# Complex equilibria and EDTA titrations (Ch 6-6,13-2,3, 15-6)

- To distinguish between $K_i$, $\beta_i$ and $K_f$.
- To determine the fractional composition of EDTA at different pH (Problem 13-2)
- To calculate and use conditional formation constant (Problem 13-3, e.g. in Sec 13-2)
- To calculate the points and sketch a curve for EDTA titration (Problem 13-7)
- To calculate metal ion concentration in a metal ion buffer. (Problem 15-36 and 15-43)



# Complex equilibria

| | Stepwise formation constant | | cumulative formation constant |
|---|---|---|---|
| $M + L \rightleftharpoons ML$ | $K_1=[ML]/([M][L])$ | | $\beta_1=K_1$ |
| $ML + L \rightleftharpoons ML_2$ | $K_2=[ML_2]/([ML][L])$ | $M + 2L \rightleftharpoons ML_2$ | $\beta_2=[ML_2]/([M][L]^2)$ $=K_1K_2$ |
| $ML_2 + L \rightleftharpoons ML_3$ | $K_3=[ML_3]/([ML_2][L])$ | $M + 3L \rightleftharpoons ML_3$ | $\beta_3=[ML_3]/([M][L]^3)$ $=K_1K_2K_3$ |
| $ML_3 + L \rightleftharpoons ML_4$ | $K_4=[ML_4]/([ML_3][L])$ | $M + 4L \rightleftharpoons ML_4$ | $\beta_4=[ML_4]/([M][L]^4)$ $=K_1K_2K_3K_4$ |

Examples

1. $M=Zn^{2+}$ $L=NH_3$ (see Sec 13-5)

This explains why $Zn(OH)_2$ redissolves in excess $NH_3$

2 $M=Pb^{2+}$ $L=I^-$ (see Sec 6-6)

This explains why $PbI_2$ redissolves in excess $I^-$.

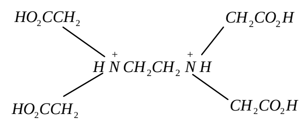
If L is a hexadentate ligand (e.g. EDTA),

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

# Fractional composition of EDTA

EDTA is a hexaprotic acid: $H_6Y^{2+}$

$pK_1 = 0.0$  $pK_2 = 1.5$ $pK_3 = 2.0$
$pK_4 = 2.66$ $pK_5 = 6.16$ $pK_6 = 10.24$



The commonly used reagent is the disodium salt, $Na_2H_2Y.2H_2O$

See Fig 11-3: Fractional composition diagram for EDTA

The fractional composition of $Y^{4-}$ is an important parameter

Example in Sec 13-2: Calculate $\alpha_{Y4-}$ at pH 6.00.



# Fractional composition of EDTA

$$a_{Y^{4-}} = \frac{[Y^{4-}]}{F}$$

$$= \frac{K_1K_2K_3K_4K_5K_6}{[H^+]^6 + [H^+]^5K_1 + [H^+]^4K_1K_2 + [H^+]^3K_1K_2K_3 + [H^+]^2K_1K_2K_3K_4 + [H^+]\ K_1K_2K_3K_4K_5 + K_1K_2K_3K_4K_5K_6}$$

$$b_2 = K_1K_2 = 10^{-0.0}10^{-1.5} = 10^{-1.5}$$

$$b_3 = K_1K_2K_3 = 10^{-0.0}10^{-1.5}10^{-2.0} = 10^{-3.5}$$

$$b_4 = K_1K_2K_3K_4 = 10^{-0.0}10^{-1.5}10^{-2.0}10^{-2.66} = 10^{-6.16}$$

$$b_5 = K_1K_2K_3K_4K_5 = 10^{-0.0}10^{-1.5}10^{-2.0}10^{-2.66}10^{-6.16} = 10^{-12.32}$$

$$b_6 = K_1K_2K_3K_4K_5K_6 = 10^{-0.0}10^{-1.5}10^{-2.0}10^{-2.66}10^{-6.16}10^{-10.24} = 10^{-22.56}$$

$$\therefore a_{Y^{4-}} = \frac{10^{-22.56}}{[10^{-6.00}]^6 + [10^{-6.00}]^5 10^{-0.0} + [10^{-6.00}]^4 10^{-1.5} + [10^{-6.00}]^3 10^{-3.5} + [10^{-6.00}]^2 10^{-6.16} + [10^{-6.00}]10^{-12.32} + 10^{-22.56}}$$

$$= 3.8\times10^{-5} \quad cf.\ \ 2.3\times10^{-5} \quad in \quad textbook$$

# Conditional formation constant

Recall formation constant, $K_f$:

