Applications of Aqueous Equilibria

第八章　　水溶液平衡的應用

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Beginning

- ***Most chemistry of the natural word occurs in aqueous solutions***
  水是自然界中生命活動的主要劇場，也是化學反應的主要舞台

- ***Acid-base reactions, solubility, complex ions formation often in equilibria in aqueous solutions***
  酸鹼反應、溶解度、錯離子形成等都經常在水溶液中達成平衡

- ***Aqueous equilibria are the foundation of environmental chemistry, biochemistry, agricultural chemistry, etc.***
  水溶液平衡是環境化學、生物化學、農業化學等領域的基礎

- ***Stability of the Chemical Species is the driving force***
  化學物質的穩定度是反應方向的決定因素

- **Common Ion Effect 共同離子效應**

HA(C_{HA})/NaA(C_{NaA})

$$\mathrm{NaA} \rightleftharpoons \underset{C_{NaA}}{\mathrm{A^-}} + \underset{C_{NaA}}{\mathrm{Na^+}}$$

$$\underset{C_{HA} - x}{\mathrm{HA}} + \mathrm{H_2O} \rightleftharpoons \underset{C_{NaA} + x}{\mathrm{A^-}} + \underset{x}{\mathrm{H_3O^+}}$$

If C_{HA} & C_{NaA} >> x

Henderson-Hasselbalch Equation

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{C_{NaA}}{C_{HA}}$$

C_{NaA} ← - - - **base form**

C_{HA} ← - - - **acid form**

- $NH_3(C_{NH3})/NH_4Cl(C_{NH4Cl})$

$$NH_4Cl \longrightarrow \underset{C_{NH4Cl}}{NH_4^+} + \underset{C_{NH4Cl}}{Cl^-}$$

$$\underset{C_{NH3} - x}{NH_3} + H_2O \rightleftharpoons \underset{C_{NH4Cl} + x}{NH_4^+} + \underset{x}{OH^-}$$

If C_{NH3} & $C_{NH4Cl} >> x$

$$pOH = pK_b + log\left(\frac{[NH_4^+]}{[NH_3]}\right) = pK_b + log\left(\frac{C_{NH_4Cl}}{C_{NH_3}}\right)$$

Buffer solution 緩衝溶液

- *A solution that is able to maintain an approximately constant pH*
  能夠維持pH值近乎不變的溶液，譬如血液

- *Resist change in pH upon addition of small amount of strong acid or base,even strong ones*
  溶液能抵抗外加的酸或鹼，而維持其pH值幾乎不變者

- *Independent of dilution*
  溶液雖經稀釋，卻能維持其pH值幾乎不變者

Preparation 緩衝溶液的製備

1 Weak acid or weak base and its corresponding salt

弱酸或弱鹼與其同離子鹽類以大致相當的莫耳比例混合者

2 Strong acid (or base) with weak base (or weak acid)

強酸與弱鹼中和或強鹼與弱酸中和至莫耳比例大致接近0.1~10者

Exact Treatment of Buffered solutions 緩衝溶液的數學

mass balance質量平衡: $[HA]_0 + [A^-]_0 = [HA] + [A^-]$…(式1)

charge balance電荷平衡: $[H^+] + [Na^+] = [OH^-] + [A^-]$…(式2)

由式2 …
$$[H^+] + [A^-]_0 = \frac{K_w}{[H^+]} + [A^-]$$

$$[A^-] = [A^-]_0 + \frac{[H^+]^2 - K_w}{[H^+]}$$

代入式1 …
$$[HA] = [A^-]_0 + [HA]_0 - [A^-]_0 - \frac{[H^+]^2 - K_w}{[H^+]}$$

$$= [HA]_0 - \frac{[H^+]^2 - K_w}{[H^+]}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]\left\{[A^-]_0 + \dfrac{[H^+]^2 - K_w}{[H^+]}\right\}}{[HA]_0 - \dfrac{[H^+]^2 - K_w}{[H^+]}}$$

If $[A^-]_0 = 0$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2 - K_w}{[HA]_0 - \dfrac{[H^+]^2 - K_w}{[H^+]}}$$

Buffer Capacity 緩衝容量

- ***The number of moles of strong acid or base that is required to cause a unit change in pH in 1 L buffer solution***
  改變1升緩衝溶液1單位的pH值時，所需要的強酸或強鹼的莫耳數

- ***Many factors such as temperature, ionic strength, solvent, colloidal particles might cause a shift in color range of one or more pH units.***
  溫度、離子強度、溶劑、膠體粒子等因素都可能造成影響

$$[H_3O^+] = K_a \frac{C_{HA}}{C_{NaA}}$$

$$pH = pK_a + \log \frac{C_{NaA}}{C_{HA}}$$

$$C_{NaOH} = \frac{m}{V} \quad m: \# \text{ of moles of NaOH}$$

$$C_{HA} = \frac{n-m}{V} \quad n: \# \text{ of moles of HA}$$

$$pH = pK_a + \log m - \log(n - m)$$

$$2.303 \frac{d(pH)}{dm} = \frac{1}{m} + \frac{1}{n-m} = \frac{n}{m(n-m)}$$

$$\frac{d^2(pH)}{dm^2} = \frac{n(2m-n)}{m^2(n-m)^2} = 0 \quad m = \frac{n}{2}$$

- **How much change will occur, when 0.01 mol of H^+ is added into 1.0 L of the following solutions?**

For example: (A) 1.00 M of NaOAc and HOAc
(B) 1.00 M NaOAc and 0.100 M HOAc
(C) 1.00 M NaOAc and 0.010 M HOAc

solution	$\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)_{before}$	$\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)_{after}$	percent change	*p*H change
A	1.00/1.00=1.00	0.99/1.01=0.98	2.00%	–0.0088
B	1.00/0.100=10.0	0.99/0.110=9.0	10.0%	–0.0458
C	1.00/0.01=100.0	0.99/0.02=49.5	50.5%	–0.305

The buffer effect does exist for all three solutions but the buffercarpacity drops substantially from A, B to C

Titration 酸鹼滴定

用已知濃度的酸或鹼定量未知濃度的鹼或酸

- $M_1V_1=M_2V_2$ M_1 = *molarity of the titrated substance*
  M_2= *molarity of the titrant*
  V_1 = *volume of the titrated substance*
  V_2= *volume of the titrant*

計量原則：滴定達當量點時，滴定劑的莫耳數與被滴定物的莫耳數相等

- ***Titration Curve*** *滴定曲線*

  - a plot of pH versus the amount of titrant.

  *滴定溶液的**pH** 值對滴定劑的量作圖所得的曲線*

Strong Acid versus Stong Base
強鹼滴定強酸

[Example]

At 25℃, 100.00 mL 0.100 M HCl titrated with 0.100 M NaOH

(a) What's the pH when *x* mL of NaOH is added?

(b) How much NaOH is needed to make a solution with pH=3.00? pH=10.00?

