I) Common-Ion Effect

Shift in equil. due to addition of an ion involved in the equil. system.

A) Addition of Strong Electrolyte

$$HF \rightleftharpoons H^+ + F^-$$

1) Add HCl

2) Add NaF

3) Ex1: What is $[OH^-]$ in a soln. made by dissolving 0.020 mole of NH_4Cl in 100.0 mL of 0.15M NH_3?

$K_b = 1.8 \times 10^{-5}$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

init.

chg.

equil.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

B) Common-Ions from Acid-Base Rx's

Common-Ion generated by an acid-base neutralization rx.

$$HF + NaOH \rightleftharpoons F^- + Na^+ + HOH$$

Rx. goes to completion

Generally, rx's between the following proceed to completion

- strong acids & strong bases
- strong acids & weak bases
- weak acids & strong bases

Neutralization rx. produces a stoichiometric amt. of F^-, leaving excess HF

- have common-ion equil. calc.

Do stoichiometry calc. for neutralization rx. in moles & then convert to Molarity for the common-ion calc.

Do NOT Forget Dilution when appropriate

1) **Ex 2**: Calc. the pH of a soln. produced by mixing 100.0 mL of 0.70 M NH_3 w. 100.0 mL of 0.40 M HCl.

a) Step 1: Neutralization rx. calc.

stoichiometry calc.

- convert to moles

$$\# \text{ moles} = V \cdot M$$

$$\text{moles } NH_3 = (0.1000 L)\left(\frac{0.70 mol}{L}\right) = 0.070 \text{ mol}$$

$$\text{moles } H^+ = (0.1000 L)\left(\frac{0.40 mol}{L}\right) = 0.040 \text{ mol}$$

	NH_3 +	H^+ $\longrightarrow$	NH_4^+
init.	0.070	0.040	0
chg.	−0.040	−0.040	+0.040
compl.	0.030	0	0.040

b) Step 2: Common-Ion Calc.

Convert moles to Molarity

- Dilution

Now have 200.0 mL soln.

Molarity $NH_3 = \frac{0.030 \text{ mol}}{0.2000 \text{ L}} = 0.15 \text{ M}$

Molarity $NH_4^+ = \frac{0.040 \text{ mol}}{0.2000 \text{ L}} = 0.20 \text{ M}$

Proceed as in Ex. 1

II) Buffers

Solutions that resist a significant change in pH when small amts. of strong acid or base are added.

A) Composition & Action of Buffers

Contain both members of

Conjugate Weak Acid-Base Pair

Acid: reacts w. added base

Base: reacts w added acid

Conj. A-B do NOT react w. each other

NH_3 & NH_4Cl

HF & NaF

1) How it Works

$$HB\,(aq) \rightleftharpoons H^+\,(aq) + B^-\,(aq)$$

$$K_a = \frac{[H^+][B^-]}{[HB]}$$

$$\boxed{[H^+] = K_a \frac{[HB]}{[B^-]}}$$

a) Add strong acid:

$$H^+ + B^- \longrightarrow HB$$

$[HB]$ Inc., $[B^-]$ Dec., chg. $\frac{[HB]}{[B^-]}$ small

$\therefore \Delta pH$ small

b) Add strong base:

$$OH^- + HB \longrightarrow H_2O + B^-$$

$[HB]\downarrow$, $[B^-]\uparrow$, $\Delta \frac{[HB]}{[B^-]}$ & ΔpH small

B) Henderson-Hasselbalch Eq.

1) Weak Acid/Salt of Acid

$$HB \rightleftharpoons H^+ + B^-$$

$$[H^+] = K_a \frac{[HB]}{[B^-]}$$

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HB]}{[B^-]}\right)$$

$$\boxed{pH = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)}$$

Note:

$$[\text{base}]_{eq} = [\text{base}]_0 + [H^+]_{eq} \cong [\text{base}]_0$$

$$[\text{acid}]_{eq} = [\text{acid}]_0 - [H^+]_{eq} \cong [\text{acid}]_0$$

$$pH = pK_a + \log\left(\frac{[\text{base}]_0}{[\text{acid}]_0}\right)$$

c) Choosing a Buffer System

To be effective, the ratio of components must be between $\frac{10}{1}$ & $\frac{1}{10}$

$$pH = pK_a + \log\left(\frac{10}{1}\right) = pK_a + 1$$

$$pH = pK_a + \log\left(\frac{1}{10}\right) = pK_a - 1$$

$\therefore$ pK_a of acid must be within 1 unit of desired pH

Note:

If equal amts. of the 2 components are present

$$pH = pK_a$$

D) Calculations

1) **Ex. 3**: What is the pH of a buffer containing 0.10M HF & 0.25 M NaF ?

$$K_{a,HF} = 6.8 \times 10^{-4}$$

$$pK_a =$$

$$pH = pK_a + \log\left(\frac{[\quad]}{[\quad]}\right)$$

2) **Ex. 4** : What is the pH of a buffer containing 0.15 M NH_3 & 0.20 M NH_4Cl ?

