1. A sample containing 26.38 mL of 0.1439 M HBr is titrated with a solution of NaOH having a molarity of 0.1219 M. Compute the pH of the titration solution added, when the titration is 1.00 mL short of the equivalence point, when the titration is at the equivalence point, and when the titration is 1.00 mL past the equivalence point.

\[ \text{HBr} \rightleftharpoons \text{H}^+ + \text{Br}^- \]

\[ \text{pH} = -\log [\text{H}^+] = -\log 0.1439 = 0.842 \]

\[ \text{# mols of HBr} = 0.1439 \text{ M} \times 0.02638 \text{ L} = 0.003796 \text{ mols} \]

Therefore, to neutralize you need \(0.003796 \text{ mols of NaOH}\), which is

\[ V = \frac{0.003796 \text{ mols}}{0.1219 \text{ M}} = 31.14 \text{ mL NaOH} \]

1.00 mL short of equivalence point:

The volume of NaOH would be 30.14 mL NaOH

\[ \text{# mols} = 0.1219 \text{ M} \times 0.03014 \text{ L} = 0.003674 \text{ mols NaOH} \]

\[ \text{# mols HBr (original)} - \text{# mols NaOH (added)} = \text{# mols of H}^+ \text{ left in solution} \]

\[ 0.003796 - 0.003674 = 1.22 \times 10^{-4} \text{ mols H}^+ \]

\[ [\text{H}^+] = 1.22 \times 10^{-4} \text{ mols} / (0.02638 \text{ L} + 0.03014 \text{ L}) = 0.002159 \text{ M} \]

\[ \text{pH} = -\log 0.002159 = 2.67 \]

At the equivalence point pH = 7

1.00 mL after the equivalence point:

\[ \text{# mols NaOH} = 0.1219 \text{ M} \times 0.03214 \text{ L} = 0.003918 \text{ mols NaOH} \]

\[ \text{# mols NaOH (total)} - \text{# mols NaOH (reacted)} = \text{# mols in solution} = \text{# mols OH}^- \]

\[ 0.003918 \text{ mols} - 0.003796 \text{ mols} = 1.22 \times 10^{-4} \text{ mols OH}^- \]

\[ \text{pOH} = -\log [1.22 \times 10^{-4} / 0.02638 + 0.03214] = 2.68 \]

\[ \text{pH} = 14 - 2.68 = 11.32 \]

2. Ammonia is a weak base with a K\(_b\) of \(1.8 \times 10^{-5}\). A 140.0 mL sample of a 0.175 M solution of aqueous ammonia is titrated with 0.106 M solution of the strong acid HCl. Write the reaction and compute the pH of the titration solution before any acid is added, when titration solution is at the half-equivalence point, and when the titration is 1.00 mL past the equivalence point.

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

\[ [\text{NH}_4^+] = [\text{OH}^-] = x \]

\[ [\text{NH}_3] = 0.175 \text{ M} - x \]

K\(_b\) = 1.8 \times 10^{-5}

K\(_b\) = [OH\(^-\)][NH\(_4^+\)] / [NH\(_3\)]

\[ 1.8 \times 10^{-5} = x^2 / 0.175 - x \]

\[ x^2 + 1.8 \times 10^{-5}x - 3.15 \times 10^{-6} = 0 \]

\[ x = 1.766 \times 10^{-3} = [\text{OH}^-] \]

\[ \text{pH} = 14 - (-\log 1.766 \times 10^{-3}) = 11.25 \]
Worksheet 5

At the half-equivalence point the pH ≅ pKₐ
pOH = pKₐ = -log 1.8 × 10⁻⁵
pOH = 4.74
pH = 14 - 4.74 = 9.26