在**25**℃用**0.100 M NaOH**溶液滴定**100.00 mL 0.100 M HCl**

(a)加入***x* mL NaOH**時溶液的**pH**值為何？

(b)需加入多少**0.100 M NaOH**，溶液的**pH**值為**3.00**或**10.00**？

(1) 20.00 mL 0.1 M NaOH is added

HCl: 100.00 mL $\times$ 0.100 M = 10.00 mmol

NaOH: 20.00 mL $\times$ 0.100 M = 2.00 mmol

$[H^+]$=(10.00 – 2.00)mmol/(100.00 + 20.00)mL=0.067 M, pH=1.18

(2) pH = 3.00

NaOH: x mL $\times$ 0.100 M = 0.100x mmol

$[H^+]$ = 0.00100 M = (10.00 – 0.100x)mmol/(100.00 + x)mL

x = 98.02 mL

(3) pH = 10.0, pOH = 14.0 – 10.0 = 4.00, $[OH^-]$ = 1.00 $\times$ 10^{-4} M

NaOH: 0.000100 M = 0.100x mmol/(200.00 + x)mL

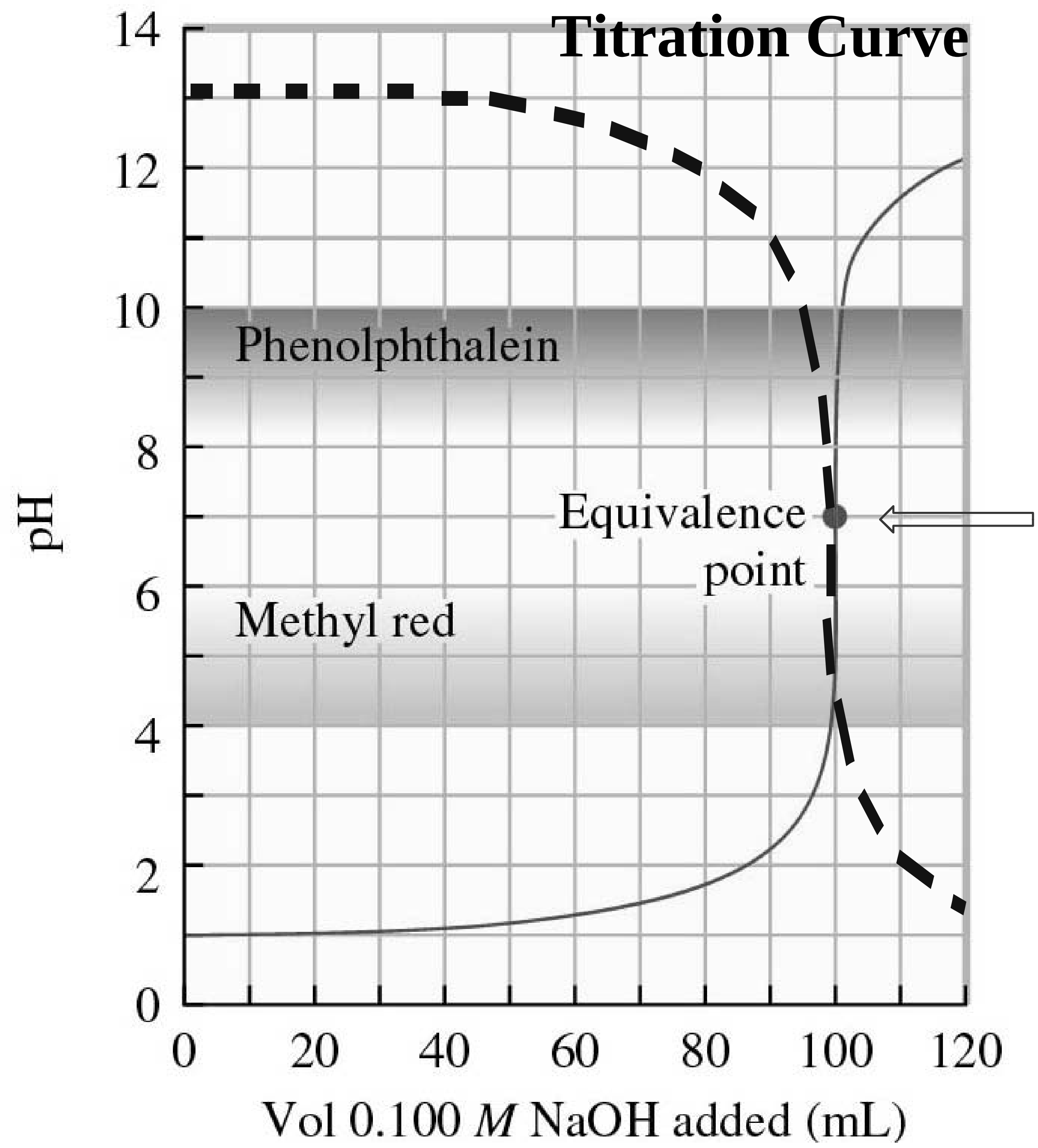
x = 0.20 mL, V_{NaOH} = (100.00 + 0.2) mL = 100.20 mL

(4) 200.00 mL NaOH is added

10.0 mmol NaOH is in excess in the solution

$[OH^-]$ = 10.0 mmol/300.0 mL= 0.033 M, pH = 12.52

Vol of NaOH added	pH	
0.00	1.00	$[H^+]=C_{HA}$
20.00	1.18	
80.00	1.95	
98.00	3.00	
99.80	4.00	
99.98	5.00	
100.00	7.00	equivalence point 當量點
100.20	10.00	
120.00	11.96	
200.00	12.52	