$K_{b, NH_3} = 1.8 \times 10^{-5}$

$pK_b = 4.74$

3) **Ex. 5**: Calc. pH of 100.0 mL of Ex 1 NH_3/NH_4^+ buffer soln. to which 10.0 mL of 0.10 M NaOH is added. Compare to pH change if base is added to water.

a) Neutralization rx. calc. (moles)

	OH^- +	NH_4^+ →	H_2O +	NH_3
init.	0.0010	0.020		0.015
chg.	− 0.0010	− 0.0010		+ 0.0010
compl.	0	0.019		0.016

Total Volume = 110.0 mL

$$[NH_4^+] = \frac{0.019\text{ mol}}{0.1100\text{ L}} = 0.173\text{ M}$$

$$[NH_3] = \frac{0.016\text{ mol}}{0.1100\text{ L}} = 0.145\text{ M}$$

b) Equilibrium - Buffer

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

0.145 M (NH3)   0.173 M (NH4+)

$$pH = pK_a + \log\left(\frac{[NH_3]}{[NH_4^+]}\right)$$

$$pH = 9.26 + \log\left(\frac{0.145}{0.173}\right)$$

$$pH = 9.18$$

The buffer soln. had pH = 9.13

- change in pH of only 0.05

c) In pure H_2O

Add 10.0 mL of 0.10 M NaOH to 100.0 mL H_2O

$$\frac{0.0010\ \text{mol}}{0.1100\ L} = 0.0091\ M\ OH^-$$

pOH = 2.04   pH = 11.96

- change of almost 5 pH units

4) Ex. 6: What ratio of conc. should be used to prepare a formic acid/formate ion buffer having a pH of 4.0?

$K_a = 1.8 \times 10^{-4}$

III) Acid-Base Titrations

Titration: Procedure for determining amt. of acid (or base) in a soln. by reacting it w. an equivalent (stoichiometric) amt. of base (or acid).

