**Solution Manual**

**Lithia Water Springs Project**

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**Introduction:** This document serves as a solution manual for the questions posed in the Lithia Water Springs Project. Instructors should feel free to use individual questions or modules in their entirety as they fit into the course material being covered. These modules may also be adapted to other samples such as wellwater or natural waters, such as freshwater and saltwater sources.

**Answers to Questions:**

*Major Inorganic Constituents*

**Q1.** Which cations and anions are represented by a single salt and which are represented by multiple salts?

From the summary of the 1915 Lithia water analysis on the engraved stone:

Cations: $Na^+$ is represented by multiple salts, and $K^+$, $Li^+$, $Ca^{2+}$, and $Mg^{2+}$ are represented by single salts.

Anions: $HCO_3^-$ is represented by multiple salts, and $Cl^-$, $SO_4^{2-}$, and $BO_2^-$ are represented by single salts.

**Q2.** Of those analytes listed on the plaque, are there any cation or anion concentrations that are unknowns based on the information provided? How can you tell?

ANALYSIS
Milligrams per liter

| | |
|---|---|
| Sodium Chloride | 4515.000 |
| Sodium Metaborate | 321.300 |
| Sodium Sulphate | 3.895 |
| Sodium Bicarbonate | 2456.000 |
| Potassium Bicarbonate | 279.500 |
| Lithium Bicarbonate | 153.820 |
| Calcium Bicarbonate | 1404.000 |
| Magnesium Bicarbonate | 1153.000 |
| Iron & Aluminum Oxides | 12.500 |
| Silica | 94.900 |

A.D. 1915

Iron and aluminum oxides are represented by a single concentration, and they would both be unknowns because it is impossible to calculate an analyte concentration when there are two unknowns and one concentration. Although it is not indicated on the plaque, based on recent analyses for the City of Ashland, instructors can assume that aluminum does not contribute significantly to the ionic content of Lithia water, and iron represents the vast majority of this Lithia water constituent. Instructors may also assume that all measured silica exists in Lithia water as $SiO_3^{2-}$, the silicate ion.

**Q3.** Based on the analysis engraved on the plaque above, how would you calculate the concentration of each ion represented by a single salt? Complete these calculations, and express the concentration in milligrams per liter (mg $L^{-1}$) and in moles per liter (M).

Listed below are the conversions of single salt concentrations to concentrations of individual cations and anions in Lithia water. Instructors may use these questions to provide students with examples of stoichiometric calculations.

    (a) Potassium

        i. $\left(\frac{279.5 \; mg \; KHCO_3}{L}\right)\left(\frac{1 \; g}{1000 \; mg}\right)\left(\frac{1 \; mol \; KHCO_3}{100.12 \; g}\right)\left(\frac{1 \; mol \; K^+}{1 \; mol \; KHCO_3}\right) = 2.792 \; x \; 10^{-3} M \; K^+$

        ii. $(2.792 \; x \; 10^{-3} M \; K^+)\left(\frac{39.098 g \; K^+}{mol \; K^+}\right)\left(\frac{1000 \; mg}{g}\right) = \frac{109.1 \; mg \; K^+}{L}$

    (b) Lithium

        i. $\left(\frac{153.82 \; mg \; LiHCO_3}{L}\right)\left(\frac{1 \; g}{1000 \; mg}\right)\left(\frac{1 \; mol \; LiHCO_3}{67.96 \; g}\right)\left(\frac{1 \; mol \; Li^+}{1 \; mol \; LiHCO_3}\right) = 2.263 \; x \; 10^{-3} M \; Li^+$

ii. $(2.263 \; x \; 10^{-3} M \; Li^+) \left( \frac{6.941g \; Li^+}{mol \; Li^+} \right) \left( \frac{1000 \; mg}{g} \right) = \frac{15.7 \; mg \; Li^+}{L}$

(c) Calcium

i. $\left( \frac{1404 \; mg \; Ca(HCO_3)_2}{L} \right) \left( \frac{1 \; g}{1000 \; mg} \right) \left( \frac{1 \; mol \; Ca(HCO_3)_2}{162.12 \; g} \right) \left( \frac{1 \; mol \; Ca^{2+}}{1 \; mol \; Ca(HCO_3)_2} \right) = $
$8.66 \; x \; 10^{-3} M \; Ca^{2+}$

ii. $(8.66 \; x \; 10^{-3} M \; Ca^{2+}) \left( \frac{40.08g \; Ca^{2+}}{mol \; Ca^{2+}} \right) \left( \frac{1000 \; mg}{g} \right) = \frac{347 \; mg \; Ca^{2+}}{L}$

(d) Magnesium

i. $\left( \frac{1153 \; mg \; Mg(HCO_3)_2}{L} \right) \left( \frac{1 \; g}{1000 \; mg} \right) \left( \frac{1 \; mol \; Mg(HCO_3)_2}{146.35 \; g} \right) \left( \frac{1 \; mol \; Mg^{2+}}{1 \; mol \; Mg(HCO_3)_2} \right) = $
$7.88 \; x \; 10^{-3} M \; Mg^{2+}$

ii. $(7.88 \; x \; 10^{-3} M \; Mg^{2+}) \left( \frac{24.31g \; Mg^{2+}}{mol \; Mg^{2+}} \right) \left( \frac{1000 \; mg}{g} \right) = \frac{192 \; mg \; Mg^{2+}}{L}$

(e) Chloride

i. $\left( \frac{4515 \; mg \; NaCl}{L} \right) \left( \frac{1 \; g}{1000 \; mg} \right) \left( \frac{1 \; mol \; NaCl}{58.44 \; g} \right) \left( \frac{1 \; mol \; Cl^-}{1 \; mol \; NaCl} \right) = 7.726 \; x \; 10^{-2} M \; Cl^-$

ii. $(7.726 \; x \; 10^{-2} M \; Cl^-) \left( \frac{35.45g \; Cl^-}{mol \; Cl^-} \right) \left( \frac{1000 \; mg}{g} \right) = \frac{2739 \; mg \; Cl^-}{L}$

(f) Metaborate

i. $\left( \frac{321.3 \; mg \; NaBO_2}{L} \right) \left( \frac{1 \; g}{1000 \; mg} \right) \left( \frac{1 \; mol \; NaBO_2}{65.80 \; g} \right) \left( \frac{1 \; mol \; BO_2^-}{1 \; mol \; NaBO_2} \right) = 4.883 \; x \; 10^{-3} M \; BO_2^-$

ii. $(4.883 \; x \; 10^{-3} M \; BO_2^-) \left( \frac{42.81g \; BO_2^-}{mol \; BO_2^-} \right) \left( \frac{1000 \; mg}{g} \right) = \frac{209 \; mg \; BO_2^-}{L}$

(g) Sulfate

i. $\left( \frac{3.895 \; mg \; Na_2SO_4}{L} \right) \left( \frac{1 \; g}{1000 \; mg} \right) \left( \frac{1 \; mol \; Na_2SO_4}{142.04 \; g} \right) \left( \frac{1 \; mol \; SO_4^{2-}}{1 \; mol \; Na_2SO_4} \right) = 2.742 \; x \; 10^{-5} M \; SO_4^{2-}$

ii. $(2.742 \; x \; 10^{-5} M \; SO_4^{2-}) \left( \frac{96.06g \; SO_4^{2-}}{mol \; SO_4^{2-}} \right) \left( \frac{1000 \; mg}{g} \right) = \frac{2.63 \; mg \; SO_4^{2-}}{L}$

(h) Silica (as silicate)

i. $\left( \frac{94.9 \; mg \; SiO_2}{L} \right) \left( \frac{1 \; g}{1000 \; mg} \right) \left( \frac{1 \; mol \; SiO_2}{60.08 \; g} \right) \left( \frac{1 \; mol \; SiO_3^{2-}}{1 \; mol \; SiO_2} \right) = 1.58 \; x \; 10^{-3} M \; SiO_3^{2-}$

ii. $(1.58 \times 10^{-3} M\ SiO_3^{2-})\left(\frac{76.08g\ SiO_3^{2-}}{mol\ SiO_3^{2-}}\right)\left(\frac{1000\ mg}{g}\right) = \frac{120.2\ mg\ SiO_3^{2-}}{L}$

(i) Iron (assuming aluminum content is negligible)

i. $\left(\frac{12.5\ mg\ Fe_2O_3}{L}\right)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol\ Fe_2O_3}{159.69\ g}\right)\left(\frac{2\ mol\ Fe^{3+}}{1\ mol\ Fe_2O_3}\right)\left(\frac{1\ mol\ Fe^{2+}}{1\ mol\ Fe^{3+}}\right) =$
$1.566 \times 10^{-4} M\ Fe^{2+}$

ii. $(1.566 \times 10^{-4} M\ Fe^{2+})\left(\frac{55.845g\ Fe^{2+}}{mol\ Fe^{2+}}\right)\left(\frac{1000\ mg}{g}\right) = \frac{8.74\ mg\ Fe^{2+}}{L}$

**Q4.** How does your approach to calculating ion concentrations represented by multiple salts differ from expressing ion concentrations represented by a single salt? Complete these calculations, and express the solute concentration in milligrams per liter (mg L$^{-1}$) and in moles per liter (M).

Multiple sources of a common ion need to be converted from mg L$^{-1}$ to mol L$^{-1}$ and then added together. Sodium ion and bicarbonate ion have a common salt so the molarity of sodium bicarbonate may first be calculated. After this calculation, the molarity of the common ions can be calculated using stoichiometric relationships and the concentrations from the previous question.