At the equivalence point:
# mols NH₃ = 0.175 M × 0.140 L = 0.0245 mols NH₃
Volume of HCl = 0.0245 mols / 0.106 M = 0.231 mols
Total volume of solution = 231 mL + 140 mL = 371 mL

\[ [\text{NH}_4^+] = 0.0245 \text{ mols} / 0.371 \text{ L} = 0.066 \text{ M} \]
\[ K_a = K_w / K_b = 1 \times 10^{-14} / 1.8 \times 10^{-5} = 5.56 \times 10^{-10} = [\text{H}_3\text{O}^+] [\text{NH}_3] / [\text{NH}_4^+] = x^2 / 0.066 \text{ M} \]
pH = -log 6.058 × 10⁻⁶ = 5.22

1.00 mL past the equivalence point:
Volume of HCl = 232 mL
\[ V_{\text{total}} = 372 \text{ mL} \]
All 231 mL of HCl added was neutralized so only 1.00 mL HCl affects the [H⁺]
# mols = 0.106 M × 0.001 L = 1.06 × 10⁻⁴
\[ M = 1.06 \times 10^{-4} \text{ mols} / 0.372 \text{ L} = 2.85 \times 10^{-4} \text{ M} \]
pH = -log 2.85 × 10⁻⁴ = 3.55

3. Oxalic acid ionizes in two stages in aqueous solution:
\[ \text{H}_2\text{C}_2\text{O}_4 (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{HC}_2\text{O}_4^- (aq) \quad K_{a1} = 5.9 \times 10^{-2} \]
\[ \text{HC}_2\text{O}_4^- (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) \text{C}_2\text{O}_4^{2-} (aq) \quad K_{a2} = 6.4 \times 10^{-5} \]

Calculate the equilibrium concentrations of \( \text{C}_2\text{O}_4^{2-} \), \( \text{HC}_2\text{O}_4^- \), \( \text{H}_2\text{C}_2\text{O}_4 \), and OH⁻ in a 0.10 M solution of sodium oxalate (Na₂C₂O₄).

You need to work the problem backwards.
\[ \text{C}_2\text{O}_4^{2-} + \text{H}_2\text{O} (l) \rightleftharpoons \text{HC}_2\text{O}_4^- + \text{OH}^- (aq) \quad K_{b2} = K_w / K_{a2} = 1 \times 10^{-14} / 6.4 \times 10^{-5} = 1.56 \times 10^{-10} \]
\[ \text{HC}_2\text{O}_4^- + \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4^- + \text{OH}^- (aq) \quad K_{b1} = 1.0 1 \times 10^{-14} / 5.9 \times 10^{-2} = 1.69 \times 10^{-13} \]

\[ [\text{HC}_2\text{O}_4^-] = x = [\text{OH}^-] \]
\[ [\text{C}_2\text{O}_4^{2-}] = 0.10 - x \]
\[ K_{b2} = 1.56 \times 10^{-10} = [\text{OH}^-][\text{HC}_2\text{O}_4^-] / [\text{C}_2\text{O}_4^{2-}] = x^2 / 0.10 - x \]
x² + 1.56 × 10⁻¹⁰x - 1.56 × 10⁻¹¹ = 0

x = 3.95 × 10⁻⁶ M = [OH⁻] = [HC₂O₄⁻]
**Worksheet 5**

\[ K_{b1} = 1.69 \times 10^{-13} = [OH^-][H_2C_2O_4] / [HC_2O_4^-] = 3.95 \times 10^{-6} [H_2C_2O_4] / 3.95 \times 10^{-6} \]

\[ x = 1.69 \times 10^{-13} M = [H_2C_2O_4] \]

\[ [C_2O_4^-] = 0.10 - 3.95 \times 10^{-6} = 0.099996 M \]

4. The pH of a drop of acid rain is 4.00. Compute the concentrations of \( H_2CO_3 \) (aq), \( HCO_3^- \) (aq), and \( CO_3^{2-} \) (aq) in the acid raindrop if the total concentration of dissolved carbonates is \( 3.6 \times 10^{-5} \) M. You will need to figure out the two stage reaction and their respective \( K_a \) at 25°C.

