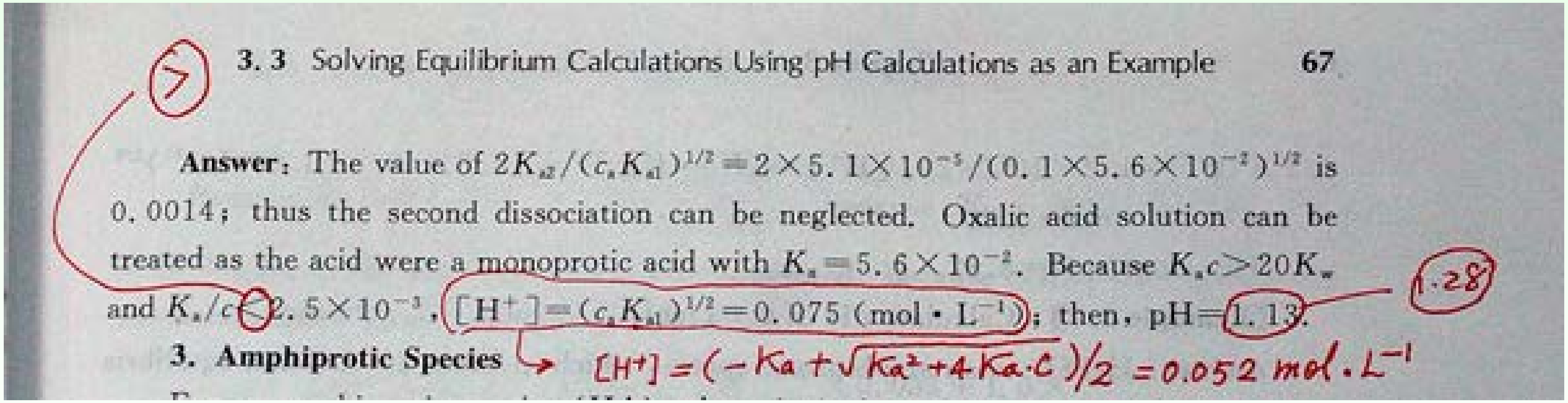
Corrections

- P66, First equation: 1.88→$10^{-5.12}$
- pH=pKa-pOH=14.00-5.12=8.88
- P67



3.3 Solving Equilibrium Calculations Using pH Calculations as an Example 67

Answer: The value of $2K_{a2}/(c_aK_{a1})^{1/2}=2\times5.1\times10^{-5}/(0.1\times5.6\times10^{-2})^{1/2}$ is 0.0014; thus the second dissociation can be neglected. Oxalic acid solution can be treated as the acid were a monoprotic acid with $K_a=5.6\times10^{-2}$. Because $K_ac>20K_w$ and $K_a/c<2.5\times10^{-3}$, $[H^+]=(c_aK_{a1})^{1/2}=0.075\ (mol\cdot L^{-1})$; then, pH=1.13.

>

1.28

$[H^+]=(-Ka+\sqrt{Ka^2+4Ka\cdot c})/2=0.052\ mol\cdot L^{-1}$

3. Amphiprotic Species

- P76
- 3.5(5) 0.01 mol•L^{-1} →0.010 mol•L^{-1}

Chapter III & IV
Acid-base Equilibrium and Acid-base Titration

- Chemical equilibria
- Acid-base equilibrium
- Acid-base titration

Volumetric Titration 容量滴定

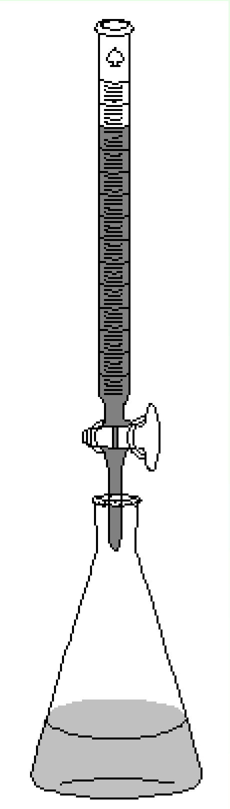
- **Theoretical Basis理论基础:**
  - **Aqueous solutions and chemical equilibria溶液与平衡**
  - **Effect of electrolytes on chemical equilibria 电解质对化学平衡的影响**
  - **Solving equilibrium problems for complex systems**
    - **Systematic Methods 系统法**
    - **Approximation近似法**
- **Volumetric Titration容量滴定**

—Neutralization酸碱中和 — Complexation络合

—Redox氧化还原 — Precipitation 沉淀

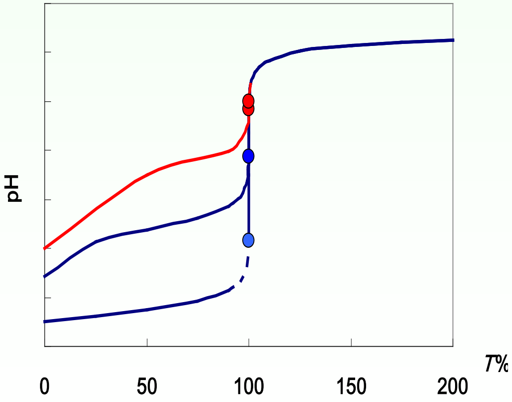
Key to Volumetric titration 容量滴定

-The Route to the End Point



- How to indicate end point (ep)如何指示终点
- How to select an indicator which changes color near the stoichiometric point (sp, 计量点）如何选择指示剂
- ep ≠ sp, how big is the error滴定误差

Find the point close to sp!!!!!!



Chemical Equilibria 化学平衡

- Equilibrium constant expressions平衡常数表达式
- Types of equilibria encountered in analytical chemistry
  - Dissociation of water: Ion-product constant

    水的解离：离子积常数
  - Dissociation of a weak acid/base: Dissociation constant

    弱酸碱解离：解离常数
  - Formation of a complex ion: Formation constant

    络合物离子的形成：形成常数
  - Oxidation-Reduction Constant 氧化-还原常数
  - Heterogeneous equilibrium of a slightly soluble substance in water: Solubility Product

    微溶性物质的异相平衡：溶度积

Acids and Bases (Brønsted-Lowry Definition)

- **An acid donates protons; a base accepts protons**
- **An acid donates protons only in the presence of proton acceptor (a base)-a conjugate base. *vise versa*反之亦然.**

  A substance acts as an acid only in the presence of a base. *vice versa*.
- **Many solvents are proton donors or proton acceptors and can thus induce basic or acidic behavior in solutes dissolved.**

protons质子; conjugate base共轭碱;

solvent溶剂; solute溶质

Acid-base Equilibrium酸碱平衡

Acid $\rightleftharpoons$ Conjugate Base 共轭碱 + Proton质子

Proton donor Proton acceptor Proton

$$HAc \rightleftharpoons Ac^- + H^+$$

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$

$$H_6Y^{2+} \rightleftharpoons H_5Y^+ + H^+$$

In General: $HA \rightleftharpoons A^- + H^+$

Amphiprotic Species两性物种

- **Amphiprotic**：Species that possess acidic & basic properties

  两性物：同时具有酸碱性的物种

- **Zwitterion**: bears a positive & a negative charge

  两极离子：同时拥有正负电荷，e.g. amino acids 如氨基酸

- **Amphiprotic solvents**：behave as acids in the presence of basic solutes and bases in the presence of acidic solutes

