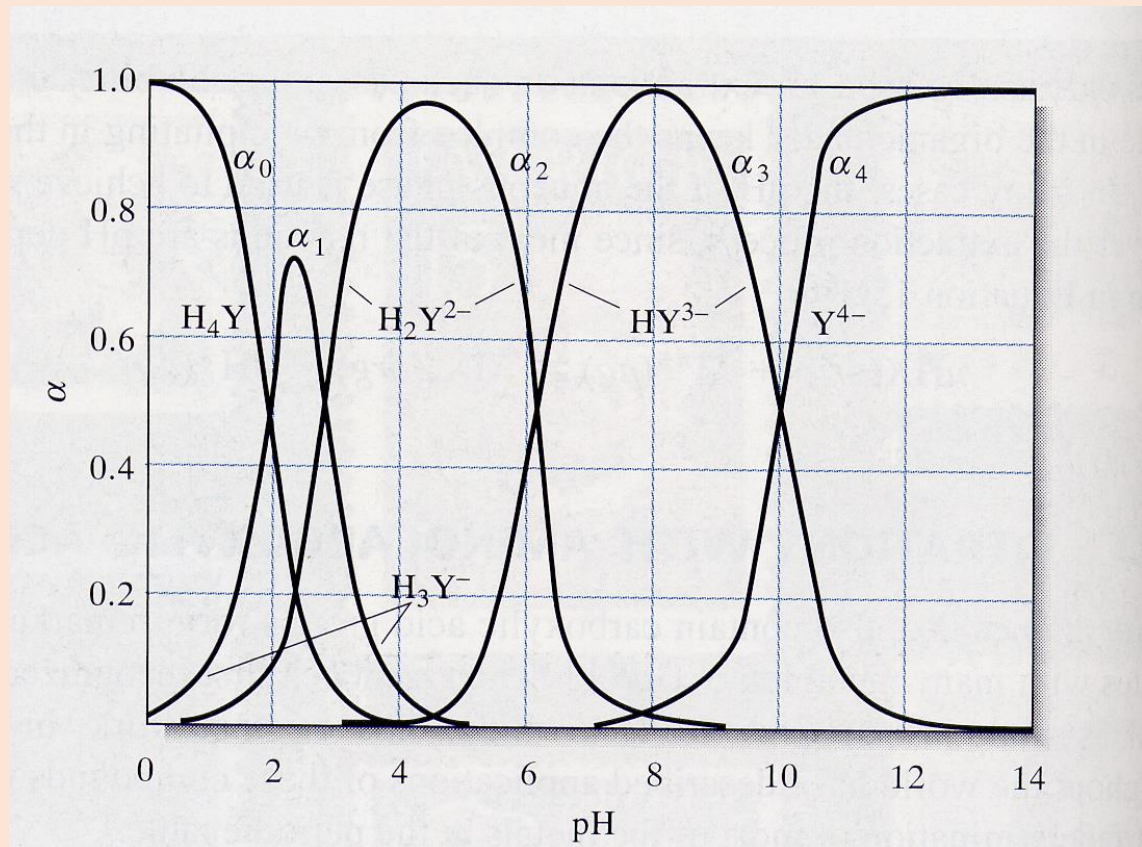




Complexometric Titration II

Equilibrium Calculations Involving EDTA

- EDTA titrations are always performed in solutions that are buffered to a known pH to avoid interferences by other cations or to ensure satisfactory indicator behavior.



