Experiments

EXPERIMENT 5
Aqueous Reactions

5.1. Safety

Aqueous solutions containing ions of transition metals should **never** be poured down the drain. Instead, these solutions should be placed in an appropriate waste containers. Most of these metal salts are toxic in large doses and the effects are cumulative. Therefore, wash your hands with soap and water frequently during the laboratory and before leaving the laboratory. Acids, such as sulfuric acid, are corrosive and can easily burn the skin or burn holes in clothing. These solutions should be handled with care. You should wash your hands after handling bottles that contain aqueous acid solutions. If acid spills on your skin, flush with copious amounts of water. If acid spills on your clothing, remove the clothing and flush the skin with copious amounts of water. If the spill occurs at your workspace, inform the people around you of the spill and contact the instructor immediately.

Before Laboratory Questions

These questions should be used to help you write your notebook and should be answered in some form before you go to the laboratory.

(1) Before writing anything in your laboratory notebook, you need to read each of the experimental procedures very carefully. You need to plan your notebook before you begin to write this notebook.
(2) What is the purpose of these experiments?
(3) How do you plan to investigate precipitation reactions? decomposition reactions? oxidation/reducation reactions? activity? Answer each of these questions as a single if/then statement.
(4) What materials are required for this experiment? Are any chemicals needed? If so, what are they? Which materials must be obtained from the stockroom, which must be obtained from the instructor, and which are in your laboratory drawer?
(5) What are the steps for each experiment?
(6) For each reaction that you select (or perform), you should create an area to write your observations. These observations need to be readable by your laboratory instructor.

5.2. Introduction

In aqueous chemistry, a chemical reaction will in general occur if [1]

- **a precipitate (i.e., an insoluble salt) is formed from a mixture of soluble salts**,
- an acid/base reaction occurs to generate a salt and water,
- a weak electrolyte (i.e., an ionic compound that does not completely dissociate in water) is formed from a mixture of strong electrolytes (i.e., ionic compounds that completely dissociate in solution), or
- **a gas is formed from a mixture of reactants**.

Aqueous chemical reactions are generally classified into four broad categories: (i) **precipitation reactions**, (ii) acid/base reactions, (iii) **decomposition reactions**, and (iv) **oxidation/reducation reactions**. In a precipitation reaction, the ions of two aqueous salts react to form an insoluble salt and a different aqueous salt. Decomposition reactions occur when a compound breaks down to form simpler substances, such as when calcium carbonate decomposes into calcium oxide and carbon dioxide at high temperatures. Acid/base reactions will be covered in more detail in Experiment 7. In this experiment, we will focus on probing precipitation, decomposition and oxidation/reduction reactions that occur in aqueous solution.

A good example of a precipitation reaction is the reaction of aqueous sodium chloride with aqueous silver nitrate to yield aqueous sodium nitrate and solid silver chloride, or

$$\mathrm{NaCl}\,(aq) \;+\; \mathrm{AgNO_3}\,(aq) \;\rightarrow\; \mathrm{NaNO_3}\,(aq) \;+\; \mathrm{AgCl}\,(s)\;. \tag{5.1}$$

The chemical equation presented in eq. (5.1) is written as a *molecular equation*, which expresses all chemical formulas as neutral species. Another way to write eq. (5.1) is as an *ionic equation*, or

$$\begin{aligned}&\mathrm{Na^+}\,(aq) \;+\; \mathrm{Cl^-}\,(aq) \;+\; \mathrm{Ag^+}\,(aq) \;+\; \mathrm{NO_3^-}\,(aq)\\ &\qquad\qquad\rightarrow\; \mathrm{Na^+}\,(aq) \;+\; \mathrm{NO_3^-}\,(aq) \;+\; \mathrm{AgCl}\,(s)\;.\end{aligned} \tag{5.2}$$

Notice that the aqueous salts in eq. (5.1) are represented as dissociated cations (postive ions) and anions (negative ions) in eq. (5.2). However, the ionic compound AgCl (s) is not soluble in water and, therefore, cannot be written as $\mathrm{Ag^+}$ (aq) and $\mathrm{Cl^-}$ (aq). You should also notice that some of the ions in eq. (5.2) appear on both sides of the equation and do not participate in the reaction. These ions are spectator ions and can be eliminated from the ionic equation. Thus, the *net ionic equation*, which is the ionic equation generated after all spectator ions have been removed, is

$$\mathrm{Cl^-}\,(aq) \;+\; \mathrm{Ag^+}\,(aq) \;\rightarrow\; \mathrm{AgCl}\,(s)\;. \tag{5.3}$$

In aqueous solution, a chemical reaction occurs only if a net ionic equation can be written for the system in question. The formation of a precipitate is strongly driven by the lattice energy of the ionic salt, where lattice energy is defined as the interaction energy between ions in the solid salt. If the lattice energy is large, then the interaction of water with the individual ions in the salt will not be large enough to overcome the lattice energy and, therefore, the compound will not dissolve in water. In this experiment, you will use qualitative observations to develop guidelines for salt solubility.

