5 – EDTA Titrations

Table 13-1 Values of $\alpha_{Y^{4-}}$ for EDTA at 20°C and μ = 0.10 M

pH	$\alpha_{Y^{4-}}$
0	1.3×10^{-23}
1	1.9×10^{-18}
2	3.3×10^{-14}
3	2.6×10^{-11}
4	3.8×10^{-9}
5	3.7×10^{-7}
6	2.3×10^{-5}
7	5.0×10^{-4}
8	5.6×10^{-3}
9	5.4×10^{-2}
10	0.36
11	0.85
12	0.98
13	1.00
14	1.00

Table 13-2 Formation constants for metal-EDTA complexes

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.79	Mn^{3+}	25.3 (25°C)	Ce^{3+}	15.98
Na^+	1.66	Fe^{3+}	25.1	Pr^{3+}	16.40
K^+	0.8	Co^{3+}	41.4 (25°C)	Nd^{3+}	16.61
Be^{2+}	9.2	Zr^{4+}	29.5	Pm^{3+}	17.0
Mg^{2+}	8.79	Hf^{4+}	29.5 (μ = 0.2)	Sm^{3+}	17.14
Ca^{2+}	10.69	VO^{2+}	18.8	Eu^{3+}	17.35
Sr^{2+}	8.73	VO_2^+	15.55	Gd^{3+}	17.37
Ba^{2+}	7.86	Ag^+	7.32	Tb^{3+}	17.93
Ra^{2+}	7.1	Tl^+	6.54	Dy^{3+}	18.30
Sc^{3+}	23.1	Pd^{2+}	18.5 (25°C, μ = 0.2)	Ho^{3+}	18.62
Y^{3+}	18.09			Er^{3+}	18.85
La^{3+}	15.50	Zn^{2+}	16.50	Tm^{3+}	19.32
V^{2+}	12.7	Cd^{2+}	16.46	Yb^{3+}	19.51
Cr^{2+}	13.6	Hg^{2+}	21.7	Lu^{3+}	19.83
Mn^{2+}	13.87	Sn^{2+}	18.3 (μ = 0)	Am^{3+}	17.8 (25°C)
Fe^{2+}	14.32	Pb^{2+}	18.04	Cm^{3+}	18.1 (25°C)
Co^{2+}	16.31	Al^{3+}	16.3	Bk^{3+}	18.5 (25°C)
Ni^{2+}	18.62	Ga^{3+}	20.3	Cf^{3+}	18.7 (25°C)
Cu^{2+}	18.80	In^{3+}	25.0	Th^{4+}	23.2
Ti^{3+}	21.3 (25°C)	Tl^{3+}	37.8 (μ = 1.0)	U^{4+}	25.8
V^{3+}	26.0	Bi^{3+}	27.8	Np^{4+}	24.6 (25°C, μ = 1.0)
Cr^{3+}	23.4				

1] The conditional formation constant K_f' for CaY^{2-} is related to K_f through which of the relationships? [1]

a) $K_f' = K_f$ at pH =0
b) $K_f' = \alpha_{Y4-}K_f$
c) $K_f = \alpha_{Y4-}K_f'$
d) $K_f' = 1 / K_f$
e) $K_f' = K_f^2$

2] In reference to EDTA titrations the symbol, α_{Y4-}, indicates which of the following? [2]

a) The fraction of metal chelated by EDTA
b) The concentration of EDTA in the Y^{4-} form.
c) The fraction of EDTA in the Y^{4-} form.
d) The analytical concentration of metal.
e) The fraction of EDTA not in the Y^{4-} form.

