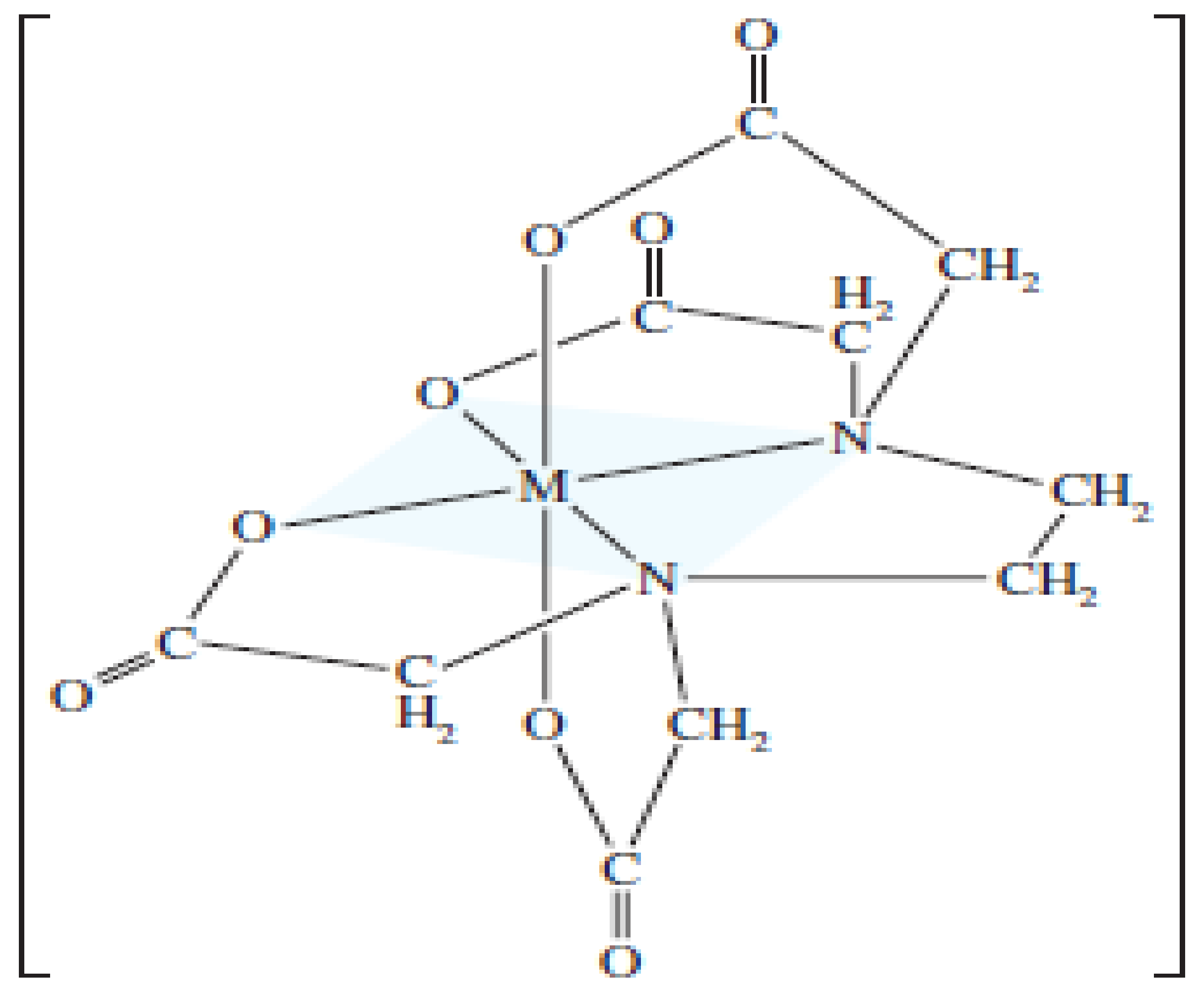
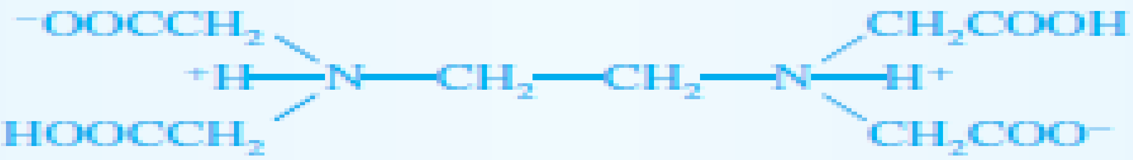
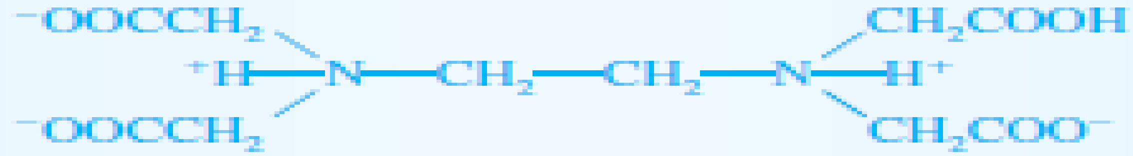
metal–EDTA complexes have a 1:1 stoichiometry

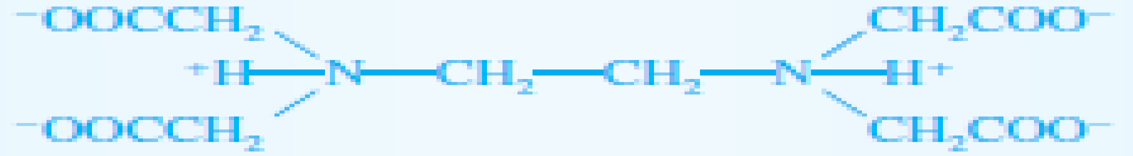




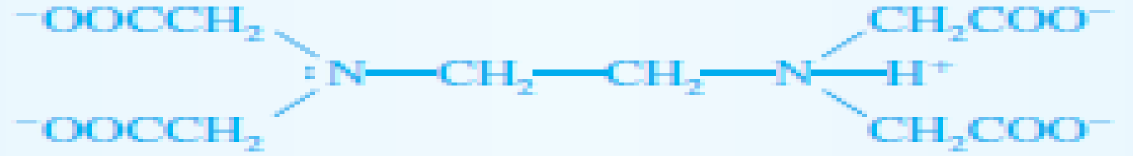
(a) H_4Y



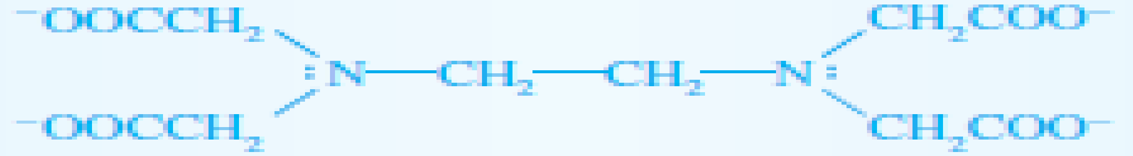
(b) H_3Y^-



(c) H_2Y^{2-}



(d) HY^{3-}



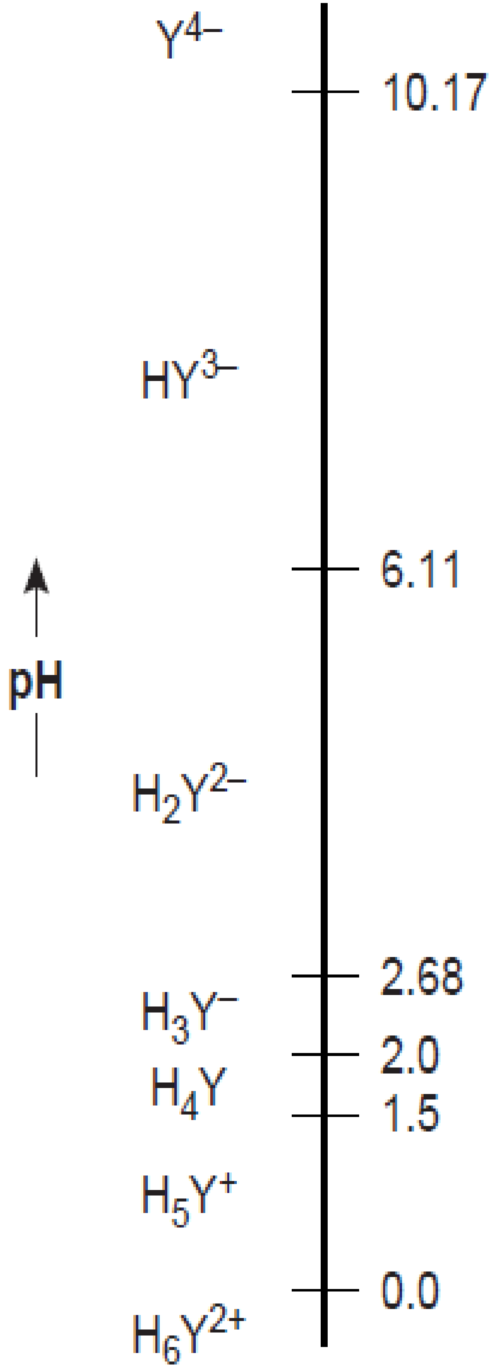


Table 9.12 Values of $\alpha_{Y^{4-}}$ for Selected pHs

pH	$\alpha_{Y^{4-}}$	pH	$\alpha_{Y^{4-}}$
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	0.35
5	3.5×10^{-7}	11	0.85
6	2.2×10^{-5}	12	0.98
7	4.8×10^{-4}	13	1.00

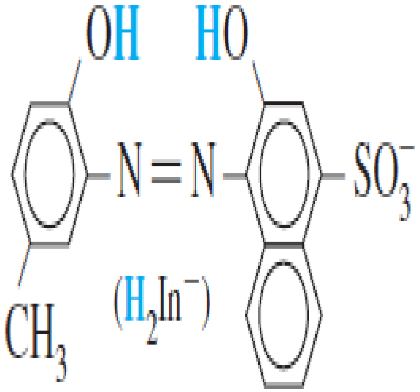
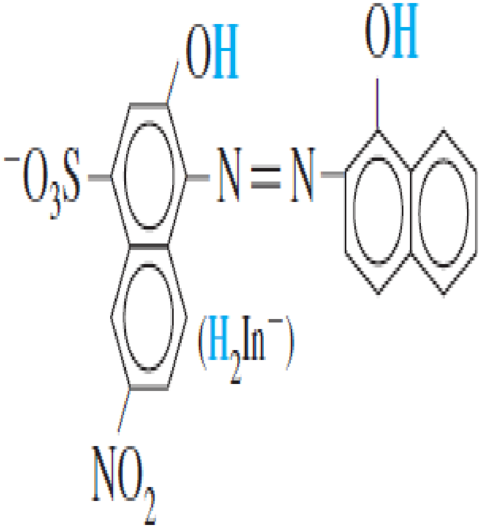
Table 9.13 Conditional Formation Constants for CdY^{2-}