However, sometimes the reaction of aqueous ions leads to the formation of a compound that is unstable. In this instance, the compound will decompose into other compounds. A good example of such a decomposition reaction is the reaction of aqueous bisulfite with a concentrated acid to give water and sulfur dioxide, or

$$\mathrm{HSO_3^-}\,(aq) \;+\; \mathrm{H^+}\,(aq) \;\rightarrow\; \mathrm{H_2SO_3}\,(aq) \;\rightarrow\; \mathrm{H_2O}\,(l) \;+\; \mathrm{SO_2}\,(g)\;. \tag{5.4}$$

The reaction in eq. (5.4) occurs because H_2SO_3 is an unstable aqueous acid. You will also investigate reactions that lead to the generation of gases.

Finally, some reactions occur by the exchange of electrons between ions in solutions. These reactions, which have been previously encountered in Experiment 4, are called oxidation/reduction reactions. The reactant that is gaining electrons is being reduced and is called the *oxidizing agent* (or *oxidant*), while the reactant that is losing electrons is being *oxidized* and is known as the *reducing agent* (or *reductant*). In this experiment, you will probe simple aqueous oxidation/reduction reactions.

5.3. Precipitation and decomposition reactions

In the previous experiments, you were given chemical reactions that had been mass and charge balanced. However, you should develop a habit of checking to verify that all reactions are charge and mass balanced before using these equations to work stoichiometry problems. If the chemical reaction is **not** balanced, you should first balance it by adjusting the coefficients in front of each of the chemical formulas in the reaction. When balancing a chemical reaction, the mole ratio of various compounds in the reaction can be adjusted to mass and charge balance the reaction. The formula of a compound does not change during the balancing of the reaction. Therefore, do not change atomic symbols or subscripts in chemical formulas. Some basic guidelines for balancing precipitation and decomposition reactions are [1]

- Balance atoms other than H and O first.
- Elements should be balanced last.
- Balance as a group those polyatomic ions that appear unchanged on both sides of the arrow.

As an example, let us balance the reaction of aqueous ammonium phosphate with aqueous sodium hydroxide to generate aqueous sodium phosphate, ammonia gas and water. Initially, we need to write the unbalanced reaction, or

$$\mathrm{(NH_4)_3PO_4}\ (aq)\ +\ \mathrm{NaOH}\ (aq)\ \rightarrow\ \mathrm{Na_3PO_4}\ (aq)\ +\ \mathrm{NH_3}\ (g)\ +\ \mathrm{H_2O}\ (l)\ .$$

Notice that we have 3 moles of Na on the right hand side (RHS) of the equation and, therefore, need 3 moles of Na on the left hand side (LHS) of the equation to mass balance sodium. This gives

$$\mathrm{(NH_4)_3PO_4}\ (aq)\ +\ 3\,\mathrm{NaOH}\ (aq)\ \rightarrow\ \mathrm{Na_3PO_4}\ (aq)\ +\ \mathrm{NH_3}\ (g)\ +\ \mathrm{H_2O}\ (l)\ .$$

We also have 3 moles of nitrogen on the LHS, which implies that we need to place a 3 in front of NH_3 to give

$$\mathrm{(NH_4)_3PO_4}\ (aq)\ +\ 3\,\mathrm{NaOH}\ (aq)\ \rightarrow\ \mathrm{Na_3PO_4}\ (aq)\ +\ 3\,\mathrm{NH_3}\ (g)\ +\ \mathrm{H_2O}\ (l)\ .$$

Finally, we notice that the PO_4^{3-} functions as a single unit as polyatomic anions will do, remaining unchanged on both sides of the equation. However, we have three other oxygen atoms from the NaOH on the LHS and, therefore, need to place a 3 in front of H_2O. When we do this, we will have a total of 15 hydrogens on the LHS of the equation and 15 hydrogens on the RHS of the equation. Therefore, the final balanced reaction equation is

$$\mathrm{(NH_4)_3PO_4}\ (aq)\ +\ 3\,\mathrm{NaOH}\ (aq)\ \rightarrow\ \mathrm{Na_3PO_4}\ (aq)\ +\ 3\,\mathrm{NH_3}\ (g)\ +\ 3\,\mathrm{H_2O}\ (l)\ .$$

5.4. Oxidation/reduction reactions

Unlike precipitation and decomposition reactions, oxidation/reduction reactions are not easily balanced by inspection because of the changing ionic charge on the species in solution. Therefore, before an oxidation/reduction reaction can be balanced, the oxidation number of each species in solution must be determined.

5.4.1. Oxidation numbers

The following guidelines can be used to assign oxidation numbers [1].

(1) All elements have an oxidation number of zero. For example, the oxidation number for each oxygen in O_2 is 0.
(2) The oxidation number of a monatomic ion is equal to the charge on the ion.
(3) The oxidation number of oxygen in oxides is -2. In peroxides (i.e., compounds with O_2^{2-}), the oxidation number on each oxygen is -1. In superoxides, the oxidation number on each oxygen is +1.
(4) The oxidation number of hydrogen is +1, except when hydrogen is bonded to a metal as a negative ion. Thus, the hydrogen in H_2O has an oxidation number of +1, while that in NaH has an oxidation number of -1.
(5) When halogens (i.e., elements in the column to the left of the perfect gases, which are in the farthest right column of the periodic table) are negative ions in an ionic compound, they have an oxidation number of -1.
(6) In a neutral molecule, the sum of the oxidation numbers of all of the atoms must be zero.
(7) In a polyatomic ion, the sum of the oxidation numbers of all the elements in the ion must be equal to the net charge on the ion.