(a) Sodium bicarbonate

i. $\left(\frac{2456\ mg\ NaHCO_3}{L}\right)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol\ NaHCO_3}{84.01\ g}\right)\left(\frac{1\ mol\ Na^+}{1\ mol\ NaHCO_3}\right) = 2.923 \times 10^{-2} M\ Na^+$

ii. $(2.923 \times 10^{-2} M\ Na^+)\left(\frac{1\ mol\ HCO_3^-}{1\ mol\ Na^+}\right) = 2.923 \times 10^{-2} M\ HCO_3^-$

(b) All sources of sodium ion

i. $(2.923 \times 10^{-2}\ M\ Na^+) + \left(7.726 \times 10^{-2}\ M\ Cl^-\left(\frac{1\ mol\ Na^+}{1\ mol\ Cl^-}\right)\right) +$
$\left(4.883 \times 10^{-3}\ M\ BO_2^-\left(\frac{1\ mol\ Na^+}{1\ mol\ BO_2^-}\right)\right) + \left(2.742 \times 10^{-5}\ M\ SO_4^{2-}\left(\frac{2\ mol\ Na^+}{1\ mol\ SO_4^{2-}}\right)\right) =$
$0.1114\ M\ Na^+$

ii. $(0.1114\ M\ Na^+)\left(\frac{22.99g\ Na^+}{mol\ Na^+}\right)\left(\frac{1000\ mg}{g}\right) = \frac{2562\ mg\ Na^+}{L}$

(c) All sources of bicarbonate ion

i.  $(2.923 \times 10^{-2} \ M \ HCO_3^-) + \left(2.792 \times 10^{-3} \ M \ K^+ \left(\frac{1 \ mol \ HCO_3^-}{1 \ mol \ K^+}\right)\right) +$
    $\left(2.263 \times 10^{-3} \ M \ Li^+ \left(\frac{1 \ mol \ HCO_3^-}{1 \ mol \ Li^+}\right)\right) + \left(8.66 \times 10^{-3} \ M \ Ca^{2+} \left(\frac{2 \ mol \ HCO_3^-}{1 \ mol \ Ca^{2+}}\right)\right) +$
    $\left(7.88 \times 10^{-3} \ M \ Mg^{2+} \left(\frac{2 \ mol \ HCO_3^-}{1 \ mol \ Mg^{2+}}\right)\right) = 0.06736 \ M \ HCO_3^-$

ii.  $(0.06736 \ M \ HCO_3^-) \left(\frac{61.02g \ HCO_3^-}{mol \ HCO_3^-}\right) \left(\frac{1000 \ mg}{g}\right) = \frac{4110 \ mg \ HCO_3^-}{L}$

**Q5.** Determine the number of milligrams of each analyte present in 25.00 mL of Lithia water from the 1915 analysis, assuming that the composition of Lithia water has not changed since 1915. Using these analyte quantities, determine appropriate analytical techniques based on the classification scheme in Table 1.

Students should recognize that multiplying the analyte concentration by a given volume will result in the mass (or moles) of analyte in that given volume. Each analyte concentration was calculated in the previous question in mg $L^{-1}$, and those concentrations can be used for the determination of milligrams of each analyte in a 25.00 mL sample of Lithia water. The analytical technique(s) listed are suggested techniques based on analyte classification. It is up to the students, in consultation with the instructor, to determine which methods are most appropriate for a given laboratory project.

**Table 1. Suggested analyte classification table for Lithia water analysis. See *Analytical Chemistry 2.0 (Chapter 3D.6, p. 51)* on the Analytical Sciences Digital Library website for additional information.**

| Analyte | Calculation | Analyte Classification (Potential Technique) |
|---|---|---|
| **Sodium** | $\left(\dfrac{2562\ mg\ Na^+}{L}\right)\left(\dfrac{1\ L}{1000\ mL}\right)(25.00\ mL) = 64.04\ mg$ | Minor (ISE) |
| **Potassium** | $\left(\dfrac{109.1\ mg\ K^+}{L}\right)\left(\dfrac{1\ L}{1000\ mL}\right)(25.00\ mL) = 2.7\ mg$ | Minor (ISE or Spectroscopy) |
| **Lithium** | $\left(\dfrac{15.7\ mg\ Li^+}{L}\right)\left(\dfrac{1\ L}{1000\ mL}\right)(25.00\ mL) = 0.4\ mg$ | Trace (ISE or Spectroscopy) |
| **Calcium** | $\left(\dfrac{347\ mg\ Ca^{2+}}{L}\right)\left(\dfrac{1\ L}{1000\ mL}\right)(25.00\ mL) = 8.7\ mg$ | Minor (Titrimetry, ISE or Spectroscopy) |
| **Magnesium** | $\left(\dfrac{192\ mg\ Mg^{2+}}{L}\right)\left(\dfrac{1\ L}{1000\ mL}\right)(25.00\ mL) = 4.8\ mg$ | Minor (Titrimetry, ISE or Spectroscopy) |
| **Iron** | $\left(\dfrac{8.74\ mg\ Fe^{2+}}{L}\right)\left(\dfrac{1\ L}{1000\ mL}\right)(25.00\ mL) = 0.2\ mg$ | Trace (Spectroscopy) |
| **Chloride** | $\left(\dfrac{2739\ mg\ Cl^-}{L}\right)\left(\dfrac{1\ L}{1000\ mL}\right)(25.00\ mL) = 68.5\ mg$ | Minor (ISE or Titrimetry) |
| **Metaborate** | $\left(\dfrac{209\ mg\ BO_2^-}{L}\right)\left(\dfrac{1\ L}{1000\ mL}\right)(25.00\ mL) = 5.2\ mg$ | Minor (Titrimetry, ISE or Spectroscopy) |
| **Sulfate** | $\left(\dfrac{2.63\ mg\ SO_4^{2-}}{L}\right)\left(\dfrac{1\ L}{1000\ mL}\right)(25.00\ mL) = 0.07\ mg$ | Trace (Spectroscopy) |
| **Bicarbonate** | $\left(\dfrac{4110\ mg\ HCO_3^-}{L}\right)\left(\dfrac{1\ L}{1000\ mL}\right)(25.00\ mL)$ $= 102.8\ mg$ | Minor (Titrimetry) |
| **Silicate** | $\left(\dfrac{120.2\ mg\ SiO_3^{2-}}{L}\right)\left(\dfrac{1\ L}{1000\ mL}\right)(25.00\ mL) = 3.0\ mg$ | Minor (Spectroscopy) |

**Q6.** Once the appropriate analytical technique(s) for each analyte have been identified based on the classification scheme in Table 1, consider, discuss, and identify additional criteria that would be important in the selection of an appropriate method for each analyte in Lithia water. An appropriate starting point for this discussion would be to read Chapter 3D in *Analytical Chemistry 2.0.*:

After students have read Chapter 3D in *Analytical Chemistry 2.0* and calculated the analyte concentrations in Q5, each group should develop a set of criteria for the selection of each analytical method. Appropriate criteria include, but are not limited to:

1. Method Sensitivity. In this project, students are guided in their selection of an analytical technique based on the analyte classification scheme in Table 1.

2. Cost of materials & equipment. In this analytical chemistry course, the selection of an analytical technique that minimizes the cost of reagents and equipment is preferable.

3. Timeframe of analysis. An analyte determination that can be completed within one laboratory period is preferable. However, it may also be acceptable if one or more group members agree to complete a determination by remaining beyond the scheduled lab period. Such arrangements should be made ahead of time, and in such cases, solution and standard preparation should be completed ahead of time if possible.

4. Is the proper equipment for performing the determination and handling any toxic or noxious reagents available in the department?

The most appropriate choice of a proper technique and method for the determination of a chosen analyte depends on the equipment, time and resources available. A student may discover that there are multiple techniques available for the determination of an analyte. If this is the case, the criteria are designed to guide each group toward the least expensive, and presumably, the least complicated analytical technique that can be used for a given determination. However, it is up to the instructor to decide how the criteria are prioritized based on course goals.

In the past, the analytical chemistry laboratory prescribed the following analytical techniques for Lithia water analytes:

- Sodium, potassium: Ion-selective electrodes
- Calcium, magnesium: Complexometric titrations
- Chloride: Precipitation titration
- Bicarbonate: Acid-base titration
- Boron, Iron, Silicate, Sulfate: Molecular spectroscopy
- Lithium: Atomic emission spectroscopy, molecular spectroscopy

**Q7.** Lithium carbonate is typically prescribed to control manic depression. A typical dosage is 900 mg day$^{-1}$ of lithium carbonate. How many liters of Lithia water would someone have to drink to ingest an equivalent amount of lithium that is present in a prescribed dose of lithium

carbonate? Based on your calculated volume of Lithia water in the previous question, are there health related issues that could arise due to the presence of other ions that are listed on the Lithia water analysis plaque? To help answer this question, perform an internet search on the health effects and the dietary intake of any of the other cations or anions in Lithia water. Cite any sources you use to support your answer.

If a typical daily dosage of lithium carbonate to treat manic depression is 900 mg per day, the volume of Lithia water needed to supply the appropriate dosage of lithium ion is:

$$\left(\frac{0.900 \; g \; Li_2CO_3}{day}\right)\left(\frac{1 \; mol \; Li_2CO_3}{73.892 \; g \; Li_2CO_3}\right)\left(\frac{2 \; mol \; Li^+}{1 \; mol \; Li_2CO_3}\right)\left(\frac{1 \; L \; Lithia \; water}{0.002263 \; mol \; Li^+}\right) = \left(\frac{10.8 \; L \; Lithia \; water}{day}\right)$$

Instructors may want to point out to their students that one of the inorganic ions in Lithia water that serves an important role in human health is sodium. Although sodium is necessary for proper electrolyte balance, which controls such functions as nerve impulse conduction, only small amounts of dietary sodium are necessary to maintain such functions. Excess sodium in the diet leads to health problems such as high blood pressure. According to the Harvard School of Public Health website on Salt and Health, U.S. government recommendations are 2300 milligrams of sodium as a maximum daily dietary intake. The sodium concentration in Lithia water, calculated in the previous question in this section, is 2573 milligrams per liter. Therefore, the volume of Lithia water that must be consumed in order to ingest the maximum daily intake of sodium ions is:

$$\left(\frac{2.300 \; g \; Na^+}{day}\right)\left(\frac{L \; Lithia \; water}{2.573 \; g \; Na^+}\right) = \left(\frac{0.894 \; L \; Lithia \; water}{day}\right)$$

This volume is twelve times less than the volume needed to supply the therapeutic amount of lithium to treat manic depression. Drinking the Lithia water from the Ashland, OR source would not be a healthy or effective way of administering a therapeutic dose of lithium.

### Origins of Lithia Water

Q8.     If the Lithia spring water was to leach ions from limestone deposits to form soda springs, what primary cations and anions would you expect to have dissolved in the spring water due to such leaching action?

Calcium ions and carbonate ions.

**Q9.** Soda springs are characterized by significant levels of $CO_2$. If the pH of a recently obtained sample of Lithia water is 6.4, draw a ladder diagram for carbonic acid, and predict the predominant form of carbonic acid in this sample of Lithia water.

The pH of Lithia water is typically 6.4, and based on the ladder diagram for the carbonic acid system, the predominant form of carbonic acid is the bicarbonate ion and carbonic acid. Since the pH of Lithia water is slightly greater than $pK_{a1}$, there is slightly more bicarbonate ion present than carbonic acid.

pH

$[CO_3^{2-}]$

$pK_{a2} = 10.33$

$[HCO_3^-]$

$pK_{a1} = 6.35$

$[H_2CO_3]$
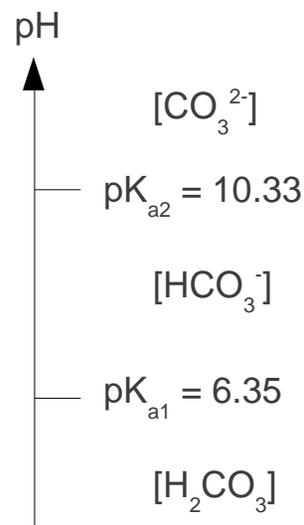
*Sample Handling & Treatment*

**Q10.** (*Sample Handling & Treatment*) Answer **Q1 – Q13** in the Chemical Equilibria and Sample Preparation section of the Lithia Water Springs document. After completing these questions, go online to the U.S. Environmental Protection Agency website (www.epa.gov) and search for documentation regarding the preservation of inorganic analytes in water samples.