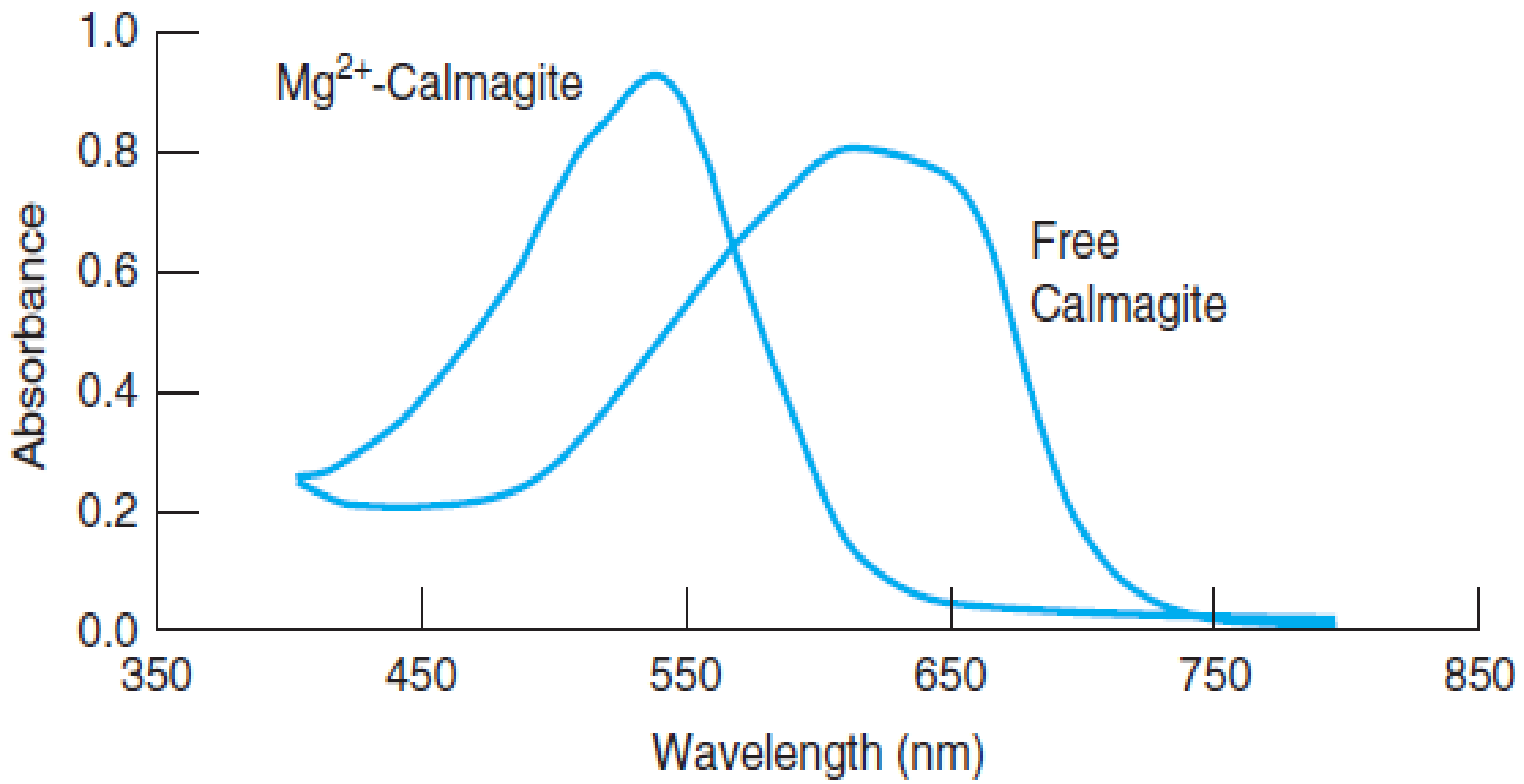
pH	K_f'	pH	K_f'
2	1.1×10^{3}	8	1.6×10^{14}
3	7.3×10^{5}	9	1.5×10^{15}
4	1.0×10^{8}	10	1.0×10^{16}
5	1.0×10^{10}	11	2.5×10^{16}
6	6.4×10^{11}	12	2.8×10^{16}
7	1.4×10^{13}	13	2.9×10^{16}

End-point detection methods:

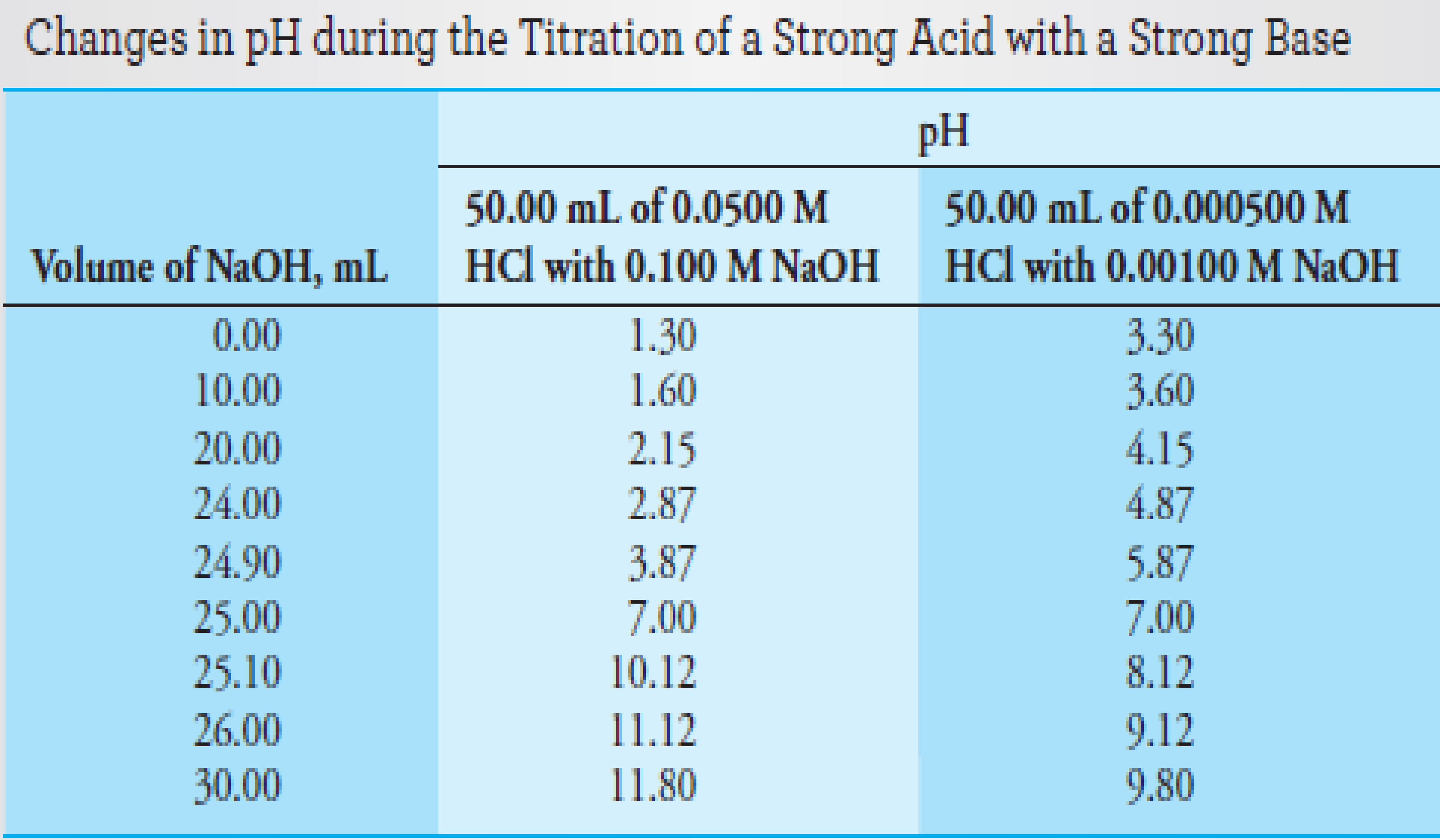
1. Metal ion indicators (Finding the End Point with a Visual Indicator)
2. 2. Mercury electrode (sensors)
3. Ion-selective electrode (sensors)
4. Glass (pH) electrode (sensors
5. Monitoring Absorbance

Indicator	Useful pH Range	Useful for
calmagite	9–11	Ba, Ca, Mg, Zn
Eriochrome Black T	7.5–10.5	Ba, Ca, Mg, Zn
Eriochrome Blue Black R	8–12	Ca, Mg, Zn, Cu
murexide	6–13	Ca, Ni, Cu
PAN	2–11	Cd, Cu, Zn
salicylic acid	2–3	Fe

Name	Structure	pK_a	Color of free indicator	Color of metal ion complex
Calmagite		$pK_2 = 8.1$ $pK_3 = 12.4$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Eriochrome black T		$pK_2 = 6.3$ $pK_3 = 11.6$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red


Mg^{2+}-Calmagite
Free Calmagite
Absorbance
1.0
0.8
0.6
0.4
0.2
0.0
350
450
550
650
750
850
Wavelength (nm)