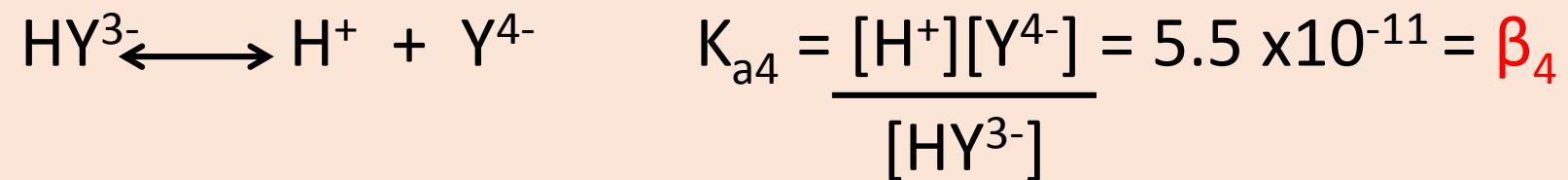
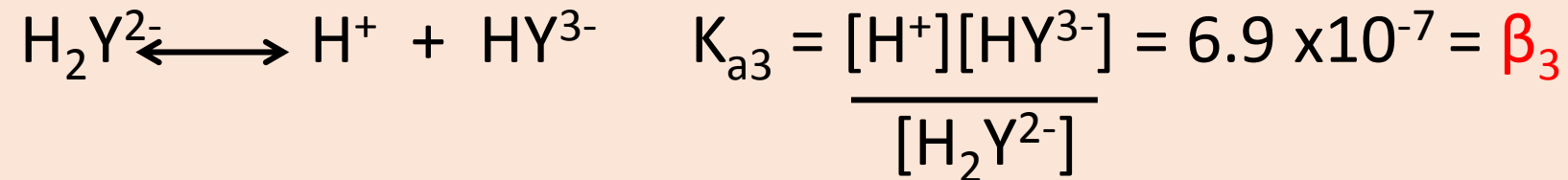
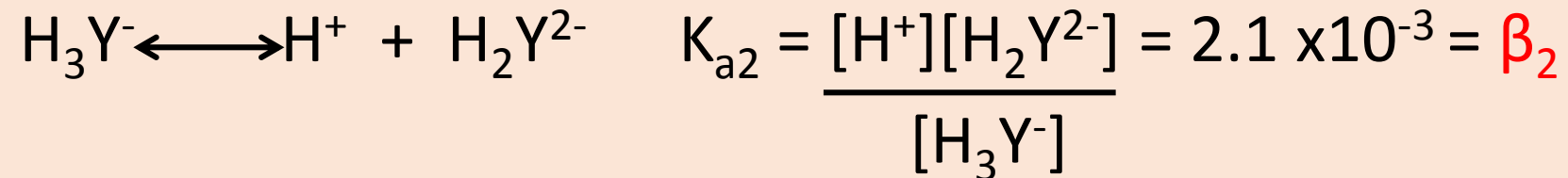
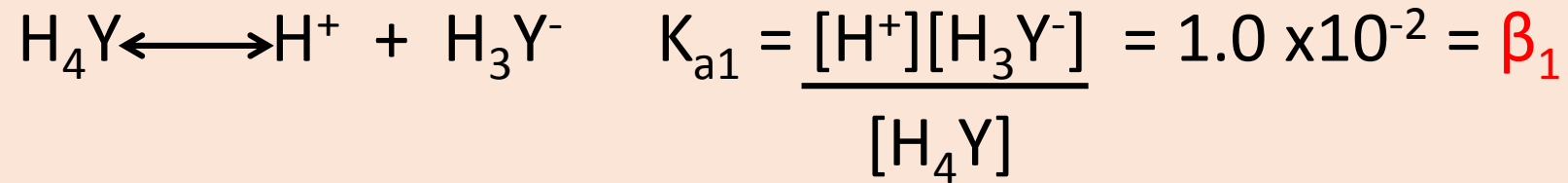


The cumulative stability constant

- $M + L = ML$ $\beta_1 = \frac{[ML]}{[M][L]} = K_1$
- $ML + L = ML_2$ $\beta_2 = \frac{[ML]^2}{[ML][L]} = K_1K_2$
- $ML_2 + L = ML_3$ $\beta_3 = \frac{[ML]^3}{[ML_2][L]} = K_1K_2K_3$
- $ML_{(n-1)} + L = ML_n$ $\beta_n = \frac{[ML]^n}{[ML_{(n-1)}][L]} = K_1K_2K_3 \dots K_n$



- Since EDTA is a tetraprotic acid, the **stepwise dissociation** of EDTA as follows :



Y^{4-} form of EDTA is the predominate form at pH greater than 10



$$\alpha_M = \frac{1}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \dots + \beta_n[L]^n}$$

$$\alpha_{ML} = \frac{\beta_1[L]}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \dots + \beta_n[L]^n}$$

$$\alpha_{ML_2} = \frac{\beta_2[L]^2}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \dots + \beta_n[L]^n}$$

$$\alpha_{ML_n} = \frac{\beta_n[L]^n}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \dots + \beta_n[L]^n}$$



$$C_{EDTA} = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^{-}] + [H_4Y]$$

$$\alpha_4 = \frac{[Y^{4-}]}{C_{EDTA}}$$

$$K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]\alpha_4 C_{EDTA}}$$



Combining the two constants α_4 and K_{MY} yields the conditional formation constant K'_{MY}

$$K'_{MY} = \alpha_4 K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]C_{EDTA}}$$

K'_{MY} is a constant only at the pH for which α_4 is applicable

- It can be used to calculate the equilibrium concentration of the metal ion and the complex at the equivalence point and where there is an excess of reactant.
- Using C_{EDTA} instead of Y^{4-} in determination of K'_{MY} simplifies calculations.



