Chapter 12 - **EDTA Titrations**

Homework: Due Friday, March 6

Problems 12-1, 12-24, 12-29, 12-30

Titration of Metals

- Allows for the determination of the quantity of the metals present in an mixture aqueous solution.
- High tech way of getting the same info is either by atomic spectroscopy (ICP or AA).
- However, many field tests are based on titration methods (such as water hardness kits).
- Additionally, chelation reactions very important to many aspects of chemistry (not just measuring metal concentrations).

Lewis acid-base concept

Lewis acid => electron pair acceptor

metal

Lewis base => electron pair donor

ligand

Coordinate covalent bond:

ligand donates both electrons of the electron pair to bond to metal ion.

Chelate Effect

- **Complexation reactions generally involve Lewis acids (electron pair acceptors - metals) and Lewis bases (electron pair donors - ligands).**
- **Many important biological molecules, such as ATP and hemoglobin, owe their function to structural changes induced by complexation with metal ions.**
- **Most metal atoms are capable of binding with six (and sometimes seven) ligands at once.**

  Example: $\mathbf{Al(H_2O)_6^{+3}}$
- **Many ligands are capable of binding at more than one site. These special ligands are called multidentate, or chelating ligands.**
- **Multidentate ligands form complexes of higher stability than do monodentate ones.**

Recall that the more negative the ΔG, the more favorable the reaction: $\Delta G = \Delta H - T\Delta S$

Consider the reactions:

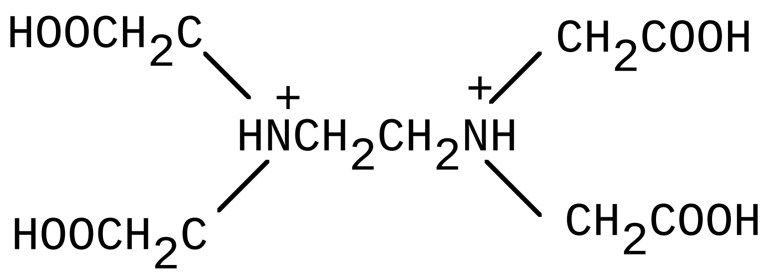
$$Ni(H_2O)_6^{+2} + 6NH_3 \text{---->} Ni(NH_3)_6^{+2} + 6\,H_2O$$

$$Ni(H_2O)_6^{+2} + 3H_2NCH_2CH_2NH_2 \rightarrow Ni(H_2NCH_2CH_2NH_2)_3^{+2} + 6H_2O$$

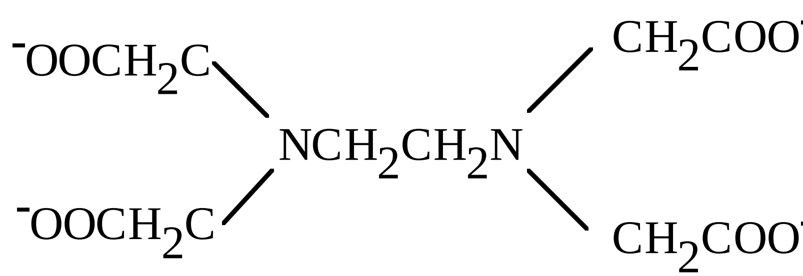
Since the same atoms (Ni and N) are binding in each case, the ΔH is about the same in each case. In the second reaction, however, 4 molecules are converted into seven, while in the first, the number of molecules stays the same. This increase in molecules increases the ΔS of the system, which makes ΔG more negative. ***This increased favorability is called the "chelate effect".***

Favorite Chelating Agent: EDTA

EDTA: The form of EDTA (ethylenediaminetetraacetic acid) the fully protonated form, is symbolized as HY^{+2}. Being a hexaprotic acid, EDTA exists in species ranging from H_2Y^{+2} to Y^{-4} .