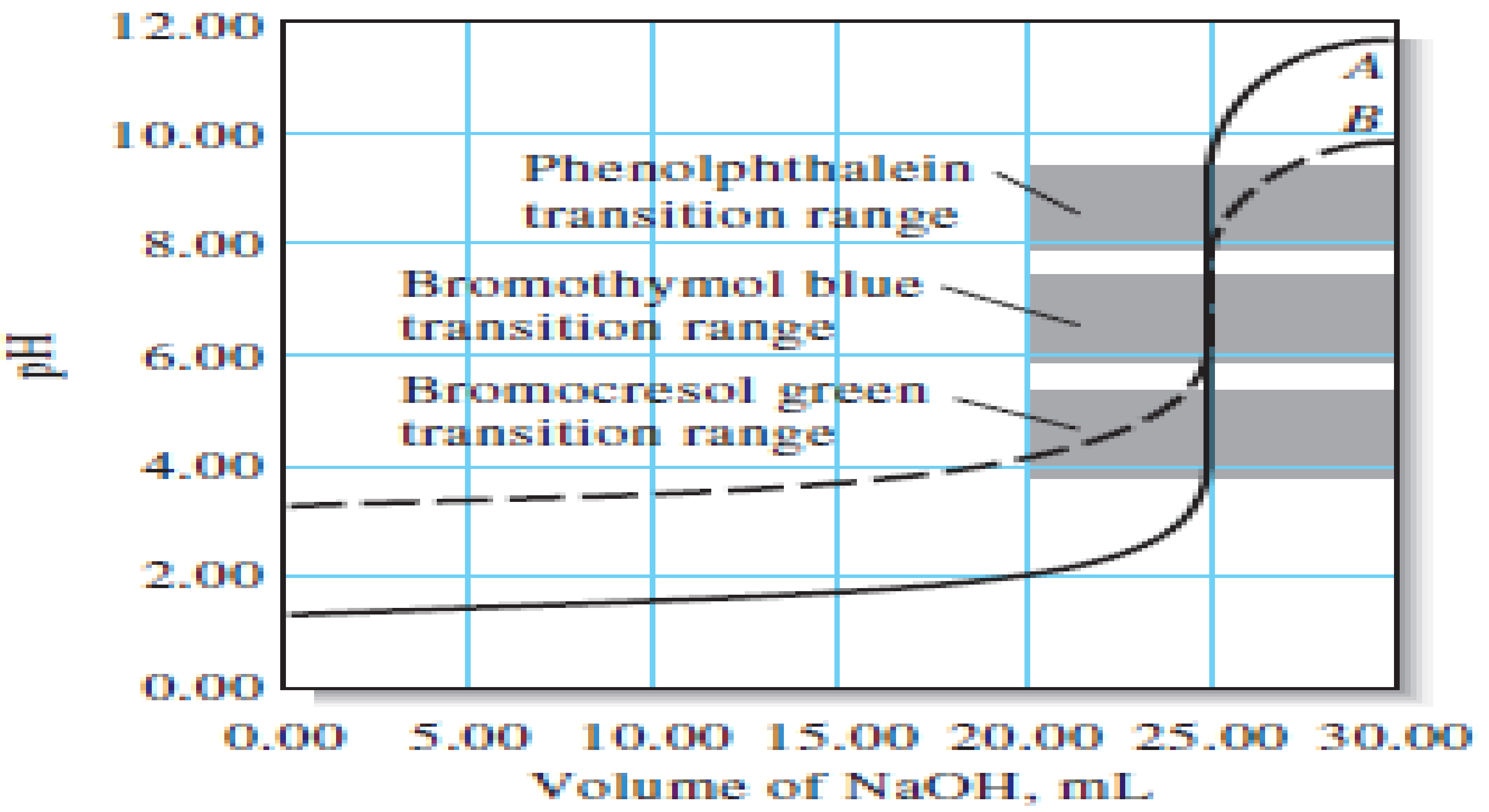
Generate the hypothetical titration curve for the titration of 50.00 mL of0.0500 M HCl with 0.1000 M NaOH

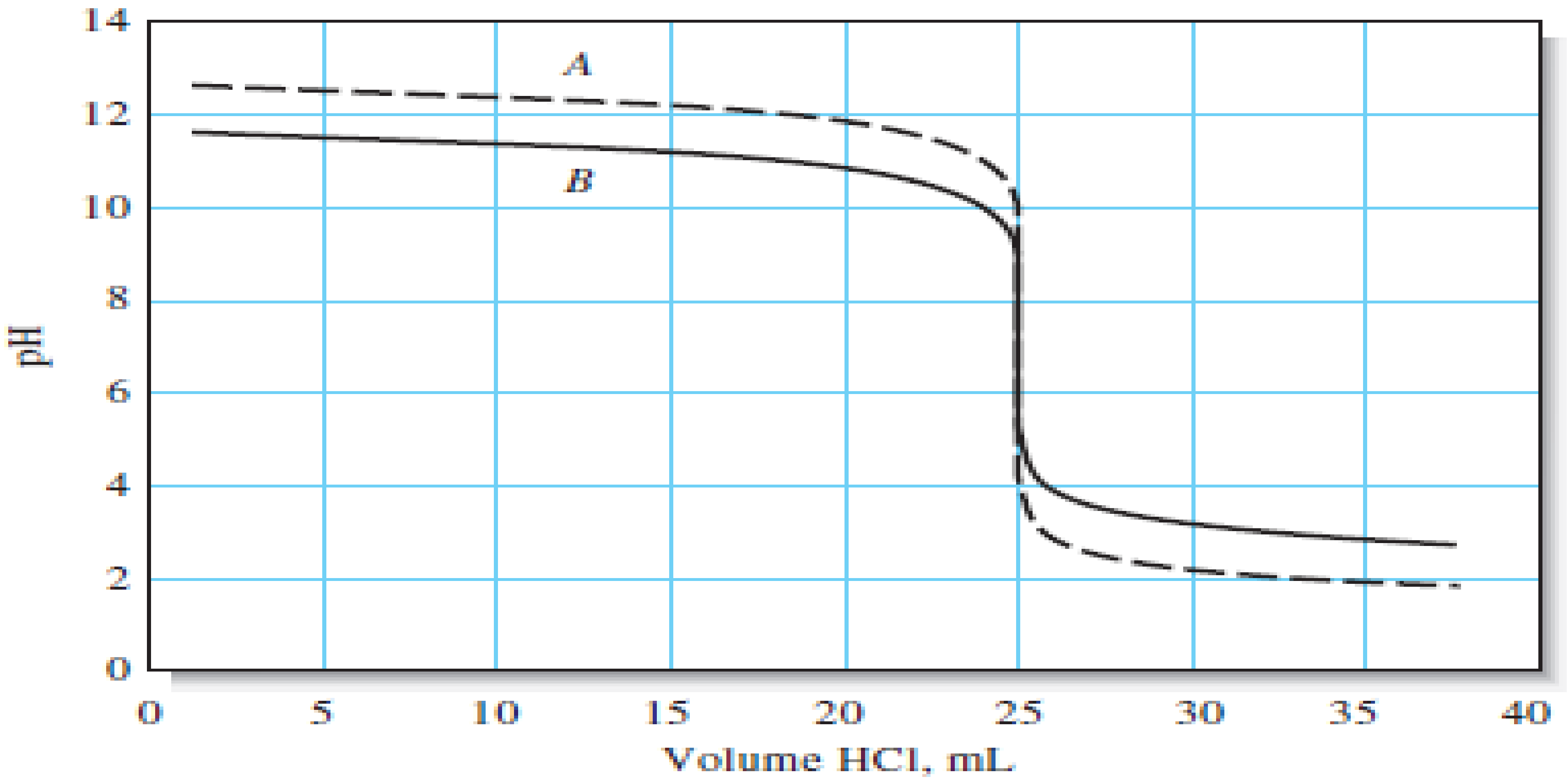


Changes in pH during the Titration of a Strong Acid with a Strong Base

Volume of NaOH, mL	pH	
	50.00 mL of 0.0500 M HCl with 0.100 M NaOH	50.00 mL of 0.000500 M HCl with 0.00100 M NaOH
0.00	1.30	3.30
10.00	1.60	3.60
20.00	2.15	4.15
24.00	2.87	4.87
24.90	3.87	5.87
25.00	7.00	7.00
25.10	10.12	8.12
26.00	11.12	9.12
30.00	11.80	9.80

The Effect of Concentration and Choosing an Indicator



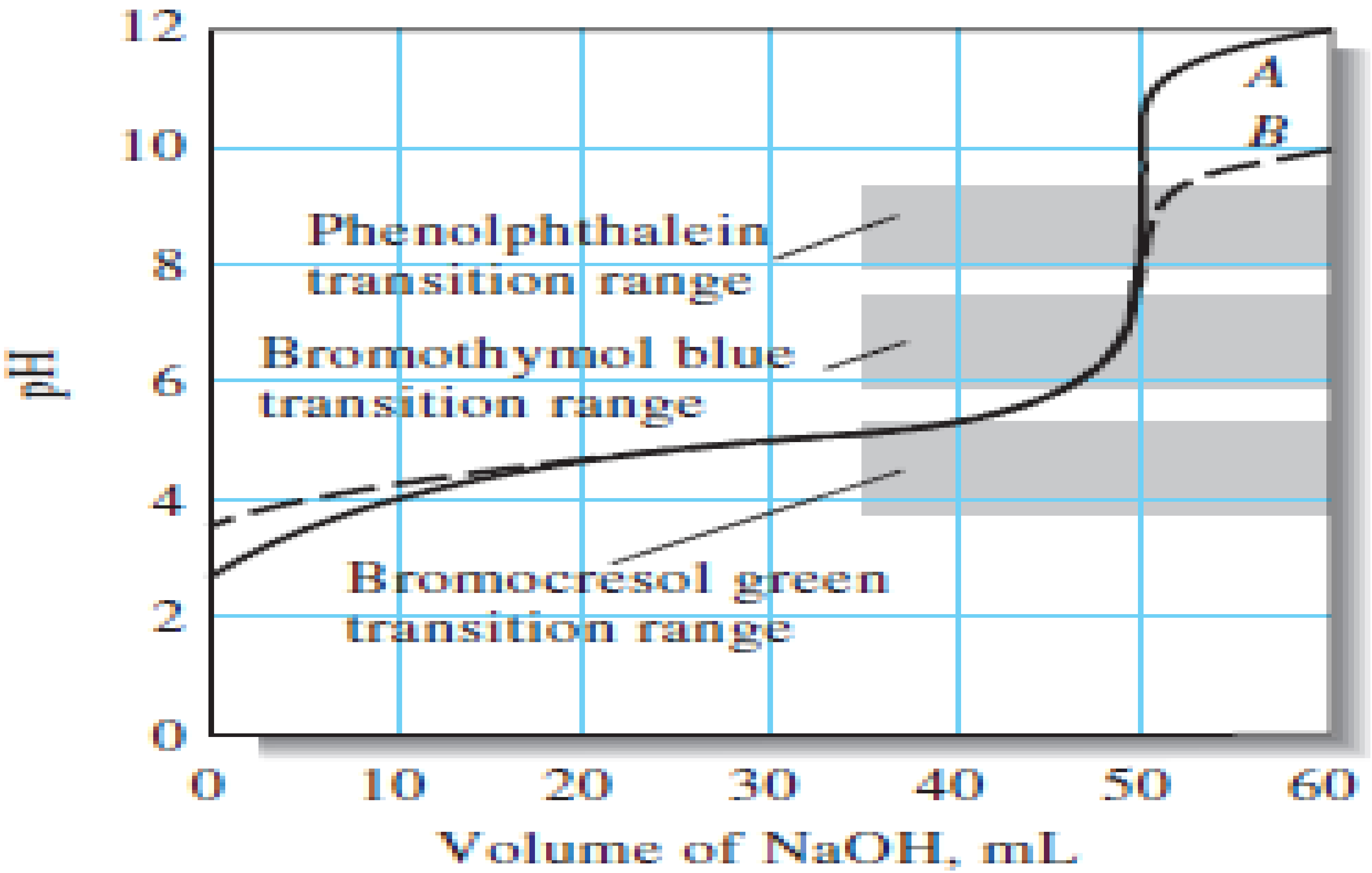


Curve *B*: 50.00 mL of 0.00500M NaOH with 0.01 M HCl.