Conditional (or effective) Formation Constant

- They are pH-dependent equilibrium constants that apply at a single pH only.
- Such constants are very useful for determining the effect of pH on the free ligand concentration in a complexation reaction.
- simplifies calculations because C_T is often known or is easily computed.

Value for α_4 for EDTA at selected pH value

pH	α_4	pH	α_4
2	3.7×10^{-14}	8	5.4×10^{-3}
3	2.5×10^{-11}	9	5.2×10^{-2}
4	3.6×10^{-9}	10	3.5×10^{-1}
5	3.5×10^{-7}	11	8.5×10^{-1}
6	2.2×10^{-5}	12	9.8×10^{-1}
7	4.8×10^{-4}		



Formation Constants for EDTA Complexes

Cation	K_{MY}^*	$\log K_{MY}$	Cation	K_{MY}	$\log K_{MY}$
Ag ⁺	2.1×10^7	7.32	Cu ²⁺	6.3×10^{18}	18.80
Mg ²⁺	4.9×10^8	8.69	Zn ²⁺	3.2×10^{16}	16.50
Ca ²⁺	5.0×10^{10}	10.70	Cd ²⁺	2.9×10^{16}	16.46
Sr ²⁺	4.3×10^8	8.63	Hg ²⁺	6.3×10^{21}	21.80
Ba ²⁺	5.8×10^7	7.76	Pb ²⁺	1.1×10^{18}	18.04
Mn ²⁺	6.2×10^{13}	13.79	Al ³⁺	1.3×10^{16}	16.13
Fe ²⁺	2.1×10^{14}	14.33	Fe ³⁺	1.3×10^{25}	25.1
Co ²⁺	2.0×10^{16}	16.31	V ³⁺	7.9×10^{25}	25.9
Ni ²⁺	4.2×10^{18}	18.62	Th ⁴⁺	1.6×10^{23}	23.2



Computing α_4 Values for EDTA Solutions

- Calculate the molar Y^{4-} concentration in a 0.0200 M EDTA solution buffered to a pH of 10.00.
- Solution

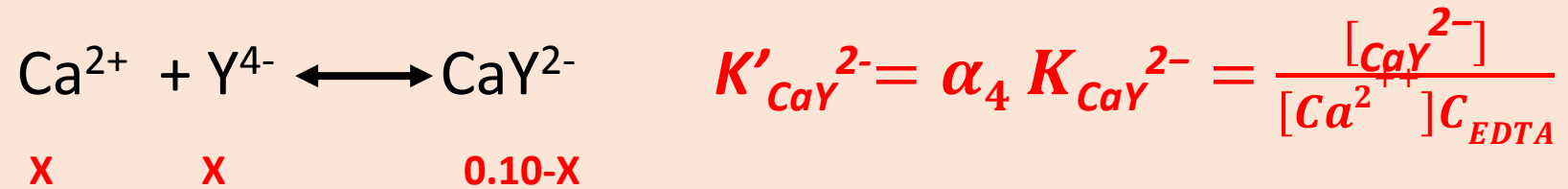
At pH 10.00, α_4 is 0.35 (*see previous table*). Thus,

$$[Y^{4-}] = \alpha_4 \times C_{\text{EDTA}} = 0.35 \times 0.0200 \text{ M}$$
$$7.00 \times 10^{-3} \text{ M}$$