$M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$

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

Below pH 10.24, the principal species of EDTA is not $Y^{4-}$,

$[Y^{4-}] = \alpha_{Y^{4-}}[EDTA]$ where [EDTA] is the total conc. of all 7 EDTA species.

$$\therefore K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]} = \frac{[MY^{n-4}]}{[M^{n+}]\alpha_{Y^{4-}}[EDTA]}$$

If the pH is controlled by a buffer, then $\alpha_{Y4-}$ is a constant that can be combined with $K_f$.

conditional formation constant: $\therefore K_f' = \alpha_{Y^{4-}} K_f = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$

This allows us to look at EDTA complex formation as if the uncomplexed EDTA were all in one form.

$M^{n+} + EDTA \rightleftharpoons MY^{n-4}$

Chem215/P.Li/EDTA titrations/P 5

# Use of the conditional formation constant

Example in Sec 13-2: Calculate the concentration of free $Fe^{3+}$ in a solution of 0.10M $FeY^-$ at pH 4.00 and pH 1.00.

$K_f(FeY^-) = 1.3\times10^{25}$ $\quad \alpha_{Y^{4-}}(pH\,4.00) = 3.8\times10^{-9}$ $\quad \alpha_{Y^{4-}}(pH\,1.00) = 1.9\times10^{-18}$

| $Fe^{3+}$ | + EDTA | $\rightleftharpoons$ | $FeY^-$ |
|---|---|---|---|
| 0 | 0 | | 0.10 |
| x | x | | 0.10-x |

$$\frac{[FeY^-]}{[Fe^{3+}][EDTA]} = \frac{0.10 - x}{x^2} = K_f' = \alpha_{Y^{4-}} K_f = 3.8\times10^{-9}\times1.3\times10^{25} = 4.9\times10^{16} \quad at \quad pH\,4.00$$

$$or \quad 1.9\times10^{-18}\times1.3\times10^{25} = 2.5\times10^{7} \quad at \quad pH\,1.00$$

$$\therefore x = 1.4\times10^{-9}\,M \quad at \quad pH\,4.00$$

$$or \quad 6.4\times10^{-5}\,M \quad at \quad pH\,1.00$$

Note that $[Fe^{3+}]$ is much lower at a higher pH at which more $Y^{4-}$ species exist. Therefore, the EP is more distinct and the titration is more effective. (see Fig 13-8)

Chem215/P.Li/EDTA titrations/P 6

# Effective EDTA titration

A titration is effective if there is at least 99.9% complexation.
$K_f$' value of $10^8$ is determined as follows:

Let the formal conc. of $FeY^-$ be F,

For 99.9% complexation,

$[Mn^{2+}]$ = [EDTA] = 0.1 % F or $10^{-3}$ F

$$K'_f = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]} = \frac{F - 10^{-3}F}{(10^{-3}F)(10^{-3}F)} \approx \frac{F}{10^{-6}F^2} = \frac{10^6}{F}$$

For F = 0.01M, $K_f$'=$10^8$.

Chem215/P.Li/EDTA titrations/P 7

# Effective EDTA titration

The minimum pH is specified arbitrarily as the pH at which $K_f$'=$10^8$.

See Fig 13-9: Minimum pH for effective EDTA titration of various metal ions at 0.01M conc.

Since $K_f$' ($FeY^-$) is 2.5x$10^7$ at pH1.00, the min. pH for EDTA titration of $Fe^{3+}$ is slightly higher than 1.00.

A solution containing both $Ca^{2+}$ and $Fe^{3+}$ can be titrated with EDTA at pH 4 without interference from $Ca^{2+}$.

Chem215/P.Li/EDTA titrations/P 8

# EDTA titration curve

Titration of 50.0 mL of 0.0500M $Mg^{2+}$ (buffered at pH 10.00) with 0.0500M EDTA. $K_f$' (pH10.00)=2.2x10$^8$

There are 3 regions.