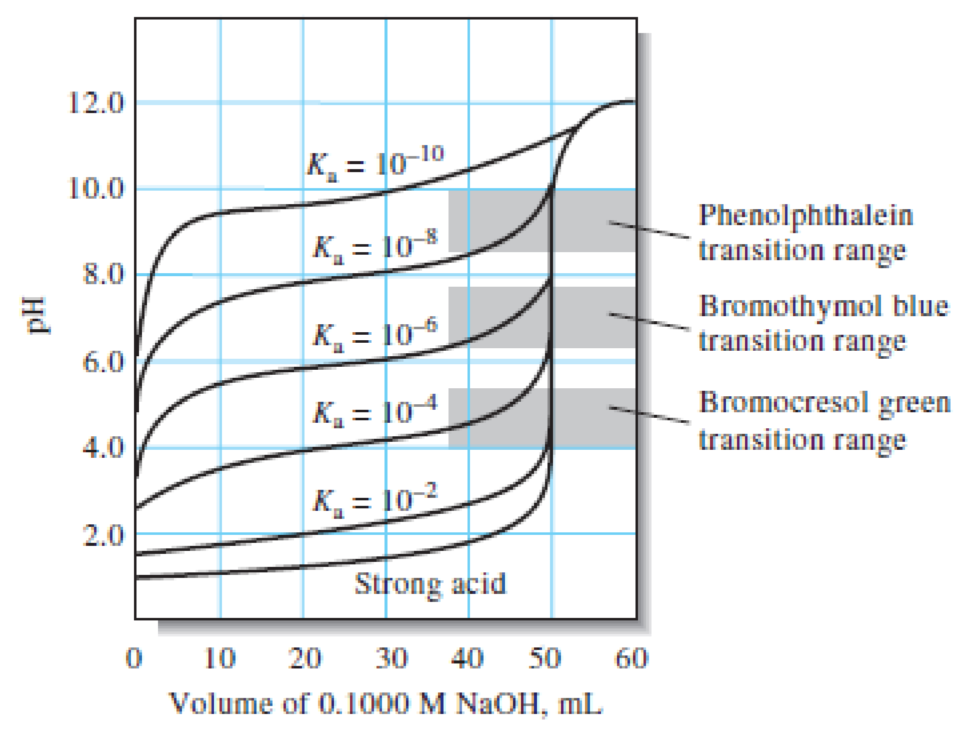
Changes in pH during the Titration of a Weak Acid with a Strong Base

	pH	
Volume of NaOH, mL	50.00 mL of 0.1000 M HOAc with 0.1000 M NaOH	50.00 mL of 0.001000 M HOAc with 0.001000 M NaOH
0.00	2.88	3.91
10.00	4.15	4.30
25.00	4.76	4.80
40.00	5.36	5.38
49.00	6.45	6.46
49.90	7.46	7.47
50.00	8.73	7.73
50.10	10.00	8.09
51.00	11.00	9.00
60.00	11.96	9.96
70.00	12.22	10.25

Curve (A) for the titration of acetic acid with sodium



The Effect of Reaction Completeness and Choosing Indicator



Precipitation Titrations

- Precipitation titrations are based on reactions that yield ionic compounds of limited solubility.
- Precipitation titrimetry is one of the oldest analytical techniques, dating back to the mid 1800s.
- Titrations with silver nitrate are sometimes called argentometric titrations.

Titration Curves

- The titration curve for a precipitation titration follows the change in either the analyte's or titrant's concentration as a function of the volume of titrant.

For example,

In an analysis for I^- using Ag^+ as a titrant

$$Ag^+(aq) + I^-(aq) \rightleftharpoons AgI(s)$$

Calculating the Titration Curve As an example, let's calculate the titration curve for the titration of 50.0 mL of 0.0500 M Cl^- with 0.100 M Ag^+. The reaction in this case is

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

The equilibrium constant for the reaction is

$$K = (K_{sp})^{-1} = (1.8 \times 10^{-10})^{-1} = 5.6 \times 10^9$$

Since the equilibrium constant is large, we may assume that Ag^+ and Cl^- react completely.

$$\text{Moles Ag}^+ = \text{moles Cl}^-$$

or

$$M_{Ag}V_{Ag} = M_{Cl}V_{Cl}$$

Solving for the volume of Ag^+

$$V_{Ag} = \frac{M_{Cl}V_{Cl}}{M_{Ag}} = \frac{(0.0500\ \text{M})(50.0\ \text{mL})}{(0.100\ \text{M})} = 25.0\ \text{mL}$$

shows that we need 25.0 mL of Ag^+ to reach the equivalence point.

Before the equivalence point Cl^- is in excess. The concentration of unreacted Cl^- after adding 10.0 mL of Ag^+, for example, is

$$[Cl^-] = \frac{\text{moles excess } Cl^-}{\text{total volume}} = \frac{M_{Cl}V_{Cl} - M_{Ag}V_{Ag}}{V_{Cl} + V_{Ag}}$$

$$= \frac{(0.0500\ \text{M})(50.0\ \text{mL}) - (0.100\ \text{M})(10.0\ \text{mL})}{50.0\ \text{mL} + 10.0\ \text{mL}}$$

$$= 2.50 \times 10^{-2}\ \text{M}$$

If the titration curve follows the change in concentration for Cl^-, then we calculate pCl as

$$\text{pCl} = -\log[Cl^-] = -\log(2.50 \times 10^{-2}) = 1.60$$

$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

Solving for the concentration of Ag^+

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{2.50 \times 10^{-2}} = 7.2 \times 10^{-9}\ M$$

gives a pAg of 8.14.

At the equivalence point, we know that the concentrations of Ag^+ and Cl^- are equal. Using the solubility product expression

$$K_{sp} = [Ag^+][Cl^-] = [Ag^+]^2 = 1.8 \times 10^{-10}$$

gives

$$[Ag^+] = [Cl^-] = 1.3 \times 10^{-5}\ M$$

At the equivalence point, therefore, pAg and pCl are both 4.89.

After the equivalence point, the titration mixture contains excess Ag^+. The concentration of Ag^+ after adding 35.0 mL of titrant is

$$[Ag^+] = \frac{\text{moles excess } Ag^+}{\text{total volume}} = \frac{M_{Ag}V_{Ag} - M_{Cl}V_{Cl}}{V_{Cl} + V_{Ag}}$$

$$= \frac{(0.100 \text{ M})(35.0 \text{ mL}) - (0.0500 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 35.0 \text{ mL}}$$

$$= 1.18 \times 10^{-2} \text{ M}$$

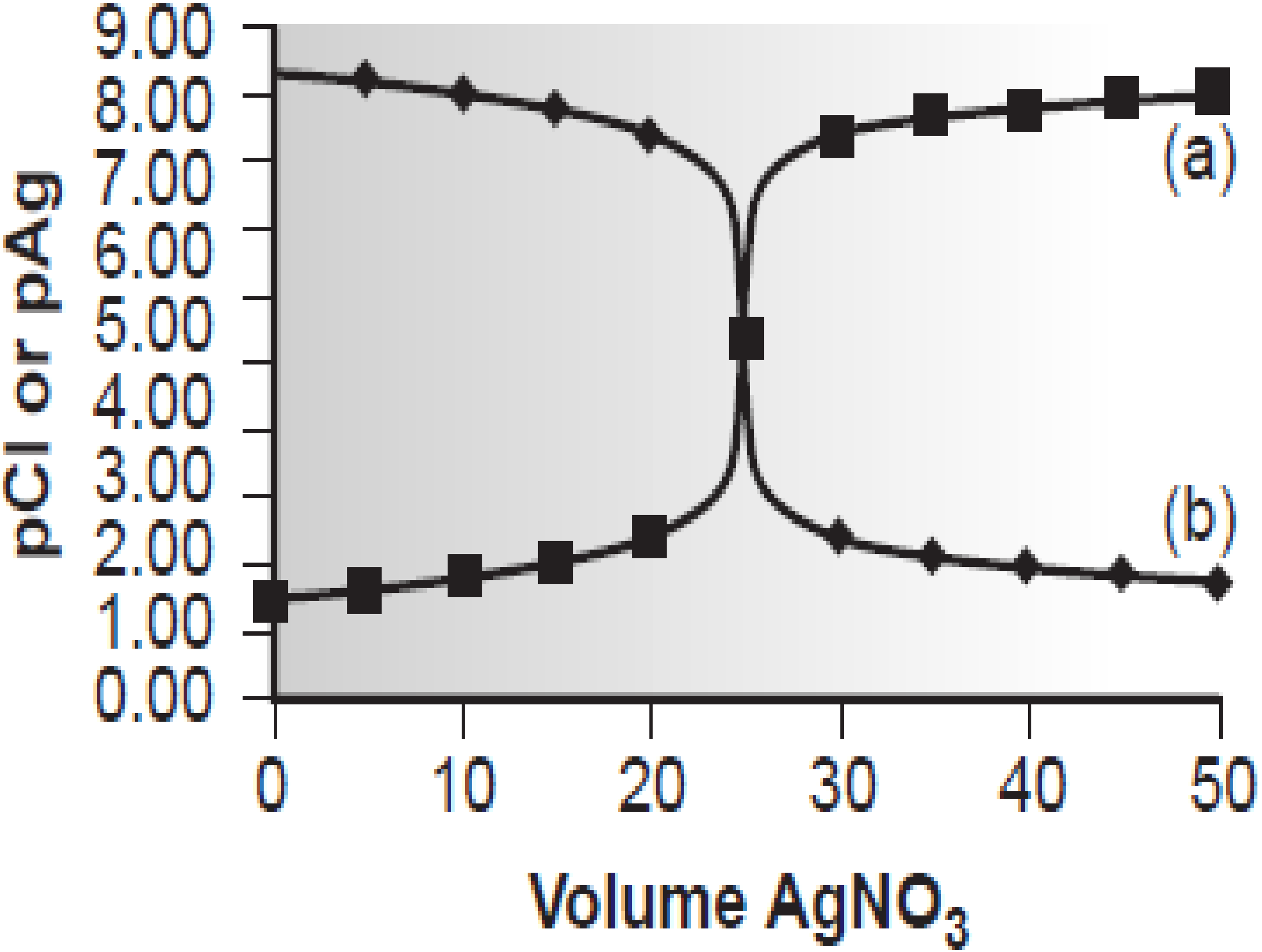
or a pAg of 1.93. The concentration of Cl^- is