As an example, the oxidation numbers for each atom in $Ca(VO_3)_2$ can be assigned as follows:

- Calcium is an alkaline earth metal. Therefore, as per guideline (4), the oxidation number on calcium is +2.
- Oxygen is not in a peroxide configuration. Thus, as per guideline (6), the oxidation number of oxygen is -2.
- Finally, guideline (9) states that the sum of the oxidation numbers of all atoms in the compound must be zero. Therefore, $1\times{+2}$ (Ca) + $6\times{-2}$ (O) + $2\,x$ (V) $=$ 0, which implies that V has an oxidation number of +5.

5.4.2. Balancing Oxidation/Reduction Reactions

With the definition of oxidation numbers, we can know define an *oxidation* as an increase in oxidation number, while *reduction* is a decrease in oxidation number. Therefore, an oxidation/reduction (redox) reaction is a chemical reaction that leads to changes in the oxidation numbers of two reactants. To balance a redox reaction, you must balance both mass and charge.

We will use an example to illustrate each step of balancing a redox reaction. This example is the reaction of hydrogen arsenite with potassium dichromate in hydrochloric acid to give hydrogen arsenate and chromium(III) chloride, or

$$H_3AsO_3\ (aq) + K_2Cr_2O_7\ (aq) + HCl\ (aq) \rightarrow H_3AsO_4\ (aq) + CrCl_3\ (aq) + KCl\ (aq)\ .$$

We should note, here, that hydrogen arsenite and hydrogen arsenate are weak acids and, therefore, do not completely dissociate in solution. The steps to mass and charge balance the above reaction are below.

(1) Write the ionic reaction equation. Ignore strong acids, since these will provide H^+ in a future step.

    Thus,

$$H_3AsO_3\ (aq) + Cr_2O_7^{2-}\ (aq) \rightarrow H_3AsO_4\ (aq) + Cr^{3+}\ (aq)\ .$$

(2) Determine the oxidation numbers for each compound in the chemical reaction equation.

For example,

- H_3AsO_3: H has an oxidation number of +1. O has an oxidation number of -2. As has an oxidation number of +3.
- $Cr_2O_7^{2-}$: O has an oxidation number of -2. Cr has an oxidation number of +6.
- H_3AsO_4: H has an oxidation number of +1. O has an oxidation number of -2. As has an oxidation number of +5.
- Cr^{3+}: Cr has an oxidation number of +3.

(3) Divide the ionic reaction equation into half reactions with one half reaction being defined by a decrease of the oxidation number from reactant to product and the other defined by an increase of oxidation number form reactant to product.

Thus,

$$\begin{gathered} H_3AsO_3\ (aq) \rightarrow H_3AsO_4\ (aq) \\ Cr_2O_7^{2-}\ (aq) \rightarrow Cr^{3+}\ (aq) \end{gathered}$$

(4) Mass balance the atoms that are under going the change in oxidation state.

Thus, in the half reaction involving As, the As is undergoing a change in oxidation number. There is one As atom on the left hand side (LHS) of the equation and one As atom on the right hand side (RHS) of the equation. Thus, As is mass balanced. For the reaction involving the change in oxidation number of Cr, there are two Cr atoms on the LHS and one Cr atom on the RHS. To mass balance the Cr requires a stoichiometric coefficient of 2 on the RHS, or

$$Cr_2O_7^{2-}\ (aq) \rightarrow 2\ Cr^{3+}\ (aq)$$

(5) Balance the number of oxygens on each side of each half-reaction equation using water.

For the example chosen above, we would obtain

$$\begin{gathered} H_2O\ (l) + H_3AsO_3\ (aq) \rightarrow H_3AsO_4\ (aq) \\ Cr_2O_7^{2-}\ (aq) \rightarrow 2\ Cr^{3+}\ (aq) + 7\ H_2O\ (l)\ . \end{gathered}$$

(6) Now balance the number of hydrogens on each side of each half-reaction equation using H^+.

For the example chosen above, we would obtain

$$\begin{gathered} H_2O\ (l) + H_3AsO_3\ (aq) \rightarrow H_3AsO_4\ (aq) + 2\ H^+\ (aq) \\ 14\ H^+\ (aq) + Cr_2O_7^{2-}\ (aq) \rightarrow 2\ Cr^{3+}\ (aq) + 7\ H_2O\ (l)\ . \end{gathered}$$

(7) Charge balance both half-reactions by using electrons e^-, with each electron giving a negative one charge.

For the example chosen, we have zero charge on the LHS of the arsenate reaction, but a +2 charge on the RHS of the reaction. Therefore, we need two electrons on the RHS of the reaction to cancel the +2 charge. Thus, we would obtain

$$H_2O\ (l) + H_3AsO_3\ (aq) \rightarrow H_3AsO_4\ (aq) + 2\ H^+\ (aq) + 2\ e^-$$

for the arsenate reaction. Since the arsenite ion is losing electrons to become arsenate, this reaction is the **oxidation half-reaction** and arsenite is the reducing agent. Similarly, we have a net charge of +12 on the LHS of the dichromate reaction and a net charge of +6 on the RHS of this same reaction. To achieve charge balance, we would need to add 6 electrons on the LHS of the reaction. Therefore, the chromate half-reaction becomes

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

The dichromate ion is gaining electrons in the process of decomposing to become the chromium (III) cation. Thus, this half-reaction is the **reduction half-reaction** and dichromate is the oxidizing agent.