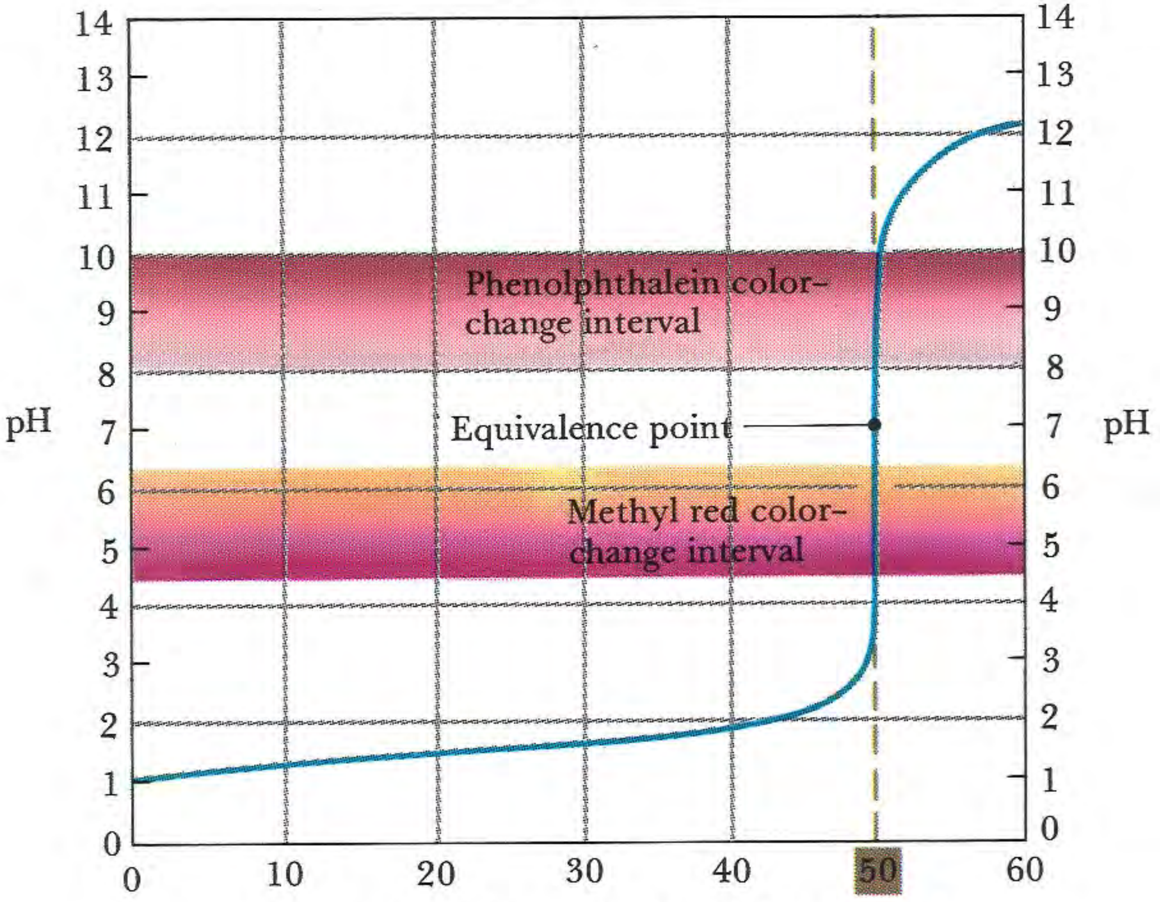
Acid-Base Titration Curve

graph of pH vs. volume of titrant added.

Equivalence Pt:

moles OH^- = # moles H^+

Transparency 119 Figure 17.5 pH curve for strong acid-strong base titration



Number of milliliters 0.100 *M* NaOH solution added to 50.0 mL 0.100 *M* HCl solution

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A) Strong Acid–Strong Base Titration

Titration of 50.0 mL of 0.100 M HCl w. 0.100 M NaOH

$$HCl + NaOH \longrightarrow NaCl + HOH$$

Net Ionic Eq.:

$$H^+ + OH^- \rightleftharpoons H_2O$$

1) Start : Before adding NaOH

$[H^+] = 0.100\ M$

pH = 1.00

2) Add 25.0 mL of NaOH

$$\#\text{ moles } H^+ = 0.0500\,L \times \frac{0.100\,mol}{L} = 0.00500$$

$$\#\text{ moles } OH^- = 0.0250\,L \times \frac{0.100\,mol}{L} = 0.00250$$

$$H^+ + OH^- \rightarrow H_2O\,(l)$$

	H^+	OH^-	$H_2O\,(l)$
	0.00500	0.00250	0
	−0.00250	−0.00250	+0.00250
comp.	0.00250	0	0.00250

Excess H^+ in 75.0 mL

$$[H^+] = \frac{0.00250\,mol}{0.0750\,L} = 0.0333\,M$$

$$pH = 1.477$$

3) Add another 25.0 mL NaOH

Total Vol. NaOH = 50.0 mL

0.00500 mol H^+ 0.00500 mol OH^-

Equivalence Pt.

Have only NaCl in H_2O

pH =

4) What Indicator Should be Used?

a) 49.9 mL of NaOH

$0.0499\ L \times \frac{0.100\ mol}{1\ L} = 0.00499\ mol$ OH^-

Excess $H^+ = 1 \times 10^{-5}$ mol

$[H^+] = \frac{\qquad}{\qquad} =$

pH =

b) 50.1 mL of NaOH

Excess $OH^- = 1 \times 10^{-5}$ mol

$[OH^-] = \frac{\qquad}{\qquad} =$

pOH =

pH =

c) Indicator

Region around eq. pt. is long & steep

pH range 4.0 – 10.0

Any indicator that changes color between 4.0 – 10.0 will signal end pt. of titration

Indicator	pK_a
methyl red	5.3
bromthymol blue	6.8
thymol blue	8.8
phenolpthalein	9.1
methyl orange	4.0
m-cresol purple	8.0
indigo carmine	12.0
bromthymol blue	7.0

5) Strong Base - Strong Acid Titration

B) Weak Acid- Strong Base

(1) Higher initial pH

(2) pH rises more rapidly in early part of titration, but more slowly near eq. pt.

The weaker the acid, less marked ΔpH near eq. pt.

