

Worksheet 5

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.



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

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

Therefore, to neutralize you need 0.003796 mols of NaOH, which is

$$V = 0.003796 \text{ mols} / 0.1219 \text{ M} = 31.14 \text{ mL NaOH}$$

1.00 mL short of equivalence point:

The volume of NaOH would be 30.14 mL NaOH

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

mols HBr (original) - # mols NaOH (added) = mols of H^+ 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 $\text{pH} = 7$

1.00 mL after the equivalence point:

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

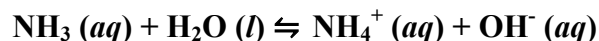
mols NaOH (total) - # mols NaOH (reacted) = # mols in solution = # mols OH^-

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

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

$$\text{pH} = 14 - 2.68 = 11.32$$

2. Ammonia is a weak base with a K_b of 1.8×10^{-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.



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

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

$$K_b = 1.8 \times 10^{-5}$$

$$K_b = [\text{OH}^-][\text{NH}_4^+] / [\text{NH}_3]$$

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

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

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

$$\text{pH} = 14 - (-\log 1.766 \times 10^{-3}) = 11.25$$

Worksheet 5

At the half-equivalence point the $\text{pH} \cong \text{pK}_a$

$$\text{pOH} = \text{pK}_b = -\log 1.8 \times 10^{-5}$$

$$\text{pOH} = 4.74$$

$$\text{pH} = 14 - 4.74 = 9.26$$

At the equivalence point:

$$\# \text{ mols NH}_3 = 0.175 \text{ M} \times 0.140 \text{ L} = 0.0245 \text{ mols NH}_3$$

$$\text{Volume of HCl} = 0.0245 \text{ mols} / 0.106 \text{ M} = 0.231 \text{ L} = 231 \text{ mL}$$

$$\text{Total volume of solution} = 231 \text{ mL} + 140 \text{ mL} = 371 \text{ mL}$$

$$[\text{NH}_4^+] = 0.0245 \text{ mols} / 0.371 \text{ L} = 0.066 \text{ M}$$

$$\text{K}_a = \text{K}_w / \text{K}_b = 1 \times 10^{-14} / 1.8 \times 10^{-5} = 5.56 \times 10^{-10} = [\text{H}_3\text{O}^+][\text{NH}_3] / [\text{NH}_4^+] = x^2 / 0.066 \text{ M}$$

$$x = 6.058 \times 10^{-6} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log 6.058 \times 10^{-6} = 5.22$$

1.00 mL past the equivalence point:

$$\text{Volume of HCl} = 232 \text{ mL}$$

$$V_{\text{total}} = 372 \text{ mL}$$

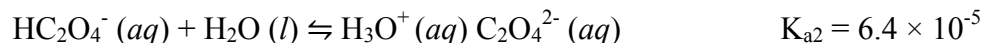
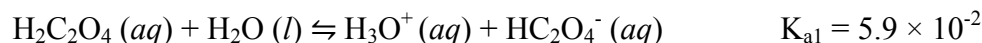
All 231 mL of HCl added was neutralized so only 1.00 mL HCl affects the $[\text{H}^+]$

$$\# \text{ mols} = 0.106 \text{ M} \times 0.001 \text{ L} = 1.06 \times 10^{-4}$$

$$\text{M} = 1.06 \times 10^{-4} \text{ mols} / 0.372 \text{ L} = 2.85 \times 10^{-4} \text{ M}$$

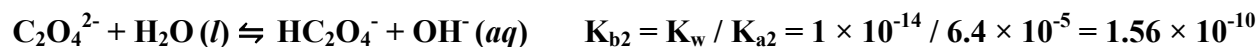
$$\text{pH} = -\log 2.85 \times 10^{-4} = 3.55$$

3. Oxalic acid ionizes in two stages in aqueous solution:



Calculate the equilibrium concentrations of $\text{C}_2\text{O}_4^{2-}$, HC_2O_4^- , $\text{H}_2\text{C}_2\text{O}_4$, and OH^- in a 0.10 M solution of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$).