(8) Make the number of electrons gained in one half-reaction equal to the number of electrons lost in the other half-reaction by multiplying all of the coefficients in each half-reaction by integers.

In our example, the oxidation half-reaction involves 2 e^-, while the reduction half-reaction involves 6 e^-. Therefore, we need to multiply all of the stoichiometry coefficients in the oxidation half-reaction by 3. This gives

$$3\ H_2O\ (l) + 3\ H_3AsO_3\ (aq) \rightarrow 3\ H_3AsO_4\ (aq) + 6\ e^- + 6\ H^+\ (aq)$$
$$14\ H^+\ (aq) + 6\ e^- + Cr_2O_7^{2-}\ (aq) \rightarrow 2\ Cr^{3+}\ (aq) + 7\ H_2O\ (l)\ .$$

(9) Now, add the two half-reactions.

In our example, we would obtain

$$\begin{aligned}&3\ H_2O\ (l) + 3\ H_3AsO_3\ (aq) + 14\ H^+\ (aq) + 6\ e^- + Cr_2O_7^{2-}\ (aq)\\ &\quad\rightarrow 3\ H_3AsO_4\ (aq) + 6\ e^- + 6\ H^+\ (aq) + 2\ Cr^{3+}\ (aq) + 7\ H_2O\ (l)\ .\end{aligned}$$

(10) Just like any algebraic equation, like terms can be collected and items can be moved to either side of the equation by adding (or subtracting) the item on each side of the equation. However, unlike standard algebraic equation, we cannot have negative stoichiometric coefficients in the final equation.

In our example, we would obtain

$$\begin{aligned}&3\ H_3AsO_3\ (aq) + 14\ H^+\ (aq) \text{ - } 6\ H^+\ (aq) + 6\ e^- \text{ - } 6\ e^- + Cr_2O_7^{2-}\ (aq)\\ &\quad\rightarrow 3\ H_3AsO_4\ (aq) + 2\ Cr^{3+}\ (aq) + 7\ H_2O\ (l) \text{ - } 3\ H_2O\ (l)\ ,\end{aligned}$$

which simplifies to a balanced net ionic equation of

$$\begin{aligned}&3\ H_3AsO_3\ (aq) + 8\ H^+\ (aq) + Cr_2O_7^{2-}\ (aq)\\ &\quad\rightarrow 3\ H_3AsO_4\ (aq) + 2\ Cr^{3+}\ (aq) + 4\ H_2O\ (l)\ .\end{aligned}$$

(11) Finally, place the spectator ions back into the equation.

In our example, the acid is aqueous hydrochloric acid and, therefore, the H^+ should be replaced with HCl (*aq*). The dichromate anion comes from potassium dichromate, so $Cr_2O_7^{-2}$ becomes $K_2Cr_2O_7$. Finally, the Cr^{3+} cation will interact with the spectator Cl^- anions creating $CrCl_3$ (*aq*). Finally, the two moles of K^+ from the potassium dichromate on the LHS are balanced by two moles of KCl on the RHS. Thus, the final balanced equation is

$$\begin{aligned}&3\ H_3AsO_3\ (aq) + K_2Cr_2O_7\ (aq) + 8\ HCl\ (aq)\\ &\quad\rightarrow 3\ H_3AsO_4\ (aq) + 2\ CrCl_3\ (aq) + 2\ KCl\ (aq)\ .\end{aligned}$$

The above reaction occurred in an acidic solution and, therefore, was balanced assuming acidic conditions. However, sometimes an oxidation/reduction reaction is more favored in a basic solution. In terms of balancing a redox reaction within a basic solution, the chemical reaction equation is first balanced as if the solution is acidic [i.e., following steps (1) - (10)]. Then, OH^- is added to both sides of the chemical reaction equation at the stoichiometric amount necessary to neutralize the acid. As an example, 8 moles of OH^- would be added to both sides of the above reaction to neutralize the 8 moles of H^+ on the LHS of the equation. This gives

$$\begin{aligned}&8\ OH^-\ (aq) + 3\ H_3AsO_3\ (aq) + 8\ H^+\ (aq) + Cr_2O_7^{2-}\ (aq)\\ &\quad\rightarrow 3\ H_3AsO_4\ (aq) + 2\ Cr^{3+}\ (aq) + 4\ H_2O\ (l) + 8\ OH^-\ (aq).\end{aligned}$$

The neutralization reaction between OH^- and H^+ gives H_2O, thus the above reaction can be rearranged and simplified to become

$$\begin{aligned}&4\ H_2O\ (l) + 3\ H_3AsO_3\ (aq) + Cr_2O_7^{2-}\ (aq)\\ &\quad\rightarrow 3\ H_3AsO_4\ (aq) + 2\ Cr^{3+}\ (aq) + 8\ OH^-\ (aq)\ .\end{aligned}$$

Because of solubility rules, which state that $Cr(OH)_3$ will be insoluble in aqueous solution and assuming that the base is potassium hydroxide, we can write a chemical equation of

$$\begin{aligned}&4\ H_2O\ (l) + 3\ H_3AsO_3\ (aq) + K_2Cr_2O_7\ (aq)\\ &\quad\rightarrow 3\ H_3AsO_4\ (aq) + 2\ Cr(OH)_3\ (s) + 2\ KOH\ (aq)\quad ,\end{aligned}$$

for the reaction between arsenous acid and potassium dichromate in a basic environment. The solubility rules are given in the Additional Information section at the end of the manual.