**Q11.** (*Sample Handling & Treatment*) Based on your search results on the U.S. EPA website and your answer to question 13 in the Chemical Equilibria and Sample Preparation section, develop a sampling plan for Lithia water so that all significant analytes can be determined.

One general approach to preserving Lithia water without compromising the determination of bicarbonate is to obtain two samples of Lithia water in Nalgene bottles, and acidify the sample that will be used to determine the concentration of all cationic species. A 1.0 mL sample of 6 M $HNO_3$ added to 60 mL of Lithia water should be sufficient to reduce the sample pH below 2.0. The unpreserved sample should be tightly capped until the bicarbonate ion determination is about to be performed.

**Activity #1:** At this point, if you are going to have your students analyze some of the constituents of a local water source, it would be an appropriate time to have them collect the samples. If students are interested in investigating changes in sample appearance upon standing, students should obtain a small, clean Nalgene bottle (60 – 250 mL capacity) and rinse it thoroughly with the water sample. After rinsing, fill the bottle completely with water and cap it tightly. Students should record any observations regarding the appearance of the water immediately after collection and a day or two afterwards. They should measure the pH of the water sample and record that value in their laboratory notebook. If students have already developed a sampling plan, appropriate steps should be taken to properly clean sample containers and preserve samples as needed.
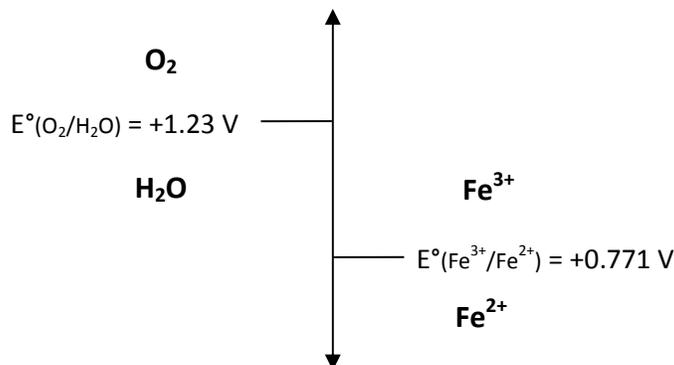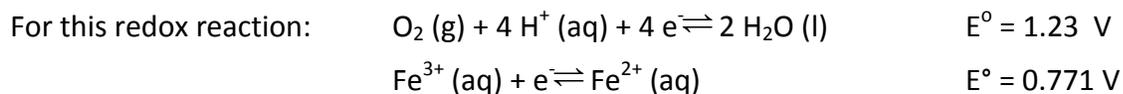
Instructors should inform their students that any change in the appearance of their natural water sample may indicate the occurrence of a chemical reaction that changes the chemical composition of the water sample. Such changes include the appearance of turbidity or precipitate, gas evolution and/or a color change. In the case of Lithia water, the Lithia water piped into downtown Ashland, Oregon is clear and colorless with a pH of approximately 6.4 and a faint sulfurous smell. After 1 – 2 days, the Lithia water sample becomes slightly turbid with a light orange precipitate at the bottom of the sample container.

### Chemical Equilibria and Sample Preparation (Q1 – Q13)

**Q1.** Which of the cationic solutes in Lithia water are main group ions? Which of the cationic solutes are transition metal ions? Evaluate whether main group and transition metal cations have lost all of their valence electrons. Can main group and/or transition metal cations potentially be oxidized by dissolved oxygen?

The only transition metal that is recognized as an inorganic constituent in Lithia water is iron. All of the other inorganic cations of historical significance determined in this course ($K^+$, $Na^+$, $Li^+$, $Ca^{2+}$, $Mg^{2+}$) are main group ions. Main group cations tend to exist in their most oxidized state. Since there are no additional valence electrons, main group cations are unable to function as reductants and cannot reduce elemental oxygen to the oxide. Ferrous ion ($Fe^{2+}$) can theoretically be oxidized to the ferric ion ($Fe^{3+}$) and act as a reductant for species such as elemental oxygen.

**Q2.** Using the standard reduction tables in *Analytical Chemistry 2.0*, draw a ladder diagram for the redox couple of dissolved oxygen and $Fe^{3+/2+}$ under standard conditions. Predict the predominant oxidation state for iron under these conditions.

For this redox reaction:
$$O_2\ (g) + 4\ H^+\ (aq) + 4\ e^- \rightleftharpoons 2\ H_2O\ (l) \qquad E^0 = 1.23\ V$$
$$Fe^{3+}\ (aq) + e^- \rightleftharpoons Fe^{2+}\ (aq) \qquad E^\circ = 0.771\ V$$

Based on this ladder diagram, the predominant species in this solution under standard conditions would be $H_2O$ and $Fe^{3+}$.

**Q3.** Using the standard reduction tables in *Analytical Chemistry 2.0*, draw a ladder diagram for the redox couple of dissolved oxygen and $Fe^{3+/2+}$ assuming the following non-standard conditions: assume that the dissolved oxygen concentration is 10 mg $L^{-1}$, the total iron concentration is 10 mg $L^{-1}$, and that the initial ratio of $[Fe^{2+}]/[Fe^{3+}]$ is 1000. Predict the predominant oxidation state for iron under these conditions and compare the result to your answer in question 2.

For the redox couple of dissolved oxygen and ferric/ferrous ion, the following calculations need to be performed before constructing the ladder diagram:
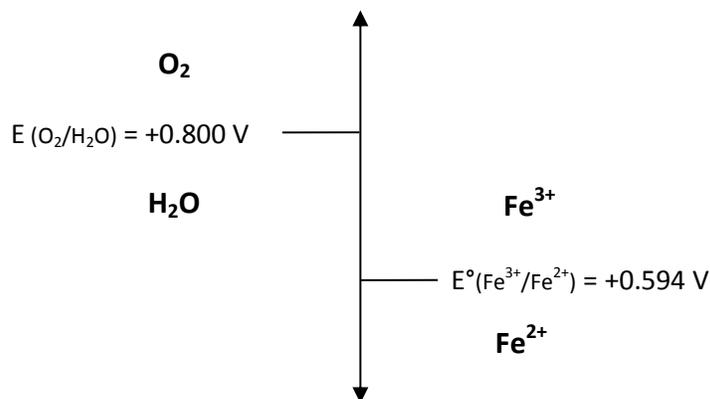
Potential of the dissolved oxygen half-reaction: $O_2$ (g) + 4 $H^+$ (aq) + 4 e $\rightleftharpoons$ 2 $H_2O$ (l)

$$[H^+] = 10^{-pH} = 10^{-6.4} = 3.98 \ x \ 10^{-7}M$$

$$[O_2] = \left(\frac{10.0 \ mg \ O_2}{L}\right)\left(\frac{1.00 \ mmol \ O_2}{32.0 \ mg \ O_2}\right)\left(\frac{1 \ mol \ O_2}{1000 \ mmol \ O_2}\right) = 3.1 \ x \ 10^{-4}M$$

$$E_{O_2} = E^o_{O_2} - \frac{0.05915}{n}log\frac{1}{[O_2][H^+]^4} = 1.23 - \frac{0.05915}{4}log\frac{1}{(3.1 \ x \ 10^{-4})(3.98 \ x \ 10^{-7})^4}$$
$$= 0.800 \ V$$

$$E_{Fe^{3+}/Fe^{2+}} = E^o_{Fe^{3+}/Fe^{2+}} - \frac{0.05915}{n}log\frac{[Fe^{2+}]}{[Fe^{3+}]} = 0.771 - \frac{0.05915}{1}log\frac{1000}{1} = 0.594 \ V$$

$O_2$

E $(O_2/H_2O)$ = +0.800 V

$H_2O$

$Fe^{3+}$

E°$(Fe^{3+}/Fe^{2+})$ = +0.594 V

$Fe^{2+}$

The predominant oxidation state for iron under these conditions is $Fe^{3+}$.

**Q4.** Refer to the plaque shown in Fig. 2 of the Major Inorganic Constituents section. What are the two predominant anions in Lithia water? Using the standard reduction tables in *Analytical*
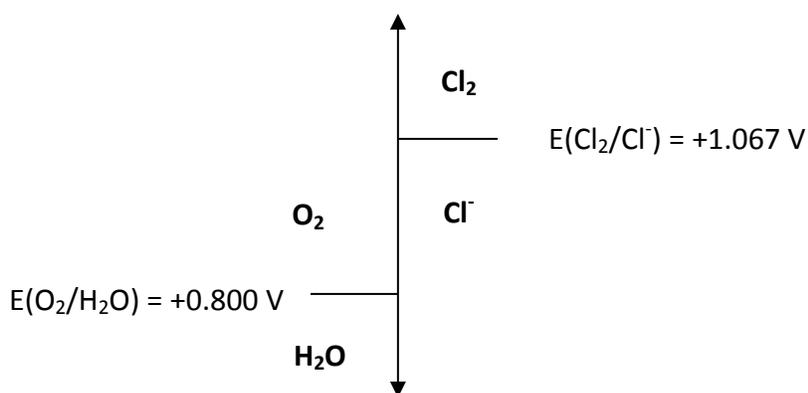
*Chemistry 2.0*, is there any reason to expect these anions to react with dissolved oxygen at concentrations expected in Lithia water? Provide appropriate support for your answer.

The two predominant anions in Lithia water are chloride and bicarbonate. Chloride ion may be oxidized to chlorine, and the Nernst equation plus a ladder diagram may be used to determine whether dissolved oxygen has sufficient capability as an oxidant under conditions found in Lithia water. Atmospheric chlorine is extremely reactive and is removed efficiently from the troposphere by chemical reactions. The smell of chlorine can be detected at 3 – 5 ppm. The determination of atmospheric chlorine in Ashland, OR has not been undertaken but a conservative estimate would be 1 pptv (part per trillion by volume) which is 1 pmol $Cl_2$ per mol of air. Assuming air is an ideal gas:

$$Cl_2 \text{ (g)} + 2e^- \rightleftharpoons 2\ Cl^- \qquad\qquad E^o = 1.396 \text{ V}$$

$$[Cl_2] = \left(\frac{1\ x\ 10^{-12} mol\ Cl_2}{mol\ air}\right)\left(\frac{1\ mol\ air}{22.4\ L}\right) = 4.5\ x\ 10^{-14}\ M\ Cl_2$$

$$E_{Cl_2/Cl^-} = E^o_{Cl_2/Cl^-} - \frac{0.05915}{n}\log\frac{[Cl^-]^2}{[Cl_2]} = 1.396 - \frac{0.05915}{2}\log\frac{(7.777x10^{-2})^2}{4.5\ x\ 10^{-14}} = 1.067\ V$$

According to the ladder diagram, dissolved oxygen and chloride ion do coexist in Lithia water. Under these conditions, dissolved oxygen is not a sufficient oxidant to oxidize chloride ion to chlorine.