酚酞顯色區
8.0~10.0

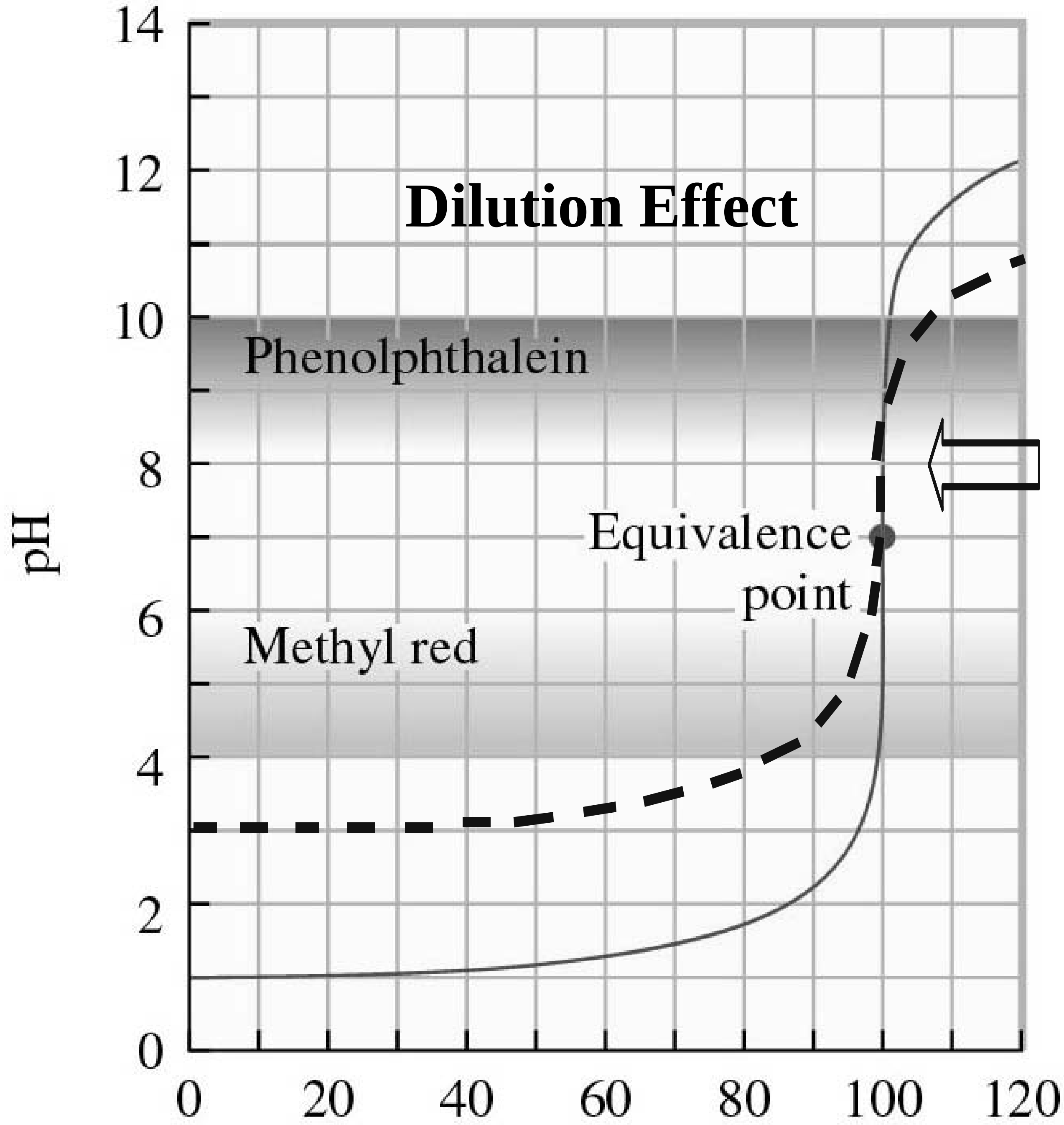
當量點 pH = 7.0

甲基橙顯色區
4.0~6.0

0.100M強酸滴定
100 mL 0.100 M
強鹼的滴定曲線

Strong Acid/Base Titration (強酸/強鹼滴定)

- ***pH has little change when HCl or NaOH is in large excess***
  鹽酸或氫氧化鈉過量時，pH值變化均不大
- ***pH has sharp change around the equivalence point with very small amount of change in titrant***
  在當量點附近，少量的滴定劑就使溶液的pH值發生極大的改變
- ***At the equivalence point:*** $N_{HCl} = N_{NaOH}$
  在當量點時，滴定劑與被滴定物的莫耳數正好相等
- ***End point : change in color of the indicator***
  滴定終點，指示劑變色後不再退色
- ***Indicator choice***
  選擇合適的指示既有助滴定的精確度



Bromothymol blue is a better indicator.
溴瑞香草藍6.0~8.0是較佳的指示劑

Weak Acid versus Stong Base
強鹼滴定弱酸

[Example]

At 25℃, 100.00 mL 0.100 M HOAc is titrated with 0.100 M NaOH

(a) What's the pH value before the titration?

(b) What's the pH when *x* mL of NaOH is added?

(c) How much NaOH is needed to make a solution with pH=3.00? pH=10.00?

在**25**℃用**0.100 M NaOH**溶液滴定**100.00 mL 0.100 M HOAc**

(a)滴定前的**pH**值為何？

(b)加入***x*** **mL NaOH**時溶液的**pH**值為何？

(c)需加入多少**0.100 M NaOH**，溶液的**pH**值為**3.00**或**10.00**？

Before NaOH is added

0.100 HOAc solution, $[H^+] = (K_a C_{HOAc})^{1/2} = 1.34 \times 10^{-3}$ M, pH = 2.87

Before the eq. pt.

10.00 mL 0.1 M NaOH is added, $[OAc^-]$ = 1.0 mmol /110 mL,

[HOAc] = 9.0 mmol/110 mL, pH = pK_a + log(1/9) = 3.79

Similarly, 20.00 mL 0.1 M NaOH is added, pH = pK_a + log(2/8) = 4.14

40.00 mL 0.1 M NaOH is added, pH = pK_a + log(4/6) = 4.56

m = n/2 50.00 mL 0.1 M NaOH is added, pH = pK_a = 4.74

60.00 mL 0.1 M NaOH is added, pH = pK_a + log(6/4) = 4.92

80.00 mL 0.1 M NaOH is added, pH = pK_a + log(8/2) = 5.34

98.00 mL 0.1 M NaOH is added, pH = pK_a + log(9.8/0.2) = 6.43

99.45 mL 0.1 M NaOH is added, pH = pK_a + log(9.945/0.055) = 7.00

At Eq. Pt.

100.00 mL 0.1 M NaOH is added, the 200 mL solution contains 0.05 M NaOAc.

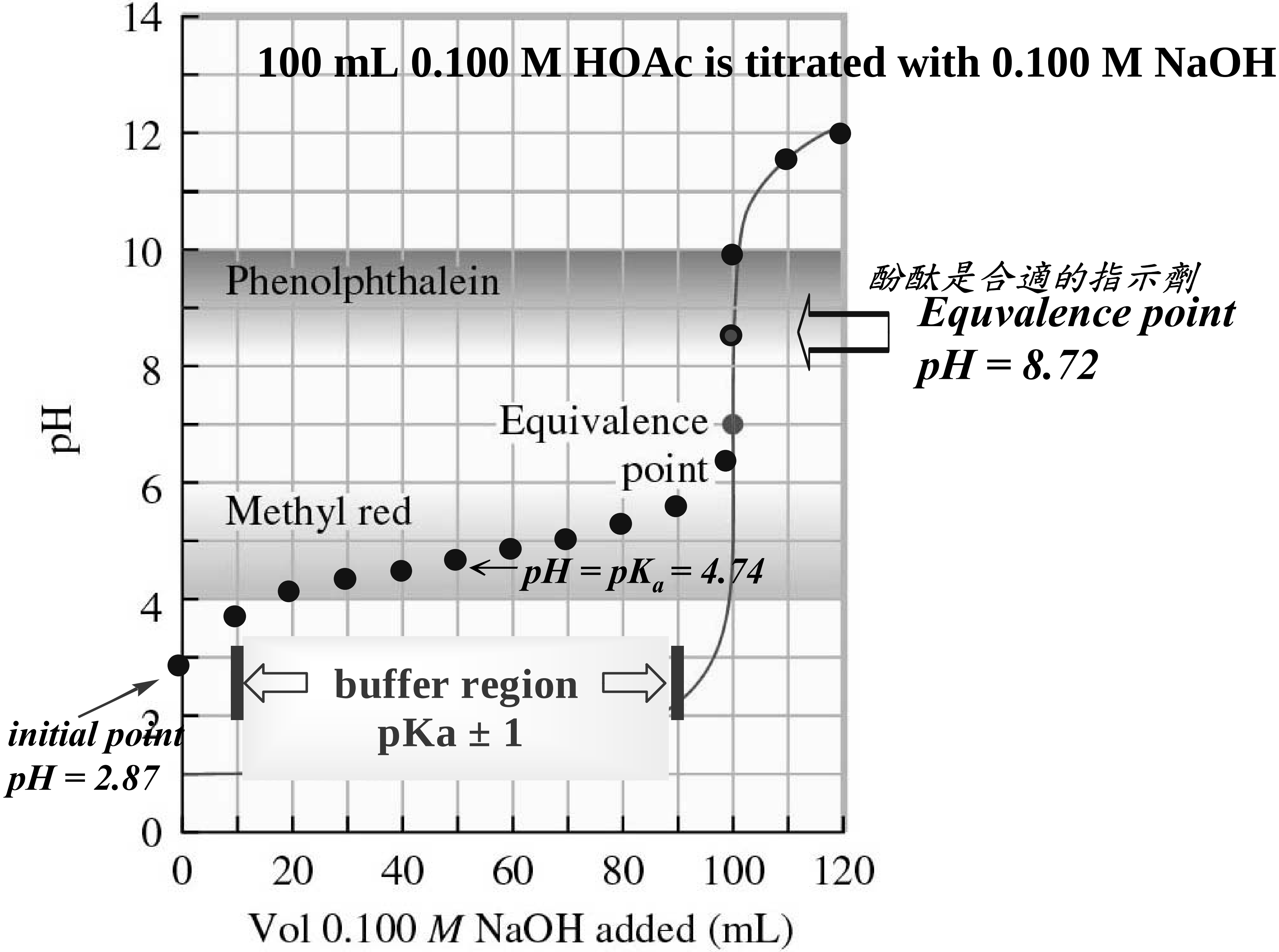
$[OH^-] = (K_b[OAc^-])^{1/2} = 5.27 \times 10^{-6}$ M, pH = 8.72