3] It is advantageous to conduct EDTA titrations of metal ions in [3]

a) acidic pH's to assist metal ion hydrolysis
b) basic pH's to prevent metal ion hydrolysis
c) basic pH's to maximize Y^{4-} fraction
d) basic pH's to minimize Y^{4-} fraction
e) acidic pH's to maximize Y^{4-} fraction

4] What is K_f' for $SrEDTA^{2-}$ at pH 11? [4]

5] The formal concentration of EDTA is 1.00 mM. What is the concentration of the Y^{4-} form at pH 4? [5]

6] What is the fraction of EDTA in the Y^{4-} form at pH 7.00? [6]

a) 1.00
b) 5.0e-4
c) 0.36
d) 0.500
e) 3.3e-14

7] What is the conditional formation constant of $CaEDTA^{2-}$ at pH 10.00? [7]

8] The fraction of free metal (α_m) in the following equilibrium can be expressed as: [8]

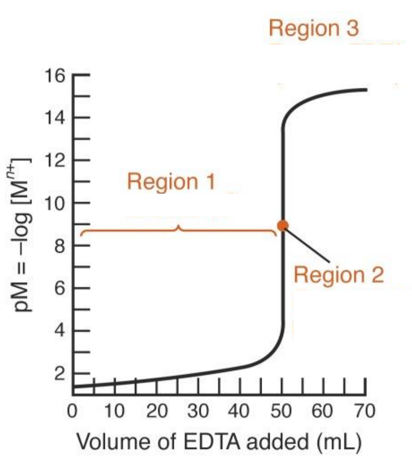
$M + L = ML \qquad \beta = [ML] / [M][L]$

9] What is the fraction of EDTA in the Y^{4-} form at pH 5? [9]

10] Given that α_{y4-} = 3.8e-9 at pH 4.00 & α_{y4-} = 1.9e-18 at pH 1.00 what is the conditional formation constant for FeY^- at those pH's. $\log K_f = 25.1$ [10]

11] Calculate the concentrations of free Fe^{3+} in a 0.10 M FeY^- solution at pH 4.00 and 1.00. [11]

12] Which of the three regions below is where moles of added EDTA equals moles of metal M^{n+}? [12]



13] For Ag^+ in the presence of NH_3, log β_1 = 3.31 and log β_2 = 7.23. The fraction of free Ag^+ in solution can be calculated from: [13]

a] $\alpha_{Ag+} = 1 / \{1+ \beta_1[NH_3] + \beta_2[NH_3]^2\}$
b] $\alpha_{Ag+} = 1 / \{1+ \beta_1[NH_3] + \beta_2[NH_3]\}$
c] $\alpha_{Ag+} = 1 / \{1+ \beta_1[NH_3]^2 + \beta_2[NH_3]\}$
d] $\alpha_{Ag+} = 1 / \{1+ \beta_1 + \beta_2\}$
e] $\alpha_{Ag+} = \{1+ \beta_1[NH_3] + \beta_2[NH_3]^2\}$

14] Calculate the concentration of free Ca^{2+} when $[Y^{4-}]$ = 4.5e-3 M, and $[CaY^{2-}]$ = 9.0e-3, at pH 10. K_f' = 1.8e10. [14]

15] A solution of 50.0-mL of 1.00×10^{-3} M $NiCl_2$(aq)is titrated with 1.00×10^{-3} M EDTA in a solution of 0.100 M NH_3 at pH 11.00. What is pNi if 25.0-mL of the titrant solution is added? Note that $\alpha_{Ni2+} = 1.34\times10^{-4}$ at 0.100 M NH_3. [15]

16] What is K_f'' for the $NiEDTA^{2-}$ complex in 0.100 NH_3 at pH 11? [16]

17] a] What is $[NiEDTA^{2-}]$ if 75.0-mL of titrant is added to the $NiCl_2$ solution in the above problem?
b] Which is true if 75.0-mL of 1.00×10^{-3} M EDTA titrant is added to the 50.0-mL of 1.00×10^{-3} M $NiCl_2$ solution in 0.1M NH_3? Assume equilibrium conditions. [17]

a) $[Ni^{2+}]$ = [EDTA]
b) $[NiEDTA^{2-}]$ > [EDTA]
c) $[NiEDTA^{2-}]$ = [EDTA]
d) $[Ni^{2+}]$ > [EDTA]

18] A] Calculate the concentration of free Mg^{2+} in a solution of 50.0 mL of 0.0500 M Mg^{2+} when 5.00 mL of 0.0500 M EDTA is added at pH 10.00. [18]

$Mg^{2+} + EDTA = MgY^{2-}$ $\qquad K_f' = \alpha_{y4-}K_f = 0.36*6.2e8 = 2.2e8$

B] When 50.0 mL of 0.0500 M EDTA is added.
C] When 51.00 of 0.0500 M EDTA is added.

