

Example question: Water Constituents

Following water quality was obtained for a drinking water sample. Answer the following.

| Chemical species | Results |
|-------------------------------|----------|
| Chloride, Cl^- | 8 mg/L |
| Sulfate, SO_4^{2-} | 16 mg/L |
| Total Dissolved Solids (TDS) | 110 mg/L |
| Bicarbonate, HCO_3^- | 73 mg/L |
| Calcium, Ca^{2+} | 15 mg/L |
| Magnesium, Mg^{2+} | 5 mg/L |
| pH | 9 |
| Potassium, K^+ | 0.7 mg/L |
| Silica, SiO_2 | 7 mg/L |
| Sodium, Na^+ | 13 mg/L |

- 1) Calculate the concentrations of H^+ and OH^- in the water in mg/L. How significant are these values compared to the values for the ions given above?

Answer)

$$[\text{H}^+] = 10^{-9} \text{ M}, [\text{OH}^-] = 10^{-5} \text{ M}$$

concentrations in mg/L:

$$\text{H}^+: 10^{-9} \text{ mole/L} \times 1 \text{ g/mole} \times 10^3 \text{ mg/g} = 10^{-6} \text{ mg/L}$$

$$\text{OH}^-: 10^{-5} \text{ mole/L} \times 17 \text{ g/mole} \times 10^3 \text{ mg/g} = 0.17 \text{ mg/L}$$

H^+ is definitely negligible.

OH^- concentration 2% of the lowest concentration (Cl^- , 8 mg/L) among anions without OH^- and 24% of the lowest concentration (K^+ , 0.7 mg/L) among all ions without H^+ and OH^- . Decision on the significance of OH^- depends on what extent the error for analysis will be accepted.

- 2) Calculate the concentrations of the ions listed in the table in milliequivalents per liter, and summarize the results in a table. Do the cations and anions appear to be in charge balance? Would including the H^+ and OH^- concentrations in the charge balance affect the results?

Answer)

| <i>Chemical species</i> | <i>Results</i> | <i>MW</i> | <i>z</i> | <i>Conc. (in meq/L)</i> |
|--|-----------------------------|-------------|----------|-----------------------------|
| <i>Anions</i> | | | | |
| <i>Cl⁻</i> | <i>8 mg/L</i> | <i>35.5</i> | <i>1</i> | <i>0.225</i> |
| <i>SO₄²⁻</i> | <i>16 mg/L</i> | <i>96.1</i> | <i>2</i> | <i>0.333</i> |
| <i>HCO₃⁻</i> | <i>73 mg/L</i> | <i>61.0</i> | <i>1</i> | <i>1.197</i> |
| <i>Anion sum (excluding OH⁻)</i> | | | | <i>1.755</i> |
| <i>OH⁻</i> | <i>0.17 mg/L</i> | <i>17.0</i> | <i>1</i> | <i>0.010</i> |
| <i>Anion sum (including OH⁻)</i> | | | | <i>1.765</i> |
| <i>Cations</i> | | | | |
| <i>Ca²⁺</i> | <i>15 mg/L</i> | <i>40.1</i> | <i>2</i> | <i>0.748</i> |
| <i>Mg²⁺</i> | <i>5 mg/L</i> | <i>24.3</i> | <i>2</i> | <i>0.412</i> |
| <i>K⁺</i> | <i>0.7 mg/L</i> | <i>39.1</i> | <i>1</i> | <i>0.018</i> |
| <i>Na⁺</i> | <i>13 mg/L</i> | <i>23.0</i> | <i>1</i> | <i>0.565</i> |
| <i>Cation sum (excluding H⁺)</i> | | | | <i>1.743</i> |
| <i>H⁺</i> | <i>10⁻⁶ mg/L</i> | <i>1.0</i> | <i>1</i> | <i>10⁻⁶</i> |
| <i>Cation sum (including H⁺)</i> | | | | <i>1.743</i> |

When *OH⁻* & *H⁺* are not included:

$$|\sum \text{anions} - \sum \text{cations}| = 1.755 - 1.743 = 0.012$$

$$0.1065 + 0.0155 \times \sum \text{anions} = 0.1065 + 0.0155 \times 1.755 = 0.134$$

$|\sum \text{anions} - \sum \text{cations}| > 0.1065 + 0.0155 \times \sum \text{anions}$ (*cations and anions in charge balance, acceptable*)

When *OH⁻* & *H⁺* are included:

$$|\sum \text{anions} - \sum \text{cations}| = 1.765 - 1.743 = 0.022$$

$$0.1065 + 0.0155 \times \sum \text{anions} = 0.1065 + 0.0155 \times 1.765 = 0.134$$

