Region 4: After the Equivalence Point

- Now we are adding NaOH to a solution of A^-.
- The base NaOH is so much stronger than the base A^- that it is fair to say that the pH is determined by the excess OH^-.

- Let's calculate the pH when V_b = 10.10 mL, which is just 0.10 mL past V_e.
- The concentration of excess OH^- is

$$[\mathrm{OH^-}] = \underbrace{(0.100\,0\ \mathrm{M})}_{\substack{\text{Initial}\\ \text{concentration}\\ \text{of OH}^-}} \underbrace{\left(\frac{\overset{\substack{\text{Volume of}\\ \text{excess OH}^-}}{0.10}}{50.00 + 10.10}\right)}_{\substack{\text{Dilution}\\ \text{factor}}} \underset{\substack{\text{Total volume}\\ \text{of solution}}}{=} 1.66 \times 10^{-4}\ \mathrm{M}$$

$$\mathrm{pH} = -\log\left(\frac{K_\mathrm{w}}{[\mathrm{OH^-}]}\right) = 10.22$$

The Titration Curve

- Calculations for the titration of MES with NaOH are shown in Table 11-2.

See Table 11-2

The Titration Curve

- The calculated titration curve in Figure 11-2 has two easily identified points.
  → One is the equivalence point, which is the steepest part of the curve.
  → The other landmark is the point where and pH = pK_a.

See Figure 11-2

- This latter point is also an inflection point, having the minimum slope.

- Figure 11-3 shows how the titration curve depends on the acid dissociation constant of HA and on the concentrations of reactants.

- As the acid becomes weaker or more dilute,

→ the end point becomes less distinct.

- It is not practical to titrate an acid or a base when its strength is too weak or its concentration too dilute.

See Figure 11-3

11.3 Titration of Weak Base with Strong Acid

- The titration of a weak base with a strong acid is the reverse of the titration of a weak acid with a strong base.

- The titration reaction is

$$B + H^+ \rightarrow BH^+$$

- Because the reactants are a weak base and a strong acid,

  → the reaction goes essentially to completion after each addition of acid.

- There are **four distinct regions** of the titration curve:

1. **Before acid is added**,

→ the solution contains just the weak base, B, in water.

→ The pH is determined by the K_b reaction.

$$\underset{F-x}{B} + H_2O \overset{K_b}{\rightleftharpoons} \underset{x}{BH^+} + \underset{x}{OH^-}$$

2. **Between the initial point and the equivalence point**,

→ there is a mixture of B and BH^+

→ The pH is computed by using

$$pH = pK_a\,(\text{for } BH^+) + \log\left(\frac{[B]}{[BH^+]}\right)$$

- In adding acid (increasing V_a),

→ we reach the special point where $V_a = \frac{1}{2}V_e$ and $pH = pK_a$ (for BH^+).

3. At the equivalence point,

→ B has been converted into BH^+, a **weak acid**.

→ The pH is calculated by considering the acid dissociation reaction of BH^+.

$$\underset{F'-x}{BH^+} \rightleftharpoons \underset{x}{B} + \underset{x}{H^+} \qquad K_a = \frac{K_w}{K_b}$$

- The formal concentration of BH^+, F′, is not the original formal concentration of B because some dilution has occurred.
- The solution contains BH^+ at the equivalence point, so it is acidic.
- The pH at the equivalence point must be below 7.

4. After the equivalence point,

→ the **excess strong acid** determines the pH.

→ We neglect the contribution of weak acid, BH^+.

11.4 Titration in Diprotic Systems

- The principles developed for titrations of monoprotic acids and bases are readily extended to titrations of polyprotic acids and bases.

See Figure 11-4

- The upper curve in Figure 11-4 is calculated for the titration of 10.0 mL of 0.100 M base (B) with 0.100 M HCl.

→ The base is dibasic, with $pK_{b1} = 4.00$ and $pK_{b2} = 9.00$.