\[ pH = -\log [H^+] \]

\[ [H^+] = 1 \times 10^{-4} \]

\[ 3.6 \times 10^{-5} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \rightarrow \text{(goes to zero)} \]

\[ H_2CO_3 + OH^- \leftrightarrow HCO_3^- + H_2O \quad K_{a1} = 4.3 \times 10^{-7} \]

\[ HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \quad K_{a2} = 4.8 \times 10^{-11} \]

\[ K_{a1} = [HCO_3^-][H_3O^+] / [H_2CO_3] = 4.3 \times 10^{-7} \]

\[ K_{a2} = [CO_3^{2-}][H_3O^+] / [HCO_3^-] = 4.8 \times 10^{-11} \]

\[ [HCO_3^-] / [H_2CO_3] = 4.3 \times 10^{-3} \]

\[ [HCO_3^-] = 4.3 \times 10^{-3} [H_2CO_3] \]

\[ [CO_3^{2-}] / [HCO_3^-] = 4.8 \times 10^{-7} \]

\[ [CO_3^{2-}] = 4.8 \times 10^{-7} [HCO_3^-] \]

\[ 3.6 \times 10^{-5} - [H_2CO_3] = [HCO_3^-] \]

\[ 3.6 \times 10^{-5} - [H_2CO_3] = 4.3 \times 10^{-3} [H_2CO_3] \]

\[ [H_2CO_3] = 3.6 \times 10^{-5} M \]

\[ [HCO_3^-] = (4.3 \times 10^{-3})(3.6 \times 10^{-5}) = 1.55 \times 10^{-7} M \]

\[ [CO_3^{2-}] = (1.55 \times 10^{-7})(4.8 \times 10^{-7}) = 7.44 \times 10^{-14} M \]

5. A 1.00 g sample of magnesium sulfate is dissolved in water, and the water is then evaporated away until the residue is bone dry. If the temperature of the water is kept between 48°C and 69°C, the solid that remains weighs 1.898 g. If the experiment is repeated with the temperature held between 69°C and 100°C, however, the solid has a mass of 1.150 g. Determine how many waters of crystallization per \( MgSO_4 \) there are in each of these two solids.

\[ m = 1.00 \text{ g} \quad MgSO_4 \times 1 \text{ mol} / 120.4 \text{ g} = 0.00831 \text{ mols} \]

1st experiment \( m_f = 1.898 \text{ g} \)

Therefore \( m = 0.898 \text{ g} \times 1 \text{ mol} / 18 \text{ g} = 0.0499 \text{ mols} \quad H_2O \)

0.00831 \( MgSO_4 \) 0.0499 \( H_2O \) divide through with 0.00831

\( MgSO_4 \) 6 \( H_2O \)

2nd experiment \( m_f = 1.150 \text{ g} \)

\( m = 0.150 \text{ g} \quad H_2O \times 1 \text{ mol} / 18 \text{ g} = 0.0083 \text{ mols} \quad H_2O \)
0.00831 MgSO₄ 0.0083H₂O
MgSO₄ H₂O

6. Thallium thiocyanate (TISCN) is only soluble in water. Its $K_{sp}$ at 25°C is $1.8 \times 10^{-4}$. Estimate the solubility of thallium thiocyanate in units of grams per 100.0 mL of water.

\[ \text{TISCN} \leftrightarrow \text{TI}^{+} + \text{SCN}^{-} \]
\[ K_{sp} = [\text{TI}^{+}][\text{SCN}^{-}] = 1.82 \times 10^{-4} \]
\[ [\text{TI}^{+}] = [\text{SCN}^{-}] = \sqrt{1.82 \times 10^{-4}} = 0.0135 \text{ M} \]
MW TISCN = 262.47 g mol⁻¹
\[ 0.0135 \text{ mol L}^{-1} \times 262.47 \text{ g mol}^{-1} = 3.54 \text{ g L}^{-1} = 0.354 \text{ g / 100 mL} \]