1. Before EP (e.g. v = 5.0 mL)

original moles of $Mg^{2+}$ — moles of EDTA added = moles of $Mg^{2+}$ reacted

$$excess\quad [Mg^{2+}] = \frac{0.0500M \times 0.0500L - 0.0500M \times 0.0050L}{(0.0500+0.0050)L} = 0.0409M$$

new volume

$$pMg^{2+} = -\log(0.0409) = 1.39$$

2. At EP (i.e $v_e$ = 50.0 mL) $V_e$ x 0.0500M = 0.0500L x 0.0500M $v_e$ = 0.0500L

moles of EDTA added =moles of $MgY^{2-}$ formed

$$[MgY^{2-}]\quad formed = \frac{0.0500M \times 0.0500L}{(0.0500+0.0500)L} = 0.0250M$$

$$\frac{[MgY^{2-}]}{[Mg^{2+}][EDTA]} = K_f' \qquad \frac{0.0250 - x}{x^2} = 2.2\times10^8 \qquad x = 1.0_7\times10^{-5}M$$

$$pMg^{2+} = 4.97$$

Chem215/P.Li/EDTA titrations/P 9

# EDTA titration curve

3. After EP (e.g. v = 51.0 mL)

V — $V_e$

$$excess\quad [EDTA] = \frac{0.0500M \times (0.0510 - 0.0500)L}{(0.0500+0.0510)L}$$

$$= 4.95\times10^{-4}M$$

$$[MgY^{2-}]\quad formed = \frac{0.0500M \times 0.0500L}{(0.0500+0.0510)L}$$

$$= 2.48\times10^{-2}M$$

$$\frac{[MgY^{2-}]}{[Mg^{2+}][EDTA]} = K_f' \qquad \frac{2.48\times10^{-2}M}{[Mg^{2+}](4.95\times10^{-4}M)} = 2.2\times10^8$$

$$[Mg^{2+}] = 2.3\times10^{-7}M \qquad pMg^{2+} = 6.64$$

Fig13-11: Titration curve for reaction of 0.0500M EDTA with 50.0 mL of 0.0500M $Mg^{2+}$ and $Zn^{2+}$ at pH 10.00

Note that EP is sharper for $Zn^{2+}$ because of higher $K_f$

Chem215/P.Li/EDTA titrations/P 10

## Indicators for complexometric titration

A metal ion indicator is a compound whose color changes when it binds to a metal ion. (Compare this to an acid indicator which changes its color when it binds to $H^{+}$).

| MgIn | + | $Y^{4-}$ | $\rightarrow$ | $MgY^{2-}$ | + | $In^{2-}$ | |
|---|---|---|---|---|---|---|---|
| red | | colorless | | colorless | | blue | for Eriochrome black T |

For a metal ion indicator to be useful, it must bind the metal less strongly than EDTA does.
Because the color of free indicator is pH-dependent, most indicators can be used only in certain pH ranges, fixed by a buffer.

See Table 13-3 for information on Eriochrome black T and other indicators.

Chem215/P.Li/EDTA titrations/P 11

## Metal ion buffer

Complexing agent, such as EDTA, can be used to maintain a constant conc. (usually low) of metal ions (e.g. $Ca^{2+}$), thus forming a metal ion buffer.

Example in section 15-6: What concentration of $NTA^{3-}$ should be added to $1.0 \times 10^{-2}$ M $CaNTA^{-}$ in 0.1 M $KNO_3$ to give $[Ca^{2+}] = 1.0 \times 10^{-6}$ M? (NTA is nitrilotriacetic acid with $pK_1 = 1.1$, $PK_2 = 1.650$, $pK_3 = 2.940$ and $pK_4 = 10.334$). What happens if pH is much lower than 7?

What is $[Mg^{2+}]$ in a solution of 50.0 mL of 0.0500M $Mg^{2+}$ (buffered at pH 10.00) mixed with 0.0500M EDTA. $K_f'$ (pH10.00)=$2.2 \times 10^{8}$ ?

It is pointless to dilute $CaCl_2$ to $10^{-6}$ M for experiments because at this low concentration, $Ca^{2+}$ ions will be lost by adsorption on glass or reaction with impurities. Plastic bottles are better than glass for storing dilute metal ion solutions.

Chem215/P.Li/EDTA titrations/P 12