  两性溶剂：在碱性溶质存在下表现为酸，在酸性溶质存在下表现为碱

  H_2O：an amphiprotic solvent溶剂

Autoprotolysis质子自递

Amphiprotic solvents undergo self-ionization 自离子化(autoprotolysis) to form a pair of ionic species

$H_2O + H_2O \leftrightharpoons H_3O^+ + OH^-$ (25℃)

$$K_w = a(H^+) \cdot a(OH^-) = 1.00 \times 10^{-14}$$

Ion - product Constant离子积常数

Why $[H_2O]$ not in K_w? Skoog Book p237

$\mathbf{CH_3OH \leftrightharpoons CH_3OH_2^+ + CH_3O^-}$

$\mathbf{HCOOH \leftrightharpoons HCOOH_2^+ \; HCOO^-}$

$\mathbf{NH_3 \leftrightharpoons NH_4^+ + NH_2^-}$

Dissociation of a Weak Acid/Base
弱酸/碱的解离

$HA + H_2O \leftrightharpoons A^- + H_3O^+$

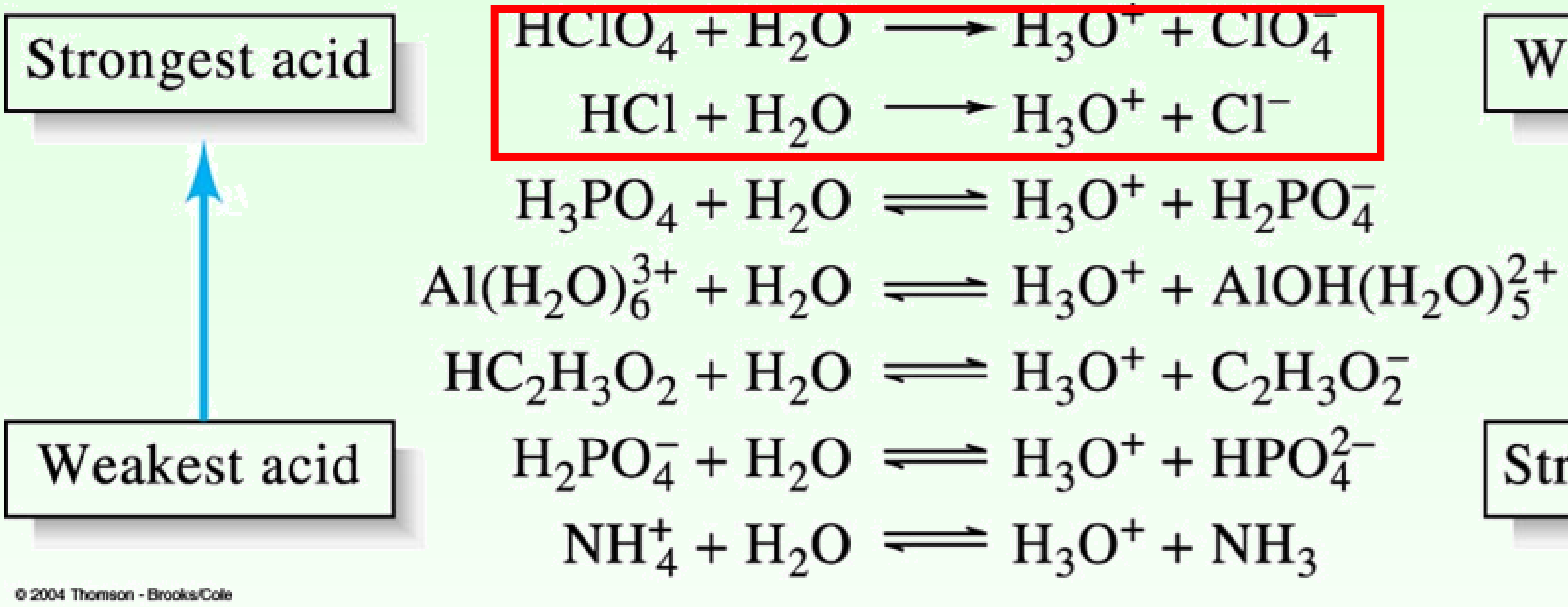
$$K_a = \frac{a(H^+) \cdot a(A^-)}{a(HA)}$$

$A^- + H_2O \leftrightharpoons HA + OH^-$

$$K_b = \frac{a(HA) \cdot a(OH^-)}{a(A^-)}$$

$$pK_a + pK_b = pK_w = 14.00\ (25°C)$$

Strength of Acids and Bases酸碱的强度



$$HClO_4 + H_2O \longrightarrow H_3O^+ + ClO_4^-$$
$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$
$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$
$$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + AlOH(H_2O)_5^{2+}$$
$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$
$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$$
$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

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Perchloric acid 高氯酸 *vs*. hydrochloric acid盐酸

- **Differentiating solvent区分溶剂: glacial acetic acid**
- **Leveling solvent拉平溶剂: H_2O**

Dissociation of Polyprotic Acids

多元酸的解离

$$H_3A \underset{K_{b_3}}{\overset{K_{a_1}}{\rightleftharpoons}} H_2A^- \underset{K_{b_2}}{\overset{K_{a_2}}{\rightleftharpoons}} HA^{2-} \underset{K_{b_1}}{\overset{K_{a_3}}{\rightleftharpoons}} A^{3-}$$

$$\boxed{\begin{aligned} pK_{b_1} &= 14.00 - pK_{a_3} \\ pK_{b_2} &= 14.00 - pK_{a_2} \\ pK_{b_3} &= 14.00 - pK_{a_1} \end{aligned}}$$

Neutralization (Titration) Reaction
中和（滴定）反应

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

$$K_t = \frac{1}{K_w} = 10^{14.00}$$

$H^+ + A^- \rightleftharpoons HA$

$$K_t = \frac{1}{K_a} \left(\frac{K_b}{K_w}\right)$$

$OH^- + HA \rightleftharpoons H_2O + A^-$

$$K_t = \frac{1}{K_b} \left(\frac{K_a}{K_w}\right)$$

***K*$_t$—Titration Constant滴定常数**

The Effect of Electrolytes on Chemical Equilibria
电解质对化学平衡的影响

$$a = \gamma[\mathrm{X}]$$

a: activity 活度
γ: activity coefficient活度系数

1. $\gamma \rightarrow 1$, $a \rightarrow [\mathrm{X}]$ and $K' \rightarrow K$
2. For uncharged molecules: $\gamma \approx 1$, then $a \rightarrow [\mathrm{X}]$
3. For solvent: $a=1$

Debye-Hückel Equation德拜- 休克尔方程

$$\boxed{-\lg \gamma_i = \frac{0.509 Z_i^2 \sqrt{I}}{1 + Ba\sqrt{I}} (I < 0.1)}$$