YH^{+2} Form

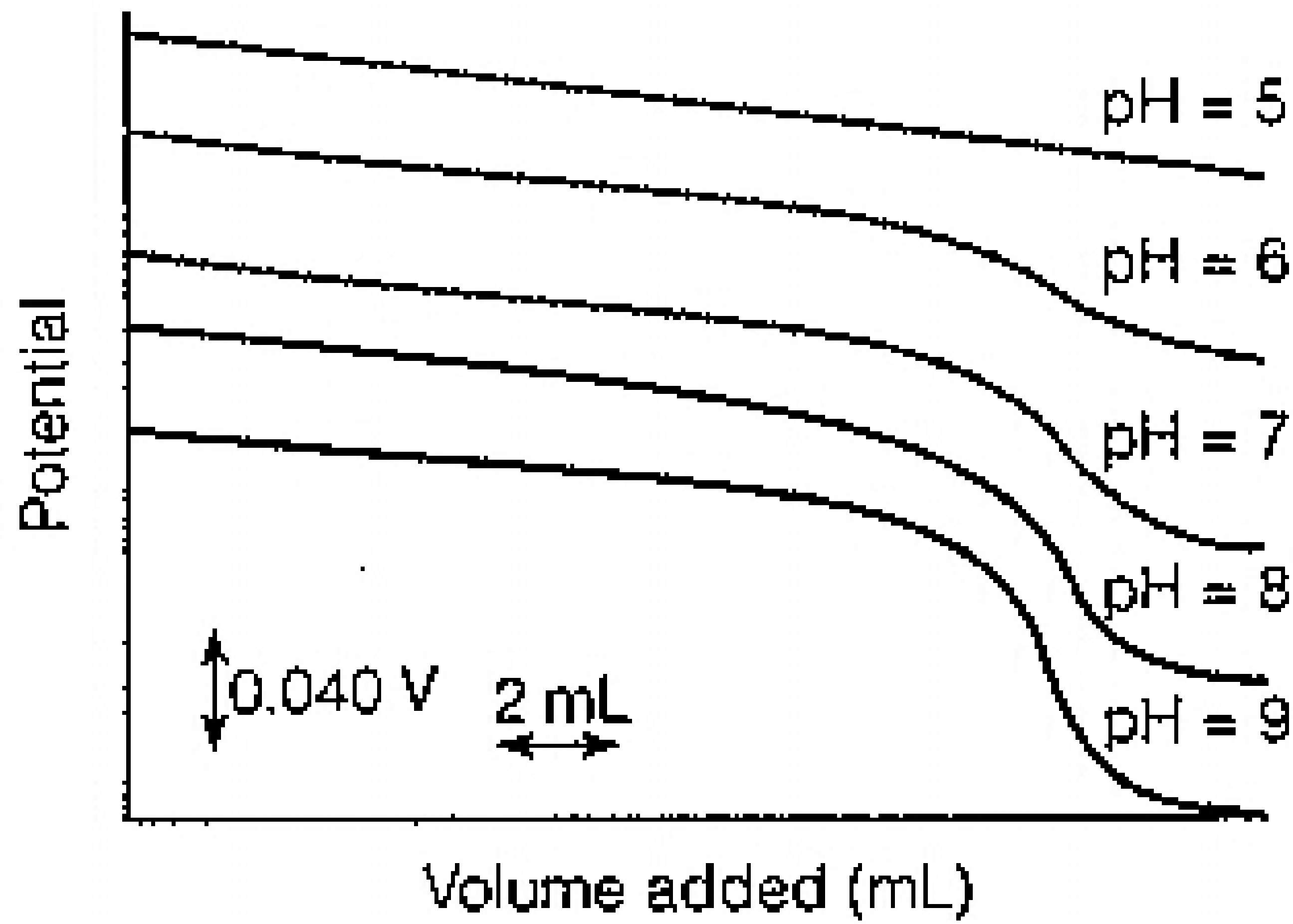


Y^{-4} Form

Control of the solution pH of an EDTA titration is important, since the Y^{-4} species is the chelator. Solutions are buffered to keep the solutions basic (pH 10 or greater).