11.4 Titration in Diprotic Systems

- The titration curve has reasonably sharp breaks at both equivalence points, corresponding to the reactions

$$B + H^+ \rightarrow BH^+$$

$$BH^+ + H^+ \rightarrow BH_2^{2+}$$

See Figure 11-4

$$B + H^+ \rightarrow BH^+$$

$$BH^+ + H^+ \rightarrow BH_2^{2+}$$

- The volume at the first equivalence point is 10.00 mL because

$$\underbrace{(V_e(\text{mL}))(0.100\text{ M})}_{\text{mmol of HCl}} = \underbrace{(10.00\text{ mL})(0.100\,0\text{ M})}_{\text{mmol of B}} \Rightarrow V_e = 10.00\text{ mL}$$

- The volume at the second equivalence point must be $2V_e$,

  → because the second reaction requires the same number of moles of HCl as the first reaction.

- The pH calculations are similar to those for corresponding points in the titration of a monobasic compound.

→ Let’s examine points A through E in Figure 11-4.

Point A

- Before acid is added,
  → the solution contains just weak base, B,
  → whose pH is governed by the reaction

$$\begin{array}{ccccc} \mathrm{B} + \mathrm{H_2O} & \overset{K_{b1}}{\rightleftharpoons} & \mathrm{BH^+} & + & \mathrm{OH^-} \\ 0.100 - x & & x & & x \end{array}$$

$$\frac{x^2}{0.100 - x} = 1.00 \times 10^{-4} \Rightarrow x = 3.11 \times 10^{-3}$$

$$[\mathrm{H^+}] = \frac{K_w}{x} \Rightarrow \mathrm{pH} = 11.49$$

- The fully basic form of a dibasic compound can be treated
  → as if it were monobasic.
  → The K_{b2} reaction can be neglected.

Point B

- At any point between A (the initial point) and C (the first equivalence point),

  → we have a **buffer** containing B and BH^+.

- Point B is halfway to the equivalence point, so $[B] = [BH^+]$.

  → The pH is calculated from the Henderson-Hasselbalch equation for the weak acid, BH^+,

  → whose acid dissociation constant is K_{a2} (for BH_2^{2+}) = $K_w/K_{b1} = 10^{-10.00}$.

$$K_{a2} = \frac{K_w}{K_{b1}} \qquad K_{a1} = \frac{K_w}{K_{b2}}$$

$$\mathrm{pH} = \mathrm{p}K_{a2} + \log\frac{[B]}{[BH^+]} = 10.00 + \log 1 = 10.00$$

→ So the pH at point B is just $\mathrm{p}K_{a2}$.

- To calculate the quotient [B]/[BH$^+$] at any point in the buffer region, → just find what fraction of the way from point A to point C the titration has progressed.

- For example, if V_a = 1.5 mL, then

$$\frac{[\mathrm{B}]}{[\mathrm{BH}^+]} = \frac{8.5}{1.5}$$

- Because 10.0 mL are required to reach the equivalence point and we have added just 1.5 mL.
→ the pH at V_a = 1.5 mL is

$$\mathrm{pH} = 10.00 + \log\frac{8.5}{1.5} = 10.75$$

Point C

- At the **first equivalence point**,

  → B has been converted into BH^+,

  → the intermediate form of the diprotic acid, BH_2^{2+}

- BH^+ is both an acid and a base.

  → From Equation 10-11, we know that

$$[H^+] \approx \sqrt{\frac{K_1K_2F + K_1K_w}{K_1 + F}}$$

→ where K_1 and K_2 are the acid dissociation constants of BH_2^{2+}.

- The formal concentration of BH^+ is calculated by considering dilution of the original solution of B.

$$F = \underbrace{(0.100\text{ M})}_{\substack{\text{Original}\\ \text{concentration}\\ \text{of B}}}\underbrace{\left(\frac{\overset{\swarrow\ \substack{\text{Initial volume}\\ \text{of B}}}{10.0}}{\underset{\nwarrow\ \substack{\text{Total volume}\\ \text{of solution}}}{20.0}}\right)}_{\substack{\text{Dilution}\\ \text{factor}}} = 0.050\,0\text{ M}$$

- Plugging all the numbers into Equation 11-3 gives

$$[H^+] = \sqrt{\frac{(10^{-5})(10^{-10})(0.050\,0) + (10^{-5})(10^{-14})}{10^{-5} + 0.050\,0}} = 3.16 \times 10^{-8}$$

$$\text{pH} = 7.50$$

- Point C in Figure 11-4 shows where the intermediate form of a diprotic acid lies on a titration curve.