You need to work the problem backwards.



$$[\text{HC}_2\text{O}_4^-] = x = [\text{OH}^-]$$

$$[\text{C}_2\text{O}_4^{2-}] = 0.10 - x$$

$$\text{K}_{b2} = 1.56 \times 10^{-10} = [\text{OH}^-][\text{HC}_2\text{O}_4^-] / [\text{C}_2\text{O}_4^{2-}] = x^2 / 0.10 - x$$

$$x^2 + 1.56 \times 10^{-10}x - 1.56 \times 10^{-11} = 0$$

$$x = 3.95 \times 10^{-6} \text{ M} = [\text{OH}^-] = [\text{HC}_2\text{O}_4^-]$$

Worksheet 5

$$K_{b1} = 1.69 \times 10^{-13} = [\text{OH}^-][\text{H}_2\text{C}_2\text{O}_4^-] / [\text{HC}_2\text{O}_4^-] = 3.95 \times 10^{-6} [\text{H}_2\text{C}_2\text{O}_4^-] / 3.95 \times 10^{-6}$$

$$x = 1.69 \times 10^{-13} \text{ M} = [\text{H}_2\text{C}_2\text{O}_4^-]$$

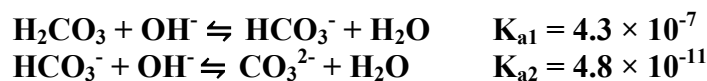
$$[\text{C}_2\text{O}_4^{2-}] = 0.10 - 3.95 \times 10^{-6} = 0.099996 \text{ M}$$

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 3.6×10^{-5} M. You will need to figure out the two stage reaction and their respective K_a at 25°C .

$$\text{pH } 4 = -\log [\text{H}^+]$$

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

$$3.6 \times 10^{-5} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + \{\text{CO}_3^{2-}\} \text{ (goes to zero)}$$



$$K_{a1} = [\text{HCO}_3^-][\text{H}_3\text{O}^+] / [\text{H}_2\text{CO}_3] = 4.3 \times 10^{-7}$$

$$K_{a2} = [\text{CO}_3^{2-}][\text{H}_3\text{O}^+] / [\text{HCO}_3^-] = 4.8 \times 10^{-11}$$

$$[\text{HCO}_3^-] / [\text{H}_2\text{CO}_3] = 4.3 \times 10^{-3}$$

$$[\text{HCO}_3^-] = 4.3 \times 10^{-3} [\text{H}_2\text{CO}_3]$$

$$[\text{CO}_3^{2-}] / [\text{HCO}_3^-] = 4.8 \times 10^{-7}$$

$$[\text{CO}_3^{2-}] = 4.8 \times 10^{-7} [\text{HCO}_3^-]$$

$$3.6 \times 10^{-5} - [\text{H}_2\text{CO}_3] = [\text{HCO}_3^-]$$

$$3.6 \times 10^{-5} - [\text{H}_2\text{CO}_3] = 4.3 \times 10^{-3} [\text{H}_2\text{CO}_3]$$

$$[\text{H}_2\text{CO}_3] = 3.6 \times 10^{-5} \text{ M}$$

$$[\text{HCO}_3^-] = (4.3 \times 10^{-3})(3.6 \times 10^{-5}) = 1.55 \times 10^{-7} \text{ M}$$

$$[\text{CO}_3^{2-}] = (1.55 \times 10^{-7})(4.8 \times 10^{-7}) = 7.44 \times 10^{-14} \text{ M}$$

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.

$$m = 1.00 \text{ g MgSO}_4 \times 1 \text{ mol} / 120.4 \text{ g} = 0.00831 \text{ mols}$$

$$1^{\text{st}} \text{ experiment } m_f = 1.898 \text{ g}$$

$$\text{Therefore } m = 0.898 \text{ g} \times 1 \text{ mol} / 18 \text{ g} = 0.0499 \text{ mols H}_2\text{O}$$

$$0.00831 \text{ MgSO}_4 \text{ } 0.0499 \text{ H}_2\text{O} \text{ divide through with } 0.00831$$

$$\text{MgSO}_4 \text{ } 6 \text{ H}_2\text{O}$$

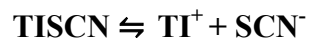
$$2^{\text{nd}} \text{ experiment } m_f = 1.150 \text{ g}$$

$$m = 0.150 \text{ g H}_2\text{O} \times 1 \text{ mol} / 18 \text{ g} = 0.0083 \text{ mols H}_2\text{O}$$

Worksheet 5

0.00831 MgSO₄ 0.0083H₂O
MgSO₄ H₂O

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



$$K_{sp} = [\text{TI}^+][\text{SCN}^-] = 1.82 \times 10^{-4}$$

$$[\text{TI}^+] = [\text{SCN}^-]$$

$$[\text{TI}^+] = [\text{SCN}^-] = \sqrt{1.82 \times 10^{-4}} = 0.0135 \text{ M}$$

$$\text{MW TISCN} = 262.47 \text{ g mol}^{-1}$$

$$0.0135 \text{ mol L}^{-1} \times 262.47 \text{ g mol}^{-1} = 3.54 \text{ g L}^{-1} = 0.354 \text{ g / 100 mL}$$

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.