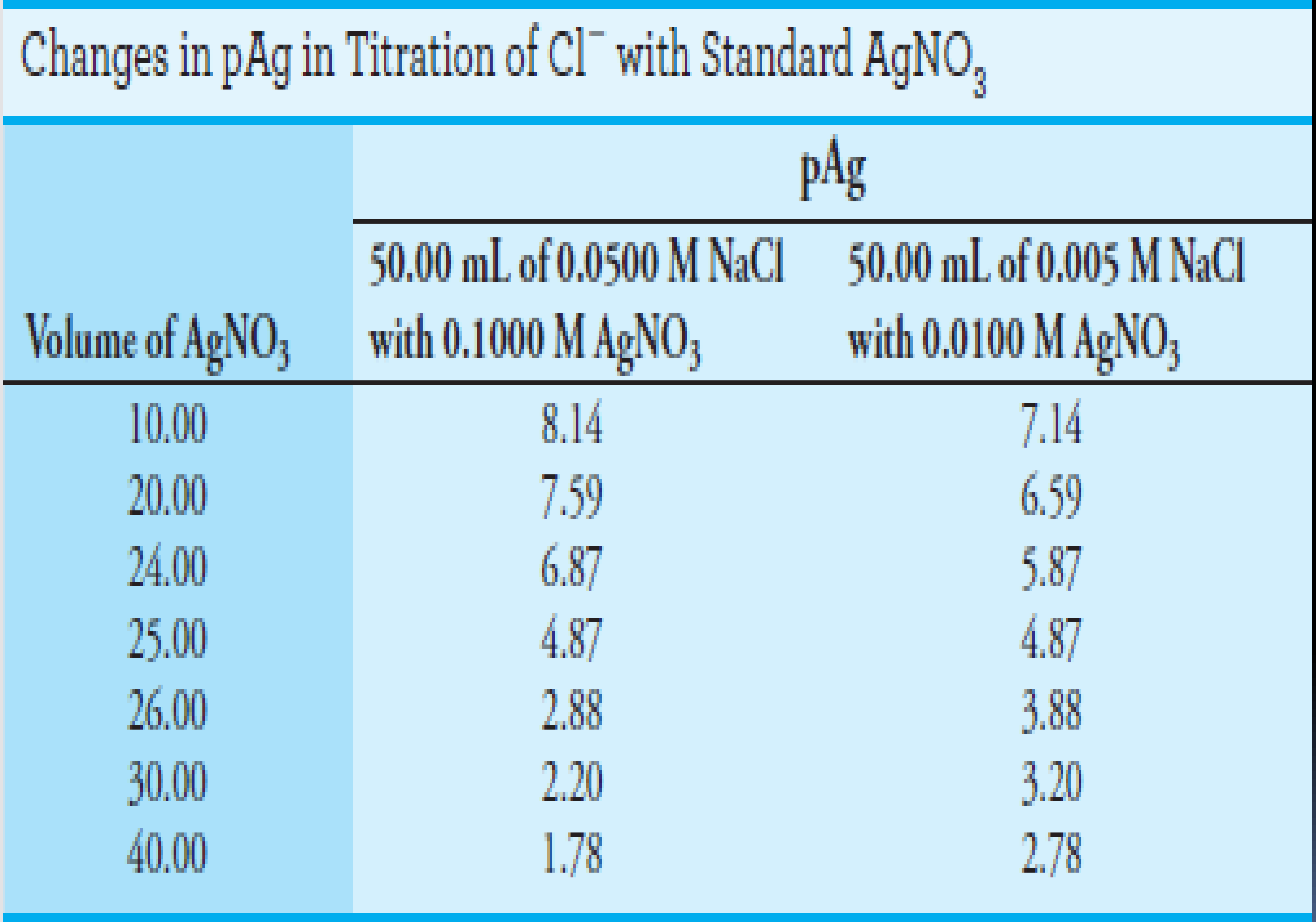
$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8 \times 10^{-10}}{1.18 \times 10^{-2}} = 1.5 \times 10^{-8} \text{ M}$$

or a pCl of 7.82.

Table 9.21 Data for Titration of 50.0 mL of 0.0500 M Cl^- with 0.100 M Ag^+

Volume $AgNO_3$ (mL)	pCl	pAg
0.00	1.30	—
5.00	1.44	8.31
10.00	1.60	8.14
15.00	1.81	7.93
20.00	2.15	7.60
25.00	4.89	4.89
30.00	7.54	2.20
35.00	7.82	1.93
40.00	7.97	1.78
45.00	8.07	1.68
50.00	8.14	1.60

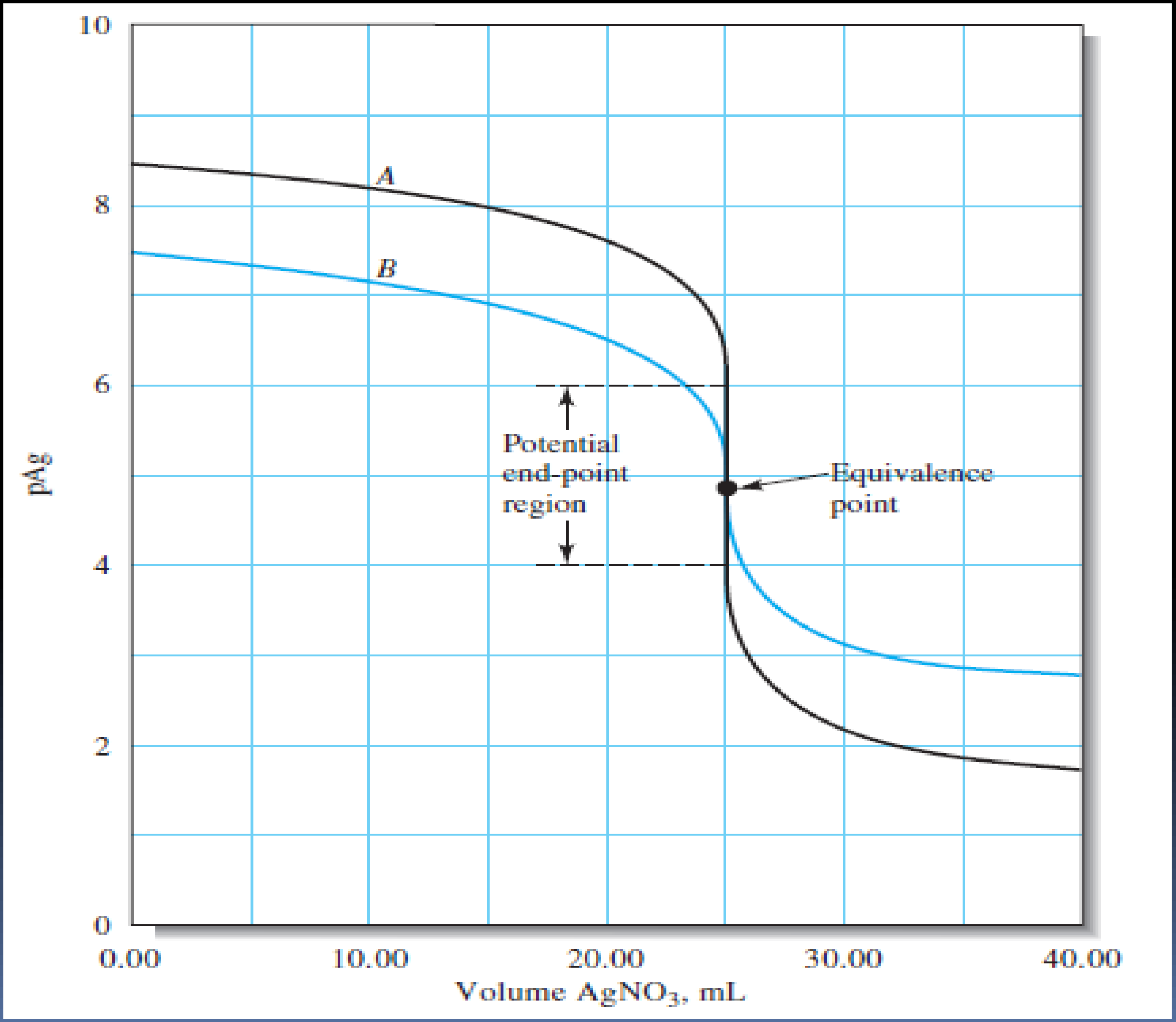

9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
pCl or pAg
(a)
(b)
0
10
20
30
40
50
Volume $AgNO_3$