19] Calculate pCa if 20.0 mL of 0.050 M of EDTA is added to 15.0 mL of 0.050 M Ca^{2+} at pH 9.0. [19]

20] Calculate pCu for the titration curve for 50.00 mL of 0.0200 F Cu^{2+} at pH 5.00 when 0, 10.00, 25.00, 30.00 mL of 0.0400 M EDTA solution are added to the titration mixture. [20]

21] Calculate the conditional formation constant of $Fe^{III}(Y)^-$ (where Y = EDTA) in presence of 0.0100 M $NaOOCH_3$ at pH 7.00, if C_{Fe3+} = 1.00e-4 M, and [EDTA] = 1.50e-4 M. [21]

22] a] Calculate the concentration of free Ag^+ for 0.010 F Ag^+ in 0.10 M NH_3.

b] Calculate pAg when a 50.00-mL of 0.010 M(or F) Ag^+ is mixed with 75.00-mL of 0.010 M EDTA at pH 10.00 in 0.10 M NH_3. [22]

23] 50 mL of 0.010 M Zn^{2+} is titrated with 0.010 M EDTA in 0.010 M NH_3 at pH 9.00. [23]

A] calculate K_f''.

B] Calculate the pZn when 50.0 mL of 0.0100 M Zn^{2+} is added to 25.0 mL of 0.0100 M EDTA in 0.010 M NH_3 at pH 9.00.

C] Calculate the pZn when 50.0 mL of 0.0100 M Zn^{2+} is added to 50.0 mL of 0.0100 M EDTA in 0.010 M NH_3 at pH 9.00.

D] Calculate the pZn when 50.0 mL of 0.0100 M Zn^{2+} is added to 75.0 mL of 0.0100 M EDTA in 0.010 M NH_3 at pH 9.00.

Answers

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[1] $K_f' = \alpha_{y4-} K_f$

[2] The fraction of EDTA in the Y^{4-} form.

[3] basic pH's to maximize Y^{4-} fraction

[4] $K_f' = \alpha_{y4-} K_f = 0.85*5.4e8 = 4.6e8$

[5] [$\mathbf{Y^{4-}}$] = 3.8e-9*1.00e-3 M = 3.8e-12 M

[6] B

[7] $K_f' = 0.36*10^{10.69} = 1.8e-10$

[8] $\alpha_m = \dfrac{1}{1+\beta[L]}$

[9] 3.7e-7

[10] $K_f = [FeY^-] / [Fe^{3+}][Y^{4-}]$ $\qquad$ $[Y^{4-}] = \alpha_{y4-}[EDTA]$

$K_f = [FeY^-] / [Fe^{3+}]\alpha_{y4-}[EDTA]$

$K_f' = \alpha_{y4-} K_f = [FeY^-] / [Fe^{3+}][EDTA]$

$Fe^{3+} + EDTA = FeY^-$ $\qquad$ $K_f' = \alpha_{y4-} K_f$

At pH 4.00 $K_f' = \alpha_{Y4-}K_f$ = 3.8e-9 * 1.3e25 = 4.9e16

At pH 1.00 K_f' = 1.9e-18 * 1.3e25 = 2.5e7

[11] Fe^{3+} + EDTA = FeY^-

0 0 0.10 M

+x +x -x

$0.10 - x / x^2 = K_f'$

x = 1.4e-9 @ pH 4.00

x = 6.3e-5 @ pH 1.00

[12] Region 2

[13] $\alpha_{Ag+} = 1 / \{1+ \beta_1[NH_3] + \beta_2[NH_3]^2\}$

[14] 1.8e10 = [9.0e-3] / $[Ca^{2+}]$[4.5e-3] $[Ca^{2+}]$ = 1.11e-10

[15] Initial mol Ni^{2+} = 50.0-mL*1.00e-3 M = 0.0500 mmol

Added mol EDTA

= 25.0-mL*1.00e-3 M

= 0.0250 mmol

Excess Ni^{2+} = 0.0500 – 0.0250 mmol = 0.0250 mmol

C_{Ni2+} = 0.0250 mmol / 75.0-mL

= 3.33e-4 M

Free $[Ni^{2+}] = \alpha_{Ni2+} C_{Ni2+}$ = 1.34e-4*3.33e-4 = 4.47e-8 M

pNi = 7.350

[16] $K_f'' = \alpha_{Ni2+}\alpha_{Y4-}*K_f = 1.34e\text{-}4*0.85*10^{18.62}$ = **4.7e14**