$$m = 0.00896 \text{ g Pb(IO}_3)_2 \times 1 \text{ mol} / 557 \text{ g} = 1.61 \times 10^{-5} \text{ mols}$$

$$S = 1.61 \times 10^{-5} \text{ mol} / 0.400 \text{ L} = 4.02 \times 10^{-5} \text{ M}$$



$$K_{sp} = [\text{Pb}^{2+}][\text{IO}_3^-]^2 = S(2S)^2$$

$$K_{sp} = (4.02 \times 10^{-5})(2 \times 4.02 \times 10^{-5})^2 = 2.6 \times 10^{-13}$$

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.

$$m = 0.090 \text{ g PbI}_2 \times 1 \text{ mol} / 461 \text{ g} = 1.95 \times 10^{-4} \text{ mols}$$



$$[\text{Pb}^{2+}] = 1.95 \times 10^{-4} \text{ M}$$

$$[\text{I}^-] = 3.90 \times 10^{-4} \text{ M}$$

$$Q = K_{sp} \text{ at } 100^\circ\text{C} = [1.95 \times 10^{-4}][3.90 \times 10^{-4}]^2 = 297 \times 10^{-11}$$

$$K_{sp} \text{ at } 25^\circ\text{C} = 1.4 \times 10^{-8}$$

$Q < K_{sp}$, 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 2.8×10^{-9} . Calculate the [Sr²⁺] and [F⁻] remaining in solution at equilibrium.



$$\text{Sr(NO}_3)_2 = 0.0032 \text{ mols}$$

Worksheet 5

KF = 0.004 mols

Because F⁻ is the limiting reagent all the F⁻ are used up to make SrF₂ and only Sr²⁺ remains in solution.

[Sr²⁺] = 0.0032 - 0.002 / 0.120 L = 0.01 M, but if some SrF₂ redissolves

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

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

10. Compare the molar solubility of Mg(OH)₂ in pure water with that in a solution buffered at pH 9.00.



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

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

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

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

buffered solution

$$\text{pH} = 14 - \text{pOH}$$

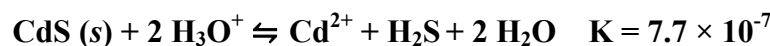
$$\text{pOH} = 5 = -\log [\text{OH}^-]$$

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

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

$$S = 0.12 \text{ M}$$

11. Calculate the [Cd²⁺] in a solution that is in equilibrium with CdS (s) and in which [H₃O⁺] = 1.0 × 10⁻³ M and [H₂S] = 0.10 M.



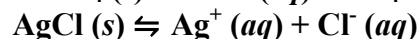
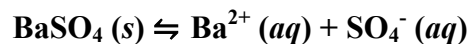
$$[\text{Cd}^{2+}][\text{H}_2\text{S}] / [\text{H}_3\text{O}^+]^2 = K$$

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

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

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

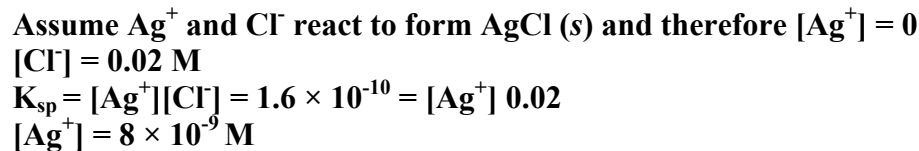
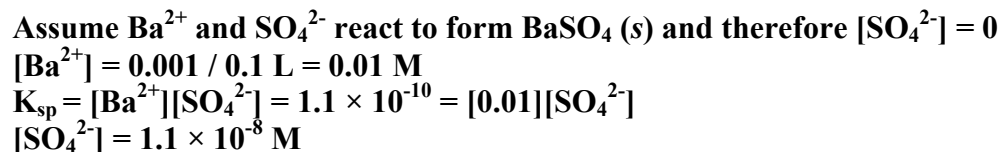
12. The two salts BaCl₂ and Ag₂SO₄ are both far more soluble in water than either BaSO₄ (K_{sp} = 1.1 × 10⁻¹⁰) or AgCl (K_{sp} = 1.6 × 10⁻¹⁰) at 25°C. Suppose 50.0 mL of 0.040 M BaCl₂ (aq) is added to 50.0 mL of 0.020 M Ag₂SO₄ (aq). Calculate the concentrations of SO₄²⁻ (aq), Cl⁻ (aq), Ba²⁺ (aq), and Ag⁺ (aq) that remain in solution at equilibrium.



$$\text{Ba}^{2+} = 0.002 \text{ mols}$$

$$[\text{Ba}^{2+}] = 0.02 \text{ M}$$

Worksheet 5



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 H_2O and NaCl . The solubility of salt will decrease as the pressure is increased.