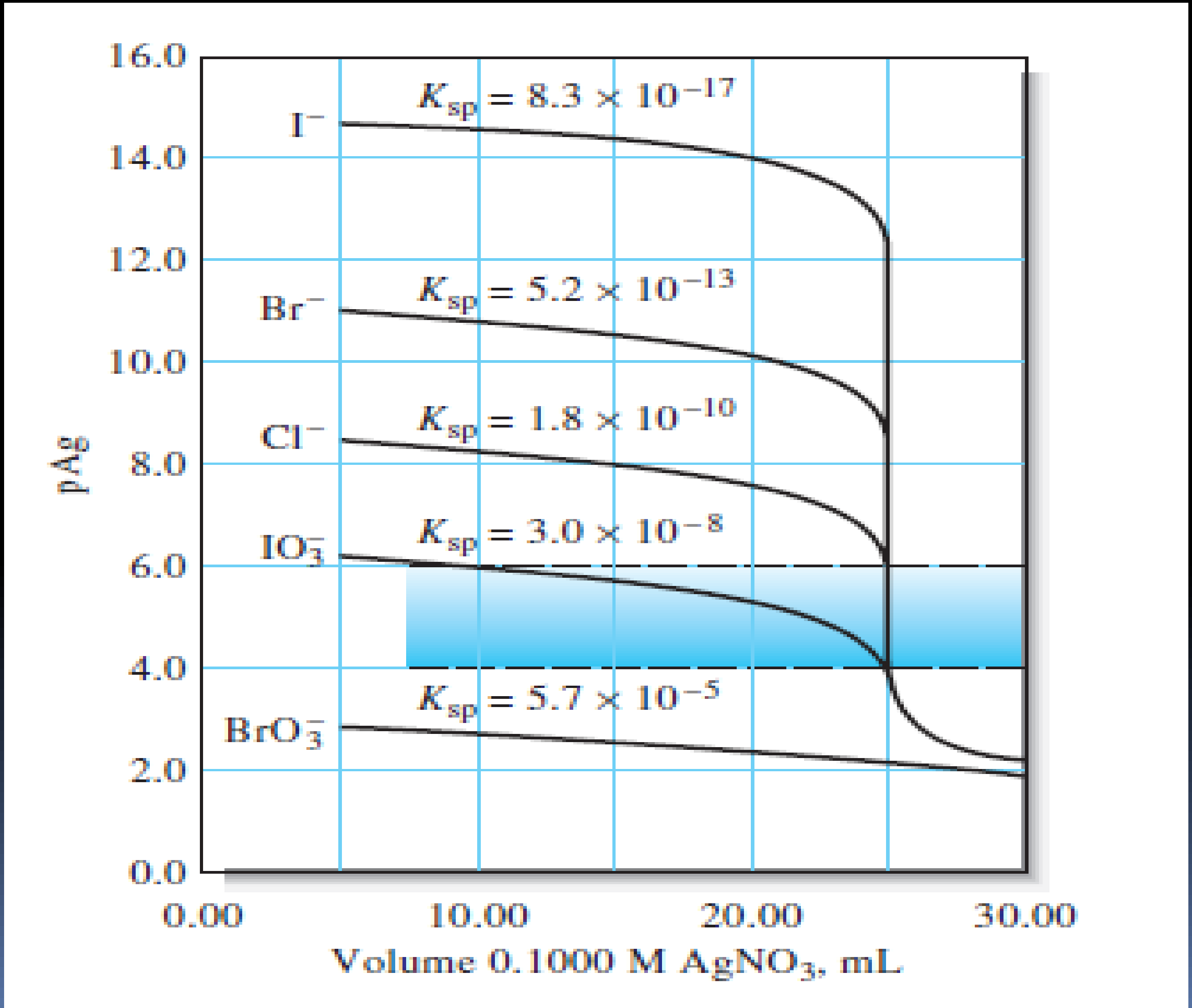
Changes in pAg in Titration of Cl^- with Standard $AgNO_3$

Volume of $AgNO_3$	pAg	
	50.00 mL of 0.0500 M NaCl with 0.1000 M $AgNO_3$	50.00 mL of 0.005 M NaCl with 0.0100 M $AgNO_3$
10.00	8.14	7.14
20.00	7.59	6.59
24.00	6.87	5.87
25.00	4.87	4.87
26.00	2.88	3.88
30.00	2.20	3.20
40.00	1.78	2.78

The Effect of Concentration on Titration Curves



The Effect of Reaction Completeness on Titration Curve



Methods for Selecting, locating and Evaluating the End Point of precipitation titration

- ☐ **Finding the End Point with a Visual Indicator.**
  - Mohr method
  - Volhard method
  - Fajan method
- ☐ **Finding the End Point Potentiometrically**

تسحيحات تكوين معقدات

Complexation Reactions and Titrations

Complexation reactions are widely used in analytical chemistry. One of the earliest uses of these reactions was for titrating cations.

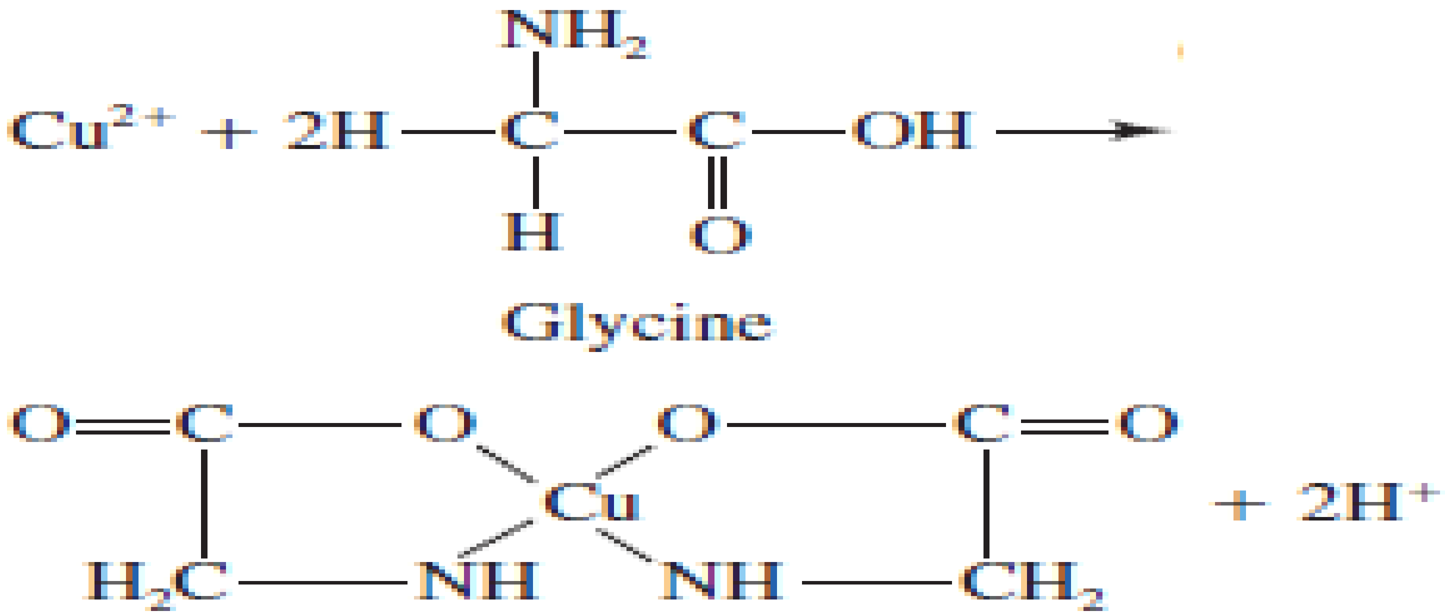
The Format ion of Complexes

- Most metal ions react with electron-pair donors to form coordination compounds or complexes.
- A ligand is an ion or a molecule that forms a covalent bond with a cation

or a neutral metal atom by donating a pair of electrons, which are then shared by the two.

- Coordination number The number of covalent bonds that a cation tends to form with electron donors.

The truly remarkable growth in their analytical application, based on a particular class of coordination compounds called chelates,



Cu^{2+} complex with glycine.

Complexation Equilibria

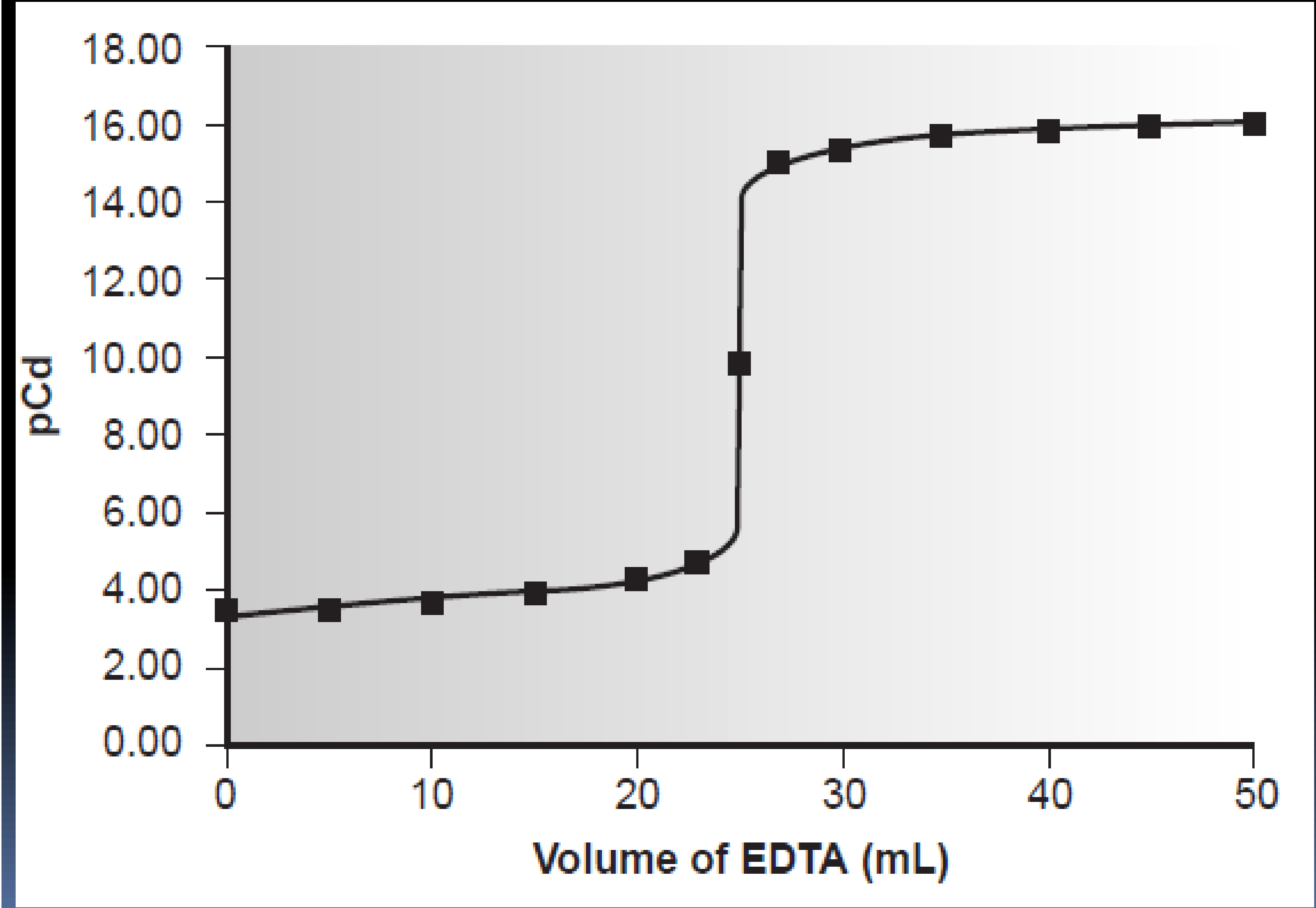
$$M + L \rightleftharpoons ML$$

$$\begin{aligned} ML + L &\rightleftharpoons ML_2 \\ ML_2 + L &\rightleftharpoons ML_3 \\ \vdots \qquad & \qquad \vdots \\ ML_{n-1} + L &\rightleftharpoons ML_n \end{aligned}$$