[17] Initial mol Ni^{2+} = 50.0-mL*1.00e-3 M = 0.0500 mmol

Added mol EDTA = 75.0-mL*1.00e-3 M = 0.0750 mmol

[NiEDTA] = 0.0500 mmol / 125.0-mL = 4.00e-4 M

Excess EDTA = 0.0250 mmol / 125.0-mL = 2.00e-4 M

K_f'' = [NiEDTA]/C_{Ni}*[EDTA] = 4.00e-4/C_{Ni}*2.00e-4 = 4.7e14

C_{Ni} = 4.3e-15

[Ni^{2+}] = 1.34e-4*4.3e-14 = 5.8e-18 M

pNi = 17.24

Therefore [$NiEDTA^{2-}$] > [EDTA]

[18] A] Initial Mg^{2+} = 0.0500 M * 50.0 mL = 2.50 mmol

Added EDTA = 0.0500 * 5.00 mL = 0.25 mmol

Mg^{2+} +	EDTA =	MgY^{2-}
2.50	0.25	0
-0.25	-0.25	+0.25
2.25	0	0.25

[Mg^{2+}] = 2.25 mmol / 55.00 mL = 0.0409pMg = 1.39

B] added EDTA = 0.0500 M * 50.0 mL = 2.50 mmol

Mg^{2+} +	EDTA =	MgY^{2-}
2.50	2.50	0
-2.50	-2.50	+2.50
0	0	2.50

[Mg^{2+}] = 2.50 mmol / 100 mL = 0.0250 M

Mg^{2+} + EDTA = MgY^{2-}

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0 0 0.0250

+x +x -x

$0.0250\text{-}x / x^2 = 2.2e8$

x = 1.07e-5 pMg = 4.97

C] added EDTA = 0.0500 M * 51.0 mL = 2.55 mmol

Mg^{2+} + EDTA = MgY^{2-}

2.50 2.55 0

-2.50 -2.50 +2.50

0 0.05 2.50

$[MgY^{2-}]$ = 2.50 mmol / 101 mL = 2.47e-2 M

[EDTA] = 0.05 mmol / 101 mL = 4.95e-4

K_f' = $[MgY^{2-}]$ / $[Mg^{2+}]$[EDTA] = 2.47e-2 M / $[Mg^{2+}]$*4.95e-4

K_f' = 2.2e8

$[Mg^{2+}]$ = 2.3e-7

pMg = 6.64

[19] mol EDTA = 20.0 mL * 0.050 M = 1.0 mmol

mol Ca^{2+} = 15.0 mL * 0.050 M = 0.75 mmol

excess EDTA region where,

$[CaY^{2-}]$ = 0.75 mmol / 35.0 mL = 2.1e-2 M

[EDTA] = 0.25 mmol / 35.0 mL = 7.1e-3 M

$K_f = [CaY^{2-}] / [Ca^{2+}]*[Y^{4-}]$

$[Y^{4-}] = \alpha_{Y4-}$ [EDTA]

$K_f * \alpha_{Y4-} = K_f' = [CaY^{2-}] / [Ca^{2+}]$*[EDTA]

