1. (45 points). "Fizzy" water is made by pressurizing pure water with pure (100%) carbon dioxide gas in a sealed bottle at a pressure of 2 atmospheres and temperature = 298K.

a) Write the reactions occurring in the bottle containing water and CO₂ gas. (5 points)

\[
\begin{align*}
\text{CO}_2(g) & \rightleftharpoons \text{H}_2\text{CO}_3^* \\
\text{H}_2\text{CO}_3^* & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \\
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- \\
\end{align*}
\]

b) Write the appropriate equilibrium equations for all the reactions. (5 points)

Henry's Law: \[ [\text{H}_2\text{CO}_3^*] = K_{H_1, \text{CO}_2} P_{\text{CO}_2} \]

Water dissociation: \[ K_w = [\text{H}^+] [\text{OH}^-] \]

Acid dissociation: \[ K_1 = \frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} \]
\[ K_2 = \frac{[\text{H}^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \]

c) Write the electroneutrality expression for the water in the bottle. (5 points)

\[ [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] \]

d) Simplify the electroneutrality expression based on the fact that carbon dioxide is an acid when it dissolves in water. (5 points)

@ pH < 7, \[ [\text{OH}^-] \ll [\text{H}^+] \]
and \[ 2[\text{CO}_3^{2-}] \ll [\text{HCO}_3^-] \text{ or } [\text{H}^+] \]
\[ \therefore [\text{H}^+] \approx [\text{HCO}_3^-] \]
e) Find the pH of the fizzy water. (5 points)

\[
[\text{H}^+] = \frac{K_1 \cdot P_{\text{CO}_2} \cdot K_{\text{H}^+}}{[\text{H}^+]}
\]

\[\text{[H}^+]^2 = 4.47 \times 10^{-7} (2 \cdot \text{m}) \cdot 0.034 \text{ M} \cdot \text{m} = 3 \times 10^{-4}, \text{[H}^+] = 1.7 \times 10^{-2}, \text{(pH} = 3.8\)]

f) Check your assumption that the terms you neglected in the complete electroneutrality expression were in fact negligible. (5 points)

\[
[\text{OH}^-] = 10^{-3.8} - 10^{-3.8} = 5.7 \times 10^{-11} \ll 1.7 \times 10^{-4}
\]

\[
[\text{CO}_3^{2-}] = \frac{K_2}{\text{[H}^+]^2} = \frac{10^{-10.33}}{10^{-3.8}} = 10^{-6.5}
\]

(i) If lemon juice (an acid) is added to the water before carbonation, so that the pH of the lemon fizzy water is less than the plain fizzy water, but the CO\(_2\) gas pressure is the same,

The molar concentration of OH\(^-\) in the lemon fizzy water will be (circle bullet for correct answer and justify) (5 points)

i) Higher than the plain fizzy water

ii) Lower than the plain fizzy water

iii) The same as the plain fizzy water

The molar concentration of H\(_2\)CO\(_3\)* in the lemon fizzy water will be (circle bullet for correct answer and justify) (5 points)

i) Higher than the plain fizzy water

ii) Lower than the plain fizzy water

iii) The same as the plain fizzy water

The molar concentration of HCO\(_3\)- in the lemon fizzy water will be (circle bullet for correct answer and justify) (5 points)

i) Higher than the plain fizzy water

ii) Lower than the plain fizzy water

iii) The same as the plain fizzy water
2. (30 points) Hypochlorous acid (HOCl) is added to water to kill bacteria. Hypochlorous acid is a weak acid that dissociates in water with the following reactions:

\[
\text{HOCl} \leftrightarrow \text{H}^+ + \text{OCl}^- \\
\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OCl}^-
\]

The HOCl (undissociated) species is a better disinfectant than the OCl\(^-\) species. In order for adequate disinfection of a drinking water supply, the HOCl concentration should be greater than 1 mg/L. The pH of the water is fixed at 7.8 and not affected by the addition of the small amount of HOCl.