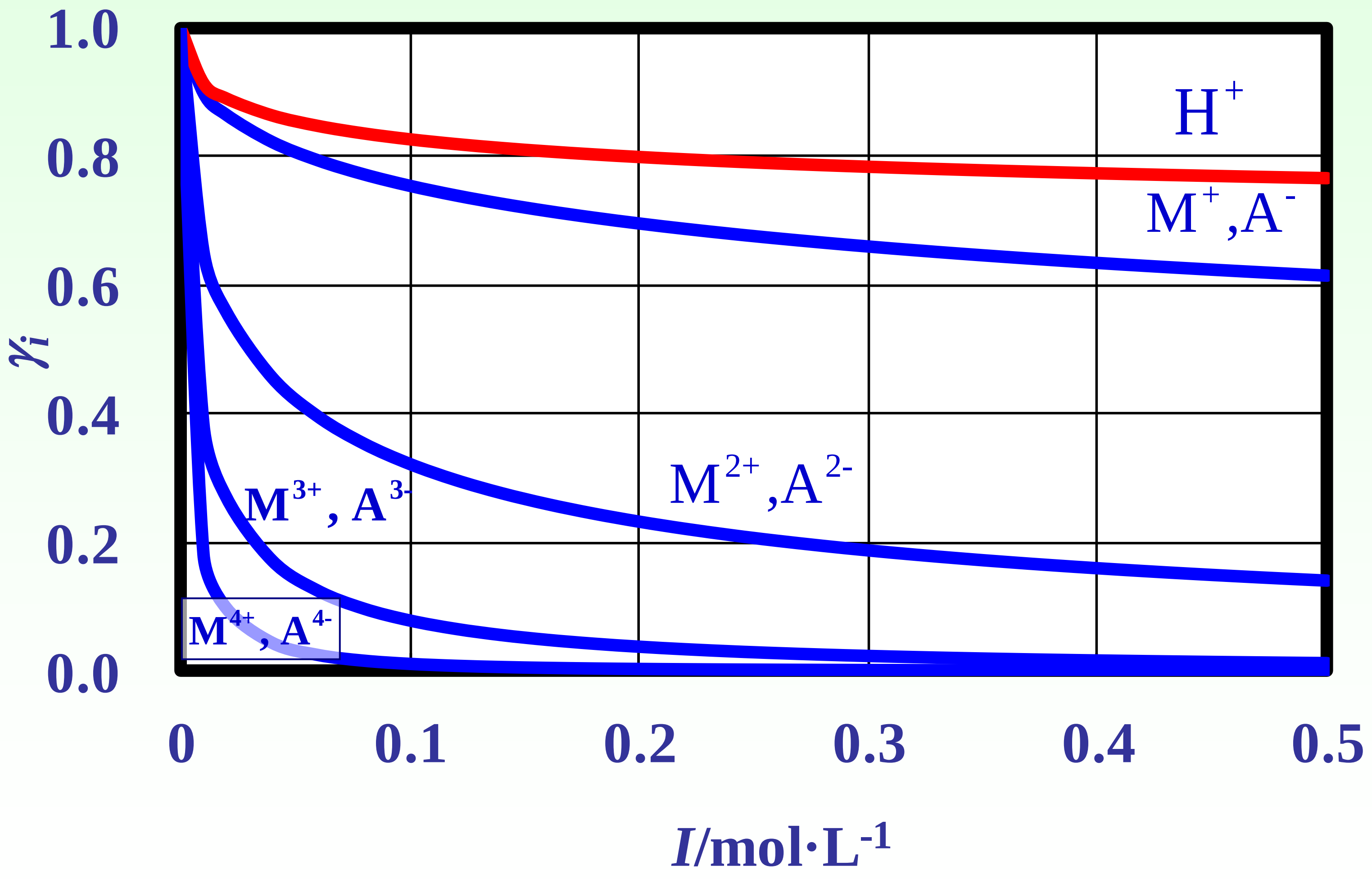
Constant: *B*=3.28 (25°C),与温度、介电常数有关

***a*: effective diameter of the hydrated ion in nanometers 水合离子有效直径（单位：nm)**

Properties of γ:

- **As *I*→0, γ→1;for uncharged molecules: γ≈1**
- **For given *I*, the γ of ions of the same charges are approximately equal.**
- **Set *I*, *Charge* ↗, γ ↘**
- **Set Charge, *I* ↗, γ↘**

Effect of Ionic Strength on Activity Coefficients
离子强度对活度的影响



The Effect of Ionic Charges on Equilibria

- The effect of added electrolyte on equilibria is **independent** of the **chemical nature of the electrolyte** but **depends on** a property of the solution called the **ionic strength (*I*)**

电解质对平衡的影响不依赖于电解质本身的性质，而是**依赖于**溶液**离子强度**

- Specifically, in the solution with *I* of 0.1 mol/L or less, the electrolyte effects is independent of the kind of ions and dependent only on the *I*.

$$I(\mu)=\tfrac{1}{2}([A]Z_A^2+[B]Z_B^2+[C]Z_c^2+\cdots)$$

A, B, and C: Ions in solution

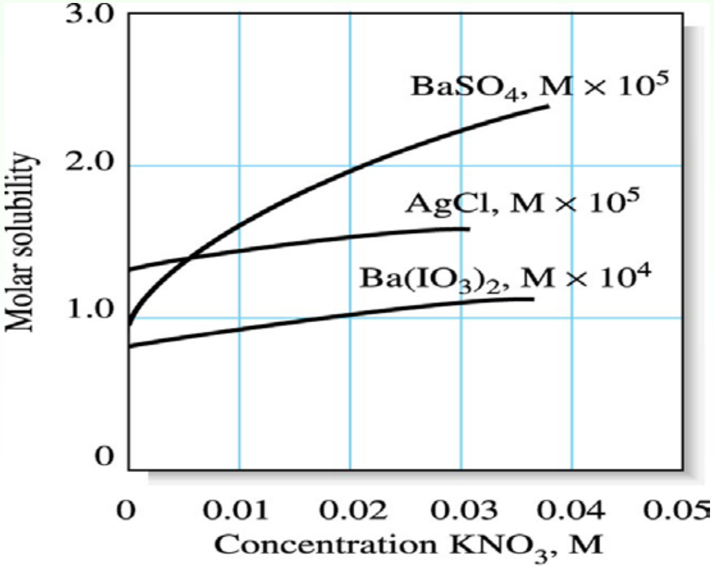
[A], [B], and [C]: Concentrations

Z_A, Z_B, and Z_c: Charges

Effect of Charge电荷 on Ionic Strength离子强度

Type of Electrolyte电解质	Example	Ionic Strength
1:1	NaCl	c
1:2	$Ba(NO_3)_2$, Na_2SO_4	$3c$
1:3	$Al(NO_3)_3$, Na_3PO_4	$6c$
2:2	$MgSO_4$	$4c$