K_f = 4.9e10

K_f' = 5.4e-2*4.9e10 = 2.6e9

2.6e9 = 2.1e-2 M / [Ca^{2+}]*7.1e-3 M [Ca^{2+}] = 1.1e-9 M

pCa = 8.94

[20] **At 0.00** [Cu^{2+}] = 0.020 M **pCu = 1.70**

At 10.00 mL

Initial mols Cu^{2+} = 0.0200 M * 50.00 mL = 1.00 mmols

Added mols EDTA = 0.040 M * 10.00 mL = 0.40 mmols

Excess Cu^{2+} = 1.00 mmol – 0.40 mmol = 0.60 mmol

$[Cu^{2+}]_{free}$ = 0.60 mmol / 60.00 mL = 0.010 M

pCu = 2.00

At 25.00 mL

Initial mols Cu^{2+} = 1.00 mmols

Added mols EDTA = 0.040 M * 25.00 mL = 1.0 mmols

This is the equivalence point therefore the formal concentration of CuEDTA is

[CuEDTA] = 1.0 mmols / 75.00 mL = 1.3e-2 M

Now Calculate free Cu^{2+}:

Cu^{2+} + EDTA ⇄ CuEDTA

+x +x 1.3e-2 –x

K_f = 6.3e18

@ pH 5.00

α_{Y4-} = 3.7e-7

$K_f' = \alpha_{Y4-} K_f$ = 3.7e-7 * 6.3e18 = 2.3$\underline{3}$e12

$1.3e\text{-}2 - x / x^2 = 2.3\underline{3}e12$

$1.3e\text{-}2 / x^2 \cong 2.3\underline{3}e12$

$x = 7.5e\text{-}8$

pCu = 7.12

At 30.00 mL

Initial mols Cu^{2+} = 1.00 mmols

Added mols EDTA = 0.0400 M * 30.00 mL = 1.20 mmols

Excess EDTA = 1.20 – 1.00 mmol = 0.20 mmol

$[EDTA]_{excess}$ = 0.20 mmol / 80.00 mL = 2.5e-3

We now have the following equilibrium to consider:

$Cu^{2+} + EDTA \rightleftarrows CuEDTA$

+x 2.5e-3+x 1.3e-2 –x

$(1.3e\text{-}2 - x) / (2.5e\text{-}3+x)\, x = 2.3\underline{3}e12$

$(1.3e\text{-}2) / (2.5e\text{-}3)\, x \cong 2.3\underline{3}e12$ $x = 2.2e\text{-}12$

pCu = 11.65

[21] $K_f(Fe^{III}(OOCH_3)^{2+}) = 10^{3.38} = 2.39\underline{8}e3$

$K_f(Fe^{III}(OOCH_3)_2^{+}) = 10^{7.1} = 1.2\underline{6}e7$

$K_f(Fe^{III}(OOCH_3)_3) = 10^{9.7} = 5.0\underline{1}e9$

$\alpha_{Fe3+} = 1 / \{1 + \beta_1[CH_3OO^-] + \beta_2[CH_3OO^-]^2 + \beta_3[CH_3OO^-]^3\}$

$= 1 / \{1 + 2.39\underline{8}e3\,[0.0100] + 1.2\underline{6}e7\,[0.0100]^2 + 5.0\underline{1}e9\,[0.0100]^3\}$

$= 1 / \{1 + 2.39\underline{8} + 1.2\underline{6}e3 + 5.0\underline{1}e3\}$

$= 1 / 6.2\underline{7}e3$

$= 1.5\underline{9}e\text{-}4$

α_{y4-} @ pH 7.00 = 5.0e-4 (Table 13-1)

$K_f = 10^{25.1}$ = 1.<u>3</u>e25 (Table 13-2)

K_f" = $\alpha_{Fe3+}\alpha_{y4-}K_f$ = 1.5<u>9</u>e-4 * 5.0e-4 * 1.<u>3</u>e25 = 1e18

[22] **<u>a] See Appendix</u>** $\beta_1 = 10^{3.31}$ = 2.04e3 $\beta_2 = 10^{7.23}$ = 1.70e7

$\alpha_{Ag+} = 1/(1 + \beta_1[NH_3] + \beta_2[NH_3]^2) = 1/(1 + 2.04e3*0.100 + 1.70e7*0.100^2)$ = 5.88e-6

