1) Write the proton transfer equilibria reaction in aqueous solution for the following bases and identify the conjugate acids of each

1a) $\text{CO}_3^{2-}$

\[
\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq) \tag{1}
\]

1b) Ammonia, $\text{NH}_3$

\[
\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \tag{2}
\]

1c) If $K_b$ for ammonia is $1.8 \times 10^{-5}$, calculate $K_a$ for its conjugate acid

\[
K_r(\text{NH}_4^+(aq)) = \frac{K_w}{K_b(\text{NH}_3(aq))} \tag{2}
\]

\[
= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \tag{1}
\]
2) Briefly explain the trend in acid strength observed in aqueous solutions of the halogen acids

\[ \text{HI(aq)} > \text{HBr(aq)} > \text{HCl(aq)} > \text{HF(aq)} \quad \text{HI(aq) (hydroiodic acid) is the strongest of the halogen} \\
\text{acids, HF(aq) (hydrofluoric acid) the weakest. The trend in bond dissociation energy is} \\
\text{HF} > \text{HCl} > \text{HBr} > \text{HI} \quad \text{(6 points)} \]

Strength of acid depends on ease with which it gives up a proton. As bond strength decreases, ease with which the molecule donates a H\(^+\) is easier.

H - I with the weakest bond amongst the halogen acids, is therefore the stronger amongst the halogen acids.

3) Determine whether aqueous solutions of the following ionic compounds have a pH equal to, greater than, or less than 7. Assume each compound is highly soluble in water. Write a chemical equation for the dissolution of each in water. If the pH will be greater than 7 or less than 7, write a chemical reaction which justifies your answer. If the pH = 7 explain why.

3a) Ammonium nitrate, NH\(_4\)NO\(_3\)

\[ \text{NH}_4\text{NO}_3(s) \rightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq) \quad (5 \text{ points}) \]

\[ \text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightarrow \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq) \quad (2) \]

\[ \text{NO}_3^-(aq) \text{ is a neutral anion.} \quad (1) \]

\[ \text{pH} < 7 \text{ because of hydrolysis of } \text{NH}_4^+(aq) \quad (2) \]

3b) Sodium acetate, CH\(_3\)COONa

\[ \text{CH}_3\text{COONa(s)} \rightarrow \text{CH}_3\text{COO}^-(aq) + \text{Na}^+(aq) \quad (5 \text{ points}) \]

\[ \text{Na}^+(aq) \text{ is a neutral cation} \quad (1) \]

\[ \text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{CH}_3\text{COOH(aq)} + \text{OH}^-(aq) \quad (2) \]

\[ \text{pH} > 7 \quad (2) \]
3c) Potassium chloride, KCl

\[ KCl (s) \rightarrow K^+ (aq) + Cl^- (aq) \]

Both \( K^+ (aq) \) and \( Cl^- (aq) \) are neutral ions, do not hydrolyze

\[ \text{pH} = 7 \]

4) A 25.0 mL sample of 0.10 M CH₃COOH(aq) is titrated with 0.10 M NaOH(aq). \( K_a (\text{CH}_3\text{COOH}) \) at 25°C = 1.8 x 10⁻⁵. For each question below, show all chemical equations relevant to solving the problem. Also show all calculations in support your answer. Credit will not be given unless you clearly show how you came to your answer.

4a) What is the initial pH of the 0.10 M CH₃COOH(aq) solution?

\[ \text{CH}_3\text{COOH} (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{CH}_3\text{COO}^- (aq) + \text{H}_3\text{O}^+ (aq) \]

\[
\begin{array}{ccc}
\text{Initial} & [\text{CH}_3\text{COOH} (aq)] & [\text{CH}_3\text{COO}^- (aq)] & [\text{H}_3\text{O}^+ (aq)] \\
0.10 & 0 & 0 & 0 \\
\text{Change} & -x & +x & +x \\
\text{Equilibrium} & 0.10-x & x & x \\
\end{array}
\]

\[ \frac{x^2}{0.10-x} = 1.8 \times 10^{-5} \]

Assume \( x \ll 0.10 \)

\( x = 1.3 \times 10^{-3} \) M.

\[ \text{pH} = 2.87 \]
4b) What is the pH after the addition of 10.0 mL of 0.10 M NaOH(aq)? (9 points)

Addition of OH⁻ to CH₃COOH

\[ \text{OH}⁻(aq) + \text{CH₃COOH} (aq) \rightarrow \text{CH₃COO}⁻ (aq) + \text{H₂O}(l) \]  