Effect of Concentration →



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Acid/Base Dissociation Constants
in K_a活度常数, K_a^c浓度常数, and K_a^M混合常数

$$\mathrm{HAc} \leftrightharpoons \mathrm{H^+} + \mathrm{Ac^-}$$

$$K_a = \frac{a(\mathrm{H^+})\cdot a(\mathrm{Ac^-})}{a(\mathrm{HAc})}, \mathrm{p}K_a = 4.76$$

$$K_a^c = \frac{[\mathrm{H^+}][\mathrm{Ac^-}]}{[\mathrm{HAc}]} = \frac{a(\mathrm{H^+})\cdot a(\mathrm{Ac^-})}{a(\mathrm{HAc})} \cdot \frac{\gamma(\mathrm{HAc})}{\gamma(\mathrm{H^+})\cdot\gamma(\mathrm{Ac^-})}$$

$$= \frac{K_a}{\gamma(\mathrm{H^+})\cdot\gamma(\mathrm{Ac^-})}$$

$$(I = 0.1,\ \gamma(\mathrm{H^+}) = 0.826,\ \ \gamma(\mathrm{Ac^-}) = 0.770)$$

$$\mathrm{p}K_a^c = 4.56$$

$$K_a^{M} = \frac{a(H^+)[Ac^-]}{[HAc]} = \frac{a(H^+)\cdot a(Ac^-)}{a(HAc)} \cdot \frac{\gamma(HAc)}{\gamma(Ac^-)} = \frac{K_a}{\gamma(Ac^-)}$$

$$pK_a^{M} = 4.65 \; (I = 0.1)$$

$$HAc: K_a^{C} > K_a^{M} > K_a$$

K_a : Thermodynamic Constant (只与 t 有关)

K_a^{C} : Concentration Constant (与 t, I 有关)

K_a^{M}: Mixed Constant (与 t, I 有关)

Solving Equilibrium Problems for Complex Systems
复杂体系中的平衡问题处理

- Mass Balance Equations质量平衡式
- Charge Balance Equation电荷平衡式
- Proton Condition Equations for acid/base solution质子条件式

- **Mass Balance物料平衡:**

  Sum of equilibrium concentration of the species in all forms equals the <u>analytical concentration</u> of the solutes.

  各物种的平衡浓度之和等于其分析浓度.

- **Charge Balance电荷平衡:(电中性原则)**

  Sum of he molar concentration of positive charge in an electrolyte solution always equals the sum of molar concentration of negative charge.

  溶液中正离子所带正电荷总数等于负离子所带负电荷总数.

- **Proton Condition质子条件:**

  In an acid-base reaction, the number of protons that an acid donated equals the number of proton that a base accepted.

  溶液中酸失去质子数目等于碱得到质子数目.

Writing the PCE

Step 1: Choose reference species/zero levels零水准

Dominant species, which is also involved in delivery of protons and includes solvent, e.g. H_2O is always the one.

选零水准(大量存在, 参与质子转移的物质包括溶剂，如水).

Step 2: Identify proton acceptors and donors

Forms of reference species accepted protons on the left of the equation, and those donated protons on the right.

得质子后的形式写在等式的左边,

失质子后的形式写在等式的右边.

Step 3: Balance the equation

-Number of Reaction Unit Conservation Principles

有关浓度项前乘上得失质子数.

期中考试安排

- 时间：2015年4月15日（周三, 8:00-9:50）
- 地点：二教411
- 考试形式：单选、填空、计算
- 请做好准备：题目多、计算量大 有效数字
  - 复习、准时、计算器
  - 答题时要有步骤、卷面要整洁
- 答疑时间：
  - 本周五2:00-430 PM
  - 4月10日（周五）、4月11日（周六）、4月12日（周日）2:00-4:30 PM

Example 2: $Na_2NH_4PO_4$ (c mol·L^{-1})

MBE: $2c = [Na^+]$ $\quad c = [NH_4^+] + [NH_3]$

$c = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]$

CBE: $[Na^+] + [NH_4^+] + [H^+]$

$= [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$

PCE: $[H^+] + [HPO_4^{2-}] + 2[H_2PO_4^-] + 3[H_3PO_4]$

$= [OH^-] + [NH_3]$

Relative Equilibrium Concentration-Fraction, *x*

弱酸(碱)型体摩尔分数及分布

HA

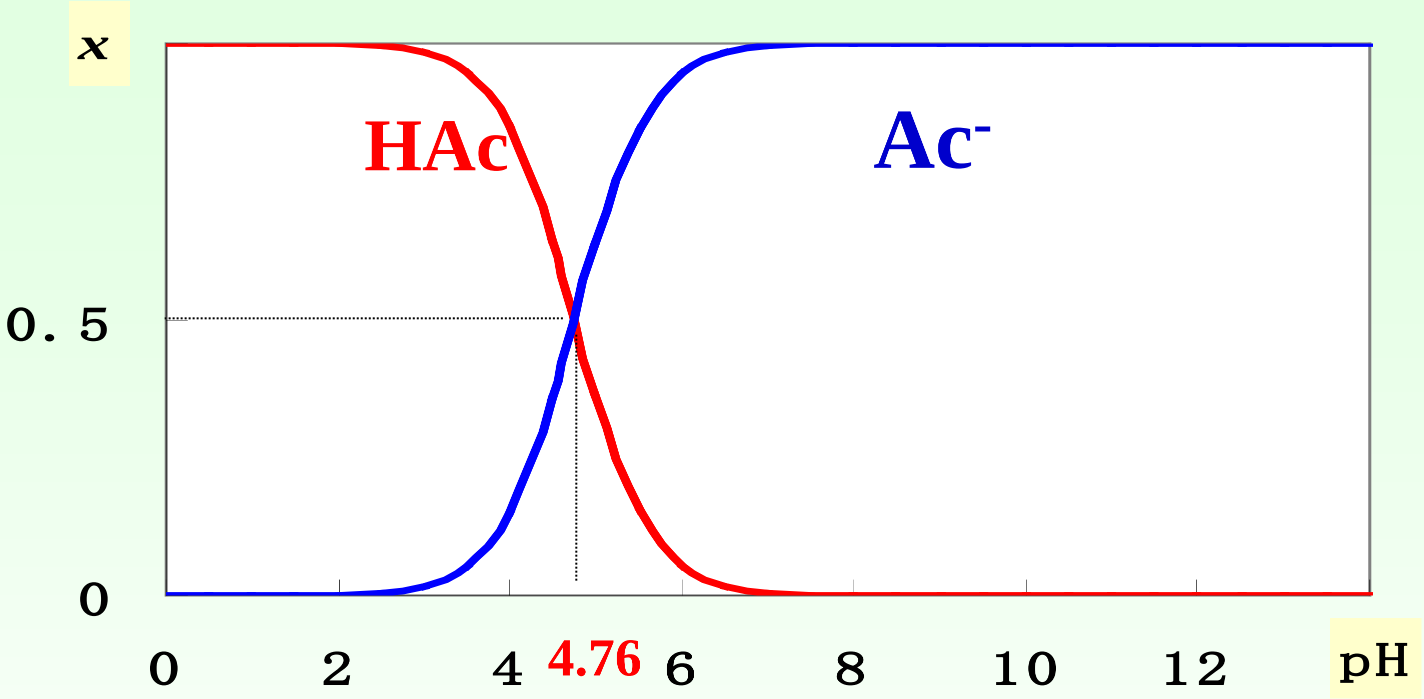
$$x(\mathrm{HA}) = \frac{[\mathrm{HA}]}{c} = \frac{[\mathrm{HA}]}{[\mathrm{HA}]+[\mathrm{A}^-]} = \frac{[\mathrm{H}^+]}{[\mathrm{H}^+]+K_\mathrm{a}}$$

$$x(\mathrm{A}^-) = \frac{[\mathrm{A}^-]}{c} = \frac{[\mathrm{A}^-]}{[\mathrm{HA}]+[\mathrm{A}^-]} = \frac{K_\mathrm{a}}{[\mathrm{H}^+]+K_\mathrm{a}}$$