After the eq. pt.

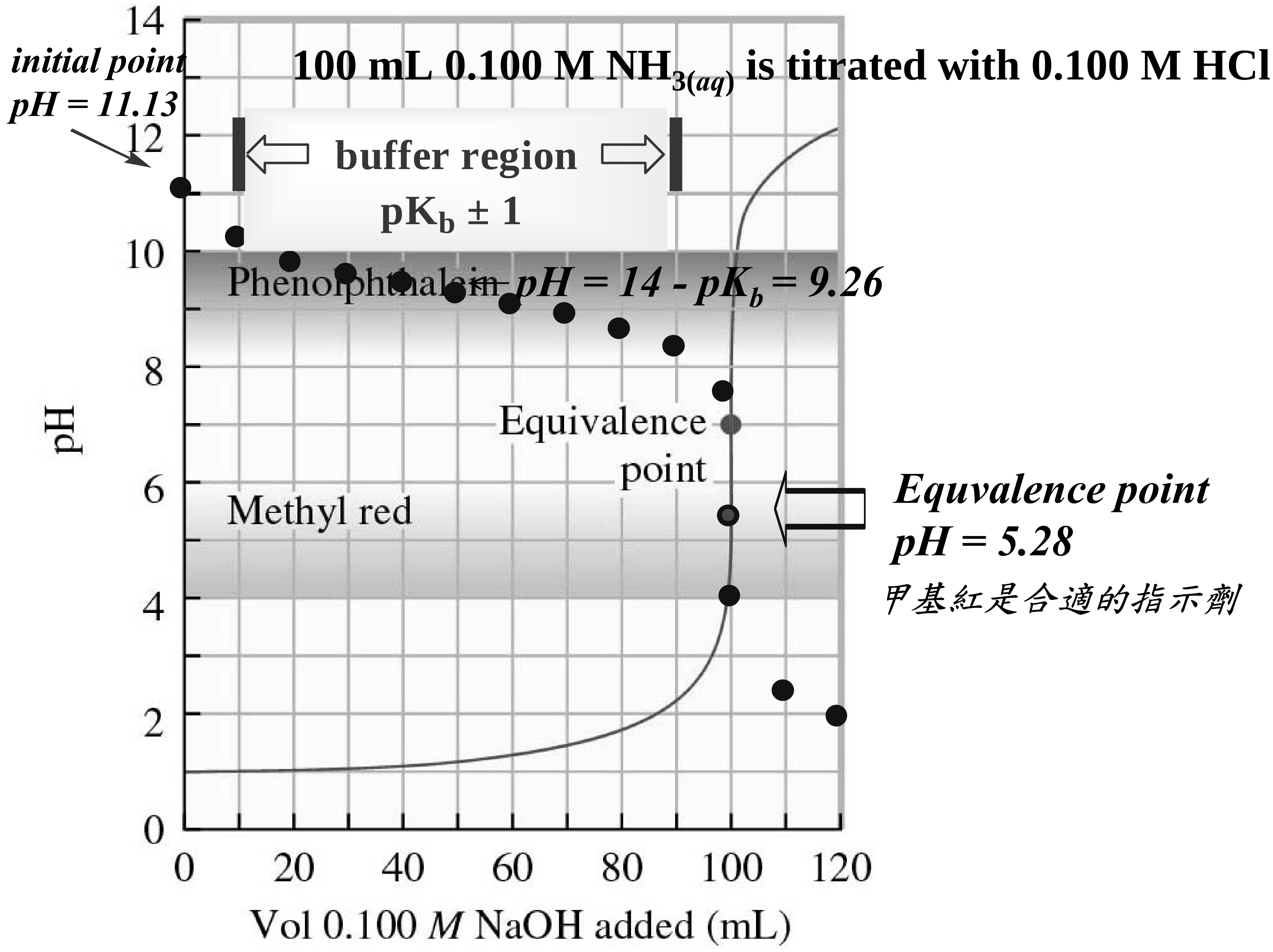
120.00 mL 0.1 M NaOH is added, $[OH^-]$ = 2.0/220 = 9.09×10^{-3} M, pH = 11.96

200.00 mL 0.1 M NaOH is added, $[OH^-]$ = 10.0/300 = $9.09 \times$ 10-3 M, pH = 12.52

Vol of NaOH added	pH	
0.00	2.87	$[H^+]=(K_aC_{HA})^{1/2}$
20.00	4.14	
50.00	4.74	$pH = pK_a$
80.00	5.34	
94.80	6.00	
99.45	7.00	
100.00	8.72	equivalence point 當量點
120.00	11.96	
200.00	12.52	



100 mL 0.100 M HOAc is titrated with 0.100 M NaOH
14
12
10
8
6
4
2
0
pH
Phenolphthalein
酚酞是合適的指示劑
Equvalence point
pH = 8.72
Equivalence point
Methyl red
pH = pKa = 4.74
buffer region
pKa ± 1
initial point
pH = 2.87
0
20
40
60
80
100
120
Vol 0.100 M NaOH added (mL)


100 mL 0.100 M NH3(aq) is titrated with 0.100 M HCl
initial point
pH = 11.13
buffer region
pKb ± 1
Phenolphthalein
pH = 14 - pKb = 9.26
Equivalence point
Methyl red
Equvalence point
pH = 5.28
甲基紅是合適的指示劑
pH
Vol 0.100 M NaOH added (mL)
0
2
4
6
8
10
12
14
0
20
40
60
80
100
120

Weak Acid/Strong Base Titration (弱酸/強鹼滴定)

- ***Initial pH is $(K_aC_{HA})^{1/2}$***
- ***When NaOH is added, the solution contains the mixture of HOAc and NaOAc.***
  加入NaOH時，形成HOAc及NaOAc的混合溶液，所以有共同離子效應
- ***$pH = pK_a$, when $[HOA] = [OAc^-]$ or $V_{NaOH} = ½V_{HOAc}$***
  NaOH的莫耳數與HOAc的莫耳數相等時，$pH = pK_a$
- ***$pK_a \pm 1$ is the buffer region.***
  $pK_a \pm 1$是緩衝溶液區
- ***At the equivalence point, the solution is a NaOAc solution with half of C_{HOAc}***
  在滴定當量點，形成醋酸鈉溶液，但是濃度僅有原來醋酸溶液的一半
- ***Phenolphthalein is a proper indicator, but not methyl red.***
  酚酞是合適的指示劑

Dilution Effect

Before NaOH is added

0.00100 HOAc solution, $K_a = [H^+][OAc^-]/[HOAc] = x^2/C_{HOAc} - x$

$[H^+] = x = 1.25 \times 10^{-4}$ M, pH = 3.90

Before the eq. pt.