a) At pH = 7.8, what fraction of the total hypochlorous acid added will be in the HOCl form? (10 points)

\[
\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \\
7.8 = 7.6 + \log \frac{[\text{OCl}^-]}{[\text{HOCl}]} \\
\frac{[\text{OCl}^-]}{[\text{HOCl}]} = 10^{-0.2} = 1.6
\]

\[
[\text{OCl}^-] = 1.6 [\text{HOCl}] \\
C_T = [\text{OCl}^-] + [\text{HOCl}] = 1.6 [\text{HOCl}] + [\text{HOCl}] = 2.6 [\text{HOCl}]
\]

\[
\frac{[\text{HOCl}]}{C_T} = 0.39 \\
39\% \text{ of added is HOCl}
\]

b) What is the minimum hypochlorous acid concentration that must be added to the water to achieve 1 mg/L as HOCl at equilibrium? (Molecular weight of HOCl = 52.5 g/mole) (10 points)

\[
0.39 C_T = 10^{-3} \text{g}.1 \text{mole} L^{-1} = 4.9 \times 10^{-5} \text{M} \text{HOCl}
\]

\[
C_T = \frac{1}{0.39} \text{mg} L^{-1} = 2.6 \text{mg} L^{-1} \text{HOCl}
\]
c) If the water pH is adjusted to 7.6, what is the savings in HOCl addition compared with the
dose required at pH = 7.8? (10 points)

\[
\text{pH} = 7.6, \quad [\text{HOCl}] = [\text{OCl}^-]
\]
and required dose is 2 mg/L
savings is \(\frac{(2.6-2)}{2.6}\) \(\times 100\% = 23\%\)

3. (15 points) The total volume of water vapor in the atmosphere is \(1.5 \times 10^{13} \text{ m}^3\) (as liquid water). Evaporation from all surfaces on the planet: ocean, land, and plants, is the only
means for water vapor entering the atmosphere, and the evaporation rate averages \(5.2 \times 10^{14} \text{ m}^3/\text{year}\) (as liquid water).

a) Assuming steady-state conditions with respect to water circulation, what is the average
residence time of water in the atmosphere? (5 points)

\[
\text{C} = \frac{1.5 \times 10^{13} \text{ m}^3}{5.2 \times 10^{14} \text{ m}^3/\text{year}} = 0.029 \text{ yr} \times 365 \frac{\text{d}}{\text{yr}} = 10.5 \text{ d}
\]

b) What is the total amount of precipitation from the atmosphere to the earth's surface, as
liquid water? (5 points)

\[
5.2 \times 10^{14} \text{ m}^3/\text{yr} \quad (= \text{evaporation})
\]

c) The surface area of the earth is approximately \(5.1 \times 10^{14} \text{ m}^2\). What is the average annual
precipitation (as water) onto the earth's surface? (5 points) (For your information, the
Denver Metro area receives \(~0.35 \text{ m/year}\) of precipitation, as water.)

\[
\text{Precipitation} = \frac{5.2 \times 10^{14} \text{ m}^3/\text{yr}}{5.1 \times 10^{14} \text{ m}^2} = \frac{1 \text{ m}}{\text{yr}}
\]
4. (9 points)

a) If an unfiltered water sample is evaporated at just over 100 °C. The dried residue is (circle bullet for correct answer): (3 points)

- i) total suspended solids
- ii) total dissolved solids
- iii) total volatile solids
- iv) total solids

b) If the evaporated residue is burned in a muffle furnace at 550 °C, The initial dried residue minus the residue left after high-temperature combustion is (circle bullet for correct answer): (3 points)

- i) total suspended solids
- ii) total dissolved solids
- iii) total volatile solids
- iv) total solids

v) If the filtrate from a filtered water sample (the part that passes through the filter) is evaporated at just over 100 °C, the residue is (circle bullet for correct answer): (3 points)

- i) total suspended solids
- ii) total dissolved solids
- iii) total volatile solids
- iv) total solids