Calculating the Cation Concentration in EDTA Solutions

- Calculate the concentration of free Ca^{2+} ion in a 0.10 M solution of CaY^{2-} at $\text{pH}=6$ and $\text{pH}=10$, *using the given values in the previous tables.*



$$K'_{\text{CaY}^{2-}} = \alpha_4 K_{\text{CaY}^{2-}} = \frac{0.10-x}{x^2}$$

At pH=6: ($\alpha_4 = 2.2 \times 10^{-5}$, $K_f = 5.0 \times 10^{10}$)

$$2.2 \times 10^{-5} \times 5.0 \times 10^{10} = \frac{0.10-x}{x^2}$$

$$\mathbf{x = 3.0 \times 10^{-4} \text{ M}}$$

At pH=10: ($\alpha_4 = 3.5 \times 10^{-1}$, $K_f = 5.0 \times 10^{10}$)

$$3.5 \times 10^{-1} \times 5.0 \times 10^{10} = \frac{0.10-x}{x^2}$$

$$\mathbf{x = 2.4 \times 10^{-6} \text{ M}}$$



Metal-EDTA titration curves

- Titration is performed by adding the chelating agent (EDTA) to the sample (metal).
- **Titration curve** is plotting the changes in metal ion concentration (pM) versus volume of titrant (EDTA)
- Example of complexometric titration is by adding 0.100 M EDTA to 100 ml 0.100 M Ca^{2+} solution buffered at pH 11





- **Before titration started** – only have Ca^{2+} solution.

$$\text{pCa} = -\log [\text{Ca}^{2+}]$$

- **Titration proceed** – part of Ca^{2+} is reacted with EDTA to form chelate. $[\text{Ca}^{2+}]$ gradually decrease.

$$\text{pCa} = -\log [\text{remaining Ca}^{2+}]$$

- **At equivalence point** – have converted all Ca^{2+} to CaY^{2-} . So pCa can be determined from the dissociation of chelate at a given pH using K_f .

$$K'_f = K_f \alpha_4 = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}] C_{\text{H}_4\text{Y}}}$$

- **Excess titrant added** – pCa can be determined from the dissociation of chelate at a given pH using K_f .



EDTA Titration Curve

Region 1

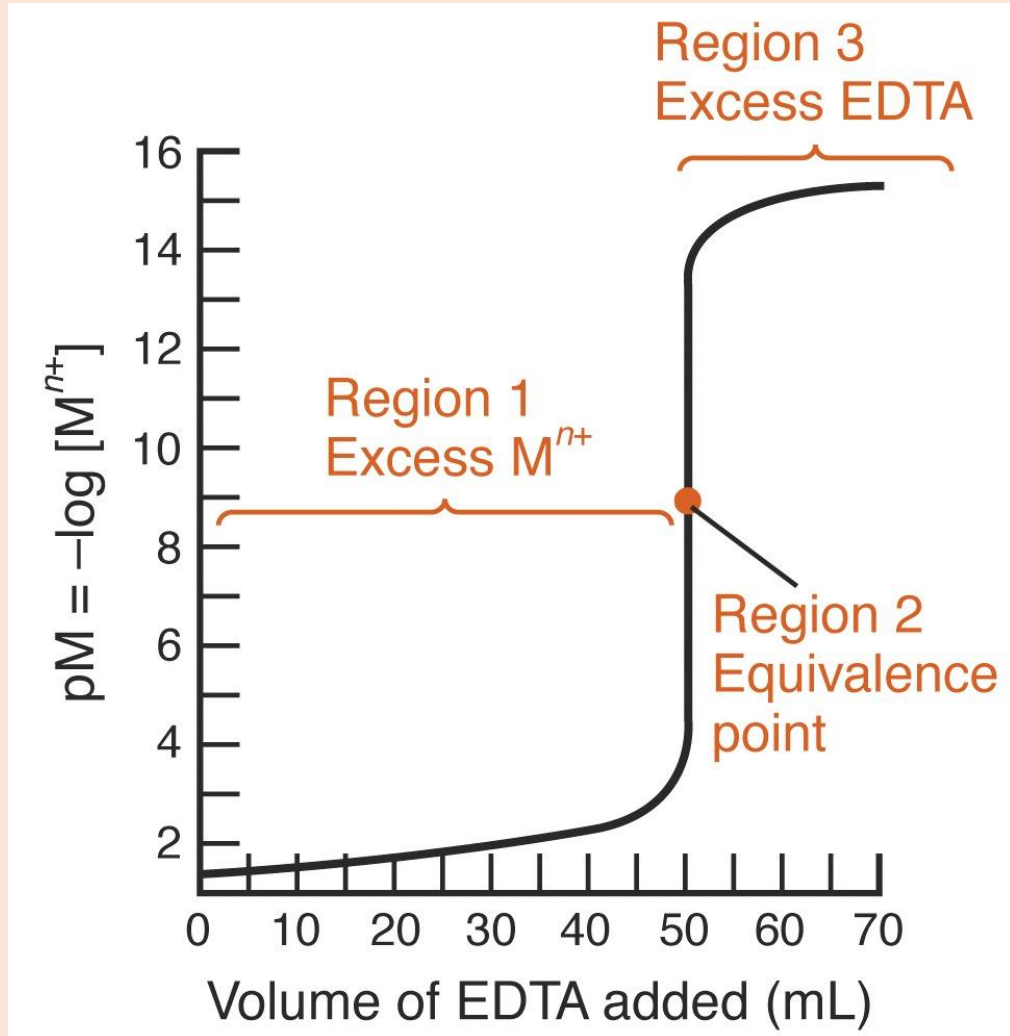
Excess M^{n+} left after each addition of EDTA. Conc. of free metal equal to conc. of unreacted M^{n+} .