(3) pH $\neq$ 7.0 at eq. pt.

pH at eq. pt. due to hydrolysis of resultant salt soln.

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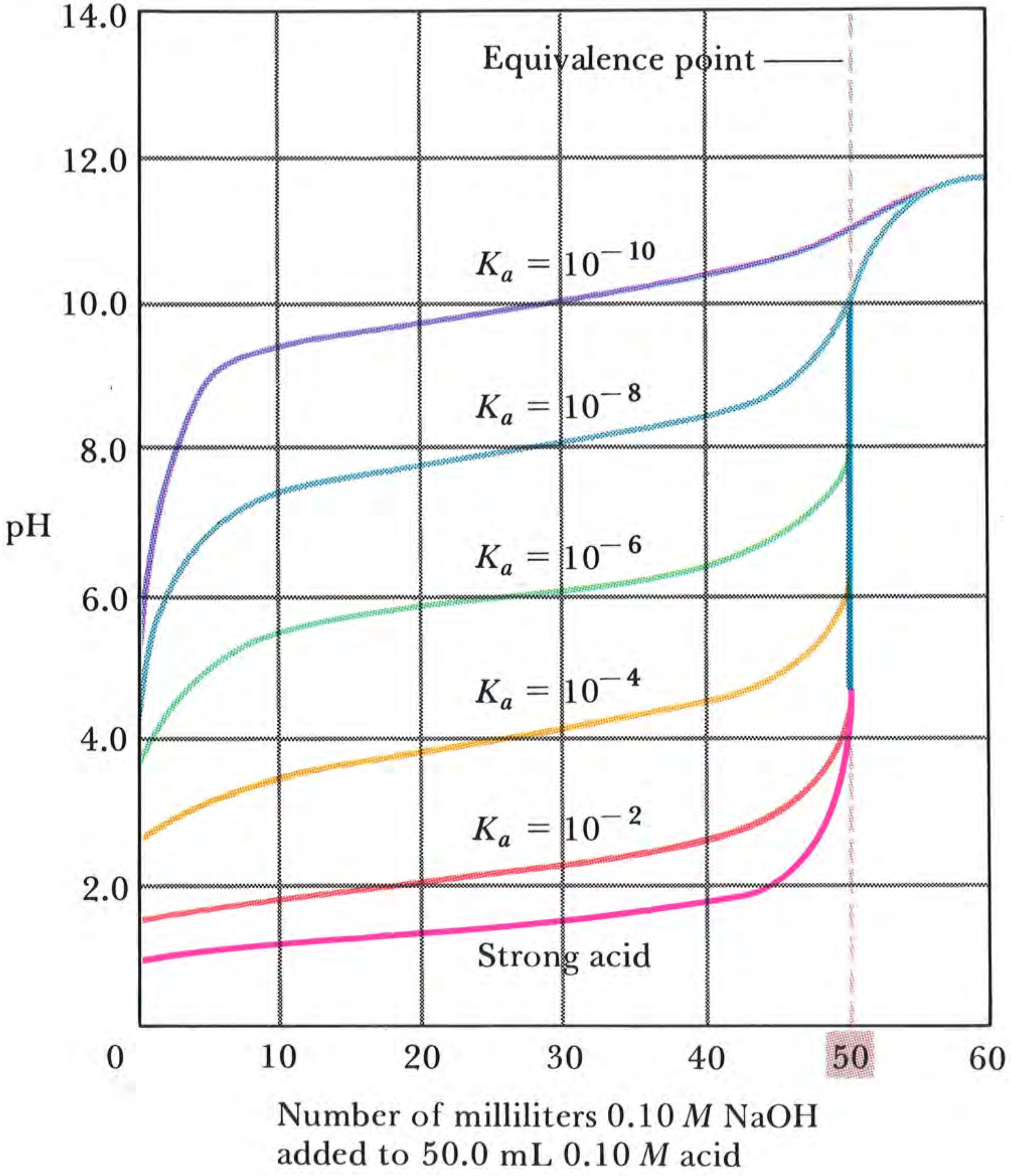
Figure 17.9 Influence of acid strength on the shape of the titration curve



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Ex 8: Titration of 50.0 mL of 0.100 M $HC_2H_3O_2$ w. 0.100 M NaOH.