$|\sum \text{anions} - \sum \text{cations}| > 0.1065 + 0.0155 \times \sum \text{anions}$ (*including OH⁻ & H⁺ does not affect the results*)

Note: Although it is not the intention of this question, it is possible to calculate the carbonate ion (CO_3^{2-}) concentration from the bicarbonate (HCO_3^-) concentration and the pH value. Note the 2nd acid dissociation constant for carbonic acid, K_{a2} :

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.3}$$

Therefore, $[CO_3^{2-}]$ can be calculated as:

$$[CO_3^{2-}] = \frac{K_{a2}[HCO_3^-]}{[H^+]} = \frac{10^{-10.3} \times (1.197 \times 10^{-3} \text{ mole/L})}{10^{-9} \text{ mole/L}}$$

$$= 6.00 \times 10^{-5} \text{ M} = 6.00 \times 10^{-2} \text{ mM} = 0.120 \text{ meq/L}$$

which can be significant.

- 3) Calculate the ionic strength of the water. Is it safe to assume that the drinking water is a dilute solution? Determine based on an acceptable error of 5% for molarity = activity.

Answer)

| Chemical species | Results | MW | C_i (mM) | z_i | $C_i z_i^2$ (mM) |
|------------------|----------|------|------------|-------|------------------|
| Anions | | | | | |
| Cl^- | 8 mg/L | 35.5 | 0.225 | 1 | 0.225 |
| SO_4^{2-} | 16 mg/L | 96.1 | 0.166 | 2 | 0.666 |
| HCO_3^- | 73 mg/L | 61.0 | 1.197 | 1 | 1.197 |
| Cations | | | | | |
| Ca^{2+} | 15 mg/L | 40.1 | 0.374 | 2 | 1.496 |
| Mg^{2+} | 5 mg/L | 24.3 | 0.206 | 2 | 0.823 |
| K^+ | 0.7 mg/L | 39.1 | 0.018 | 1 | 0.018 |
| Na^+ | 13 mg/L | 23.0 | 0.565 | 1 | 0.565 |
| Sum | | | | | 4.990 |

$$I = 0.5 \times 4.99 \text{ mM} = 2.50 \times 10^{-3} \text{ M}$$

$$\log \gamma_i = -\frac{0.5 z_i^2 I^{0.5}}{1 + I^{0.5}}$$

For divalent ions (e.g., SO_4^{2-} , Ca^{2+} , Mg^{2+}):

$$\log \gamma_i = -\frac{0.5 \times 2^2 \times 0.00499^{0.5}}{1 + 0.00499^{0.5}} = -0.0952$$

$$\gamma_i = 0.803$$

For monovalent ions (e.g., Cl^- , HCO_3^- , K^+ , Na^+):

$$\log \gamma_i = -\frac{0.5 \times 1^2 \times 0.00499^{0.5}}{1 + 0.00499^{0.5}} = -0.0238$$

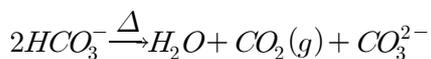
$$\gamma_i = 0.947$$

Creates more than 5% error for both cases. For accurate calculations, we should not assume molarity=activity for this water sample.

- 4) In the common method for measuring the total dissolved solids of a sample, drying of the sample by heating converts bicarbonate to carbon dioxide, water, and carbonate. Write a balanced equation for this reaction and employ the result to compute the TDS for the water sample. What could be the reasons for the difference between the calculated/measured TDS?

Answer)

Conversion of HCO_3^- to others during heating:



So, the contribution of HCO_3^- to TDS should be:

$$73 \text{ mg/L} \times \frac{60.0 \text{ mole/L}}{2 \times 61.0 \text{ mole/L}} = 35.9 \text{ mg/L}$$

Adding other anions, cations, and silica:

$$\text{calculated TDS: } (8 + 16 + 35.9) + (15 + 5 + 0.7 + 13) + 7 = 100.6 \text{ mg/L} \approx 101 \text{ mg/L}$$

The calculated TDS and measured TDS (=110 mg/L) are slightly different.

Note:

For TDS measurement, the water sample is filtered and the filtered water is heated to evaporate all the water. The HCO_3^- conversion reaction will occur during this heating, resulting in CO_3^{2-} remaining as solids and CO_2 and H_2O releasing out as vapors.

Possible reasons:

error in ions analysis; error in TDS analysis; reporting only 1-2 effective numbers for ion analysis (computation error); presence of other minor ions