10.00 mL 0.1 M NaOH is added, pH = $pK_a + \log([OAc^-]/[HOAc])$

Note: $[OAc^-]/[HOAc] \neq 1:9$ (> 1/9)

At Eq. Pt.

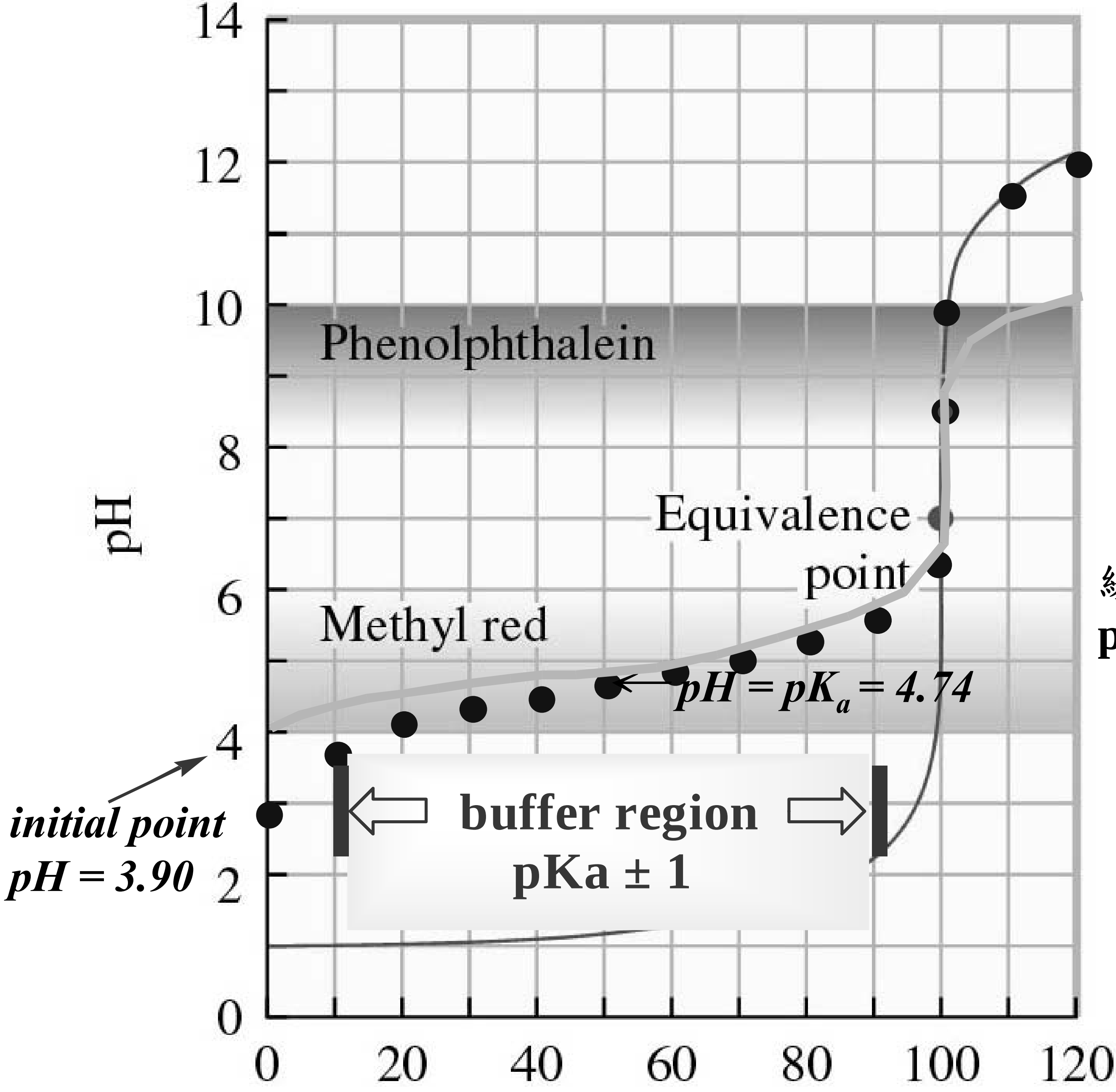
100.00 mL 0.1 M NaOH is added, the 200 mL solution contains 0.0005 M NaOAc.

$$K_b = \frac{[OH^-]^2 - K_w}{[OAc^-]_0 - \dfrac{[OH^-]^2 - K_w}{[OH^-]}}$$

After the eq. pt.

