. Give the oxidation number for each atom in the following ions: Ni^{2+} ; NO_3^- ; CO_3^{2-}; SO_4^{2-} ; NH_4^+ ; ClO_4^- ; MnO_4^- ; CN^- ; IF_4^+ ; PO_4^{3-}.

3. Give the oxidation number for each atom in the following molecules: $NiCl_2$; HNO_3 ; Na_2CO_3 ; $Al_2(SO_4)_3$; NH_4Cl ; $KMnO_4$; KCN ; $HClO_4$.

4. Give the oxidation number for each atom in the following ions: HCO_3^- ; HSO_4^- ; $H_2PO_4^-$; NH_2^- ; $Cr_2O_7^{2-}$.

5. Give the oxidation number for each atom in the following molecules: CH_3OH ; CH_3CH_2OH ; H_2CCH_2 ; CH_3Cl ; CCl_4 .

6. Give the oxidation number of N and H in NH_3. What is the oxidation number of Cu in $Cu(NH_3)_4{}^{2+}$?

7. Give the oxidation number of O and H in OH^-. What is the oxidation number of Al in $Al(OH)_4{}^-$?

8. An oxidation number need not be an integer. Give the oxidation number for each atom in the following molecules: P_4O_7 ; P_4O_6 ; P_4O_8 ; P_4O_9 .

9. Which of the following are redox reactions?
   a) $3\ H_2(g) + N_2(g) \rightleftharpoons 2\ NH_3(g)$
   b) $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$
   c) $C(s) + O_2(g) \rightleftharpoons CO_2(g)$
   d) $H_2CCH_2(g) + H_2(g) \rightleftharpoons H_3CCH_3(g)$
   e) $3\ Cu(s) + 8\ H^+(aq) + 2\ NO_3^-(aq) \rightleftharpoons 3\ Cu^{2+}(aq) + 2\ NO(g) + 4\ H_2O$
   f) $H_2(g) + Cl_2(g) \rightleftharpoons 2\ HCl(g)$
   g) $Cu^{2+}(aq) + 4\ NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$

10. When natural gas (methane) burns, the chemical reaction is

$$CH_4(g) + 2\ O_2(g) \rightleftharpoons CO_2(g) + 2\ H_2O(g) \quad .$$

Is this an oxidation-reduction reaction?

11. When iron corrodes, the chemical reaction is

$$2\ Fe(s) + O_2(aq) + 2\ H_2O(\ell) \rightleftharpoons 2\ FeO{\bullet}H_2O(s) \quad .$$

Is this an oxidation-reduction reaction?

12. Plants convert carbon dioxide and water into carbohydrates and dioxygen by a series of reactions called photosynthesis. The overall chemical reaction is

$$6\ CO_2(g) + 6\ H_2O(\ell) \rightleftharpoons C_6H_{12}O_6(aq) + 6\ O_2(g)$$

Is this an oxidation-reduction reaction?

Problem

1. Give the oxidation number for the bromine atom in each of the species below, and then describe the relationship between the oxidation number on the bromine and the relative acidity of these compounds: $HOBrO_2$; $HOBr$; $HOBrO$.