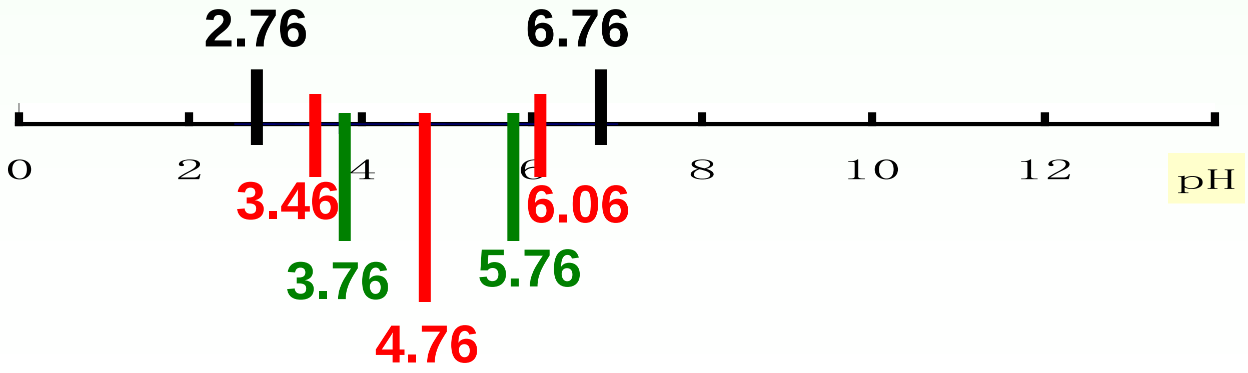
$$x(\mathrm{HA}) + x(\mathrm{A}) = 1$$

$$[\mathrm{HA}] = c \cdot x(\mathrm{HA}),\ [\mathrm{A}] = c \cdot x(\mathrm{A})$$

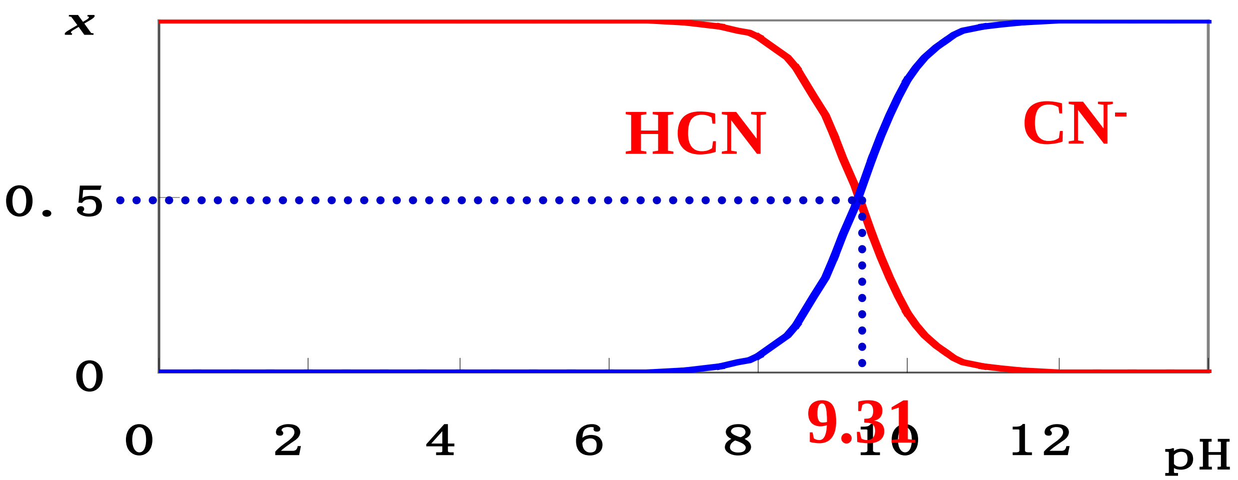
x-pH Plots for HAc (pK_a=4.76)