- This is the **least-buffered point** on the whole curve,
→ because the pH changes most rapidly if small amounts of acid or base are added.

- There is a misconception that the intermediate form of a diprotic acid behaves as a buffer when, in fact, it is the worst choice for a buffer.

See Figure 11-4

Point D

- At any point between C and E,

  → there is a **buffer** containing BH^+ (the base) and BH_2^{2+} (the acid).

- When V_a = 15.0 mL, $[BH^+] = [BH_2^{2+}]$ and

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{a1}} + \log \frac{[\mathrm{BH}^+]}{[\mathrm{BH}_2^{2+}]} = 5.00 + \log 1 = 5.00$$

Point E

- Point E is the **second equivalence point**,

  → at which the solution is formally the same as one prepared by dissolving BH_2Cl_2 in water.

- The formal concentration of BH_2^{2+} is

$$F = (0.100\ \text{M})\left(\frac{\overset{\text{Original volume of B}}{10.0}}{\underset{\text{Total volume of solution}}{30.0}}\right) = 0.033\ 3\ \text{M}$$

- The pH is determined by the acid dissociation reaction of BH_2^{2+}.

$$\underset{F - x}{BH_2^{2+}} \rightleftharpoons \underset{x}{BH^+} + \underset{x}{H^+} \qquad K_{a1} = \frac{K_w}{K_{b2}}$$

$$\frac{x^2}{0.033\,3 - x} = 1.0 \times 10^{-5} \Rightarrow x = 5.72 \times 10^{-4} \Rightarrow pH = 3.24$$

- **Beyond the second equivalence point** (V_a > 20.0 mL),

  → the **pH of the solution** can be calculated from the volume of **strong acid added** to the solution.

- For example, at V_a = 25.00 mL,

  → there is an excess of 5.00 mL of 0.100 M HCl in a total volume of 10.00 + 25.00 = 35.00 mL.

  → The pH is found by writing

$$[\mathrm{H}^+] = (0.100\ \mathrm{M})\left(\frac{5.00}{35.00}\right) = 1.43 \times 10^{-2}\ \mathrm{M} \Rightarrow \mathrm{pH} = 1.85$$

Analytical Chemistry

Chapter 12. EDTA Titrations

In this chapter,

→ How to find the quantities of metal ions in a solution from an EDTA titration curve

i) Formation of metal-chelate complexes
ii) Shapes of EDTA titration curves

12.1 Metal-Chelate Complexes

- Metal ions (Lewis acids)

  → accepting electron pairs from electron-donating ligands (Lewis bases)

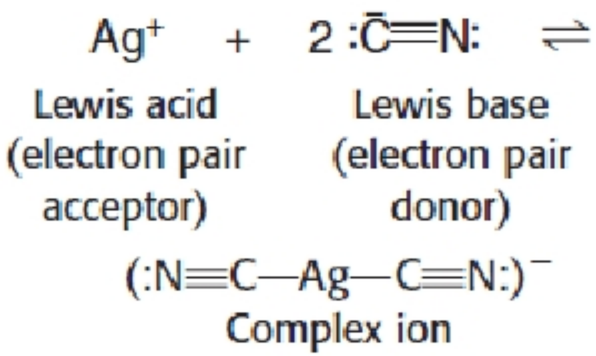
- Most transition metal ions bind six ligand atoms.
- A ligand binds to a metal ion through only one atom

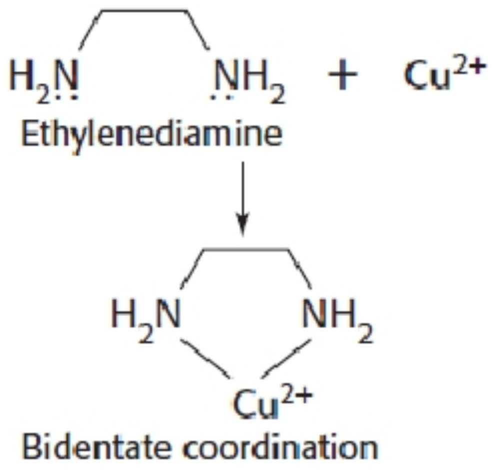
  → called a **monodentate ligand**

  → the carbon atom in cyanide (CN)