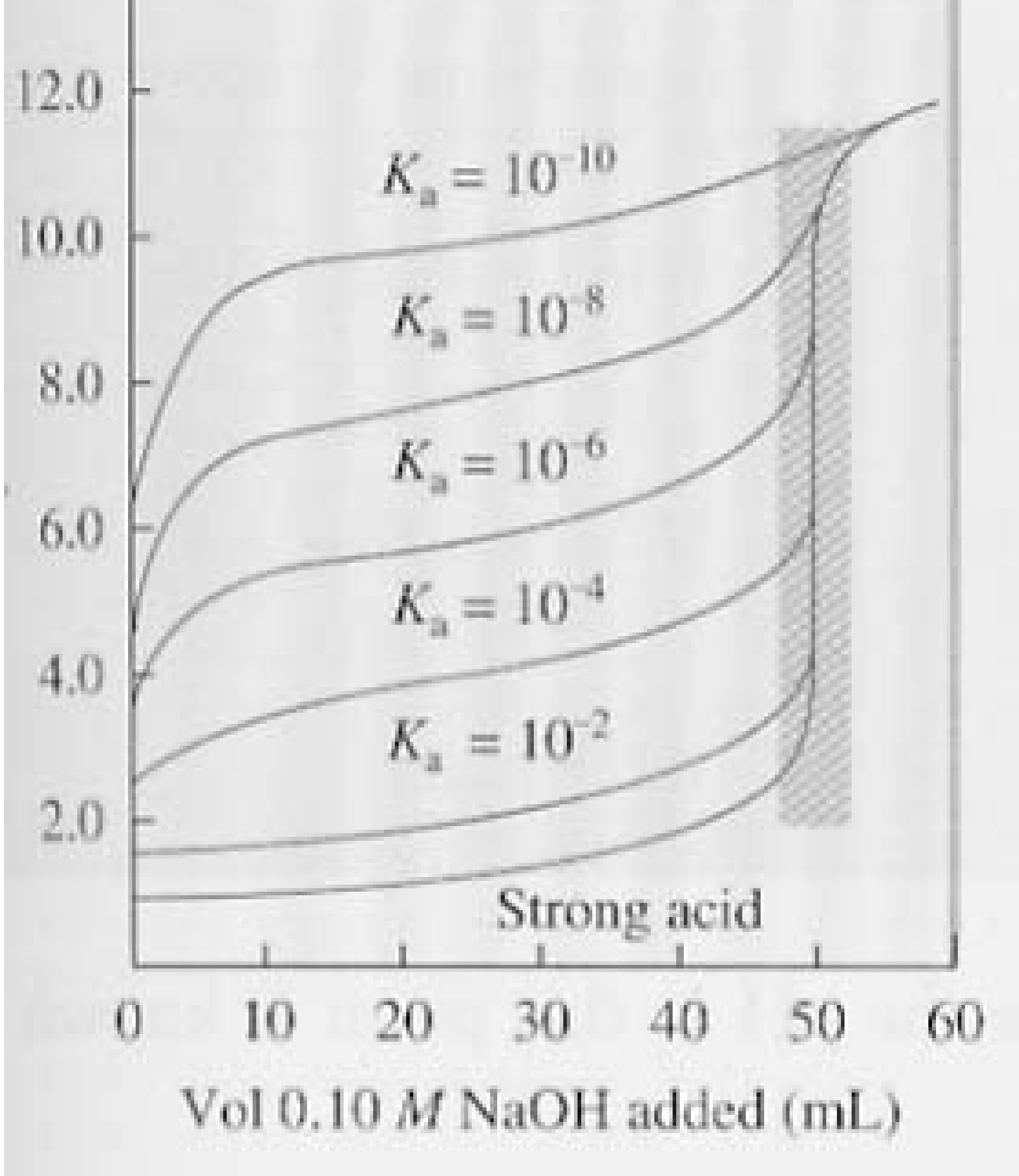
200.00 mL 0.001 M NaOH is added, $[OH^-] = 0.100/300 = 3.33 \times 10^{-4}$ M, pH = 10.52