5.5. Experiment 5A. Precipitation reactions

Use small test tubes for all reactions performed during this experiment. All solutions have a concentration of 0.1 M, unless otherwise specified. Procedures for all reactions are listed below:

(1) Place 1 mL of Solution A into a clean test tube.
(2) Add approximately 1 mL of Solution B to Solution A.
(3) Record your observations in your laboratory notebook.
(4) Test the results using a second reaction that you develop using the list of reagents available in the laboratory.

For example, let us consider a possible reaction where Solution A is mercury(II) nitrate and Solution B is potassium iodide. When Solution B is added to Solution A, we obtain a red-orange precipitate, which settles to the bottom of the test tube, and a colorless solution. We know that the red-orange precipitate cannot be mercury(II) nitrate or potassium iodide. Therefore, the precipitate must be either mercury(II) iodide or potassium nitrate. We can determine whether the precipitate is mercury(II) iodide or potassium nitrate by performing a second reaction. If the precipitate is potassium nitrate, we should obtain the same red-orange precipitate by reacting sodium nitrate with potassium iodide. However, when sodium nitrate is mixed with potassium iodide, no precipitate forms. Therefore, we can conclude the the precipitate formed from the reaction of mercury(II) nitrate and potassium iodide must be mercury(II) iodide. Similarly, we could have chosen to test the initial reaction by mixing sodium iodide with mercury(II) nitrate. In this instance, we would have observed the formation of the same red-orange precipitate, indicative of the red-orange precipitate being mercury(II) iodide.

You should select five reactions from the list below and perform these reactions. Each reaction should involve at least two different anions or cations from previous reactions. (For example, you cannot do Reaction 1 and Reaction 2, since three of the four ions are common to the two reactions.) You must show your list of reactions to your instructor for approval before you start the experiment. Once you have performed the initial five reactions, you should develop a set of test reactions. The test reactions should also be shown to the laboratory instructor for approval before being performed. All observations should be recorded in your laboratory notebook.

Possible precipitation reactions:

- Reaction A1. Solution A: Potassium (or sodium) iodide. Solution B: Lead(II) nitrate.
- Reaction A2. Solution A: Potassium (or sodium) chloride. Solution B: Lead(II) nitrate.
- Reaction A3. Solution A: Potassium (or sodium) iodide. Solution B: Silver nitrate.
- Reaction A4. Solution A: Potassium (or sodium) chloride. Solution B: Silver nitrate.

- Reaction A5. Solution A: Potassium (or sodium) iodide. Solution B: Barium nitrate.
- Reaction A6. Solution A: Potassium (or sodium) chloride. Solution B: Barium nitrate.
- Reaction A7. Solution A: Potassium (or sodium) iodide. Solution B: Calcium nitrate.
- Reaction A8. Solution A: Potassium (or sodium) chloride. Solution B: Calcium nitrate.
- Reaction A9. Solution A: Potassium (or sodium) sulfate. Solution B: Barium nitrate.
- Reaction A10. Solution A: Ammonium sulfate. Solution B: Barium nitrate.
- Reaction A11. Solution A: Potassium (or sodium) sulfate. Solution B: Calcium chloride.
- Reaction A12. Solution A: Potassium (or sodium) carbonate. Solution B: Barium nitrate.
- Reaction A13. Solution A: Potassium (or sodium) carbonate. Solution B: Ammonium sulfate.
- Reaction A14. Solution A: Potassium (or sodium) sulfide. Solution B: Barium nitrate.
- Reaction A15. Solution A: Potassium (or sodium) sulfide. Solution B: Ammonium sulfate.
- Reaction A16. Solution A: Potassium (or sodium) sulfite. Solution B: Barium nitrate.
- Reaction A17. Solution A: Potassium (or sodium) sulfite. Solution B: Ammonium sulfate.
- Reaction A18. Solution A: Silver nitrate. Solution B: Potassium (or sodium) carbonate.
- Reaction A19. Solution A: Lead(II) nitrate. Solution B: Potassium (or sodium) carbonate.
- Reaction A20. Solution A: Lead(II) nitrate. Solution B: Potassium (or sodium) acetate.
- Reaction A21. Solution A: Silver nitrate. Solution B: Potassium (or sodium) acetate.
- Reaction A22. Solution A: Barium nitrate. Solution B: Potassium (or sodium) acetate.
- Reaction A23. Solution A: Lead(II) nitrate. Solution B: Potassium (or sodium) chlorate.
- Reaction A24. Solution A: Silver nitrate. Solution B: Potassium (or sodium) chlorate.
- Reaction A25. Solution A: Barium nitrate. Solution B: Potassium (or sodium) chlorate.