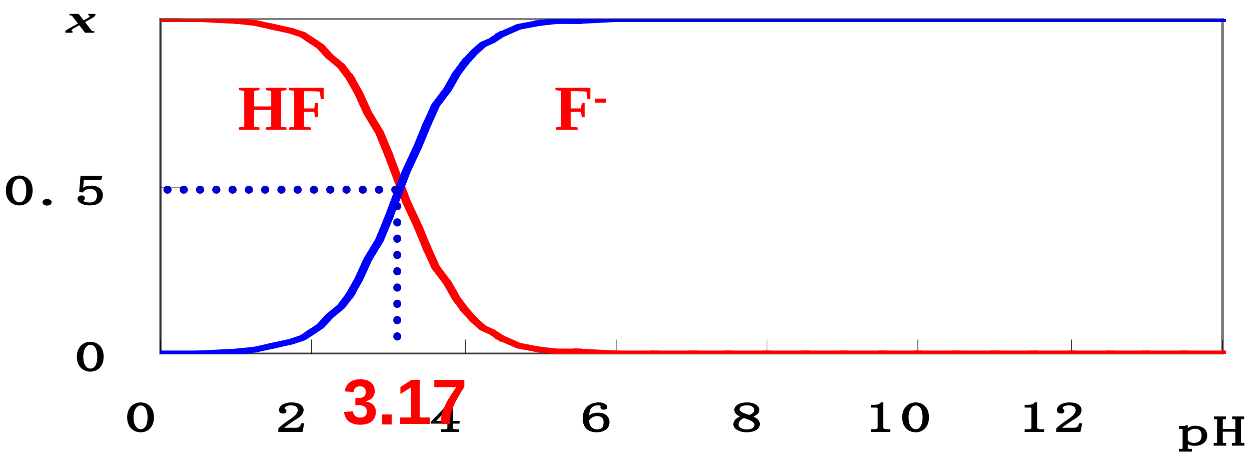


Predominant-area (Ladder) diagram优势区域图



x-pH Plots for HCN and HF





x for Diprotic Weak Acid
二元弱酸H_2A的摩尔分数

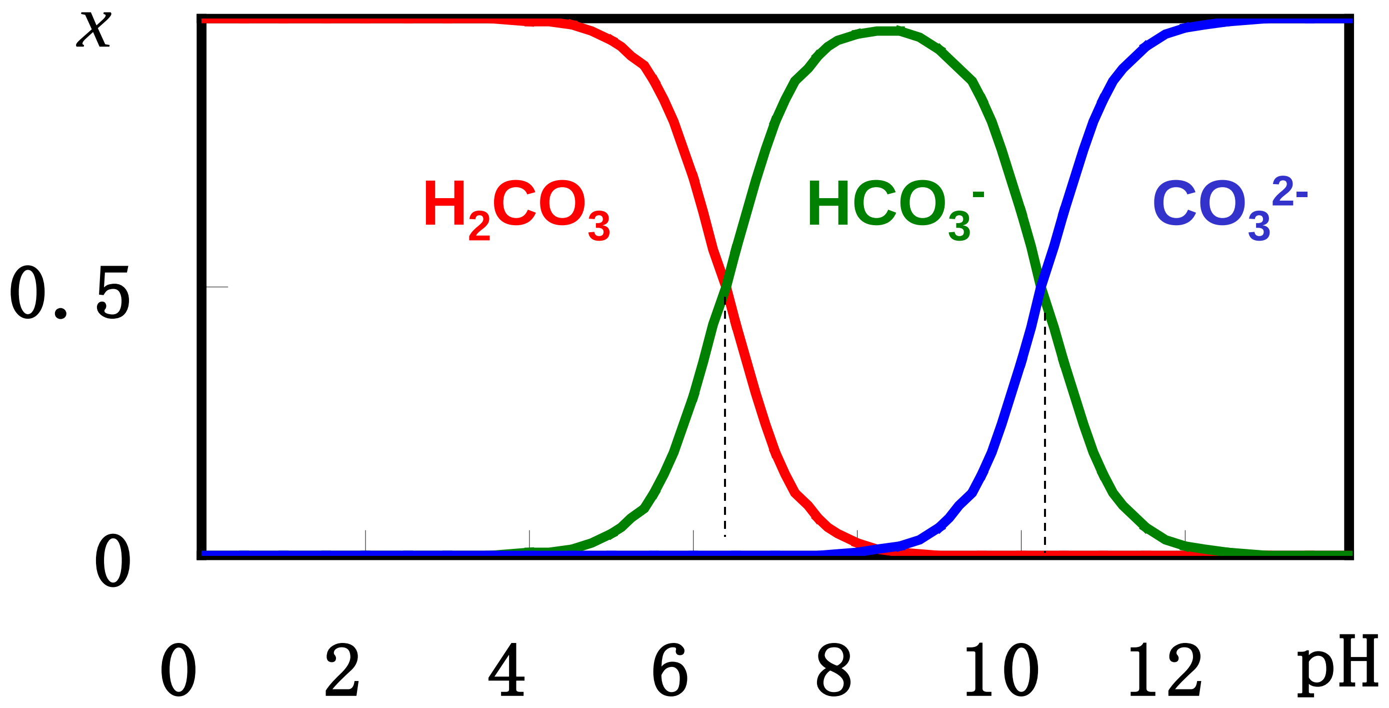
$$x_2 = \frac{\left[\mathrm{H}^+\right]^2}{\left[\mathrm{H}^+\right]^2 + K_{\mathrm{a}_1}\left[\mathrm{H}^+\right] + K_{\mathrm{a}_1}K_{\mathrm{a}_2}} = \frac{[\mathrm{H_2A}]}{[\mathrm{H_2A}]+[\mathrm{HA^-}]+[\mathrm{A^{2-}}]}$$

$$x_1 = \frac{K_{\mathrm{a}_1}\left[\mathrm{H}^+\right]}{\left[\mathrm{H}^+\right]^2 + K_{\mathrm{a}_1}\left[\mathrm{H}^+\right] + K_{\mathrm{a}_1}K_{\mathrm{a}_2}} = \frac{[\mathrm{HA^-}]}{[\mathrm{H_2A}]+[\mathrm{HA^-}]+[\mathrm{A^{2-}}]}$$

$$x_0 = \frac{K_{\mathrm{a}_1}K_{\mathrm{a}_2}}{\left[\mathrm{H}^+\right]^2 + K_{\mathrm{a}_1}\left[\mathrm{H}^+\right] + K_{\mathrm{a}_1}K_{\mathrm{a}_2}} = \frac{[\mathrm{A^{2-}}]}{[\mathrm{H_2A}]+[\mathrm{HA^-}]+[\mathrm{A^{2-}}]}$$

$$\boxed{\left[\mathrm{H_2A}\right] = c \cdot x_2; \quad \left[\mathrm{HA^-}\right] = c \cdot x_1; \quad \left[\mathrm{A^{2-}}\right] = c \cdot x_0}$$

x-pH for H_2CO_3

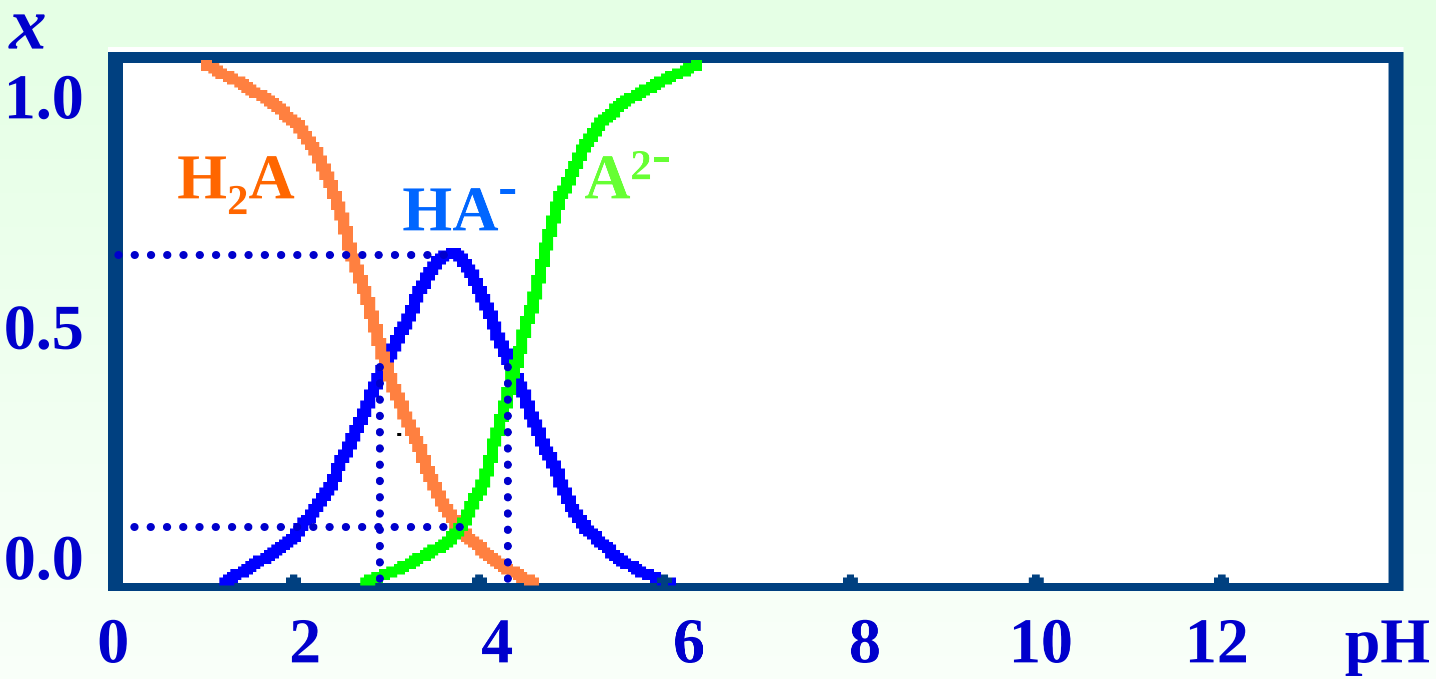


6.38 10.25

H_2CO_3 pK_{a_1} HCO_3^- pK_{a_2} CO_3^{2-}

$\triangle pK_a = 3.87$

x-pH for Tartaric Acid酒石酸(H_2A)