In the bicarbonate ion, the oxidation number for carbon is +4, which is the highest oxidation state for carbon since elemental carbon has only four valence electrons. Therefore, dissolved oxygen cannot oxidize the bicarbonate ion.

**Q5.** Using the standard reduction tables in *Analytical Chemistry 2.0*, is there any reason to expect main group cations to react with transition metal cations present in Lithia water? Provide appropriate support for your answer.

The predominant main group cations in Lithia water are $Li^+$, $Na^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$. The predominant transition metal in Lithia water is $Fe^{2+}$. The standard reduction potentials for the main group cations to their zero valent state and the standard reduction potential for the ferric-ferrous redox couple are listed in the table below:

| Standard Reduction Half-Reaction | E° (V) |
|---|---|
| $Li^+ + e^- \rightleftharpoons Li$ (s) | -3.04 |
| $Na^+ + e^- \rightleftharpoons Na$ (s) | -2.713 |
| $K^+ + e^- \rightleftharpoons K$ (s) | -2.93 |
| $Mg^{2+} + 2e^- \rightleftharpoons Mg$ (s) | -2.356 |
| $Ca^{2+} + 2e^- \rightleftharpoons Ca$ (s) | -2.84 |
| $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ (aq) | +0.771 |

All of the main group cations exist in their fully oxidized state and are extremely weak oxidants as evidenced by the extremely negative (unfavorable) standard reduction potentials. The oxidation of ferrous ion to ferric ion is unfavorable except in the presence of a strong oxidant. Although an instructor may want students to construct a ladder diagram and use the Nernst equation to calculate the electrochemical potential for each half-cell, one can determine by inspection that the reduction of Group IA and IIA cations by the oxidation of ferrous ions to ferric ions is extremely unfavorable. Therefore, no redox reaction should take place among the main group ions and ferrous ions.

**Q6.** Briefly summarize the redox chemistry that can take place among the major inorganic cations in Lithia water.

Dissolved oxygen acts as an oxidant to oxidize ferrous ions to ferric ions. The oxidation of ferrous ions to ferric ions leads to the precipitation of ferric hydroxide, which appears as a fine orange precipitate at the bottom of the Lithia water sample. The main group cations are stable in Lithia water as they have large negative standard reduction potentials, which make them extremely weak oxidants.

**Q7.** Using the solubility rules provided above and the primary inorganic constituents in Lithia water, which inorganic salts would be most likely to form a precipitate in Lithia water?

Carbonates and hydroxides would be the most likely inorganic salts to form a precipitate in Lithia water.

**Q8.** Why is there no term for the solid calcium carbonate in the $K_{sp}$ expression?

Unlike the concentration of dissolved ions in aqueous solution, which is an extensive property and varies based on the number of ions in a given volume of solvent, the concentration of a pure solid (or a pure liquid) is an intensive property and is constant. Equilibrium constant expressions do not contain concentration terms for pure solids or liquids, and they are given a value of 1 in the equilibrium constant expression.

**Q9.** Write expressions that relate the concentration of calcium ion and the concentration of phosphate ion to the solubility of calcium phosphate in water.

$$Ca_3(PO_4)_2 \text{ (s)} \rightleftharpoons 3\ Ca^{2+} \text{ (aq)} + 2\ PO_4^{3-} \text{ (aq)}$$

| | $Ca_3(PO_4)_2$ (s) | $3\ Ca^{2+}$ (aq) | $2\ PO_4^{3-}$ (aq) |
|---|---|---|---|
| Initial (I) | ------ | 0 | 0 |
| Change (C) | -X | +3X | +2X |
| Equilibrium (E) | ------ | 3X | 2X |

If the molar solubility of calcium phosphate is X, then

$3X = [Ca^{2+}]$     or     $X = [Ca^{2+}]/3$

$2X = [PO_4^{3-}]$     or     $X = [PO_4^{3-}]/2$

So the molar solubility of $Ca_3(PO_4)_2$ can be expressed as either $([Ca^{2+}]/3)$ or $([PO_4^{3-}]/2)$.

**Q10.** Calculate the solubility of calcium hydroxide in a solution that has a pH of 12. Note: The pH has been adjusted to 12 by some other means than the dissolution of calcium hydroxide. If calcium hydroxide is added to the water with a pH of 12, some of the calcium hydroxide will dissolve to satisfy the $K_{sp}$ equilibrium expression for calcium hydroxide.

The solubility equilibrium established in a saturated solution of $Ca(OH)_2$ is:

$$Ca(OH)_2 \text{ (s)} \rightleftharpoons Ca^{2+} \text{ (aq)} + 2\ OH^- \text{ (aq)}$$
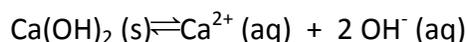
The equilibrium constant expression for $Ca(OH)_2$ is:

$$K_{sp} = [Ca^{2+}][OH^-]^2$$

The molar solubility of $Ca(OH)_2$ can be defined as $[Ca^{2+}]$ because dissolving one mole of $Ca(OH)_2$ provides one mole of calcium ions. Solving for the molar solubility of $Ca(OH)_2$ may be accomplished using the following steps:

$$[H^+] = 10^{-pH} = 1.0 \times 10^{-12} \ M$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-12}} = 1.0 \times 10^{-2} \ M$$

$$[Ca^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{6.5 \times 10^{-6}}{(0.010)^2} = 0.065 \ M$$

**Q11.** What is the molar solubility and mass solubility (i.e. solubility in grams of solid per liter of solution) of each of the metal hydroxides listed in Table 1 at pH values of 10.0, 6.0, and 2.0? How is the solubility of a metal hydroxide affected by pH? Offer an explanation for this behavior using LeChatelier's principle.

To solve for the molar solubility of each metal hydroxide at each pH, the hydroxide ion concentration must be calculated at each pH and substituted into the equilibrium constant expression to solve for the molar solubility of the salt. The molar solubility can be converted to mass solubility by multiplying the molar solubility by the molar mass of the salt.

Step 1: Calculate the hydroxide ion concentration at pH 10.0, 6.0, and 2.0

$$[H^+] = 10^{-pH} = 10^{-10.0} = 1.0 \times 10^{-10} \ M$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-10}} = 1.0 \times 10^{-4} \ M$$

$$At \ pH \ 6.0, [OH^-] = 1.0 \times 10^{-8} M$$

$$At \ pH \ 2.0, [OH^-] = 1.0 \times 10^{-12} \ M$$

Step 2: Calculate the molar solubility of calcium hydroxide at each pH level

$$At \ pH \ 10.0, [Ca^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{6.5 \times 10^{-6}}{(1.0 \times 10^{-4}M)^2} = 6.5 \times 10^2 \ M$$

$$At \ pH \ 6.0, [Ca^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{6.5 \times 10^{-6}}{(1.0 \times 10^{-8}M)^2} = 6.5 \times 10^{10} \ M$$

$$At \ pH \ 2.0, \ [Ca^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{6.5 \times 10^{-6}}{(1.0 \times 10^{-12}M)^2} = 6.5 \times 10^{18} \ M$$

Step 3: Calculate the mass solubility (S) of calcium hydroxide at each pH level

$$At \; pH \; 10.0, S_{Ca(OH)_2} = [Ca^{2+}]MW_{Ca(OH)_2}$$

$$= (6.5 \; x \; 10^2 M \; Ca^{2+}) \left( \frac{1 \; mol \; Ca(OH)_2}{1 \; mol \; Ca^{2+}} \right) \left( \frac{74.093 \; g \; Ca(OH)_2}{1 \; mol \; Ca(OH)_2} \right)$$

$$= \frac{4.8 \; x \; 10^4 \; g \; Ca(OH)_2}{L \; solution}$$

$$At \; pH \; 6.0, S_{Ca(OH)_2} = \frac{4.8 \; x \; 10^{12} \; g \; Ca(OH)_2}{L \; solution}$$

$$At \; pH \; 2.0, S_{Ca(OH)_2} = \frac{4.8 \; x \; 10^{19} \; g \; Ca(OH)_2}{L \; solution}$$

The table below contains the molar solubility and mass solubility for all the hydroxide salts from Table 1 in the Chemical Equilibria document.

| Salt | $K_{sp}$ | Molar Solubility (M) | | | Mass Solubility (g/L) | | |
|---|---|---|---|---|---|---|---|
| | | pH 10 | pH 6 | pH 2 | pH 10 | pH 6 | pH 2 |
| $Ca(OH)_2$ | $6.5 \; x \; 10^{-6}$ | $6.5 \; x \; 10^2$ | $6.5 \; x \; 10^{10}$ | $6.5 \; x \; 10^{18}$ | $4.8 \; x \; 10^4$ | $4.8 \; x \; 10^{12}$ | $4.8 \; x \; 10^{18}$ |
| $Mg(OH)_2$ | $7.1 \; x \; 10^{-12}$ | $7.1 \; x \; 10^{-4}$ | $7.1 \; x \; 10^4$ | $7.1 \; x \; 10^{12}$ | $4.1 \; x \; 10^{-2}$ | $4.1 \; x \; 10^6$ | $4.1 \; x \; 10^{14}$ |
| $Al(OH)_3$ | $4.6 \; x \; 10^{-33}$ | $4.6 \; x \; 10^{-21}$ | $4.6 \; x \; 10^{-9}$ | $4.6 \; x \; 10^3$ | $3.6 \; x \; 10^{-19}$ | $3.6 \; x \; 10^{-7}$ | $3.6 \; x \; 10^5$ |
| $Fe(OH)_2$ | $8.0 \; x \; 10^{-16}$ | $8.0 \; x \; 10^{-8}$ | $8.0 \; x \; 10^0$ | $8.0 \; x \; 10^8$ | $7.2 \; x \; 10^{-6}$ | $7.2 \; x \; 10^2$ | $7.2 \; x \; 10^{10}$ |
| $Fe(OH)_3$ | $1.6 \; x \; 10^{-39}$ | $1.6 \; x \; 10^{-27}$ | $1.6 \; x \; 10^{-15}$ | $1.6 \; x \; 10^{-3}$ | $1.7 \; x \; 10^{-25}$ | $1.7 \; x \; 10^{-13}$ | $1.7 \; x \; 10^{-1}$ |

Note that for salts having a relatively large $K_{sp}$ or under acidic conditions, the predicted molar solubility and mass solubility are unrealistically large. In these cases, the solubility is no longer dependent on the solubility equilibrium but on the number of moles of solvent required to interact with each mole of solute. The molarity of water is 55.6 M, and each ion would be surrounded by several molecules of water. It is, therefore, unreasonable to expect that the solute concentration under low pH conditions would exceed several moles per liter.

The solubility of metal hydroxides increases with decreasing pH. Metal hydroxides that have a cation with an oxidation state of +2 exhibit a one hundred-fold increase in their solubility for every unit decrease in pH. Metal hydroxides that have a cation with an oxidation state of +3 exhibit a one thousand-fold increase in their solubility for every unit decrease in pH.