$[Ag^+] = \alpha_{Ag+}C_{Ag+}$ = 5.88e-6*0.010 M = 5.88e-8 M

<u>b] K_f" = $K_f\alpha_{Ag+}\alpha_{Y4-}$ = $10^{7.32}$*5.88e-6*0.36 = 44.2</u>

Initial mol Ag^+ = 50.00-mL*0.010 M = 0.500 mmol

Added mol EDTA = 75.00-mL*0.010 M = 0.750 mmol

All Ag^+ is complexed with EDTA with leftover EDTA

$[AgY^{3-}]$ = 0.500 mmol / 125.00-mL = 4.00e-3 M

$[EDTA]_{free}$ = 0.250 mmol / 125.00-mL = 2.00e-3 M

K_f" = $[AgY^{3-}]$ / C_{Ag+} [EDTA]

44.2 = 4.00e-3 M / C_{Ag+} 2.00e-3 M

C_{Ag+} = 4,52e-2

$[Ag^+] = \alpha_{Ag+}C_{Ag+}$ = 5.88e-6 * 4.52e-2 M = 2.66e-7 M

pAg = 6.575

[23] A] *Appendix I in your text has*

log β_1 *= 2.18* β_1 *= 151*

log β_2 *= 4.43* β_2 *= 2.69e4*

log β_3 *= 6.74* β_3 *= 5.50e6*

log β_4 *= 8.70* β_4 *= 5.01e8*

$\alpha_M = 1 / \{1+ \beta_1[L] + \beta_2[L]^2 +\ldots + \beta_n[L]^n \}$

$\alpha_{Zn2+} = 1 / \{1 + 151[0.010] + 2.69e4[0.010]^2 + 5.50e6[0.010]^3 + 5.01e8[0.010]^4 \}$

$\alpha_{Zn2+} = 1 / \{1 + 1.51 + 2.69 + 550.0 + 5010.0\}$

$= 1.79e-4$

$K_f = 3.2e16$ *Table 13-2*

$\alpha_{y4-} = 5.4e-2$ *Table 13-1*

$K_f'' = K_f \alpha_{Zn2+} \alpha_{y4-} = 3.2e16 * 5.4e-2 * 1.79e-4 = 3.1e11$

B] *Initial* Zn^{2+} *= 50.0 mL * 0.0100 M = 0.500 mmol*

*Added EDTA = 25.0 mL * 0.0100 M = 0.250 mmol*

Excess Zn^{2+} *= 0.500 – 0.250 = 0.250 mmol*

$C_{zn2+} = 0.250$ *mmol / 75.0 mL = 3.33e-3 M*

$[Zn^{2+}] = \alpha_{Zn2+} C_{zn2+} = 1.79e-4 * 3.33e-3$ *M*

pZn = 6.225

C] *Initial* Zn^{2+} *= 50.0 mL * 0.0100 M = 0.500 mmol*

*Added EDTA = 50.0 mL * 0.0100 M = 0.500 mmol*

Initial Zn^{2+} *= Added EDTA* $\therefore$ *eq. pt.*

Initial $[ZnY^{2-}]$ *= 0.500 mmol / 100.0 mL = 5.00e-3 M*

$ZnY^{2-} = C_{Zn2+} +$ *EDTA*

5.00e-3 0 0

-x +x +x

$K_f'' = 3.1e11 = (5.00e-3 - x) / x^2$

$x = C_{zn2+}$

x = 1.27e-7 M

$[Zn^{2+}] = \alpha_{Zn2+} C_{zn2+} = 1.79e-4 * 1.27e-7$ *M*

$[Zn^{2+}] = 2.27e\text{-}11\ M$

pZn = 10.64

D] Initial Zn^{2+} = 50.0 mL * 0.0100 M = 0.500 mmol

Added EDTA = 75.0 mL * 0.0100 M = 0.750 mmol

Excess EDTA = 0.250 mmol

$[ZnY^{2-}]$ = 0.500 mmol / 125.0 mL = 4.00e-3

[EDTA] = 0.250 mmol / 125.0 mL = 2.00e-3 M

K_f'' = 3.1e11 = $[ZnY^{2-}] / C_{zn2+}$*[EDTA]

3.1e11 = 4.00e-3 / C_{zn2+}* 2.00e-3

C_{zn2+} = 6.45e-12

$[Zn^{2+}] = \alpha_{Zn2+}\ C_{zn2+}$ = 1.79e-4 * 6.45e-12M = 1.15e-15

pZn = 14.94