3.04 4.37

pK_{a_1} pK_{a_2}

H_2A HA^- A^{2-}

ΔpK_a 1.33

x for Triprotic acid (H_3A)

Denominator 分母 is composed of 4 terms

$\mathbf{M} = [H^+]^3+[H^+]^2K_{a_1}+[H^+]K_{a_1}K_{a_2}+K_{a_1}K_{a_2}K_{a_3}$

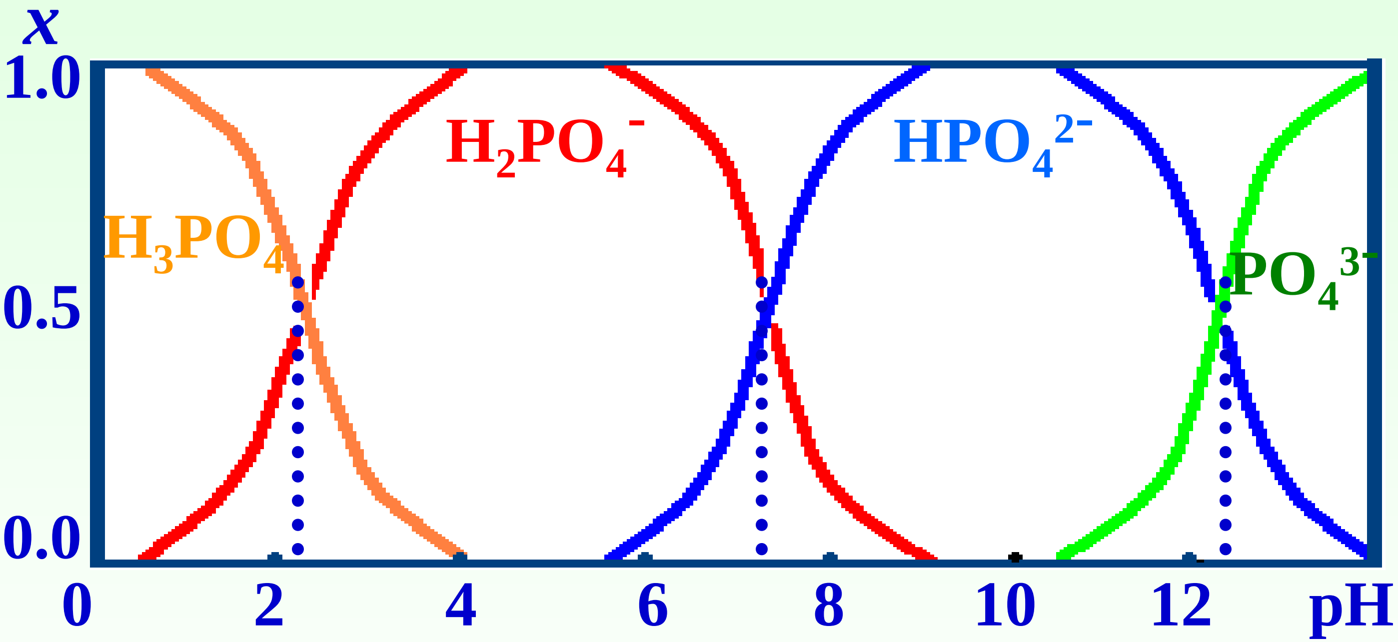
$x_3 = [H_3A]/c= [H^+]^3/\mathbf{M}$

$x_2 = [H_2A^-]/c= [H^+]^2K_{a_1}/\mathbf{M}$

$x_1 = [HA^{2-}]/c= [H^+]K_{a_1}K_{a_2}/\mathbf{M}$

$x_0 = [A^{3-}]/c=K_{a_1}K_{a_2}K_{a_3}/\mathbf{M}$

x-pH for Phosphoric acid 磷酸(H_3A)