1) Start: weak acid ionization

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

2) Add 25.0 mL of NaOH

$HC_2H_3O_2$	+ OH^-	→ $C_2H_3O_2^-$	+ H_2O
0.00500	0.00250	0	
− 0.00250	−0.00250	+ 0.00250	
0.00250	0	0.00250	

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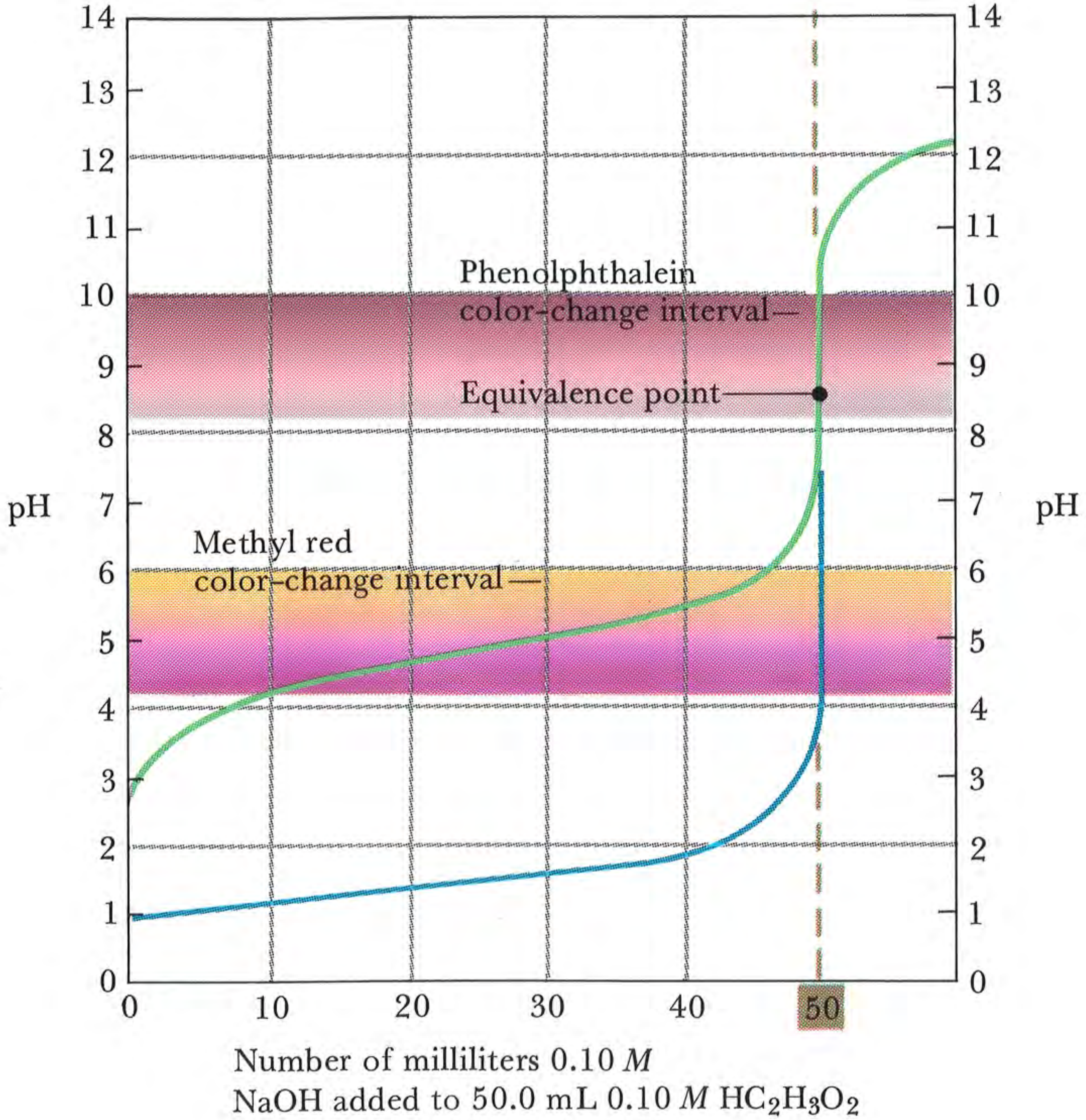
Figure 17.8 pH curve for weak acid-strong base titration



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$$[HC_2H_3O_2] = \frac{0.00250\ mol}{0.0750\ L} = 0.0333\ M$$

$$[C_2H_3O_2^-] = \frac{0.00250\ mol}{0.0750\ L} = 0.0333\ M$$

Buffer!!!

$$pH = pK_a + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

$$= 4.745 + \log\frac{(0.0333)}{(0.0333)}$$

$$= 4.745 + 0$$

$$pH = 4.745$$

<u>NOTE:</u> Halfway to eq. pt.

$$\boxed{pH = pK_a}$$

3) Add another 25.0 mL NaOH

Total Vol. NaOH = 50.0 mL

Equivalence Pt.