- A ligand that attaches to a metal ion through more than one ligand atom

  → said to be **multidentate** or a **chelating ligand**



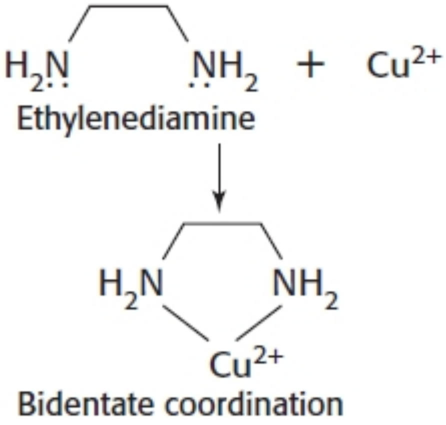


- A simple chelating ligand

  → 1,2-diaminoethane, also called ethylenediamine

- Ethylenediamine is bidentate

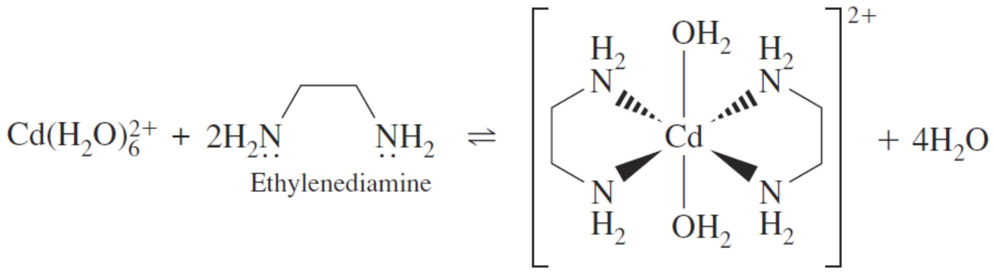
  → because it binds to the metal through two ligand atoms.



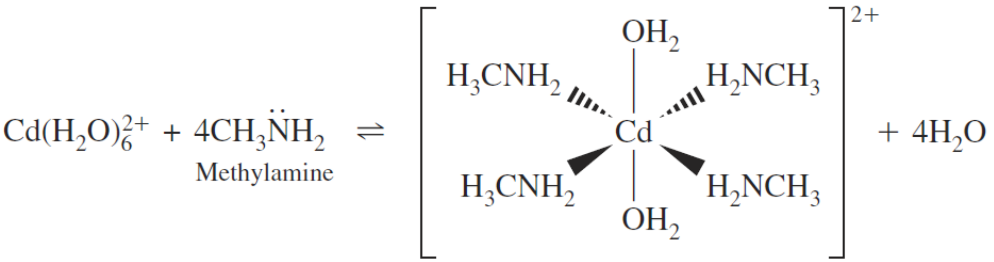
- The **chelate effect**

→ the ability of multidentate ligands to form more stable metal complexes than those formed by similar monodentate ligands.

- For example, the reaction of $Cd(H_2O)_6^{2+}$ with two molecules of ethylenediamine is more favorable than its reaction with four molecules of methylamine:



$K \equiv \beta_2 = 8 \times 10^9$



$K \equiv \beta_4 = 4 \times 10^6$

- At pH 12 in the presence of 2 M ethylenediamine and 4 M methylamine,

→ the quotient $[Cd(ethylenediamine)_2^{2+}]$ $/[Cd(methylamine)_4^{2+}]$ is 30.

- A titration based on complex formation

  → called a **complexometric titration** .
- Ligands other than NTA in Figure 12-4 form strong 1:1 complexes with all metal ions except univalent ions such as Li, Na, and K.
- The stoichiometry is 1:1 regardless of the charge on the ion.

See Figure 12-4

- Aminocarboxylic acids in Figure 12-4 are synthetic chelating agents.
- Amine N atoms and carboxylate O atoms are potential ligand atoms in these molecules (Figures 12-5 and 12-6).
- When these molecules bind to a metal ion, the ligand atoms lose their protons.