100 mL 0.001M HOAc is titrated with 0.001 M NaOH



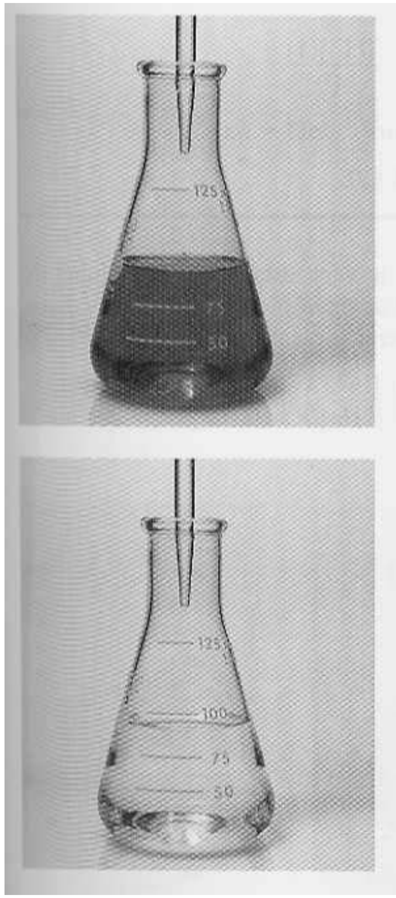
緩衝溶液抵抗稀釋引起
pH值的改變優於強酸

Titration curves for the acids of different acid strength

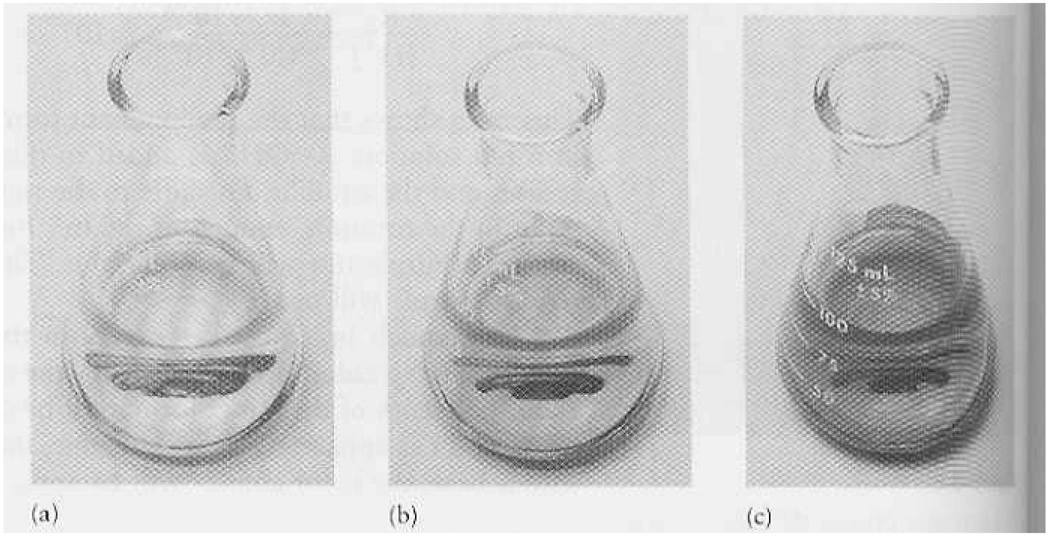


Acid-Base Indicator 酸鹼指示劑

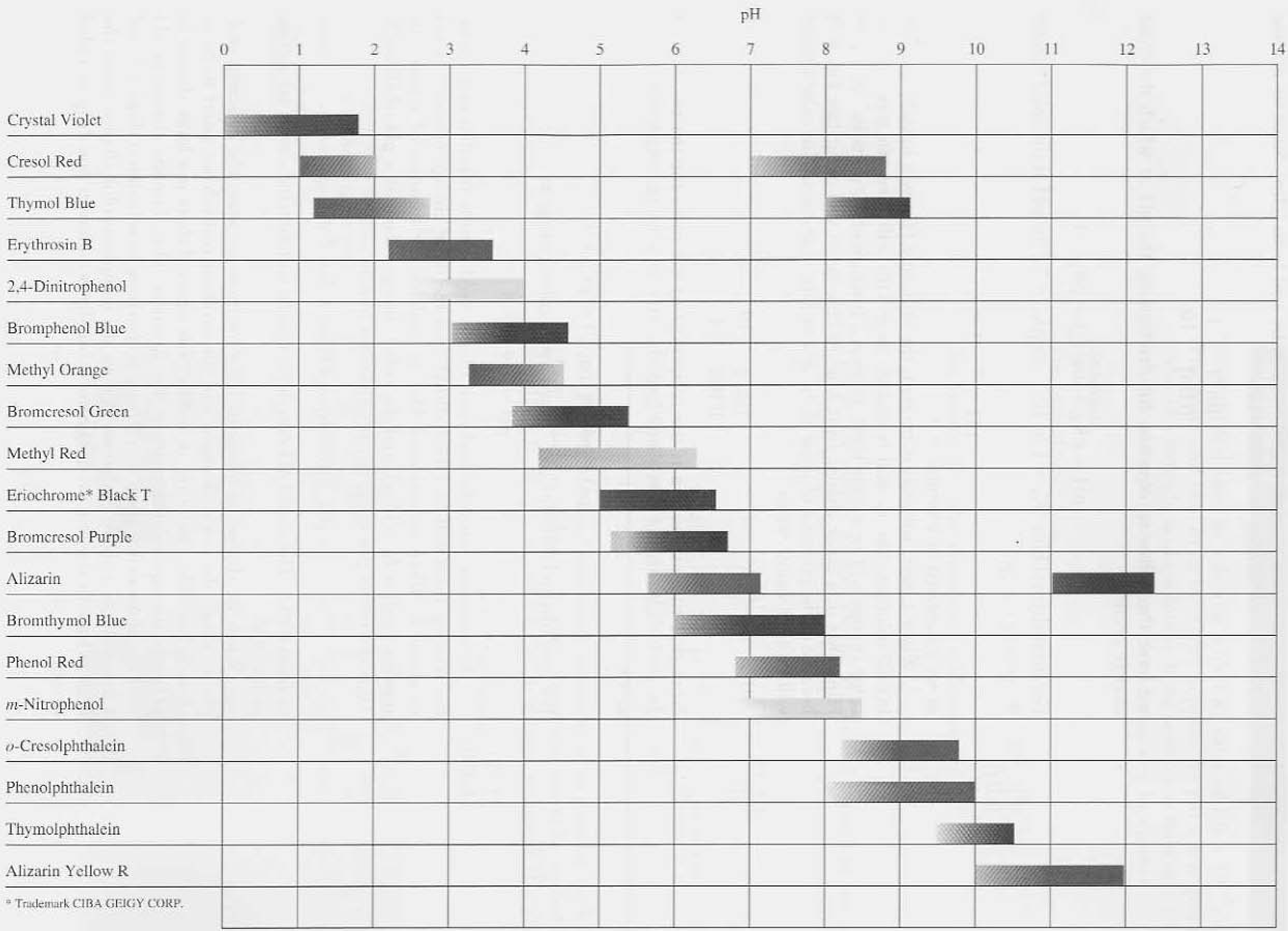
- *酸鹼指示劑是弱酸性或弱鹼性的物質，其酸式與鹼式可以顯出不同的顏色*



bromothymol blue 溴瑞香草藍



phenophthalein 酚酞



The pH ranges shown are approximate. Specific transition ranges depend on the indicator solvent chosen.