- converted ALL $HC_2H_3O_2$ to $C_2H_3O_2^-$

Hydrolysis!!

$$\underset{?M}{C_2H_3O_2^-} + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$

Need $[C_2H_3O_2^-]_{eq.\,pt.}$

mol $C_2H_3O_2^-$ at eq. pt $=$ mol $HC_2H_3O_2$ at start

$[C_2H_3O_2^-] =$

$$\begin{array}{llll}
C_2H_3O_2^- & + H_2O \rightleftharpoons & HC_2H_3O_2 & + OH^- \\
0.0500\,M & & 0 & 0 \\
-x & & +x & +x \\
\hline
0.0500 - x & & x & x
\end{array}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$\frac{x^2}{(0.0500 - x)} = 5.6 \times 10^{-10}$$

$$x = [OH^-] = 5.3 \times 10^{-6}$$

$$pOH = 5.28$$

$$pH = 8.72 \quad (\text{NOT } 7)$$

4) Add another 0.1 mL NaOH

Total Vol. NaOH = 50.1 mL

$[OH^-] \cong$ conc. excess NaOH

$$\frac{0.0001\,L \times \frac{0.100\,mol}{L}}{0.1001\,L} = 9.99 \times 10^{-5}\,M$$

OH^-

pOH = 4.0

pH = 10.0

c) Weak Base – Strong Acid

Calc. pH at the eq. pt. when 10.0 mL of 0.36 M ethylamine is titrated w. 0.12 M HCl

$$[C_2H_5NH_2]_0 \neq [HCl]_0$$

$$\therefore \text{Vol. HCl at eq. pt.} \neq V_{0,\,\text{base}}$$

$$C_2H_5\ddot{N}H_2 + H^+ \rightleftharpoons C_2H_5NH_3^+$$

Initially,

$$0.0100\,\text{L} \times \frac{0.36\,\text{mol}}{\text{L}} = 0.0036\,\text{mol}\ C_2H_5NH_2$$

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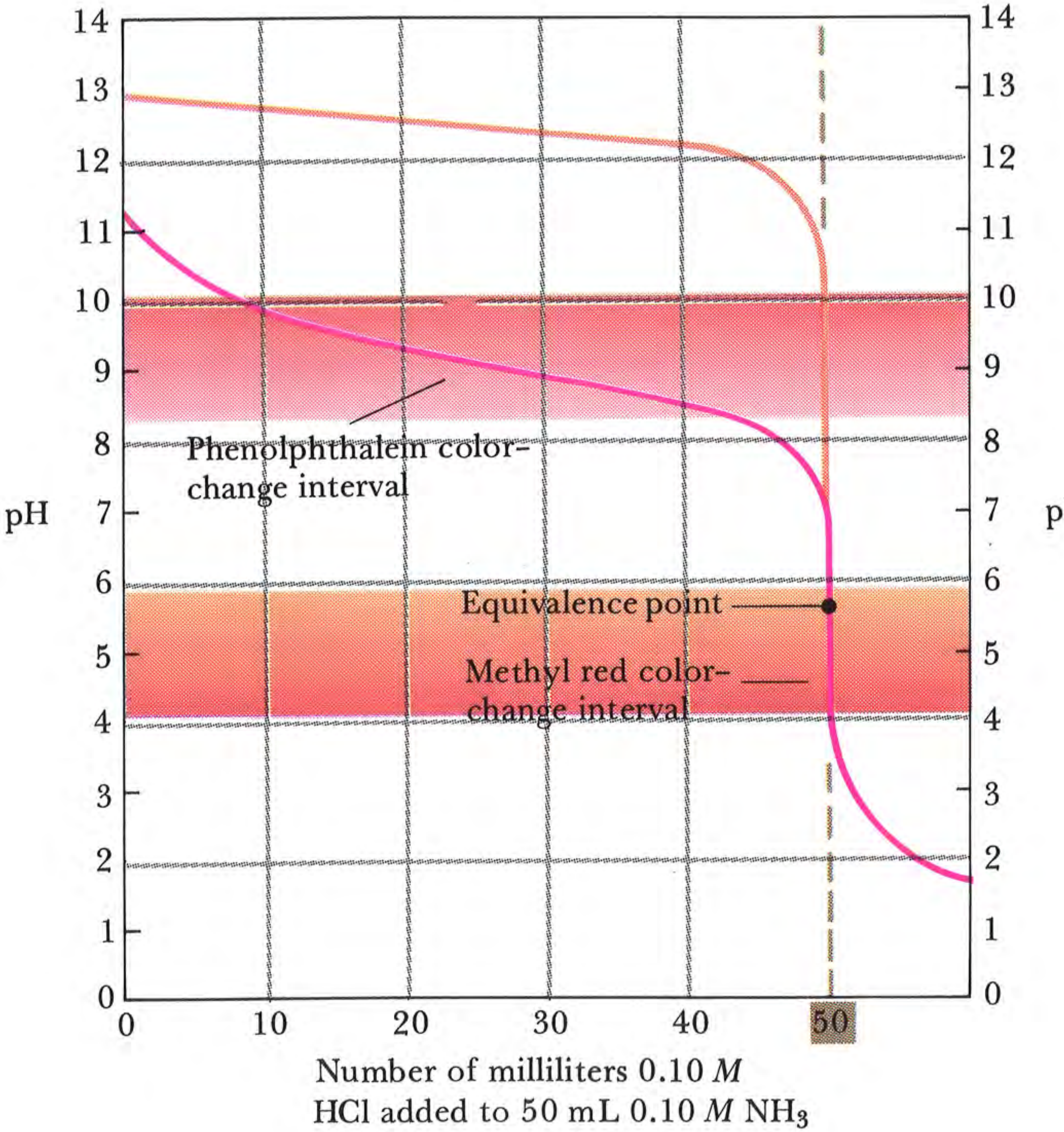
Figure 17.10 pH curve for strong acid-weak base titration