7. At 25°C, 400 mL of water can dissolve 0.00896 g of lead iodate, Pb(IO₃)₂. Calculate $K_{sp}$ for lead iodate.

\[ m = 0.00896 \text{ g Pb(IO}_3\text{)_2} \times 1 \text{ mol / 557 g} = 1.61 \times 10^{-5} \text{ mols} \]
\[ S = 1.61 \times 10^{-5} \text{ mol / 0.400 L} = 4.02 \times 10^{-5} \text{ M} \]
\[ \text{Pb(IO}_3\text{)_2} \leftrightarrow \text{Pb}^{2+} + 2 \text{IO}_3^{-} \]
\[ K_{sp} = [\text{Pb}^{2+}][\text{IO}_3^{-}]^2 = S(2S)^2 \]
\[ K_{sp} = (4.02 \times 10^{-5})(2 \times 4.02 \times 10^{-5})^2 = 2.6 \times 10^{-13} \]

8. A solution is prepared by dissolving 0.090 g of PbI₂ in 1.00 L of hot water and cooling the solution to 25°C. Will solid precipitate result from this process, according to the solubility product expression? Explain.

\[ m = 0.090 \text{ g PbI}_2 \times 1 \text{ mol / 461 g} = 1.95 \times 10^{-4} \text{ mols} \]
\[ \text{PbI}_2 \leftrightarrow \text{Pb}^{2+} + 2\Gamma \]
\[ [\text{Pb}^{2+}] = 1.95 \times 10^{-4} \text{ M} \]
\[ [\Gamma] = 3.90 \times 10^{-4} \text{ M} \]
\[ Q = K_{sp} \text{ at 100°C} = (1.95 \times 10^{-4})(3.90 \times 10^{-4})^2 = 297 \times 10^{-11} \]
\[ K_{sp} \text{ at 25°C} = 1.4 \times 10^{-8} \]
\[ Q < K_{sp}, \text{ Thus no precipitate will form.} \]

9. When 40.0 mL of 0.0800 M Sr(NO₃)₂ and 80.0 mL of 0.0500 M KF are mixed, a precipitate of strontium fluoride (SrF₂) is formed. The solubility product of strontium fluoride in water at 25°C is $2.8 \times 10^{-9}$. Calculate the $[\text{Sr}^{2+}]$ and $[\text{F}^-]$ remaining in solution at equilibrium.

\[ \text{Sr}^{2+} + 2 \text{F}^- \leftrightarrow \text{SrF}_2 \]
\[ \text{Sr(NO}_3\text{)_2} = 0.0032 \text{ mols} \]
Worksheet 5

**KF** = 0.004 mols

Because F\(^-\) is the limiting reagent all the F\(^-\) are used up to make SrF\(_2\) and only Sr\(^{2+}\) remains in solution.

\[[Sr^{2+}] = 0.0032 - 0.002 / 0.120 \text{ L} = 0.01 \text{ M}, \text{ but if some SrF}_2 \text{ redissolves}

\[K_{sp} = [Sr^{2+}][F^-]^2 = 2.8 \times 10^{-9}\]

\[[F^-] = \sqrt{2.8 \times 10^{-9} / 0.01} = 5.29 \times 10^{-4} \text{ M}\]

**10.** Compare the molar solubility of Mg(OH)\(_2\) in pure water with that in a solution buffered at pH 9.00.

\[\text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{2+} + 2 \text{OH}^-\]

\[S = [\text{Mg}^{2+}]\]

\[2S = [\text{OH}^-]\]

\[K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = S(2S)^2 = 1.2 \times 10^{-11}\]

\[S = 1.4 \times 10^{-4} \text{ M}\]

**buffered solution**

\[\text{pH} = 14 - \text{pOH}\]

\[\text{pOH} = 5 = -\log [\text{OH}^-]\]

\[[\text{OH}^-] = 1 \times 10^{-5} \text{ M}\]

\[K_{sp} = 1.2 \times 10^{-11} = S(10^{-5})^2\]

\[S = 0.12 \text{ M}\]