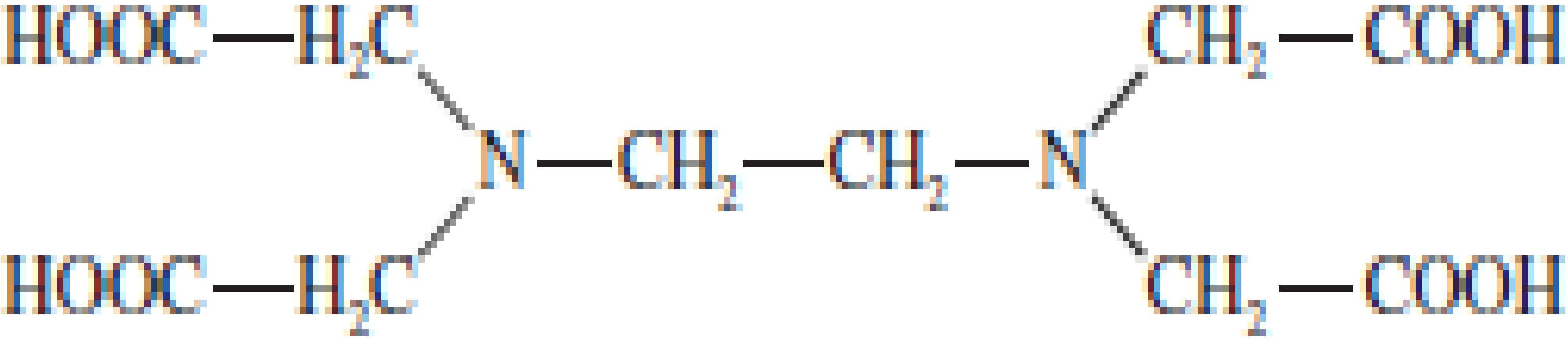
For example, Cu(II), with a maximum coordination number of 4, can form complexes with ammonia that have the formulas

$Cu(NH_3)^{2+}$, $Cu(NH_3)_2{}^{2+}$, $Cu(NH_3)_3{}^{2+}$, and $Cu(NH_3)_4{}^{2+}$

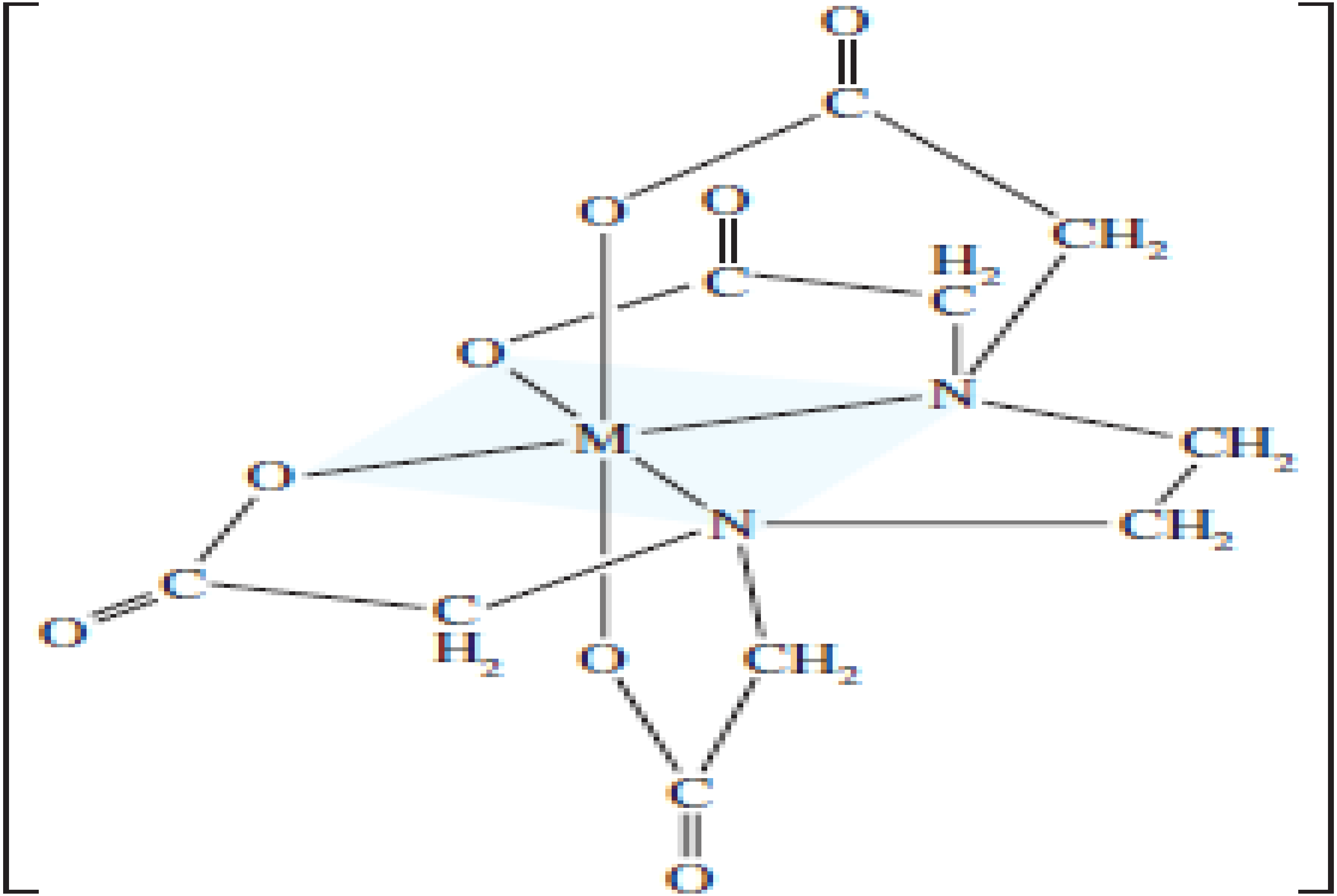
Titrations Curves

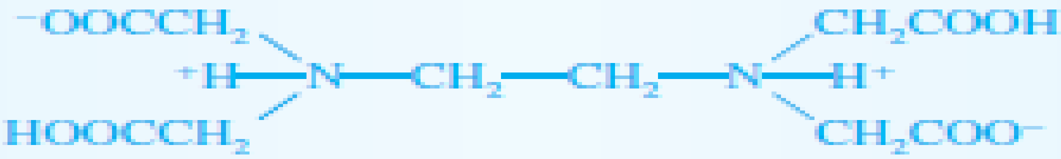


Ethylenediaminetetraacetic Acid (EDTA)

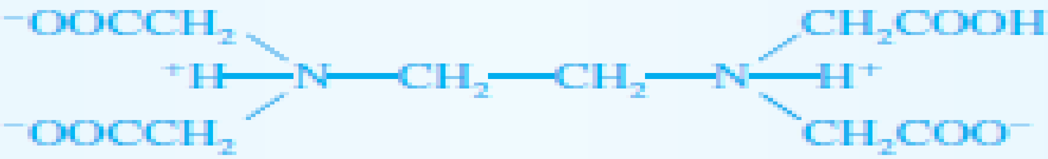


Structural formula of EDTA.