5.6. Experiment 5B. Decomposition reactions

Use small test tubes for all reactions performed during this experiment. All solutions have a concentration of 0.1 M, unless otherwise specified. Procedures for all reactions are listed below:

(1) Place 1 mL of Solution A into a clean test tube.
(2) Add approximately 1 mL of Solution B to Solution A.
(3) Record your observations in your laboratory notebook.

You should select two of the following reactions to be investigated. Record all of your observations in your laboratory notebook.

Possible decomposition reactions:

- Reaction B1. Solution A: Potassium (or sodium) carbonate. Solution B: 3 M hydrochloric acid.
- Reaction B2. Solution A: Potassium (or sodium) sulfide. Solution B: 3 M hydrochloric acid.
- Reaction B3. Solution A: Potassium (or sodium) bicarbonate. Solution B: 3 M hydrochloric acid.
- Reaction B4. Solution A: Potassium (or sodium) sulfite. Solution B: 3 M hydrochloric acid.
- Reaction B5. Solution A: Potassium (or sodium) bisulfite. Solution B: 3 M hydrochloric acid.

5.7. Experiment 5C. Oxidizing power of halogens

At the reagent shelf are bottles of chlorine water, bromine water and iodine water (or a 0.05 M I_2 in methanol solution). These reagents consist of water saturated with the halogen. The first step is to familiarize your self with the color of halogens in hexane.

(1) Obtain three vials with caps from the stockroom.
(2) In each vial, place 3 mL of water and 0.5 mL of the halogen water. Be sure to clearly label each vial.
(3) Add to each vial 1 mL of hexane. Close the cap and shake.
(4) Open the cap to vent any hexane vapor produced by the shaking.
(5) Record your observations in your laboratory notebook. The hexane layer will be the top layer. An example of what is occurring is

$$\mathrm{Br_2}\ (aq,\ \text{colorless}) + \text{hexane} \rightarrow \mathrm{Br_2}\ (aq,\ \text{colorless}) + \mathrm{Br_2}\ (\text{hexane, red/brown})$$

Thus, color in the top layer indicates that Cl_2, Br_2 and I_2 were present in the aqueous layer before hexane was added.

(6) Close the caps and place the vials on the top of the laboratory bench for future reference.

To investigate the oxidation/reduction reactions for halogens, we will now perform a series of reactions, namely

- Reaction C1: sodium (or potassium) bromide and chlorine water [i.e., Cl_2 (aq)],
- Reaction C2: sodium (or potassium) iodide and chlorine water,
- Reaction C3: sodium (or potassium) chloride and bromine water [i.e., Br_2 (aq)],
- Reaction C4: sodium (or potassium) iodide and bromine water,
- Reaction C5: sodium (or potassium) chloride and iodine water [i.e., I_2 (aq)], and
- Reaction C6: sodium (or potassium) bromide and iodine water.

The steps for each reaction are

(1) Label a test tube with the reaction.
(2) Add 2 mL of 0.1 M aqueous sodium (or potassium) salt solution.
(3) Add 1 mL of the halogen water, cover the test tube and shake.
(4) Add 1 mL of hexane. Cover the test tube and shake.
(5) Compare your results with the reference vials to help determine what is present in the hexane layer. For instance, if the following reaction occurs

$$2\ \mathrm{Br}^-\ (aq) + \mathrm{Cl_2}\ (aq) \rightarrow 2\ \mathrm{Cl}^-\ (aq) + \mathrm{Br_2}\ (aq)\ ,$$

we would expect to observe a red/brown hexane layer caused by Br_2 dissolving into hexane.

Table 5.1: Cations of some of the transition metals and post transition metals.

Name	Cations	Name	Cations
bismuth	Bi^{3+}	lead	Pb^{2+}, Pb^{4+}
cadmium	Cd^{2+}	manganese	Mn^{2+}, Mn^{3+}
chromium	Cr^{2+}, Cr^{3+}	mercury	Hg_2^{2+}, Hg^{2+}
cobalt	Co^{2+}, Co^{3+}	nickel	Ni^{2+}
copper	Cu^{+}, Cu^{2+}	silver	Ag^{+}
gold	Au^{+}, Au^{4+}	tin	Sn^{2+}, Sn^{4+}
iron	Fe^{2+}, Fe^{3+}	zinc	Zn^{2+}

(6) Write your results in your laboratory notebook. The most reactive halogen is the halogen that reacts with the other two. The least reactive is the halogen that reacts with none of the other halogens.
(7) Once you have finished all of the reactions in this experiment, empty all test tubes and vials into an appropriate waste bin. Then wash the vials for use in Experiment 5D.

5.8. Experiment 5D. Metal Activity

An activity series is a listing of chemical species in order of increasing (or decreasing) reactivity. Metals tend to react by losing one or more electrons (per atom). Non-metals tend to gain electrons when they react. Metals are considered more active than non-metals since they are more easily oxidized. One way an activity series may be determined is to observe the spontaneity of reaction of a set of metals with a single oxidizing agent.

The ion formed from the metal in the reaction depends on the chemical nature of the metal. Periodic Groups IA, IIA, and IIIA are very consistent in this matter. Group IA metals form +1 ions, etc. Transition metals are not as easily predictable, but the charges on their cations are known from experiment. Transition metals and post-transition metals can form cations of various charges. Table 5.1 gives the cations for some of the transition and post-transition metals. In this experiment you will probe the activity of various metals.