Titration of Ca^{+2} with EDTA at various pHs

Fig. 13-8, pg. 265



$EDTA^{-4} \Rightarrow Y^{-4}$ (Chelating Form)

+1 cations:	$Ag^{+} + Y^{-4} = AgY^{-3}$
+2 cation:	$Hg^{+2} + Y^{-4} = HgY^{-2}$
+3 cation:	$Fe^{+3} + Y^{-4} = FeY^{-1}$
+n ion:	$M^{+n} + Y^{-4} = MY^{(n-4)+}$

- EDTA chelates with cations of any oxidation state.
- Universal chelating agent.
- Different formation contants for each EDTA/metal complex

End point detection:

- End points in EDTA titration are determined with metal ion indicators that respond to the presence (or absence) of metal ions.
- These indicators also form complexes with metals, although not as strongly as EDTA.
- As EDTA is added to the mixture, it first complexes with the free metal ion, then begins to react with the metal ion that is bound to the indicator, since it's K_f with the metal is so much larger than the indicators.
- The point at which the majority of the indicator is no longer bound to a metal ion, a color change takes place.
- For the majority of metal ion indicators, the color change is from red to blue.

$$\underset{\text{(red)}}{\text{M(In)}} + \text{EDTA} \rightarrow \text{M(EDTA)} + \underset{\text{(blue)}}{\text{In}}$$

EDTA Indicators

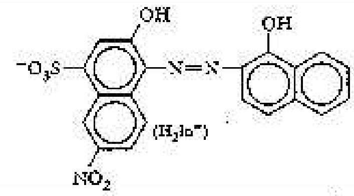
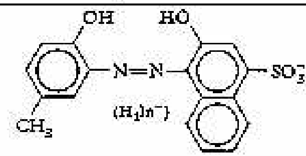
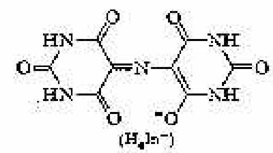
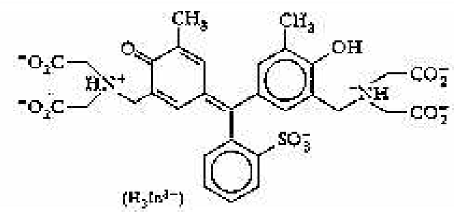
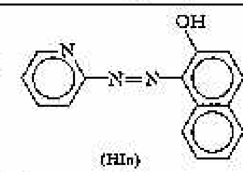
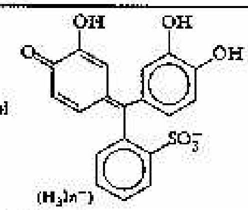
Table 13-3, pg. 273

Most common: Erichrome Black T

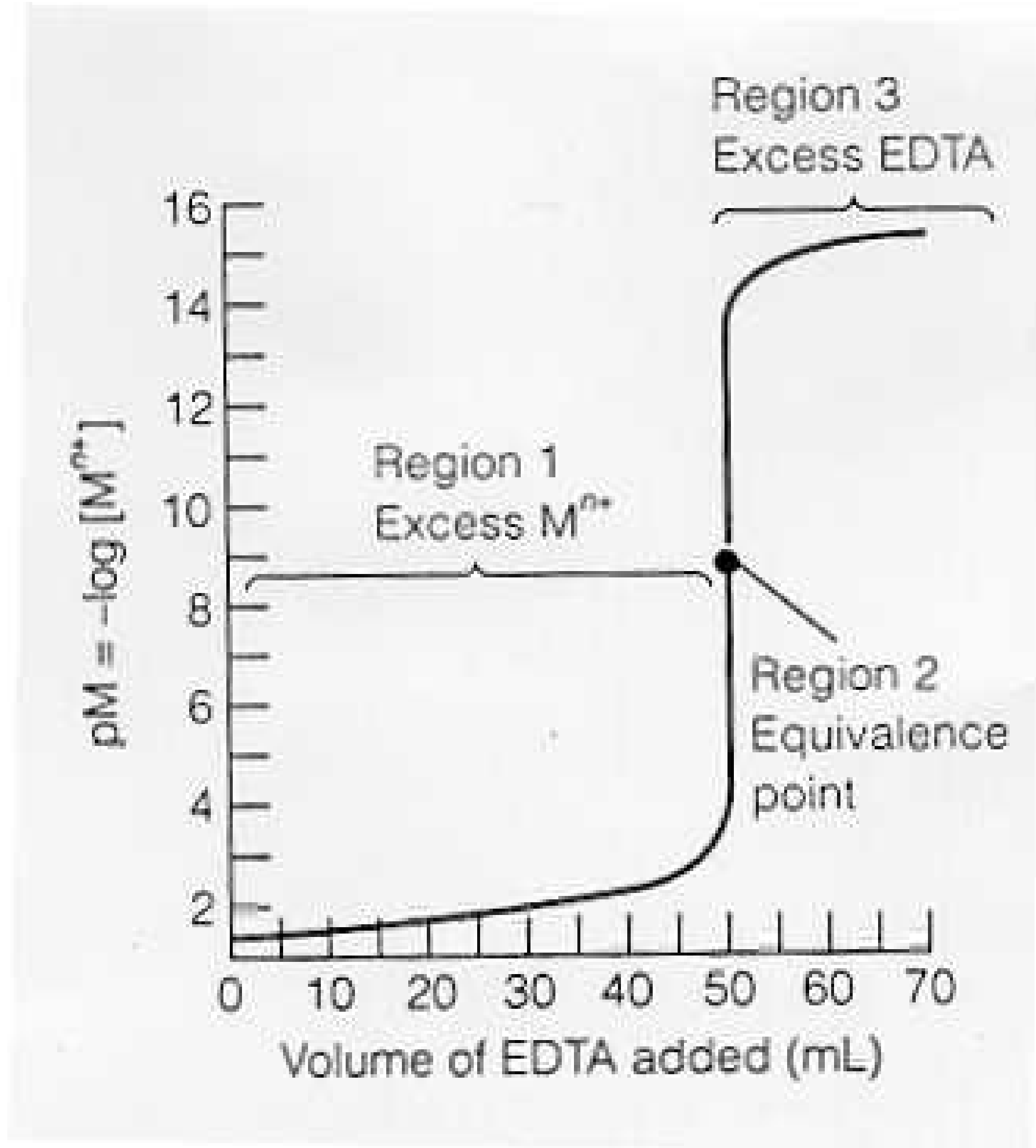
MgIn + EDTA =
(red)