**Q12.** Integrating the ideas of redox chemistry and solubility expressed in this module, summarize the chemical and physical changes you would expect over time in a sample of Lithia water? What sample preparation step could be used to prevent such changes from occurring?

Previous questions on redox chemistry (see **Q6** in this guide) indicate that dissolved oxygen does not affect the concentration or oxidation state of main group metals, but that dissolved oxygen is predicted to oxidize ferrous ion to ferric ion. Previous questions on analyte solubility as a function of pH indicate that metal hydroxides of interest in the analysis of Lithia water tend to be insoluble under basic to slightly acidic conditions, but that most of these hydroxides are moderately to freely soluble at low pH. The $K_{sp}$ of ferric hydroxide is orders of magnitude lower than ferrous hydroxide, which results in the precipitation of ferric hydroxide in Lithia water after the oxidation of ferrous ion by dissolved oxygen occurs. Observations in the author's laboratory indicated that most of the ferrous ion in Lithia water is oxidized and precipitates as ferric hydroxide within the first 24 hours after sample collection. However, at low pH ($\leq$ 2.0), even the least soluble of the metal hydroxides, ferric hydroxide, is moderately soluble at pH 2.0, with a mass solubility of 170 mg $L^{-1}$. Therefore, it is suggested that if the pH of the Lithia water is adjusted to a pH of 2.0 or less, analytes that form insoluble hydroxides can be prevented from precipitating by acidification with trace-metal grade or reagent grade acid. Instructors are encouraged to address this question as students are observing changes in their mineral water sample.

**Q13.** Collection of samples for trace metal analysis in drinking water is described in the Sample Collection, Preservation, and Storage section of EPA method 200.5, Determination of Trace Elements in Drinking Water by Axially Viewed Inductively Coupled Plasma - Atomic Emission Spectrometry (http://www.epa.gov/nerlcwww/ordmeth.htm). After reading this document, suggest a general approach to preserving Lithia water prior to analysis. Would this work for all analytes of interest in Lithia water? Explain.

EPA method 200.5 is a protocol for the determination of a large set of cations in drinking water. In the Collection, Preservation, and Storage section of EPA method 200.5, to properly keep all inorganic cations in solution, the analyst is instructed to acidify a one liter water sample with 3.0 mL of (1+1) nitric acid, and after 16 hours of cold storage, verify that the pH of the acidified sample is below 2.0.

The effect of sample acidification on the solubility of sparingly soluble salts is introduced in the Lithia water module entitled *Chemical Equilibria*. In the case of Lithia water, students are expected to discover that dissolved oxygen oxidizes the ferrous ion to ferric ion. Because iron (III) hydroxide is significantly less soluble than iron (II) hydroxide, a layer of iron (III) hydroxide settles out of solution as an orange precipitate in 1-2 days unless the sample is acidified. However, while sample acidification keeps metal ions in solution, sample acidification also protonates the bicarbonate ion to form carbonic acid, which subsequently dissociates into carbon dioxide and water. Therefore, students analyzing Lithia water should suggest the collection of two samples; one acidified sample for the determination of iron and another

unacidified sample for the remaining analytes. Lithia water students can also suggest, based on EPA method 200.5, that the acidified sample be used for the determination of metal ions, and the unacidified sample be used for the determination of anions.

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***Solubility Equilibria – Advanced Topics***

**Q14.** Calculate the alpha values for the three carbonic acid species ($H_2CO_3$, $HCO_3^-$, $CO_3^{2-}$) at a pH of 6.4. Do these values agree with your predictions based on the carbonic acid ladder diagram?

The ladder diagram for the carbonic acid system is shown to the right ($K_{a1} = 4.47 \times 10^{-7}$, $K_{a2} = 4.68 \times 10^{-11}$). Once students are introduced to alpha values, they should realize that at a given pH, the fraction of each form of the analyte can be calculated using only the $K_a$ values and the pH.

pH

$[CO_3^{2-}]$

$pK_{a2} = 10.33$

$[HCO_3^-]$

$pK_{a1} = 6.35$
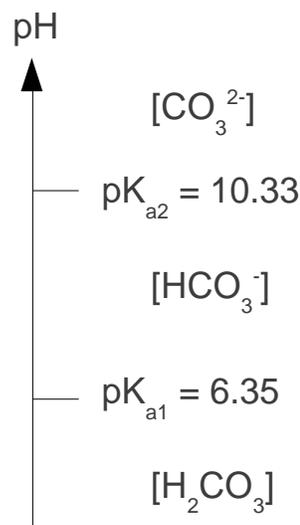
$[H_2CO_3]$

$$[H^+] = 10^{-pH} = 10^{-6.4} = 3.98 \times 10^{-7}\,M$$

$$\alpha_{H_2CO_3} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}} =$$

$$\frac{(3.98 \times 10^{-7}\,M)^2}{(3.98 \times 10^{-7}\,M)^2 + (3.98 \times 10^{-7}\,M)(4.47 \times 10^{-7}) + (4.47 \times 10^{-7})(4.68 \times 10^{-11})}$$

$$\alpha_{H_2CO_3} = 0.471$$

$$\alpha_{HCO_3^-} = \frac{[H^+]K_{a1}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}} =$$

$$\frac{(3.98 \times 10^{-7}\,M)(4.47 \times 10^{-7})}{(3.98 \times 10^{-7}\,M)^2 + (3.98 \times 10^{-7}\,M)(4.47 \times 10^{-7}) + (4.47 \times 10^{-7})(4.68 \times 10^{-11})}$$

$$\alpha_{HCO_3^-} = 0.529$$

$$\alpha_{CO_3^{2-}} = \frac{K_{a1}K_{a2}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}} =$$

$$\frac{(4.47 \times 10^{-7})(4.68 \times 10^{-11})}{(3.98 \times 10^{-7}\,M)^2 + (3.98 \times 10^{-7}\,M)(4.47 \times 10^{-7}) + (4.47 \times 10^{-7})(4.68 \times 10^{-11})}$$

$$\alpha_{CO_3^{2-}} = 0.000062$$

The calculated fractions of each carbonate species make sense since the pH (6.4) is close to but slightly more basic than the $pK_{a1}$ (6.35) for carbonic acid. When pH is equal to $pK_{a1}$, then the fraction of each species involved in the equilibrium described by $K_{a1}$ by definition equals 0.50.

**Q15.** Given that the pH of the Lithia water is 6.4, what is the total concentration of all species in the carbonic acid equilibrium?

The introduction of alpha values enables students to account for the acid-base behavior of ionic species in solution. In the stoichiometric calculations used to determine the concentrations of inorganic constituents in Lithia water (Major Inorganic Constituents – **Q3** and **Q4**), it was determined that the bicarbonate concentration in Lithia water, based on the analysis on the 1915 plaque, was 0.06736 M. Assuming that the pH of the water was 6.4, 52.9% of the species in the carbonic acid equilibrium exist as bicarbonate. Therefore, the total concentration of all species in the carbonic acid equilibrium is:

$$c_T = \frac{0.06736\ M}{0.529} = 0.1273\ M$$

This concentration represents the sum of all carbonate-based species in the carbonic acid equilibrium (i.e. $c_T = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]$)

**Q16.** What is the concentration of carbonate ion?

$$[CO_3^{2-}] = \alpha_{CO_3^{2-}} c_T = (0.000062)(0.1273M) = 7.92\ x\ 10^{-6}M$$

**Q17.** Using this concentration of carbonate, calculate the concentration of calcium that you would expect in Lithia water from the dissolution of calcium carbonate.

$K_{sp} = [Ca^{2+}][CO_3^{2-}]$

$$[Ca^{2+}][CO_3^{2-}] = K_{sp} = 4.5\ x\ 10^{-9}$$

$$[Ca^{2+}] = \frac{K_{sp}}{[CO_3^{2-}]} = \frac{4.5\ x\ 10^{-9}}{7.92\ x\ 10^{-6}} = 5.68\ x\ 10^{-4}\ M$$

And the mass solubility (S)

$$S = (5.68\ x\ 10^{-4}M\ Ca^{2+})\left(\frac{40.08\ g\ Ca^{2+}}{1\ mol\ Ca^{2+}}\right)\left(\frac{1000\ mg}{1\ g}\right) = 22.8\ mg\ L^{-1}$$

**Q18.** Compare this value to the value of calcium on the plaque.

In the section on Major Inorganic Constituents, the concentration of calcium in Lithia water was determined to be 347 mg $L^{-1}$. This concentration was based on the analysis engraved on the 1915 plaque. This concentration is approximately fifteen times higher than the calcium ion content calculated in the previous problem, which indicates that the acid-base chemistry of the carbonic acid system is not the only factor that controls the calcium ion concentration in Lithia water.Instructors may want to stress this difference between calculated and determined calcium concentrations as an introduction to the effect of ionic strength on solubility.

**Q19.** What effect would raising the ionic strength of a solution have on the solubility of a sparingly soluble salt? Think about what relatively high concentrations of other ions (e.g., $Na^+$ and $Cl^-$) might have in a solution containing smaller amounts of $Ca^{2+}$ and $CO_3^{2-}$.

In the case of the solubility of a sparingly soluble salt, analyte ions ($Ca^{2+}$ and $CO_3^{2-}$) experience coulombic interactions with the supporting electrolyte of opposite charge (e.g. $CO_3^{2-}$ ions interact with $Na^+$, and $Ca^{2+}$ ions interact with $Cl^-$) . The ions from the supporting electrolyte partially screen the charge of each analyte ion. These interactions decrease the activity, or the effective concentration, of the analyte ions.The solubility equilibrium and equilibrium constant expression of calcium carbonate is expressed by:

$$CaCO_3 \text{ (s)} \rightleftharpoons Ca^{2+} \text{ (aq)} + CO_3^{2-} \text{ (aq)} \qquad\qquad K_{sp} = a_{Ca^{2+}} a_{CO_3^{2-}}$$
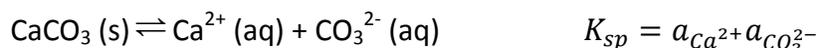
As the ionic strength of a solution increases, the screening of the analyte ions increases, and the analyte ion activity decreases. According to LeChatelier's principle, if the activity of the dissolved ions decreases, then more of the solid should dissolve so that the product of the calcium ion and carbonate ion concentrations once again equals the solubility product. Instructors should keep in mind that students do not need to know the Debye-Hückel equation in order to answer this question.

**Q20.** Calculate the molar solubility of AgCl under infinite dilution conditions (i.e. $\mu = 0$) with its solubility in 0.10 M $NaNO_3$. The hydrated ion diameters and thermodynamic equilibrium constants may be obtained from *Analytical Chemistry 2.0*.