The reactions that will be investigated are

- Reaction D1: copper metal with ferrous sulfate
- Reaction D2: zinc metal with ferrous sulfate
- Reaction D3: magnesium metal with ferrous sulfate
- Reaction D4: zinc metal with copper(II) sulfate
- Reaction D5: iron metal with copper(II) sulfate
- Reaction D6: manganese metal with copper(II) sulfate
- Reaction D7: copper metal with zinc sulfate
- Reaction D8: iron metal with zinc sulfate
- Reaction D9: magnesium metal with zinc sulfate
- Reaction D10: copper metal with magnesium(II) sulfate
- Reaction D11: zinc metal with magnesium(II) sulfate
- Reaction D12: iron metal with magnesium(II) sulfate

The steps for this investigation are as follows:

(1) Prepare a fresh solution of ferrous sulfate heptahydrate by dissolving 0.3 g of the hydrate in 10 mL of water.
(2) Add a small amount of metal to the bottom of a clean test tube. (If the iron is rusty, it should be cleaned in 6 M H_2SO_4, then rinsed in water before use).
(3) Add approximately 3 mL of the metal sulfate solution to the solid metal.

(4) Observe to see if a reaction occurs. Normally, reactions do not generate very shiny metal pieces but, instead, create small black or brown powders. This is caused by the finally divided crystals that are created during the reaction.
(5) If a reaction does not occur, place the test tube in a boiling water bath and heat for a few minutes. (Do not allow the solution in the test tube to boil.) Check the reaction mixture again for evidence of a chemical reaction.
(6) Record your results in your laboratory notebook. The most reactive metal is the one that reacts with all other metal cations. If you have to heat to generate a reaction, then this metal is not as reactive as the metal in a system that does not have to be heated.
(7) After the experiment, decant the liquid into the appropriate waste containers. If metals are generated or no reaction occurs, keep the metals for future use. The laboratory instructor will show you where to place these metals. Clean the test tubes for use in the next experiment.

5.9. Experiment 5E. Metal reactions with H^+ (aq)

The next oxidizing agent to be investigated is the hydronium ion $H_3O^+{}_{\text{(aq)}}$, which is present in all strong aqueous acids. Frequently, this species is simply called the hydrogen ion, or even the hydrated proton, $H^+{}_{\text{(aq)}}$, since in aqueous solution it is hydrated.

The product formed when $H^+{}_{\text{(aq)}}$ is the oxidizing agent is $H_2{}_{\text{(g)}}$, neutral molecular hydrogen, which can only be formed if $H^+{}_{\text{(aq)}}$ can take an electron from the metal. Since active metals produce $H_2{}_{\text{(g)}}$ when reacting with a strong acid, these reactions are often used to generate $H_2{}_{\text{(g)}}$.

The reactions investigated here are:

- Reaction E1: iron with concentrated acid
- Reaction E2: zinc with concentrated acid
- Reaction E3: copper with concentrated acid
- Reaction E4: magnesium with concentrate acid

The ability of each of the metals to reduce H^+ to H_2 (g) will be tested as follows:

(1) Place a small amount of metal in a clean test tube.
(2) Add approximately 1 mL of 6 M HCl.
(3) Observe the reaction.
(4) If no bubbles form, warm the solution gently in a hot water bath. Do not boil and do not mistake water bubbles for hydrogen gas bubbles.
(5) Record your observations in your laboratory notebook.

5.10. References

1. J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 5th ed. (Wiley, New York, 2007).

After Laboratory Questions

These questions should be used to help you write your notebook and should be answered in some form after completion of the laboratory.

(1) For each reaction performed write the balanced chemical reaction equation. Indicate phase [i.e., (s) for solid, (g) for gas, and (aq) for aqueous] for each reactant and product. For precipitates give the color of the precipitate under the product. For gases, give the color and/or smell of the gas under the gas. For reactions that do not occur, write *no reaction*.

(2) For each of the reactions, assume that you start with 0.5 mL of each reactant and calculate the amount of solid (or gaseous) product that you would expect based on your balanced chemical reaction.

(3) Write redox couples (i.e., X_2/X^-) for each of the halogens and their ions. Arrange these couples with the strongest reducing agent at the left of the list and the strongest oxidizing agent at the right of the list.

(4) Write redox couples for each of the metals and their cations (i.e., M^x+/M) and arrange the redox couples with the strongest reducing agent at the left of the list and the strongest oxidizing agent at the right of the list. Place the H^+/H_2 redox couple in its proper place in this list.

5.11. Reminders

Remember to get your results signed before leaving the laboratory and to submit your laboratory notebook pages.

5.12. Appendix 5.I. Solubility rules

The standard solubility rules to determine whether a salt will precipitate are given below. In Chemistry 114, you will learn the nuisances of precipitation reactions and will see instances when these rules may not apply.