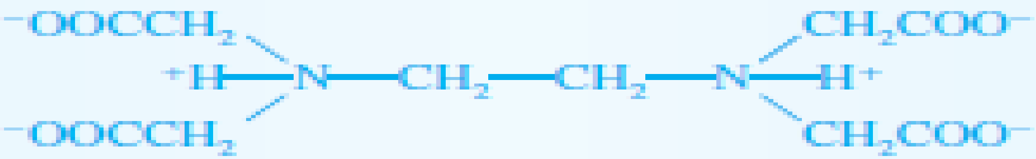

O
C
O
O
C
CH₂
H₂
C
O
N
M
CH₂
O
N
CH₂
C
O
C
H₂
O
CH₂
C
O



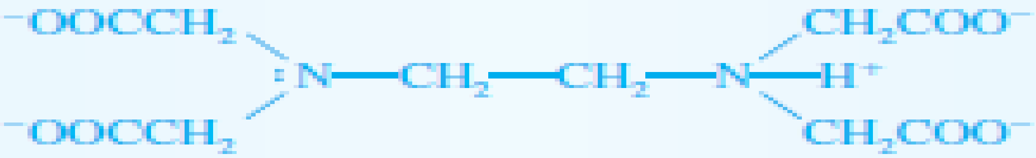
(a) H_4Y



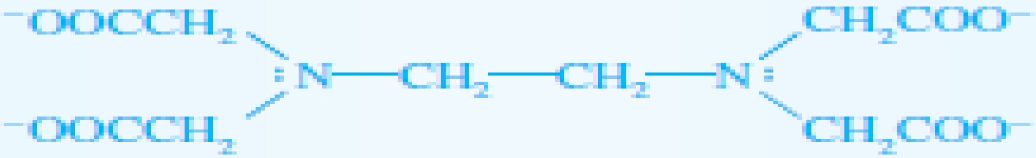
(b) H_3Y^-



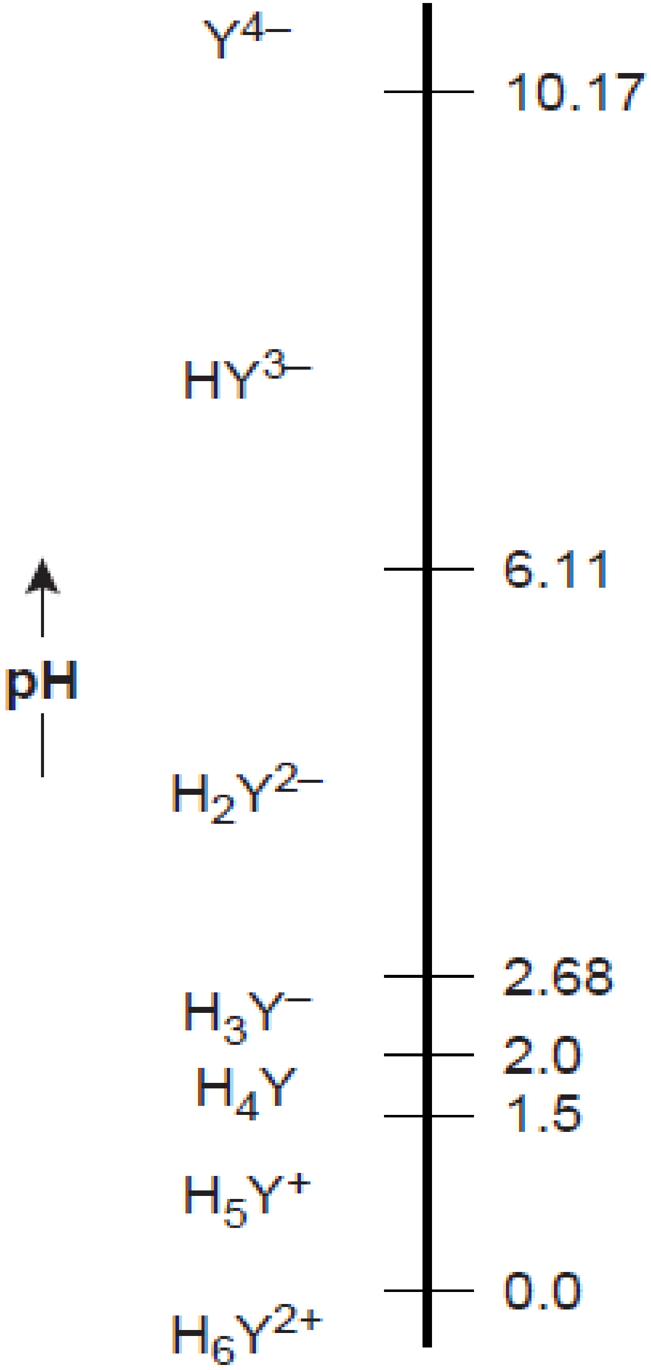
(c) H_2Y^{2-}



(d) HY^{3-}



(e) Y^{4-}



Conditional Metal-Ligand

$$C_{EDTA} = [H_6Y^{2+}] + [H_5Y^{+}] + [H_4Y] + [H_3Y^{-}] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

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

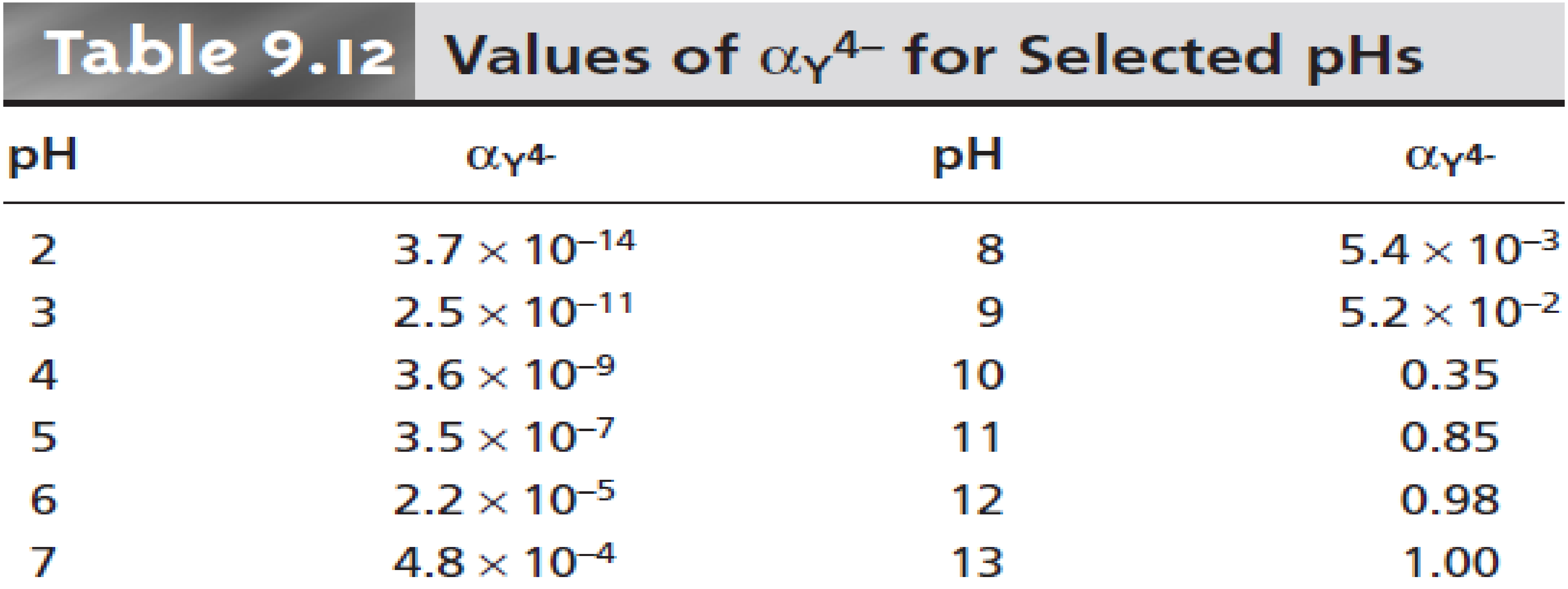


Table 9.12 Values of $\alpha_{Y^{4-}}$ for Selected pHs

pH	$\alpha_{Y^{4-}}$	pH	$\alpha_{Y^{4-}}$
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	0.35
5	3.5×10^{-7}	11	0.85
6	2.2×10^{-5}	12	0.98
7	4.8×10^{-4}	13	1.00

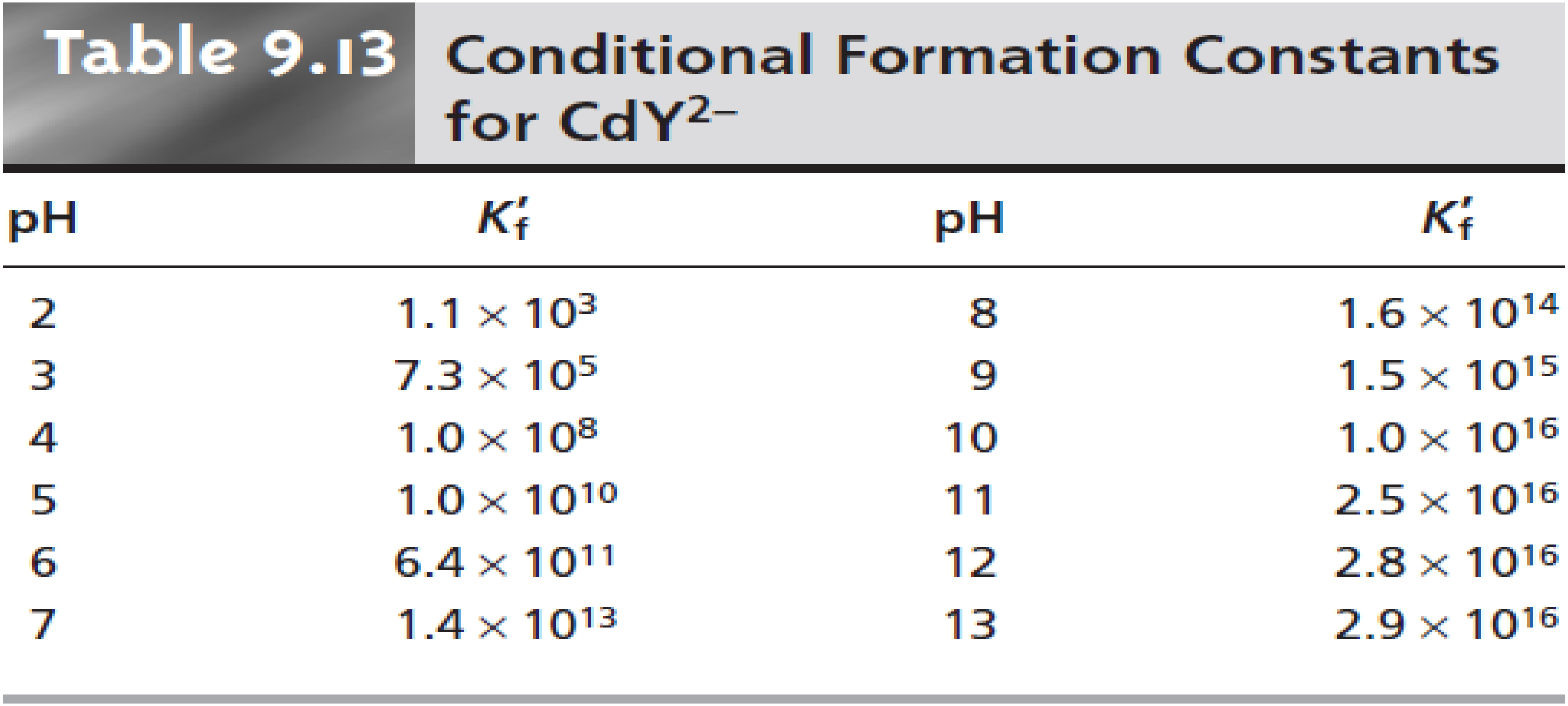


Table 9.13 Conditional Formation Constants for CdY^{2-}

pH	K'_f	pH	K'_f
2	1.1×10^{3}	8	1.6×10^{14}
3	7.3×10^{5}	9	1.5×10^{15}
4	1.0×10^{8}	10	1.0×10^{16}
5	1.0×10^{10}	11	2.5×10^{16}
6	6.4×10^{11}	12	2.8×10^{16}
7	1.4×10^{13}	13	2.9×10^{16}

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\alpha_{Y^{4-}} C_{EDTA}}$$

$$K'_f = \alpha_{Y^{4-}} \times K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]C_{EDTA}}$$

مزاحمة الـ EDTA مع ليكندات اخرى

$$C_{Cd} = [Cd^{2+}] + [Cd(NH_3)^{2+}] + [Cd(NH_3)_2^{2+}] + [Cd(NH_3)_3^{2+}] + [Cd(NH_3)_4^{2+}]$$

$$\alpha_{Cd^{2+}} = \frac{[Cd^{2+}]}{C_{Cd}}$$

$$K'_f = \alpha_{Y^{4-}} \times K_f = \frac{[CdY^{2-}]}{\alpha_{Cd^{2+}} C_{Cd} C_{EDTA}}$$

$$K''_f = \alpha_{Cd^{2+}} \times \alpha_{Y^{4-}} \times K_f = \frac{[CdY^{2-}]}{C_{Cd} C_{EDTA}}$$

Table 9.15 Data for Titration of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA at a pH of 10.0 and in the Presence of 0.0100 M NH_3

Volume of EDTA (mL)	pCd
0.00	3.36
5.00	3.49
10.00	3.66
15.00	3.87
20.00	4.20
23.00	4.62
25.00	9.77
27.00	14.91
30.00	15.31
35.00	15.61
40.00	15.78
45.00	15.91
50.00	16.01