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Requires ? moles H^+ for neut'n.

D) Conclusions

1) Indicator must be chosen to change color at a pH close to eq. pt.

2) Use pH meter instead. Graph pH vs. Vol. of titrant & estimate vol. corresponding to midpoint of steeply rising portion of curve.

3) Use titration curve to determine K_a of weak acid. Find $V = \frac{1}{2} V_{eq. pt.}$,

$\frac{1}{2}$ neutralized

$$\therefore \quad pH = pK_a$$

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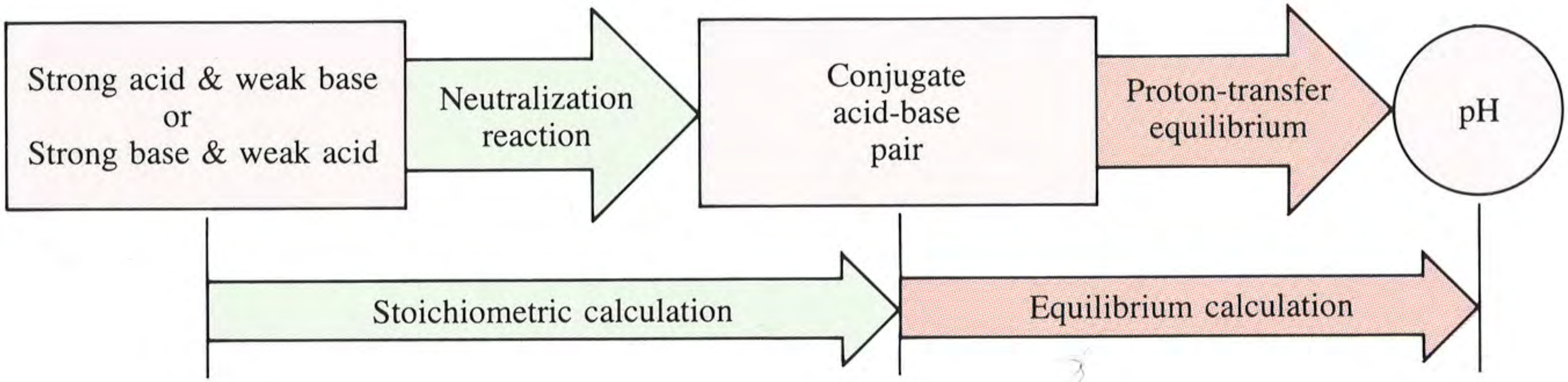
Figure 17.1 Calculating pH for a partially neutralized acid-base mixture