Figure 8.8

Why does an indicator work? 酸鹼指示劑原理

$$HIn \rightleftharpoons H^+ + In^-$$

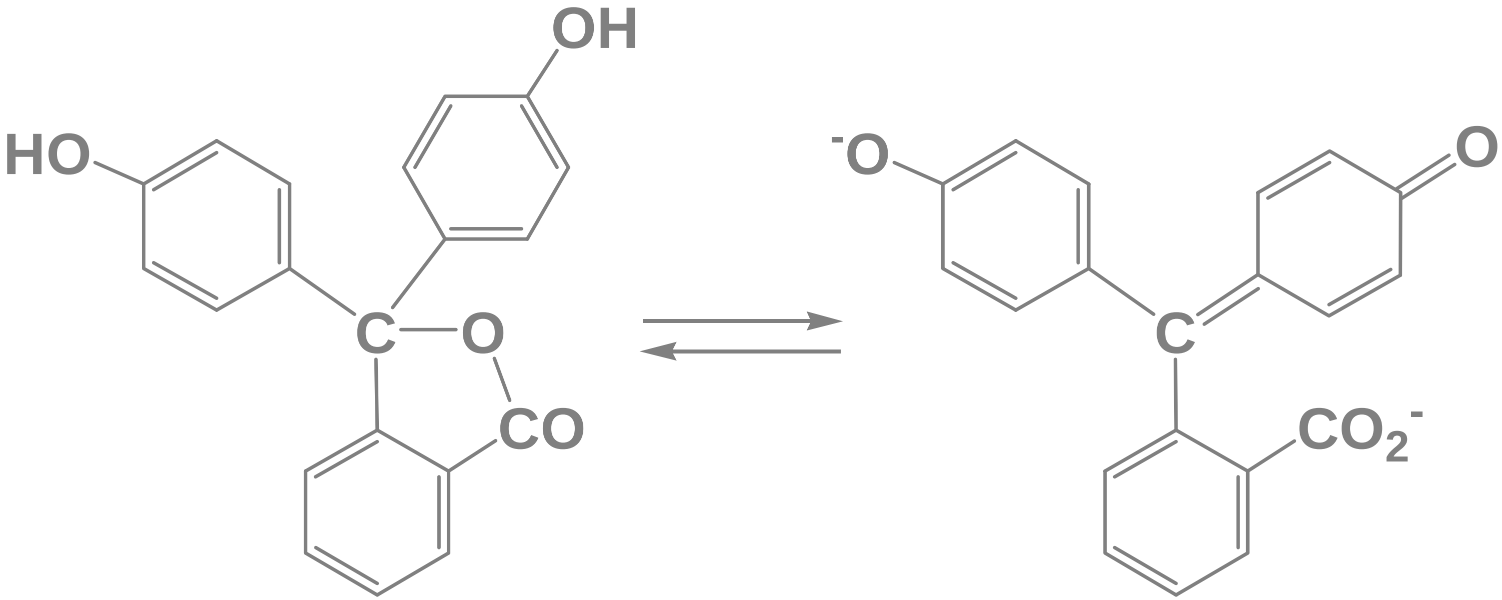
$$pH = pK_{HIn} + log([In]/[HIn])$$

$$[In]/[HIn] = 10, pK_{HIn} = pH + 1$$

$$[In]/[HIn] = 0.1, pK_{HIn} = pH - 1$$

$$0.1 \le [In]/[HIn] \le 10 \quad ，pK_{HIn} = pH(eq.\ pt.) \pm 1$$

HIn 的 pK_{HIn} 值在滴定當量點±1的範圍內，其鹼式與酸式的量可相差約十倍，有明顯的顏色差異，就是合適的指示劑



acid form ***base form***

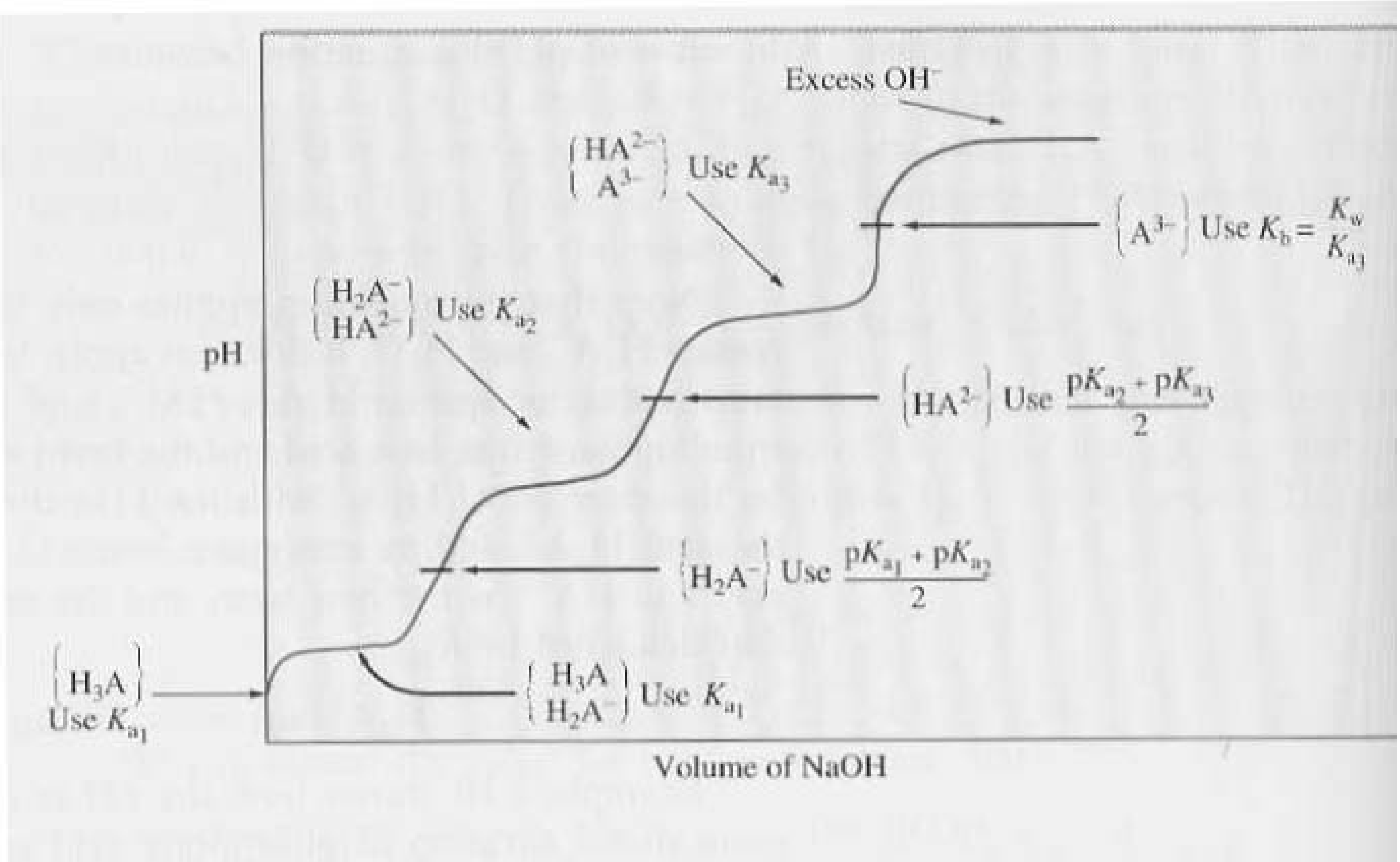
phenolphthalein

Titratiin a polyprotic acid 強鹼滴定多質子酸

Table 8.4 A Summary of Various Points in the Titration of a Triprotic Acid

Point in the Titration	Major Species Present	Equilibrium Expression Used to Obtain the pH
No base added	H_3A, H_2O	$K_{a_1} = \frac{[H^+][H_2A^-]}{[H_3A]}$
Base added		
Before the first equivalence point	H_3A, H_2A^-, H_2O	$K_{a_1} = \frac{[H^+][H_2A^-]}{[H_3A]}$
At the first equivalence point	H_2A^-, H_2O	See the following discussion
Between the first and second equivalence points	H_2A^-, HA^{2-}, H_2O	$K_{a_2} = \frac{[H^+][HA^{2-}]}{[H_2A^-]}$
At the second equivalence point	HA^{2-}, H_2O	See the following discussion
Between the second and third equivalence points	HA^{2-}, A^{3-}, H_2O	$K_{a_3} = \frac{[H^+][A^{3-}]}{[HA^{2-}]}$
At the third equivalence point	A^{3-}, H_2O	$K_b = \frac{K_w}{K_{a_3}} = \frac{[HA^{2-}][OH^-]}{[A^{3-}]}$
Beyond the third equivalence point	A^{3-}, OH^-, H_2O	pH determined by excess OH

Titratiin a polyprotic acid　強鹼滴定多質子酸



Solubility Equilibria　溶解度平衡

- ***As acid-base chemistry, solubility is governed by the chemical equilibria***

  物質的溶解度遵守化學平衡定則

- ***When an ionic solid dissolves in water, the solubility product constant is defined according to the law of mass action.***

  離子固體的溶解度積常數是溶液中離子濃度冪次的乘積

$$CaF_2 \qquad Ca^{2+}_{(aq)} + 2F^{-}_{(aq)} \quad K_{sp} = [Ca^{2+}][F^{-}]^2$$

- ***Solubility is the amount (concentration) of a substance that dissolves in a given volume of solvent at a given temparature.***

  物質的溶解度是其溶解在定量溶液中的量，通常以 g/100 g soln’或體積莫耳濃度表示

- ***Solubility of ionic solids is influenced by common ion effect, pH value, temparature, etc.***

  電解質的溶解度會受同離子效應、pH值、溫度等影響

Relative Solubilities 相對溶解度

Example: Compare the solubilities for CuS, Ag_2S, Bi_2S_3.

	K_{sp} (25 ^oC)	solubility (M)
$CaSO_4$	6.1×10^{-5}	7.2×10^{-3}
CuI	5.0×10^{-12}	2.2×10^{-6}
AgI	1.5×10^{-16}	1.7×10^{-8}
CuS	8.5×10^{-45}	9.2×10^{-23}
Ag_2S	1.6×10^{-49}	3.4×10^{-17}
Bi_2S_3	1.1×10^{-73}	1.0×10^{-15}

AgI → Ag^+ + I^- $K_{sp} = [Ag^+][I^-]$,
the solubility of AgI is x, $(x)^2 = 1.5 \times 10^{-16}$, $x = 1.2 \times 10^{-8}$ M

Bi_2S_3 → 2 Bi^{3+} + 3 S^{2-} $K_{sp} = [Bi^{3+}]^2[S^{2-}]^3$
the solubility of Bi_2S_3 is x, $(2x)^2(3x)^3 = 1.1 \times 10^{-73}$, $x = 1.0 \times 10^{-15}$ M

Common Ion Effect 共同離子效應

Example: Ag_2CrO_4 in a 0.100 M $AgNO_3$, $[Ag^+]$ = ? $[CrO_4^{2-}]$ = ?

$Ag_2CrO_4 \rightarrow 2\ Ag^+ + CrO_4^{2-}$ $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$,

the solubility of Ag_2CrO_4 is x, $(2x)^2(x) = 9.0\text{x}10^{-12}$, $x = 1.3\text{x}10^{-4}$

$[Ag^+] = 2x = 2.6\text{x}10^{-4}\ M$

$[CrO_4^{2-}] = x = 1.3\text{x}10^{-4}\ M$

Considering the common ion effect,

the solubility of Ag_2CrO_4 is x

$[Ag^+] = 2x + 0.100$, $[CrO_4^{2-}] = x$,

$(2x + 0.100)^2(x) = 9.0\text{x}10^{-12}$, $x << 0.100$, $x = 9.0\text{x}10^{-10}\ M$

$[Ag^+] = 0.100\ M$

$[CrO_4^{2-}] = x = 9.0\text{x}10^{-10}\ M$