Form a buffer CH₃COOH/CH₃COO⁻

Moles of OH⁻ added = 0.0010 moles

Moles of CH₃COO⁻ formed = 0.0010 moles

Moles of CH₃COOH unreacted = 0.0025 - 0.0010 = 0.0015 moles

Concentration of CH₃COOH = \( \frac{0.0015 \text{ moles}}{0.0250 \text{ L} + 0.0100 \text{ L}} \) = 4.3 x 10⁻² M

Concentration of CH₃COO⁻ = \( \frac{0.0010 \text{ moles}}{0.0350 \text{ L}} \) = 2.9 x 10⁻³ M

pH determined by reaction:

\[ \text{CH₃COOH}(aq) + \text{H₂O}(l) \rightleftharpoons \text{CH₃COO}⁻(aq) + \text{H}_3\text{O}⁺(aq) \]

\[
\begin{array}{c|c|c|c}
\text{Initial} & \text{[CH₃COOH] } & \text{[CH₃COO⁻]} & \text{[H}_3\text{O}⁺] \\
\text{4.3 x 10⁻² M} & \text{2.9 x 10⁻³ M} & \text{0} & \\
\text{Equilibrium} & 4.3 x 10⁻² - x & 2.9 x 10⁻³ + x & x \\
\end{array}
\]

\[
x(2.8 x 10⁻¹² + x) = 1.8 x 10⁻⁵ \\
x = 2.7 x 10⁻⁵ \text{ M} \\
\text{pH} = 4.56 \quad \text{(1)}
\]
4c) What volume of 0.10 M NaOH(aq) is required to reach halfway to the equivalence point?

\[ \text{Halfway point reached when } \text{mol OH}^- \text{ added = } \frac{1}{2} \text{ mol CH}_3\text{COOH initially present.} \]

\[ \text{CH}_3\text{COOH} (aq) + \text{OH}^- (aq) \rightarrow \text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O(l)} \]

Initial number of mol CH\(_3\)COOH = 0.025mol

Number of mol CH\(_3\)COOH added at halfway = 0.00125mol

Need 12.5 mL of 0.10 M NaOH to reach halfway point.

4d) Calculate the pH at the equivalence point.

At equivalence, enough OH\(^-\) added to completely react with CH\(_3\)COOH

\[ \text{CH}_3\text{COOH} (aq) + \text{OH}^- (aq) \rightarrow \text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O(l)} \]

At equivalence, hydrolysis of CH\(_3\)COO\(^-\) determines pH

\[ \text{CH}_3\text{COO}^- (aq) \rightarrow \text{CH}_3\text{COOH} (aq) + \text{OH}^- (aq) \]

At equivalence,

\[ \left[ \text{CH}_3\text{COO}^- (aq) \right] = \frac{0.0025\text{ mol}}{0.025\text{ mol} + 0.025\text{ mol}} = 0.05\text{ M} \]

\[ \begin{array}{ccc}
\text{CH}_3\text{COO}^- & \text{CH}_3\text{COOH} & \text{OH}^- \\
0.05\text{ M} & 0 & x \\
-x & x & x \\
\end{array} \]

\[ \frac{x^2}{0.05-x} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \]

Assume x < 0.05

\[ x = 5.27 \times 10^{-6}\text{ M} \]

\[ \text{pOH} = 5.28 \]

\[ \text{pH} = 8.72 \]
5) Determine the pH required for the onset of precipitation of \( \text{Ni(OH)}_2(s) \) from a 0.060 M \( \text{NiSO}_4(\text{aq}) \) solution. (6 points)

\[
\text{NiSO}_4(\text{aq}) \rightarrow \text{Ni}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})
\]

\[
[\text{Ni}^{2+}(\text{aq})] = 0.060 \text{ M}
\]

\[
\frac{[\text{Ni}^{2+}][\text{OH}^-]^2}{\text{K}_s} = 6.5 \times 10^{-18}
\]

\[
[\text{OH}^-] = \sqrt{\frac{6.5 \times 10^{-18}}{0.060}}
\]

\[
\text{pOH} = 8
\]

\[
\text{pH} = 6
\]

6) Which anion fluoride (F\(^-\)) or carbonate (CO\(_3^{2-}\)), would be a better choice for separating Ba\(^{2+}\) ions from Ca\(^{2+}\) ions from an aqueous solution containing both ions? Briefly explain your choice of anion. Also predict which salt would precipitate first on addition of the anion you decide is better for separating the two cations. (7 points)

\[
\begin{align*}
\text{BaF}_2 & : \text{K}_s = 1.7 \times 10^{-6} \\
\text{BaCO}_3 & : \text{K}_s = 8.1 \times 10^{-9} \\
\text{CaF}_2 & : \text{K}_s = 4.0 \times 10^{-11} \\
\text{CaCO}_3 & : \text{K}_s = 8.7 \times 10^{-9}
\end{align*}
\]

\[
\text{K}_s \text{ of BaF}_2 \text{ and CaF}_2 \text{ differ by \( \log 5 \) order of magnitude}
\]

\[
\text{K}_s \text{ of BaCO}_3 \text{ and CaCO}_3 \text{ very similar}
\]