(1) Almost all salts of ammonium and the alkali metals are soluble.
(2) Halide salts are generally soluble. The following are the exceptions to this rule:
    (a) Silver, mercury(I) and lead(II) form insoluble salts with chloride, bromide and iodide.
    (b) Mercury(II) forms an insoluble salt with bromide and iodide.
    (c) Magnesium, calcium, strontium, barium and lead(II) form insoluble salts with fluoride.
(3) Chlorate, nitrate and acetate sats generally from soluble salts. (Acetate salts of silver and mercury(I) are only moderately soluble.)
(4) Sulfate salts are generally soluble except for those formed from strontium, barium, mercury(I), mercury(II), and lead(II). (Calcium sulfate and silver sulfate are only moderately soluble.)
(5) Phosphate, carbonate, chromate and oxalate salts are insoluble except for those formed from ammonium and the alkali metals.
(6) All metallic oxides are insoluble except for those formed from ammonium and the alkali metals.
(7) All metallic hydroxides are insoluble except for those formed from the alkali and alkali earth metals. (The heavier alkali earth metal hydroxides are only moderately soluble.)
(8) All sulfide salts are insoluble except for those formed from ammonium, alkali metals and alkali earth metals.

5.13. Practice problems

The problems below are excellent practice problems for the laboratory quiz and the laboratory practical. Since these problems will not be graded, the answers are given in Appendix I.

(1) Assign oxidation numbers to each element in the following compounds:
   (a) $VOCl_3$
   (b) $S_2O_3^{2-}$
   (c) BrO^-
   (d) NO_2
   (e) H_2PtCl_6
   (f) OsO_4
   (g) $V_2O_7^{2-}$

(2) Predict whether a precipitation reaction will occur when aqueous solutions of the following substances are mixed:
   (a) $NaOH + HClO_4$
   (b) $(NH_4)_2SO_4 + NiCl_2$
   (c) $FeCl_2 + KOH$
   (d) $MnCl_2 + Na_2S$

(3) Write balanced net ionic equations for the following reactions in acidic solution:
   (a) $Zn\ (s) + VO^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + V^{3+}\ (aq)$

   (b) $H_2O_2\ (aq) + Cr_2O_7^{2-}\ (aq) \rightarrow O_2\ (g) + Cr^{3+}\ (aq)$

   (c) $IO_3^-\ (aq) + Re\ (s) \rightarrow ReO_4^-\ (aq) + I^-\ (aq)$

   (d) $S_4O_6^{2-}\ (aq) + Al\ (s) \rightarrow H_2S\ (aq) + Al^{3+}\ (aq)$

(4) Write balanced net ionic equations for the following reactions in basic solution:
   (a) $P\ (s) + PO_4^{2-}\ (aq) \rightarrow HPO_3^{2-}\ (aq)$

   (b) $Tl_2O_3\ (s) + NH_2OH\ (aq) \rightarrow TlOH\ (s) + N_2\ (g)$

   (c) $Cu(NH_3)_4^{2+}\ (aq) + S_2O_4^{2-}\ (aq) \rightarrow SO_3^{2-}\ (aq) + Cu\ (s) + NH_3\ (aq)$

   (d) $S_2O_3^{2-}\ (aq) + I_2\ (aq) \rightarrow S_4O_6^{2-}\ (aq) + I^-\ (aq)$

(5) The following three solutions are mixed: 100.0 mL of 0.100 M sodium sulfate, 50.0 mL of 0.300 M zinc chloride, and 100.0 mL of 0.200 M barium cyanide.
   (a) What ionic compound or compounds will precipitate out of solution?
   (b) How many grams of the precipitate will be formed?
   (c) What is the molarity of each ion remaining in the solution assuming complete precipitation of all insoluble salts?

(6) A 250.0 g sample of a white solid is known to be a mixture of potassium nitrate, barium chloride, and sodium chloride. When 100.0 g of this mixture is dissolved in water and allowed to react with excess sulfuric acid, 67.3 g of a white precipitate is collected. When the remaining 150.0 g of the mixture is dissolved in water and allowed to react with excess silver nitrate, 197.6 g of a second precipitate is collected.
   (a) What are the formulas of the two precipitates?

(b) What is the mass of each substance in the original 250.0 g mixture?

(7) To 100.0 mL of a solution that contains 0.120 M chromium(II) nitrate and 0.500 M nitric acid is added 20.0 mL of 0.250 M potassium dichromate. The dichromate and chromium(II) ions react to give chromium(III) ions.

(a) Write a balanced net ionic equation for the reaction.

(b) Calculate the concentrations of all ions in the solution after the reaction.

(8) Use the following reactions to arrange the elements A, B, C, and D in order of their decreasing ability as reducing agents:

$C + B^+ \rightarrow C^+ + B$

$A^+ + D \rightarrow$ no reaction

$C^+ + A \rightarrow$ no reaction

$D + B^+ \rightarrow D^+ + B$

Given the information above, which of the following reactions would you expect to occur and why?

(1) $A^+ + C \rightarrow A + C^+$

(2) $A^+ + B \rightarrow A + B^+$

(9) How could you use a precipitation reaction to separate each of the following pairs of cations? Write the formula for each reactant you would add, and write a balanced net ionic equation for each reaction.

(a) K^+ and Hg_2^{2+}

(b) Ca^{2+} and NH_4^+

(c) Pb^{2+} and Ni^{2+}

(d) Fe^{2+} and Ba^{2+}