MgEDTA + In
(colorless) (blue)

TABLE 13-3 Common metal ion indicators

Name	Structure	pK_a	Color of free indicator	Color of metal ion complex
Eriochrome black T		$pK_2 = 6.3$ $pK_3 = 11.6$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Calmagite		$pK_2 = 8.1$ $pK_3 = 12.4$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Murexide		$pK_2 = 9.2$ $pK_3 = 10.9$	H_4In^- red-violet H_3In^{2-} violet H_2In^{3-} blue	Yellow (with Co^{2+}, Ni^{2+}, Cu^{2+}); red with Ca^{2+}
Xylenol orange		$pK_2 = 2.32$ $pK_3 = 2.85$ $pK_4 = 6.70$ $pK_5 = 10.47$ $pK_6 = 12.23$	H_5In^- yellow H_4In^{2-} yellow H_3In^{3-} yellow H_2In^{4-} violet HIn^{5-} violet In^{6-} violet	Red
Pyridylazo-naphthol (PAN)		$pK_a = 12.3$	HIn orange-red In^- pink	Red
Pyrocatechol violet		$pK_1 = 0.2$ $pK_2 = 7.8$ $pK_3 = 9.8$ $pK_4 = 11.7$	H_4In red H_3In^- yellow H_2In^{2-} violet HIn^{3-} red-purple	Blue

Three Regions of EDTA Titration Fig. 13-10, pg. 267



Water Hardness

- Water hardness is defined as the ($[Ca^{+2}]$ + $[Mg^{+2}]$) is present in the water.
- Water is "harder" in the Western U.S. compared to the East.
- Water hardness kits used to test for hardness based on EDTA titration and Erichrome Black T indicator.
- What's wrong with hard water?
- How is water "softened"?

Why is EDTA important?

- It is used in many products (detergents, hair products, etc.).
- It binds readily to metals which can make them more soluable.
- It can act to mobilize metals that would have otherwise "stayed put"; thus, EDTA can act indirectly to move toxic metals from one site to another through ground water, flooding, spring run off, etc.

EDTA is ubiquitous – it is found in many consumer products.

Abbreviation for EDTA - ethylenediaminetetraacetic acid, an ADDITIVE used in some processed foods to eliminate the possibility of rancidity caused by the transfer of trace metals during the manufacturing process. EDTA has a wide variety of nonculinary uses, including the treatment of lead poisoning.

Life Enhancement Products offers a variety of formulations containing EDTA