$AgCl(s) \rightleftharpoons Ag^+ \text{ (aq)} + Cl^- \text{ (aq)}$ $\qquad\qquad\qquad$ $K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$

Under infinite dilution conditions:

$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$

Let X be the molar solubility of AgCl

$[Ag^+][Cl^-] = (X)(X) = X^2 = 1.8 \times 10^{-10}$

$X = 1.34 \times 10^{-5}$ M

Taking ionic strength into account:

- Calculation of ionic strength ($\mu$)
  - $\mu = \frac{1}{2}\Sigma c_i z_i^2 = \frac{1}{2}\left((0.10 \ M \ Na^+)(+1)^2 + (0.10 \ M \ NO_3^-)(-1)^2\right) = 0.10$
- Calculation of activity coefficients ($\gamma$) using Debye – Hückel equation

$$\log \gamma_x = \frac{-0.51\, z^2 \sqrt{\mu}}{1 + 3.3\alpha_x\sqrt{\mu}}$$

$$\gamma_{Ag^+} = 10^{\frac{-0.51\, z^2 \sqrt{\mu}}{1+3.3\alpha_x\sqrt{\mu}}} = 10^{\frac{(-0.51)\left(1^2\right)\sqrt{0.10}}{1+3.3(0.25\ \text{nm})\sqrt{0.10}}} = 0.7449$$

$$\gamma_{Cl^-} = 10^{\frac{-0.51\, z^2 \sqrt{\mu}}{1+3.3\alpha_x\sqrt{\mu}}} = 10^{\frac{(-0.51)\left(-1^2\right)\sqrt{0.10}}{1+3.3(0.3\ \text{nm})\sqrt{0.10}}} = 0.7537$$

- Calculation of a concentration-based solubility product and molar solubility of AgCl
  - $K'_{sp} = \dfrac{K_{sp}}{\gamma_{Ag^+}\gamma_{Cl^-}} = \dfrac{1.8\ x\ 10^{-10}}{(0.7449)(0.7537)} = 3.2\ x\ 10^{-10}$
  - $X^2 = 3.2\ x\ 10^{-10}$
  - $X = 1.79\ x\ 10^{-5} M$

**Q21.** Calculate the concentration-based equilibrium constant for $CaCO_3$, $H_2CO_3$, and $HCO_3^-$, and use these constants to predict the calcium concentration in Lithia water at pH 6.4. The ionic strength of Lithia water may be calculated from the solute molarities reported on the plaque from the Major Inorganic Constituents section, and the hydrated ion diameters and thermodynamic equilibrium constants may be obtained from *Analytical Chemistry 2.0*.

For the solubility equilibrium

$CaCO_3$ (s) $\rightleftharpoons Ca^{2+}$ (aq) + $CO_3^{2-}$ (aq)
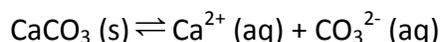
Taking ionic strength into account:

- Calculation of ionic strength ($\mu$): This calculation involves the analyte molarities that were calculated from the 1915 analysis of Lithia water.

  - $\mu = \frac{1}{2}\sum c_i z_i^2 = \frac{1}{2}\begin{pmatrix}(0.1114\ M\ Na^+)(+1)^2+(0.002792\ M\ K^+)(+1)^2+(0.002263\ M\ Li^+)(+1)^2+ \\ (0.00866\ M\ Ca^{2+})(+2)^2+(0.00788\ M\ Mg^{2+})(+2)^2+ \\ (0.0001566\ M\ Fe^{2+})(+2)^2+ (0.07726\ M\ Cl^-)(-1)^2 \\ (0.06736\ M\ HCO_3^-)(-1)^2 + (0.004883\ M\ BO_2^-)(-1)^2 + \\ + (0.00002742\ M\ SO_4^{2-})(-2)^2+ (0.00158\ M\ SiO_3^{2-})(-2)^2\end{pmatrix} = 0.170$
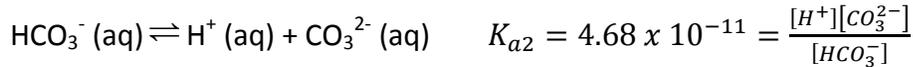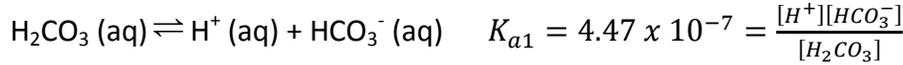
- Calculation of activity coefficients ($\gamma$) using the Debye – Hückel equation for inorganic salt

$$\log \gamma_x = \frac{-0.51\, z^2 \sqrt{\mu}}{1 + 3.3\alpha_x\sqrt{\mu}}$$

$$\gamma_{Ca^{2+}} = 10^{\frac{-0.51\, z^2 \sqrt{\mu}}{1+3.3\alpha_x\sqrt{\mu}}} = 10^{\frac{(-0.51)\left(2^2\right)\sqrt{0.170}}{1+3.3(0.60\ \text{nm})\sqrt{0.170}}} = 0.3443$$

$$\gamma_{CO_3^{2-}} = 10^{\frac{-0.51\,z^2\sqrt{\mu}}{1+3.3\alpha_x\sqrt{\mu}}} = 10^{\frac{(-0.51)(-2^2)\sqrt{0.170}}{1+3.3(0.45\,nm)\sqrt{0.170}}} = 0.3008$$

For the weak acid equilibria

$H_2CO_3$ (aq) $\rightleftharpoons$ $H^+$ (aq) + $HCO_3^-$ (aq)    $K_{a1} = 4.47\ x\ 10^{-7} = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]}$

$HCO_3^-$ (aq) $\rightleftharpoons$ $H^+$ (aq) + $CO_3^{2-}$ (aq)    $K_{a2} = 4.68\ x\ 10^{-11} = \dfrac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$

- Calculation of activity coefficients (γ) using Debye – Hückel equation for weak acid

$$\gamma_{H^+} = 10^{\frac{-0.51\,z^2\sqrt{\mu}}{1+3.3\alpha_x\sqrt{\mu}}} = 10^{\frac{(-0.51)(+1^2)\sqrt{0.170}}{1+3.3(0.9\,nm)\sqrt{0.170}}} = 0.8044$$

$$\gamma_{CO_3^{2-}} = 10^{\frac{-0.51\,z^2\sqrt{\mu}}{1+3.3\alpha_x\sqrt{\mu}}} = 10^{\frac{(-0.51)(-2^2)\sqrt{0.170}}{1+3.3(0.45\,nm)\sqrt{0.170}}} = 0.3008$$

$$\gamma_{HCO_3^-} = 10^{\frac{-0.51\,z^2\sqrt{\mu}}{1+3.3\alpha_x\sqrt{\mu}}} = 10^{\frac{(-0.51)(-1^2)\sqrt{0.170}}{1+3.3(0.45\,nm)\sqrt{0.170}}} = 0.7406$$

- Calculation of a concentration-based acid dissociation constant and the molar concentration of the carbonate ion

$$K'_{a2} = \frac{K_{a2}\gamma_{HCO_3^-}}{\gamma_{H^+}\,\gamma_{CO_3^{2-}}} = \frac{(4.68\ x\ 10^{-11})(0.7406)}{(0.8044)(0.3008)} = 1.43\ x\ 10^{-10}$$

$$1.43\ x\ 10^{-10} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

Based on the 1915 analysis, $[HCO_3^-]$ = 0.06736 M, and assuming that the pH is 6.4 ($[H^+]$ = 3.98 x $10^{-7}$ M):

$$1.43\ x\ 10^{-10} = \frac{(3.98\ x\ 10^{-7}M)[CO_3^{2-}]}{(0.06736\ M)}$$

$$2.42\ x\ 10^{-5}M = [CO_3^{2-}]$$

- Calculation of a concentration-based solubility product and both the molar solubility and mass solubility for calcium carbonate in Lithia water

  o $K'_{sp} = \dfrac{K_{sp}}{\gamma_{Ca^{2+}}\gamma_{CO_3^{2-}}} = \dfrac{4.5\ x\ 10^{-9}}{(0.3443)(0.3008)} = 4.35\ x\ 10^{-8}$

  o $K'_{sp} = [Ca^{2+}][CO_3^{2-}]$

- $4.35 \times 10^{-8} = [Ca^{2+}](2.42 \times 10^{-5} M)$

- $[Ca^{2+}] = 1.79 \times 10^{-3} M$

- $S_{CaCO_3} = 1.79 \times 10^{-3} M \left(\frac{100.09 \ g \ CaCO_3}{mol}\right)\left(\frac{1000 \ mg}{g}\right) = \frac{179.6 \ mg \ Ca^{2+}}{L}$

Students should be able to communicate that although the mass solubility of calcium carbonate in Lithia water is within a factor of two of the reported solubility from the 1915 analysis, there still may be another factor left unexplained which would account for the additional calcium in the Lithia water.

**Q22.** Remembering that the Lithia water contains carbonate ion, use LeChatelier's principle to explain what effect the addition of carbonic acid has on the concentration of carbonate ion in Lithia water?

The carbonate buffer system consists of carbonic acid, hydrogen carbonate ion (bicarbonate), and the carbonate ion, and all three of these chemical species contain the carbonate ion. Carbonic acid is the fully protonated form in the buffer system and carbonate ion is the fully deprotonated form in the buffer system. When carbonic acid is introduced to a solution containing carbonate ion, the dissociation of protons from carbonic acid shifts the carbonate equilbrium in Lithia water favoring the protonation of carbonate ion to form bicarbonate ion:

$$H_3O^+ \ (aq) + CO_3^{2-} \ (aq) \rightleftharpoons HCO_3^- \ (aq) + H_2O \ (l)$$
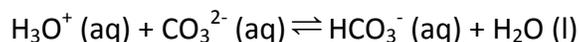
This reaction decreases the concentration of the carbonate ion in solution.

**Q23.** Considering your answer to the preceding question, what effect would the addition of carbonic acid have on the solubility of calcium carbonate and other sparingly soluble carbonate salts?

For the solubility equilibrium

$$CaCO_3 \ (s) \rightleftharpoons Ca^{2+} \ (aq) + CO_3^{2-} \ (aq)$$
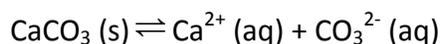
The addition of carbonic acid would reduce the carbonate ion concentration. Based on Le Chatelier's principle, if the concentration of a product is decreased in a chemical equilibrium, then the equilibrium would shift towards the products to reestablish equilibrium. This shift in the solubility equilibrium of calcium carbonate would increase the solubility of calcium carbonate.

**Q24.** The concentration of calcium ion based on the 1915 analysis of Lithia water is 347 mg L$^{-1}$. Assuming that the calcium ion concentration in Lithia water is controlled by the carbonate ion

concentration in Lithia water, calculate the carbonate ion concentration in Lithia water using the concentration-based equilibrium constant for calcium carbonate.