**11.** Calculate the [Cd\(^{2+}\)] in a solution that is in equilibrium with CdS (s) and in which [H\(_3\)O\(^+\)] = 1.0 \times 10^{-3} \text{ M} and [H\(_2\)S] = 0.10 M.

\[\text{CdS} (s) + 2 \text{H}_3\text{O}^+ \rightleftharpoons \text{Cd}^{2+} + \text{H}_2\text{S} + 2 \text{H}_2\text{O} \quad K = 7.7 \times 10^{-7}\]

\[[\text{Cd}^{2+}][\text{H}_2\text{S}] / [\text{H}_3\text{O}^+]^2 = K\]

\[[\text{H}_2\text{S}] = 0.10 \text{ M}\]

\[[\text{H}_3\text{O}^+] = 1.0 \times 10^{-3} \text{ M}\]

\[[\text{Cd}^{2+}] = (7.7 \times 10^{-7})(1 \times 10^{-3})^2 / 0.10 = 7.7 \times 10^{-12} \text{ M}\]

**12.** The two salts BaCl\(_2\) and Ag\(_2\)SO\(_4\) are both far more soluble in water than either BaSO\(_4\) (K\(_{sp}\) = 1.1 \times 10^{-10}) or AgCl (K\(_{sp}\) = 1.6 \times 10^{-10}) at 25°C. Suppose 50.0 mL of 0.040 M BaCl\(_2\) (aq) is added to 50.0 mL of 0.020 M Ag\(_2\)SO\(_4\) (aq). Calculate the concentrations of SO\(_4^{2-}\) (aq), Cl\(^-\) (aq), Ba\(^{2+}\) (aq), and Ag\(^+\) (aq) that remain in solution at equilibrium.

\[\text{BaSO}_4 (s) \rightleftharpoons \text{Ba}^{2+} (aq) + \text{SO}_4^{2-} (aq)\]

\[\text{AgCl} (s) \rightleftharpoons \text{Ag}^+ (aq) + \text{Cl}^- (aq)\]

\[\text{Ba}^{2+} = 0.002 \text{ mols} \quad \text{[Ba}^{2+}] = 0.02 \text{ M}\]
\[ \text{Ag}^{+} = 0.002 \text{ mols} \quad [\text{Ag}^{+}] = 0.02 \text{ M} \]
\[ \text{Cl}^{-} = 0.004 \text{ mols} \quad [\text{Cl}^{-}] = 0.04 \text{ M} \]
\[ \text{SO}_4^{2-} = 0.001 \text{ mols} \quad [\text{SO}_4^{2-}] = 0.01 \text{ M} \]

Assume \( \text{Ba}^{2+} \) and \( \text{SO}_4^{2-} \) react to form \( \text{BaSO}_4 \) (s) and therefore \( [\text{SO}_4^{2-}] = 0 \)
\[ [\text{Ba}^{2+}] = \frac{0.001}{0.1} \text{ L} = 0.01 \text{ M} \]
\[ K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10} = [0.01][\text{SO}_4^{2-}] \]
\[ [\text{SO}_4^{2-}] = 1.1 \times 10^{-8} \text{ M} \]

Assume \( \text{Ag}^{+} \) and \( \text{Cl}^{-} \) react to form \( \text{AgCl} \) (s) and therefore \( [\text{Ag}^{+}] = 0 \)
\[ [\text{Cl}^{-}] = 0.02 \text{ M} \]
\[ K_{sp} = [\text{Ag}^{+}][\text{Cl}^{-}] = 1.6 \times 10^{-10} = [\text{Ag}^{+}] 0.02 \]
\[ [\text{Ag}^{+}] = 8 \times 10^{-9} \text{ M} \]

13. The volume of a certain saturated solution is greater than the sum of the volumes of the water and salt from which it is made. Predict the effect of increased pressure on the solubility of this salt.

Using Le Chatelier’s principle we know that increased pressure favors the states with smaller volume, namely they separate \( \text{H}_2\text{O} \) and \( \text{NaCl} \). The solubility of salt will decrease as the pressure is increased.