Region 2

Equivalence point: $[M^{n+}] = [EDTA]$
Some free M^{n+} generated by
 $MY^{n-4} \Leftrightarrow M^{n+} + EDTA$

Region 3

Excess EDTA. Virtually all metal in MY^{n-4} form.





Exercise

Calculate pCa in 100 ml of a solution of 0.100 M Ca^{2+} at pH10 after addition of 0, 50, 100, 150 ml of 0.100 M EDTA. K_f for CaY^{2-} is 5.0×10^{10} and α_4 is 0.35.

Solution

$$\begin{aligned}K'_f &= K_f \times \alpha_4 \\ &= 5.0 \times 10^{10} \times 0.35 \\ &= \mathbf{1.75 \times 10^{10}}\end{aligned}$$

a) Addition of 0.00 ml EDTA

$$\begin{aligned}[\text{Ca}^{2+}] &= 0.100 \text{ M} \\ \text{pCa} &= -\log 0.100 \\ &= \mathbf{1.00}\end{aligned}$$



b) Addition of 50.00 ml EDTA

Initial mmol Ca²⁺ = 100ml x 0.100 M = 10 mmol

mmol EDTA added = 50ml x 0.100 M = 5 mmol

mmol Ca²⁺ left = 5 mmol

$$[\text{Ca}^{2+}] = \frac{5 \text{ mmol}}{(100+50)\text{ml}} = 0.0333 \text{ M}$$

$$\text{pCa} = -\log 0.0333 = \mathbf{1.48}$$



c) Addition of 100 ml EDTA

Initial mmol Ca²⁺ = 100ml x 0.100 M = 10 mmol

mmol EDTA added = 100ml x 0.100 M = 10 mmol

Equivalence point is reached. We have convert all Ca²⁺ to CaY²⁻. mmol CaY²⁻ = mmol initial Ca²⁺

$$[\text{CaY}^{2-}] = \frac{10 \text{ mmol}}{(100+100)\text{m}} = 0.05 \text{ M}$$

$$K'_f = K_f \alpha_4 = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}] C_{\text{H}_4\text{Y}}}$$

$$K'_f = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}] C_{\text{H}_4\text{Y}}} = 1.75 \times 10^{10}$$
$$\frac{0.05}{(x)(x)} = 1.75 \times 10^{10}$$

$x = 1.7 \times 10^{-6}$ so pCa = - log 1.7x10⁻⁶ = **5.77**



d) Addition of 150 ml EDTA

Initial mmol Ca²⁺ = 100ml x 0.100 M = 10 mmol

mmol EDTA added = 150ml x 0.100 M = 15 mmol

mmol EDTA excess = 5 mmol

$$C_{H_4Y} = \frac{5 \text{ mmol}}{(100+150)\text{ml}} = \mathbf{0.02M} \quad [CaY^{2-}] = \frac{10}{(100+150)\text{ml}} = \mathbf{0.04M}$$

$$K_f = \frac{[CaY^{2-}]}{[Ca^{2+}](0.02)} = 1.75 \times 10^{10}$$

$$\frac{0.04}{(x)(0.02)} = 1.75 \times 10^{10}$$

$$x = 1.14 \times 10^{-10} \quad \text{so } pCa = -\log 1.14 \times 10^{-10} = \mathbf{9.94}$$