Strong acid & weak base
or
Strong base & weak acid

Neutralization reaction

Conjugate acid-base pair

Proton-transfer equilibrium

pH

Stoichiometric calculation

Equilibrium calculation

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4) Weak Acid – Strong Base or
Weak Base – Strong Acid

---

a) initially weak acid or
weak base ionization

b) after add'n. of titrant
Buffer

c) at Eq. Pt.
Hydrolysis

d) conc's determined by
neut. rx. to completion
& then equil. rx. w.
common-ion

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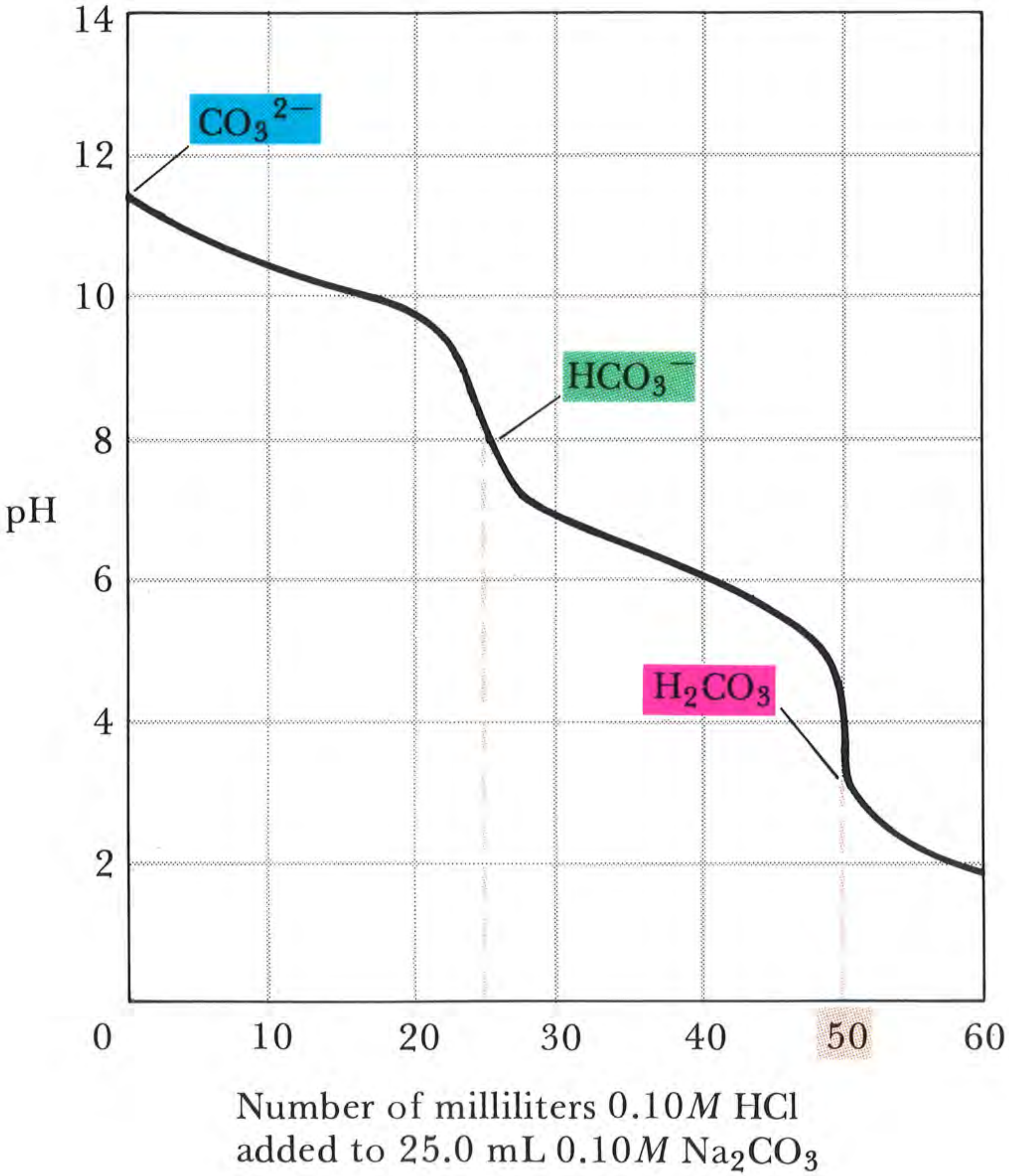
Figure 17.12 Titration curve for Na_2Co_3 with HCl



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