F\(^-\) is a better choice to separate Ba\(^{2+}\) & Ca\(^{2+}\)

If F\(^-\) added expect CaF\(_2 \) to precipitate first
7) Answer the following questions. For each YES response write a balanced overall balanced cell reaction and calculate the standard cell potential. For a NO answer briefly explain why your answer is no.

7 a) Can H$_2$ reduce Ni$_{2+}$(aq) ions to nickel metal?

\[ \text{Ni}^{2+} (aq) + 2e^- \rightarrow \text{Ni(s)} \quad E^0 = -0.23 \text{V} \quad \boxed{2} \]

\[ 2\text{H}^+ (aq) + 2e^- \rightarrow \text{H}_2(g) \quad E^0 = 0 \text{V} \quad \boxed{2} \]

Reduction of Ni$_{2+}$(aq) by H$_2$ in the following reaction

\[ \text{H}_2(g) + \text{Ni}^{2+}(aq) \rightarrow \text{Ni(s)} + 2\text{H}^+(aq) \]

involves oxidation of H$_2 \rightarrow$ H$^+$ and reduction of Ni$^{2+}$ to Ni.$^5$

\[ \Delta E^0 = E^0 \text{(redox)} - E^0 \text{(ox/red)} \]

\[ = E^0 \text{Ni}^{2+/0} - E^0 \text{H}^+/H_2 \]

\[ = -0.23 \text{V} - 0 = -0.23 \text{V} \]

Since \( \Delta E^0 < 0 \) reaction is not spontaneous

hence H$_2$ cannot reduce Ni$^{2+}$

7 b) Can permanganate ions (MnO$_4^-$) ions oxidize copper metal to Cu$^{2+}$ (aq) ions in an acidic solution?

\[ \text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O(l)} \quad \boxed{2} \]

\[ E^0 = +1.51 \text{V} \]

\[ \text{Cu}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cu(s)} \quad E^0 = +0.34 \text{V} \quad \boxed{2} \]

MnO$_4^-$ (aq) in acidic solution can oxidize Cu(s) to Cu$^{2+}$

Overall cell reaction

\[ 2\text{MnO}_4^-(aq) + 16\text{H}^+(aq) + 5\text{Cu(s)} \rightarrow 2\text{Mn}^{2+}(aq) + 8\text{H}_2\text{O(l)} + 5\text{Cu}^{2+}(aq) \]

\[ \Delta E^0 = +1.17 \text{V} \quad \boxed{1} \]
8) Determine the cell voltage for the following galvanic cell at 25°C
Cr(s) | Cr\textsuperscript{3+} (aq, 0.37 mol/L) || Pb\textsuperscript{2+} (aq, 9.5 \times 10^{-3} \text{ mol/L}) | Pb(s)

Write a balanced overall cell reaction for this cell.

\[ \text{Anode: } \text{Cr(s)} \rightarrow \text{Cr}^{3+} (aq) + 3e^- \]
\[ \text{Cathode: } \text{Pb}^{2+} (aq) + 2e^- \rightarrow \text{Pb(s)} \]

Overall cell reaction

\[ 2\text{Cr(s)} + 3\text{Pb}^{2+} (aq) \rightarrow 3\text{Pb(s)} + 2\text{Cr}^{3+} (aq) \]

\[ \Delta E^0 = E^0_{\text{Pb}^{2+}/\text{Pb}} - E^0_{\text{Cr}^{3+}/\text{Cr}} = -0.13 \text{ V} - (-0.74 \text{ V}) = +0.61 \text{ V} \]

\[ \Delta E = \Delta E^0 - \frac{RT}{nF} \ln \frac{Q}{6} \]

\[ = 0.61 - \frac{0.02569 \ln \left( \frac{[\text{Cr}^{3+}\text{(aq)}]^2}{[\text{Pb}^{2+}\text{(aq)}]^3} \right)}{6} \]

\[ = 0.61 - \frac{0.02569 \ln \left( \frac{(0.37)^2}{(9.5 \times 10^{-3})^3} \right)}{6} \]

\[ \Delta E = 0.56 \text{ V} \]