Review

Calculating the pH during a titration involves:

1. Identify the stoichiometric (non-equilibrium, one-way) reaction that takes place, and calculate the quantities of reactants that are consumed and of products that are made.

2. Identify the equilibrium reaction, if any, that takes place, and calculate the quantity of H^+ or OH^- produced to reach equilibrium.

3. Convert the value of H^+ or OH^- into a pH value.

So far, we have covered how to calculate the pH in three regions of a titration curve:

1. The initial point, before the titration begins, when only the sample is present. Note the sample could be a strong acid, weak acid, strong base, or weak base. (Chapter 15)
2. At the equivalence point. (combination of Chapters 4, 5, 15 and 16)
3. Before the equivalence and after the initial point (the buffer region). (combination of Chapters 4, 5, 15 and 16)

The half-equivalence point is a special case in the buffer region.

At the half-equivalence point, the solution is a buffer with equal amounts of weak acid and its conjugate weak base.

In the example from last time, the strong base converted half of the weak acid HA into its conjugate base A^-. We had 0.0025 moles of HA and 0.0025 moles of A^-. Using the total volume, we had 0.0333 M HA and 0.0333 M A^-.

With equal molarity of conjugate acid and base:

$pH = pK_a + \log([\text{conj. base}]/[\text{conj. acid}])$

$pH = pK_a + \log(0.0333\text{ M} / 0.0333\text{ M})$

$pH = pK_a + \log(1) = pK_a$

At the half-equivalence point, $pH = pK_a$ when titrating a weak acid.

pH after equivalence point

After the equivalence point, the stoichiometric reaction has neutralized all the sample, and the pH depends on how much excess titrant has been added.

<u>Example: Strong acid – strong base titration</u>

To reach equivalence point

HNO_3 + KOH $H_2O(l)$ + $KNO_3(aq)$

I   0.100 moles each
(sample+titrant)

C

End

After equivalence point, any excess strong base KOH determines the pH. If total KOH added was 0.150 moles, then excess OH^- = 0.050 moles.

$pOH = -\log[OH^-]$ (excess)

$pH = 14 - pOH$ (Fig. 16.5, p. 589.)

Example: Weak acid - strong base titration

To reach equivalence point

$HA + OH^- \qquad\qquad H_2O(l) + A^-$

I 0.100 moles each
(sample+titrant)

C

End

Although, $A^- + H_2O(l) \qquad HA + OH^-$ produces a small amount of OH^-, the excess OH^- from the strong base dominates and determines the pH. If total OH^- from strong base was 0.150 moles, then excess $OH^- = 0.050$ moles.

$pOH = -\log[OH^-]$ (excess)

$pH = 14 - pOH$

Excess strong base results in $pH > 7$ (basic).

Fig. 16.6, p. 591.

Example: Weak base - strong acid titration

To reach equivalence point

NH_3 + HCl $\qquad\qquad$ H_2O(l) + NH_4Cl(aq)

I $\quad$ 0.100 moles each
$\quad$ (sample+titrant)

C

End

Although, NH_4^+ + H_2O(l) $\qquad$ NH_3 + H_3O^+ produces a small amount of H_3O^+, the excess strong acid HCl dominates and determines the pH. If total H_3O^+ from HCl was 0.150 moles, then excess H_3O^+ = 0.050 moles.

pH = [H_3O^+] (excess)

pH = -log[H_3O^+]

Excess strong acid results in pH < 7 (acidic).

Fig. 16.7, p. 593.

Types of titration calculations

1. Initial point
   -pH depends on concentration of sample and whether sample is a strong acid, weak acid, strong base, or weak base (Chapter 15 calculations)

2. Before the equivalence point (buffer region, including the half-equivalence point)
   -pH depends on how much unreacted sample remains and how much conjugate has been produced (Chapters 4, 5, 15 and 16 calculations)

3. At the equivalence point
   -pH depends on whether the salt formed is acidic, basic, or neutral (Chapter 15 calculations)

4. After equivalence point
   -pH depends on amount of excess base or acid added beyond equivalence point (Chapter 4, 5, and 15 calculations)

Solubility is not the same as K_{sp}

Solubility (also called molar solubility) is a concentration value that is included in the definition of the solubility constant K_{sp}, which is a mathematical expression.

Which compound, $SrSO_4$ ($K_{sp} = 2.8 \times 10^{-7}$) or PbI_2 ($K_{sp} = 8.7 \times 10^{-9}$), has a higher solubility in water at 25 °C?

Le Chatelier’s principle and solubility

When a system at equilibrium is disturbed, the system will shift in a way that partially counteracts the disturbance. (Chapter 13)

<u>Greater solubility due to acid</u>:
Consider $CaCO_3(s)$ $\quad\quad$ $Ca^{2+} + CO_3^{2-}$

$2H_3O^+ + CO_3^{2-}$ $\quad\quad$ H_2CO_3 $\quad\quad$ $CO_2(g) + H_2O(l)$
$+ 2H_2O(l)$

<u>Lesser solubility due to common ion effect</u>:
Calculate solubility of $ZnCO_3$ in a 0.050 M solution of $Zn(NO_3)_2$.

$ZnCO_3(s)$ $\quad\quad$ $Zn^{2+} + CO_3^{2-}$ $\quad$ $K_{sp} = 1.5 \times 10^{-11}$

Equilibrium, solubility, and precipitation

From Chapter 14, a saturated solution has reached its maximum solubility of solute and is at equilibrium between dissolved and undissolved solute ($Q = K$). No additional precipitate forms, and no additional solute dissolves.

An unsaturated solution has not reached the solubility limit of the solute and has not reached equilibrium ($Q < K$). Additional solute can be dissolved in the solution.

A supersaturated solution has exceeded the solubility limit of the solute, and the concentration of the solute exceeds its maximum equilibrium concentration ($Q > K$). Solute must precipitate to reach equilibrium.

Example: An aqueous solution contains 0.100 M Pb^{2+} and 0.0100 M Ag^{+} ions. Gaseous HCl is bubbled into the solution. For each ion, determine the concentration of HCl at which the ion begins to precipitate as a chloride salt.

Practice: A 0.050 M $AgNO_3$ solution is saturated with AgCl. Determine the concentration of chloride ion.

Titration example: calculations involving pOH, Fig. 16.6, p. 591. 50.0 mL of 0.100 M acetic acid is titrated with 0.100 M NaOH solution. Calculate the pH after 50.0 mL of titrant has been added and after 75.0 mL has been added.