See Figure 12-5, 12-6

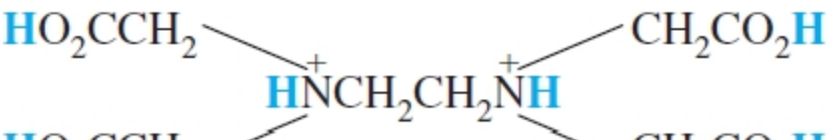
12.2 EDTA

- Ethylenediaminetetraacetic acid (EDTA)
- EDTA is, by far, the most widely used chelator in analytical chemistry.
- One mole of EDTA reacts with one mole of metal ion.
- EDTA engulfs the metal ion, forming the **six coordinate** species in Figure 12-1.
- Every element of the periodic table can be measured with EDTA.

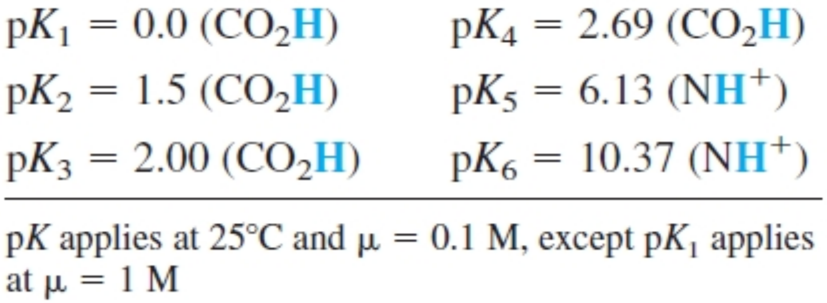
See Figure 12-1

Acid-Base Properties

- EDTA is a **hexaprotic** system, designated H_6Y^{2+} .
- The highlighted, acidic hydrogen atoms are the ones that are lost upon metal-complex formation.



H_6Y^{2+}



$pK_1 = 0.0\ (CO_2H)$
$pK_2 = 1.5\ (CO_2H)$
$pK_3 = 2.00\ (CO_2H)$
$pK_4 = 2.69\ (CO_2H)$
$pK_5 = 6.13\ (NH^+)$
$pK_6 = 10.37\ (NH^+)$

pK applies at 25°C and $\mu = 0.1$ M, except pK_1 applies at $\mu = 1$ M

- The first four pK values apply to carboxyl protons
- The last two are for the ammonium protons.
- The neutral acid is tetraprotic, with the formula H_4Y.

- The fraction (α) of EDTA in each of its protonated forms at a certain pH
- As in Section 10-5, we can define α for each species as the fraction of EDTA in that form.
- For example, α_{Y4-} is defined as

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[H_6Y^{2+}] + [H_5Y^{+}] + [H_4Y] + [H_3Y^{-}] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]}$$

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[EDTA]} \qquad \textbf{(12-3)}$$

→ where [EDTA] is the total concentration of all free EDTA species in the solution.

- By “free,” we mean EDTA not complexed to metal ions.

- Following the derivation in Section 10-5, we can show that is given by

$$\alpha_{Y^{4-}} = \frac{K_1K_2K_3K_4K_5K_6}{D}$$

$$D = [H^+]^6 + [H^+]^5K_1 + [H^+]^4K_1K_2 + [H^+]^3K_1K_2K_3 + [H^+]^2K_1K_2K_3K_4 + [H^+]K_1K_2K_3K_4K_5 + K_1K_2K_3K_4K_5K_6$$

- Table 12-1 gives values for α_{Y4-} as a function of pH.

See Table 12-1

- The fraction of EDTA in each of its protonated forms is plotted in Figure 12-7.

See Figure 12-7

EDTA Complexes

- The equilibrium constant for the reaction of a metal with a ligand

  → called the **formation constant, K_f**, or the **stability constant** :

Formation constant:

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4} \qquad K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]}$$

- Note that K_f for EDTA is defined in terms of the species Y^{4-} reacting with the metal ion.
- The equilibrium constant could have been defined for any of the other six forms of EDTA in the solution.
- The equation above should not be interpreted to mean that only Y^{4-} reacts with metal ions.

- Table 12-2 shows that formation constants for most EDTA complexes are large

  → tend to be larger for more positively charged cations.

See Table 12-2