From **Q21 (Solubility Equilibria)**:

- $K'_{sp} = \dfrac{K_{sp}}{\gamma_{Ca^{2+}}\gamma_{CO_3^{2-}}} = \dfrac{4.5 \; x \; 10^{-9}}{(0.3443)(0.3008)} = 4.35 \; x \; 10^{-8}$
- $K'_{sp} = [Ca^{2+}][CO_3^{2-}]$

From **Q3 (Major Inorganic Constituents)**:

- $4.35 \; x \; 10^{-8} = (8.66 \; x \; 10^{-3} \; M)[CO_3^{2-}]$

  - $[CO_3^{2-}] = 5.02 \; x \; 10^{-6} M$

*Principle of Electroneutrality*

**Q1.** List the cations and anions that were determined this term

This answer will differ based on the type of sample available, time spent on the project, etc.In any case, the answer to this question will guide the student toward constructing the appropriate charge balance equation. For Lithia water, a typical list of ions is:

Cations: $Na^+$, $K^+$, $Li^+$, $Ca^{2+}$, $Mg^{2+}$, $Fe^{2+}$

Anions: $HCO_3^-$, $Cl^-$, $BO_2^-$, $SO_4^{2-}$, $SiO_3^{2-}$

**Q2.** Based on the principle of electroneutrality, what should be true about the concentration of cationic charge and anionic charge in Lithia water.

The number of moles of positive charge should equal the number of moles of negative charge.

**Q3.** Assuming that the inorganic constituents of Lithia water have been completely characterized, write down an appropriate charge balance equation for all dissolved ions in Lithia water.

Based on the list of ions in Q1 of this section, and assuming that silica exists in solution as the silicate ion, the appropriate charge balance equation for the inorganic ions in Lithia water would be:

$$[Na^+] + [K^+] + [Li^+] + 2[Ca^{2+}] + 2[Mg^{2+}] + 2[Fe^{2+}] = [HCO_3^-] + [Cl^-] + [BO_2^-] + [SO_4^{2-}] + [SiO_3^{2-}]$$
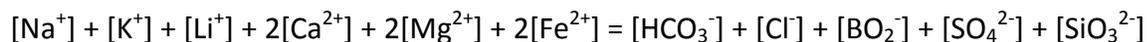
Because the pH of Lithia water is 6.4 and the concentration of the other ions is large, the contribution of $H^+$ and $OH^-$ to the charge balance reaction can be neglected. In other cases, such as solutions having low ionic strength, it may be necessary to include these species in the calculation of electroneutrality.

**Q4.** Use the error propagation equations described in Chapter 4 of *Analytical Chemistry 2.0* to propagate the experimental error in the following analytical determinations

     **a.**     A solution with a volume of 1.000 ± 0.012 mL was determined to have a mass of 1.008 ± 0.023 g. What is the density of the solution and its uncertainty?

$$D = \frac{M}{V} = \frac{1.008\ g}{1.000\ mL} = 1.008\ g\ mL^{-1}$$

To estimate the uncertainty of an experimental result that is calculated using solely multiplication and division:

$$\frac{u_D}{D} = \sqrt{\left(\frac{u_M}{M}\right)^2 + \left(\frac{u_V}{V}\right)^2}$$

$$\frac{u_D}{1.008 \; g \; mL^{-1}} = \sqrt{\left(\frac{0.023 \; g}{1.008 \; g}\right)^2 + \left(\frac{0.012 \; mL}{1.000 \; mL}\right)^2}$$

$$u_D = 0.026 \; g \; mL^{-1}$$

The density of the solution is 1.008 ± 0.026 g mL$^{-1}$.

**b.** The volume delivered by a buret ($\Delta V$) is the difference between the initial volume ($V_i$) and the final volume ($V_f$) read on the scale of the buret. If $V_i$ is (5.36 ± 0.02) mL and $V_f$ is (15.68 ± 0.02) mL, calculate the volume delivered and its uncertainty.

$$\Delta V = V_f - V_i = 15.68 \; mL - 5.36 \; mL = 10.32 \; mL$$

To estimate the uncertainty of an experimental result that is calculated using solely addition and subtraction:

$$u_{\Delta V} = \sqrt{u_{V_f}^2 + u_{V_i}^2}$$

$$u_{\Delta V} = \sqrt{(0.02 \; mL)^2 + (0.02 \; mL)^2} = 0.028 \; mL$$

Rounded to the nearest hundredth of a milliliter, the delivered volume is (10.32 ± 0.03) mL.

**c.** The density of a liquid was determined by measuring the mass of a 100-mL volumetric flask filled with the liquid, subtracting the mass of the empty 100-mL volumetric flask, and dividing the mass difference by the volume of the 100-mL volumetric flask. If the mass of the full flask is 248.3 ± 0.1 g, the mass of the empty flask is 45.5 ± 0.1 g, and the volume of the flask is 100.0 ± 0.08 mL, calculate the density of the liquid and its uncertainty.

$$D_{liq} = \frac{(M_{full} - M_{empty})}{V_{flask}} = \frac{(248.3 \; g - 45.5 \; g)}{100.0 \; mL} = 2.028 \; g \; mL^{-1}$$

To estimate the uncertainty of an experimental result that is calculated using two or more sets of mathematical operations (in this case, addition and/or subtraction followed by multiplication and/or division), one must propagate error through one set of operations (in this case, subtraction of two masses) followed by propagating the error through the remaining set of operations (in this case, dividing volume into mass):

$$(M_{full} - M_{empty}) = (248.3 \; g - 45.5 \; g) = 202.8 \; g$$

$$u_{\Delta M} = \sqrt{u^2_{M_{full}} + u^2_{M_{empty}}}$$

$$u_{\Delta V} = \sqrt{(0.1\ g)^2 + (0.1\ g)^2} = 0.141\ g$$

*(keep additional 1 or 2 digits to minimize rounding errors)*

$$\frac{u_D}{D} = \sqrt{\left(\frac{u_M}{M}\right)^2 + \left(\frac{u_V}{V}\right)^2}$$

$$\frac{u_D}{2.028\ g\ mL^{-1}} = \sqrt{\left(\frac{0.141\ g}{202.8\ g}\right)^2 + \left(\frac{0.08\ mL}{100.0\ mL}\right)^2}$$

$$u_D = 0.002\ g\ mL^{-1}$$

The density of the liquid is 2.028 ± 0.002 g mL$^{-1}$.

**Q5.** Based on your reading of Chapter 4 in *Analytical Chemistry 2.0*, what statistical approach would you use to determine whether equivalent amounts of cationic charge and anionic charge were determined in Lithia water?

A t-test for two experimental means would be the appropriate statistical test for determining whether statistically equivalent amounts of cationic charge and anionic charge were determined in Lithia water.

**Q6.** The Nutrition Facts label on a bottle of local mineral water contains the following information on select inorganic solutes (standard deviations provided by author, assume each result based on triplicate readings (n=3)):

| Solute | Concentration (mg L$^{-1}$) |
|---|---|
| Bicarbonate | 466 (± 24) |
| Magnesium | 124 (± 5) |
| Calcium | 2.67 (± 0.10) |
| Sodium | 3.31 (± 0.15) |
| Zinc | 4.45 (± 0.10) |

At the 95% confidence level, determine whether all of the major inorganic solutes have been reported on the Nutrition Facts label from this bottle of mineral water.

**Step 1:** Convert all solute concentrations and uncertainties into molarities

$$\left(\frac{466\ mg\ HCO_3^-}{L}\right)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol\ HCO_3^-}{61.02\ g\ HCO_3^-}\right) = 7.637\ x\ 10^{-3}M\ HCO_3^-$$

$$\left(\frac{24\ mg\ HCO_3^-}{L}\right)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol\ HCO_3^-}{61.02\ g\ HCO_3^-}\right) = 0.393\ x\ 10^{-3}M\ HCO_3^-$$

$$\left(\frac{124\ mg\ Mg^{2+}}{L}\right)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol\ Mg^{2+}}{24.305\ g\ Mg^{2+}}\right) = 5.102\ x\ 10^{-3}M\ Mg^{2+}$$

$$\left(\frac{5\ mg\ Mg^{2+}}{L}\right)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol\ Mg^{2+}}{24.305\ g\ Mg^{2+}}\right) = 0.206\ x\ 10^{-3}M\ Mg^{2+}$$

$$\left(\frac{2.67\ mg\ Ca^{2+}}{L}\right)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol\ Ca^{2+}}{40.08\ g\ Ca^{2+}}\right) = 6.662\ x\ 10^{-5}M\ Ca^{2+}$$

$$\left(\frac{0.10\ mg\ Ca^{2+}}{L}\right)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol\ Ca^{2+}}{40.08\ g\ Ca^{2+}}\right) = 0.250\ x\ 10^{-5}M\ Ca^{2+}$$

$$\left(\frac{3.31\ mg\ Na^+}{L}\right)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol\ Na^+}{22.9898\ g\ Na^+}\right) = 1.440\ x\ 10^{-4}M\ Na^+$$

$$\left(\frac{0.15\ mg\ Na^+}{L}\right)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol\ Na^+}{22.9898\ g\ Na^+}\right) = 0.065\ x\ 10^{-4}M\ Na^+$$

$$\left(\frac{4.45\ mg\ Zn^{2+}}{L}\right)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol\ Zn^{2+}}{65.37\ g\ Zn^{2+}}\right) = 6.807\ x\ 10^{-5}M\ Zn^{2+}$$

$$\left(\frac{0.10\ mg\ Zn^{2+}}{L}\right)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol\ Zn^{2+}}{65.37\ g\ Zn^{2+}}\right) = 0.153\ x\ 10^{-5}M\ Zn^{2+}$$

| Solute | Concentration (mg L$^{-1}$) | Concentration (M x 10$^3$) |
|---|---|---|
| Bicarbonate | 466 (± 24) | (7.637 ± 0.393) |
| Magnesium | 124 (± 5) | (5.102 ± 0.206) |
| Calcium | 2.67 (± 0.10) | (0.066 ± 0.002) |
| Sodium | 3.31 (± 0.15) | (0.144 ± 0.007) |
| Zinc | 4.45 (± 0.10) | (0.068 ± 0.002) |

**Step 2:** Create a charge balance equation for the bottled spring water sample based on the nutrition label.

$$[HCO_3^-] = 2[Mg^{2+}] + 2[Ca^{2+}] + [Na^+] + 2[Zn^{2+}]$$

**Step 3:** Use the charge balance equation and error propagation to determine the total cationic charge and total anionic charge including their associated uncertainties.

Anionic Charge: 7.637 mM

Anionic Charge Uncertainty: $s_- = 0.393 \; mM$

(bicarbonate ion is the only anionic species in this charge balance equation)

Cationic Charge: 2(5.102 mM) + 2(0.066 mM) + (0.144 mM) + 2(0.068 mM) = 10.616 mM

Cationic Charge Uncertainty:
$$s_+ = \sqrt{(2(0.206 \; mM))^2 + (2(0.0025 \; mM))^2 + (0.0065 \; mM)^2 + (2(0.0015 \; mM))^2}$$

$$s_+ = 0.412 \; mM$$

**Step 4:** Use the F-test to see if the variance for the anionic charge is significantly different than the variance of the cationic charge. If so, the t-test for two experimental means with equal variances can be used to compare the concentrations of the anionic charge and cationic charge. If not, the t-test for two experimental means with unequal variances must be used to compare the concentrations of the anionic charge and cationic charge.

$$F_{exp} = \frac{s_+^2}{s_-^2} \qquad \text{(larger variance is always in the numerator)}$$

$$F_{exp} = \frac{(0.412 \; mM)^2}{(0.393 \; mM)^2} = 1.10$$

$$At \; 95\% \; confidence \; level: \quad F_{crit}(0.05, 2, 3) = 16.04$$

$$degrees \; of \; freedom: \nu_{num} = 2$$

*(variance in numerator based on triplicate determinations of bicarbonate ion*

$$\nu_{denom} = 3$$

*(there are four cationic analytes)*

$$Since \; F_{exp} < F_{crit},$$

*the variances of the two groups are statistically equivalent @ 95% confidence level*

**Step 5:** Use the t-test for two experimental means with equal variances to determine if the anionic and cationic solute concentrations are statistically equivalent at the 95% confidence level.

$$t_{exp} = \frac{|\bar{X}_+ - \bar{X}_-|}{s_{pooled}\sqrt{\frac{1}{n_+} + \frac{1}{n_-}}}$$

$$where \; s_{pooled} = \sqrt{\frac{(n_+ - 1)s_+^2 + (n_- - 1)s_-^2}{(n_+ + n_- - 2)}}$$

$$s_{pooled} = \sqrt{\frac{(4 - 1)(0.412 \; mM)^2 + (3 - 1)(0.393 \; mM)^2}{(4 + 3 - 2)}} = 0.405 \; mM$$

$$t_{exp} = \frac{|10.616 \; mM - 7.637 \; mM|}{(0.405 \; mM)\sqrt{\frac{1}{4} + \frac{1}{3}}} = 9.63$$

$$t_{critical}(0.05,5) = 2.571, and \; therefore, t_{expt} > t_{critical}$$

*the difference in the ionic concentrations is statistically significant at the 95% c.l.*

***Assessment Question Set #1 – Solubility Equilibria***

**Q1.**   Write the balanced reaction for the dissolution of iron (III) hydroxide in water.

Q1 is a knowledge-based question for quantitative analysis students. Chemistry students at this level should be able to write the chemical formula of an ionic compound and express the dissociation of an ionic compound in water, which is general chemistry material.

$$Fe(OH)_3 \text{ (s)} \rightleftharpoons Fe^{3+} \text{ (aq)} + 3\ OH^- \text{ (aq)}$$
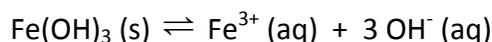
**Q2.**   Write the equilibrium constant expression for the solubility of iron (III) hydroxide.

Q2 is a comprehension-based question for quantitative analysis students. If a chemistry student can recall the definition of an equilibrium constant expression, then that student can modify the definition of an equilibrium constant expression for any solubility equilibrium.

$$K_{sp} = [Fe^{3+}][OH^-]^3$$

**Q3.**   Calculate the molar solubility of iron (III) hydroxide in pure water.

Q3 is an application-based question for determining the solubility of an ionic compound in water.

In pure water, pH = pOH = 7.00. Therefore, in pure water, $[OH^-] = 1.0 \times 10^{-7}$ M :

$$Fe(OH)_3 \text{ (s)} \rightleftharpoons Fe^{3+} \text{ (aq)} + 3\ OH^- \text{ (aq)}$$

| | | | |
|---|---|---|---|
| Initial | ----- | 0 | $1.0 \times 10^{-7}$ |
| Change | -X | +X | +3X |
| Equilibrium | ----- | X | $1.0 \times 10^{-7}$ + 3X |

*Assume that X represents the molar solubility of iron (III)hydroxide*

$$K_{sp} = [Fe^{3+}][OH^-]^3$$

$$1.6\ x\ 10^{-39} = (X)(1.0\ x\ 10^{-7} + 3X)^3$$

*assuming* $3X \ll 1.0\ x\ 10^{-7}M$

$$1.6\ x\ 10^{-39} = (X)(1.0\ x\ 10^{-7})^3$$

$$1.6\ x\ 10^{-18}M = X$$

*using* 5% *rule,*    $3X < (0.05)(1.0\ x\ 10^{-7}M)$

$$3(1.6 \ x \ 10^{-18} \ M) < 5.0 \ x \ 10^{-9}M, assumption \ holds$$

**Q4.** Calculate the molar solubility of iron (III) hydroxide at pH 6.4, and compare it to the calculated molar solubility of iron (III) hydroxide in Q3.

Q4 is an analysis-based question because it requires that a student differentiate between the solubility of iron hydroxide in a solvent where one of the ion concentrations (i.e. hydroxide) is held constant (i.e. a buffer) and where the concentration is not held constant.

In a pH buffer, the hydronium ion concentration, and therefore the hydroxide ion concentration, is constant. In a buffered solution with a pH of 6.4:

$$pH + pOH = 14$$

$$pOH = 14 - pH = 14 - 6.4 = 7.6$$

$$[OH^-] = 10^{-pOH} = 10^{-7.6} = 2.5 \ x \ 10^{-8} \ M$$

$$K_{sp} = [Fe^{3+}][OH^-]^3$$

$$1.6 \ x \ 10^{-39} = (X)(2.5 \ x \ 10^{-8}M)^3$$

$$1.0 \ x \ 10^{-16}M = X$$

$$since \ 1.0 \ x \ 10^{-16} \ M > 4.8 \ x \ 10^{-18}M,$$

$$the \ solubility \ of \ Fe(OH)_3 \ increases \ as \ the \ solution \ becomes \ more \ acidic$$

**Q5.** Calculate the molar solubility of iron (III) hydroxide when the ionic strength of the pH 6.4 buffer is 0.10 mol L$^{-1}$.

Q5 is a synthesis-based question because it requires a student to understand how ionic strength controls the activity coefficient of an analyte, to understand how this activity coefficient changes the magnitude of the equilibrium constant, and to apply these concepts in the determination of the molar solubility of the ionic compound. In this problem, a student needs to:

- Use the Debye-Hückel equation to calculate the activity coefficient of each ionic species in the iron (III) hydroxide solubility equilibrium

$$\log \gamma_x = \frac{-0.51 \ z^2 \sqrt{\mu}}{1 + 3.3\alpha_x\sqrt{\mu}}$$

$$\gamma_{Fe^{3+}} = 10^{\frac{-0.51\, z^2 \sqrt{\mu}}{1+3.3\alpha_x\sqrt{\mu}}} = 10^{\frac{(-0.51)\left(+3^2\right)\sqrt{0.10}}{1+3.3(0.9\,\text{nm})\sqrt{0.10}}} = 0.1784$$

$$\gamma_{OH^-} = 10^{\frac{-0.51\, z^2 \sqrt{\mu}}{1+3.3\alpha_x\sqrt{\mu}}} = 10^{\frac{(-0.51)\left(-1^2\right)\sqrt{0.10}}{1+3.3(0.35\,\text{nm})\sqrt{0.10}}} = 0.7619$$

- Calculate the concentration-based equilibrium constant using the thermodynamically-based equilibrium constant and the activity coefficients calculated in the previous step

$$K'_{sp} = \frac{K_{sp}}{\gamma_{Fe^{3+}}(\gamma_{OH^-})^3} = \frac{1.6\ x\ 10^{-39}}{(0.1784)(0.7619)^3} = 2.0\ x\ 10^{-38}$$

- Calculate the molar solubility of the ionic compound using the concentration-based equilibrium constant

$$K'_{sp} = [Fe^{3+}][OH^-]^3$$

$$2.0\ x\ 10^{-38} = (X)(2.5\ x\ 10^{-8}M)^3$$

$$1.3\ x\ 10^{-15}M = X$$

**Q6.** To prevent precipitation of iron (III) hydroxide in household water systems, hydrogen peroxide is often added as an oxidizing agent to municipal water sources containing iron (II) ion concentrations above 0.3 mg $L^{-1}$. Compare the effectiveness of this treatment at pH 6.4 versus pH 2.0 at a dissolved iron (i.e. $Fe^{2+}$) concentration of 0.3 mg $L^{-1}$..

Q6 is an evaluation-based question as it asks the student to use equilibrium chemistry to compare the effectiveness of iron removal during water purification under two sets of conditions.

Since hydrogen peroxide is used as an oxidizing agent to remove iron, the first step for the student is to recognize that there is a large difference in solubility constants between iron (II) hydroxide and iron (III) hydroxide, and that this difference may lead to marked differences in solubility between the two salts. The second step is to use each solubility equilibrium constant expression to determine the molar solubility of each salt at each pH and compare it to the analyte concentration of interest (0.3 mg $L^{-1}$) to evaluate the effectiveness of hydrogen peroxide.

The critical molarity of dissolved iron in water for this problem is:

$$\left(\frac{0.3 \; mg \; Fe}{L}\right)\left(\frac{1 \; g}{1000 \; mg}\right)\left(\frac{1 \; mol \; Fe}{55.85 \; g \; Fe}\right) = 5.4 \; x \; 10^{-6} M \; Fe$$

At pH 6.4:

Iron (III) hydroxide

$$K_{sp} = [Fe^{3+}][OH^-]^3$$

$$1.6 \; x \; 10^{-39} = (X)(2.5 \; x \; 10^{-8}M)^3$$

$$1.0 \; x \; 10^{-16}M = X$$

Iron (II) hydroxide

$$K_{sp} = [Fe^{3+}][OH^-]^2$$

$$8.0 \; x \; 10^{-16} = (X)(2.5 \; x \; 10^{-8}M)^2$$

$$1.3M = X$$

When the solution pH is slightly acidic, the oxidation of ferrous ion by the addition of hydrogen peroxide results in the formation of an iron (III) hydroxide salt which is substantially less soluble than the iron (II) hydroxide salt. Under these conditions, hydrogen peroxide is effective at decreasing the dissolved iron concentration below the 0.3 mg L$^{-1}$ threshold.

At pH 2.0:

Iron (III) hydroxide

$$K_{sp} = [Fe^{3+}][OH^-]^3$$

$$1.6 \; x \; 10^{-39} = (X)(1.0 \; x \; 10^{-12}M)^3$$

$$1.6 \; x \; 10^{-3}M = X$$

Iron (II) hydroxide

$$K_{sp} = [Fe^{3+}][OH^-]^2$$

$$8.0 \; x \; 10^{-16} = (X)(1.0 \; x \; 10^{-12}M)^2$$

$$8 \; x \; 10^8 M = X \; (unrealistically \; large - interpret \; as \; freely \; soluble)$$

Under highly acidic conditions, both iron hydroxide salts are more soluble than the 0.3 mg L$^{-1}$ threshold for dissolved iron. This example highlights the significance of sample acidification below pH 2.0 as a method of sample preservation for metals analysis.