2.16 ΔpK_a 5.05 7.21 ΔpK_a 5.11 12.32

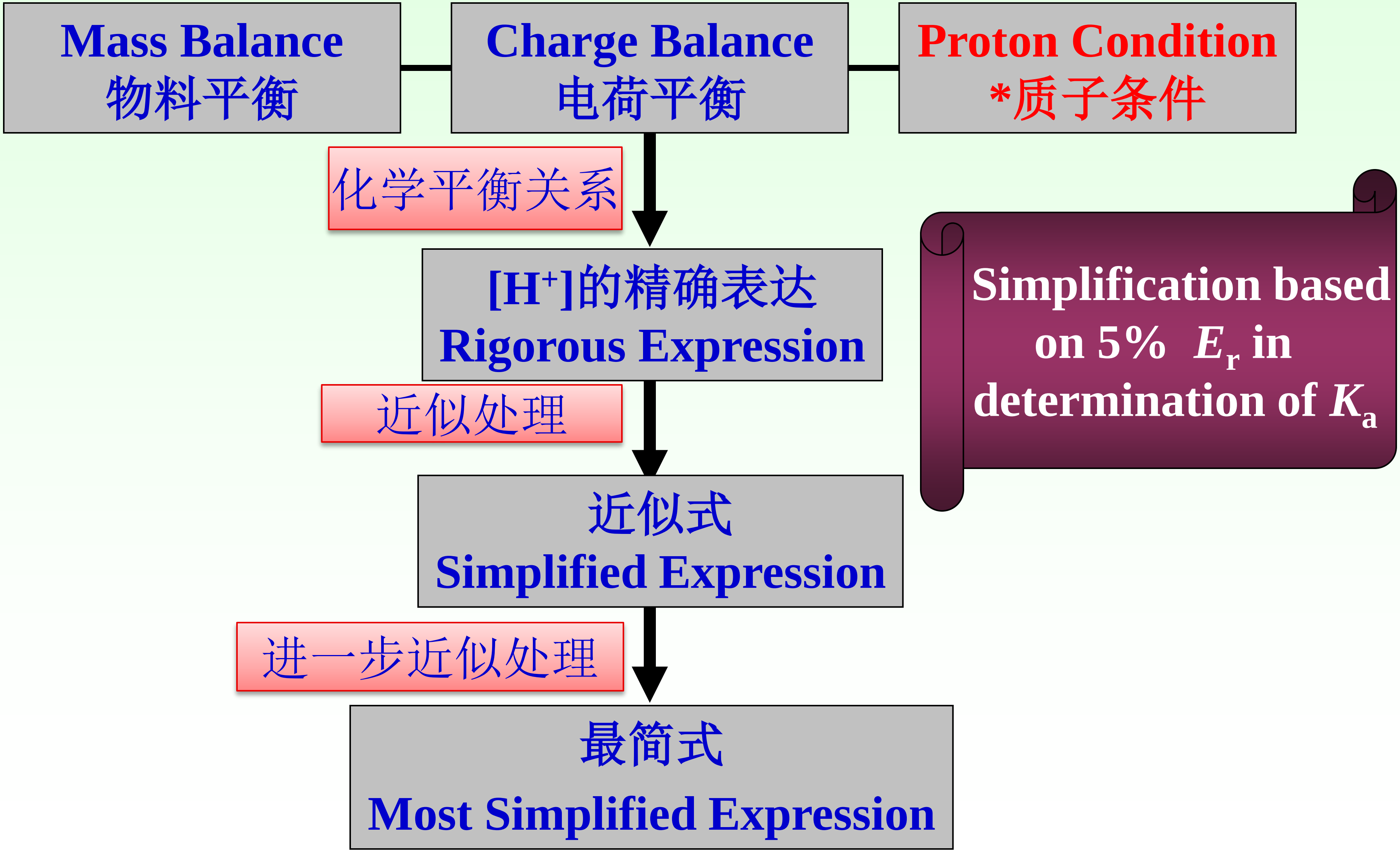
pK_{a_1} pK_{a_2} pK_{a_3}

H_3PO_4 $H_2PO_4^-$ HPO_4^{2-} PO_4^{3-}

Steps for Solving Equilibrium Problems

- **Step 1 list**
  - **all pertinent chemical reactions 所有有关化学反应**
  - **all equilibrium expressions所有平衡表达式**
  - **mass balance equations质量平衡式**
  - **charge balance equation电荷平衡式**
- **Step 2 count**
  - **the number of unknown concentrations未知浓度的个数**
  - **the number of equations developed must equal the number of unknowns. 方程的个数=未知数的个数**
- **Step 3 Calculation**
  - **Approach #1 Using a computer program.计算机**
  - **Approach #2 Making suitable approximations.近似简化**
- **Step 4 Check the validity of the approximation. 检验近似的合理性**

pH of a Acid/Base Solution



Mass Balance
物料平衡

Charge Balance
电荷平衡

Proton Condition
***质子条件**

化学平衡关系

[H$^+$]的精确表达
Rigorous Expression

近似处理

近似式
Simplified Expression

进一步近似处理

最简式
Most Simplified Expression

Simplification based on 5% E_r in determination of K_a

Paper Selection

1 **刘通，杨晶辉，周旭豪**
2
3 李佼峰，黄子川，马丽娜
4 周家宇 周俊良
5
6
7
8
9
10
11吴斌 薛一斌 张翔
12范围 胡亦旻
13徐霖 白英杰 张隽之
14范如本，林之
15黎俊岑，娄鸣鹤，全柏峄
16
17冯晟 刘逸芸 张清韵
18宋汝怿、罗翌阳、冯轩宇
19
20
21刘浩源和屈沛, 陈天阳 孙维维 张隽晔
22
23
24周小洲 陆作雨
25

Monoprotic Acid (HA,一元弱酸)

PCE: $[H^+] = [A^-] + [OH^-]$

Using Equilibrium $$[H^+] = \frac{K_a[HA]}{[H^+]} + \frac{K_w}{[H^+]}$$

Rigorous Expression精确式

$$[H^+] = \sqrt{K_a[HA] + K_w}$$

Substitute替代 $$[HA] = \frac{c_a[H^+]}{[H^+] + K_a}$$ **for [HA]**

$$[H^+]^3 + K_a[H^+]^2 - (K_a c_a + K_w)[H^+] - K_a K_w = 0$$

$$[\mathrm{H}^+] = \sqrt{K_\mathrm{a}[\mathrm{HA}] + K_\mathrm{w}}$$

When $K_\mathrm{a}c > 20K_\mathrm{w}(10^{-12.7})$, K_w is negligible可忽略

$[\mathrm{HA}] = c_\mathrm{a} - [\mathrm{A}^-] = c_\mathrm{a} - ([\mathrm{H}^+] - [\mathrm{OH}^-]) \approx c_\mathrm{a} - [\mathrm{H}^+]$

Simplified简化/近似式, $\boxed{[\mathrm{H}^+] = \sqrt{K_\mathrm{a}(c_\mathrm{a} - [\mathrm{H}^+])}}$

Rearrange to a quadratic equation变换成二次方程

$[\mathrm{H}^+]^2 + K_\mathrm{a}[\mathrm{H}^+] - c_\mathrm{a}K_\mathrm{a} = 0$

If $\alpha < 0.05$, i.e. $K_\mathrm{a}/c < 2.5\mathrm{x}10^{-3}$, then, $c_\mathrm{a} - [\mathrm{H}^+] \approx c_\mathrm{a}$

Finally simplified最简式, $\boxed{[\mathrm{H}^+] = \sqrt{K_\mathrm{a}c_\mathrm{a}}}$

Example 1: 0.20 mol·L^{-1} $Cl_2CHCOOH$ (pK_a=1.26)

$$K_a c = 10^{-1.26} \times 0.20 = 10^{-1.96} >> 20K_w$$

$$K_a / c = 10^{-1.26} / 0.20 = 10^{-0.56} > 2.5 \times 10^{-3}$$

$$[H^+] = \sqrt{K_a(c_a - [H^+])}$$

$$[H^+] = 10^{-1.09} \quad , \quad pH = 1.09$$

Using $[H^+] = \sqrt{K_a c_a}$ $[H^+] = 10^{-0.98}$, $E_r = 29\%$

Example2:

1.0×10^{-4} mol·L^{-1} HCN (pK_a= 9.31)

$$K_a c = 10^{-9.31}\times1.0\times10^{-4} = 10^{-13.31} < 20K_w$$

$$K_a/c = 10^{-9.31}/1.0\times10^{-4} = 10^{-5.31} < 2.5\times10^{-3}$$

$$[\mathrm{H}^+]=\sqrt{K_a c+K_w}=10^{-6.61}$$

If $[\mathrm{H}^+]=\sqrt{K_a c}=10^{-6.66}$, $E_r=11\%$

Monobase一元碱: A

PCE: $[H^+] + [HA] = [OH^-]$

$$[\mathrm{OH^-}] = \frac{K_b[\mathrm{A}]}{[\mathrm{OH^-}]} + \frac{K_w}{[\mathrm{OH^-}]}$$

Rigorous Expression精确式

$$[\mathrm{OH^-}] = \sqrt{K_b[\mathrm{A}] + K_w}$$

When $K_b c_b > 20K_w (10^{-12.7})$, K_w is negligible

$$[\mathrm{OH^-}] = \sqrt{K_b(c_b - [\mathrm{OH^-}])}$$

When $\alpha < 0.05$, i.e. $K_b/c_b < 2.5 \times 10^{-3}$,

$$[\mathrm{OH^-}] = \sqrt{K_b c_b}$$

Amphiprotic Species两性物(HA^-)

PCE: $[H_2A] + [H^+] = [A^{2-}] + [OH^-]$

Using Equilibrium

$$\frac{[H^+][HA^-]}{K_{a_1}} + [H^+] = \frac{K_{a_2}[HA^-]}{[H^+]} + \frac{K_w}{[H^+]}$$

Rigorous Expression

$$[H^+] = \sqrt{\frac{K_{a_2}[HA^-] + K_w}{1 + [HA^-]/K_{a_1}}} = \sqrt{\frac{K_{a_2}c(HA^-) + K_w}{1 + c(HA^-)/K_{a_1}}}$$

If $K_{a_1} >> K_{a_2}$(if $\alpha \leq 5\ \%$, $\Delta pK_a \geq 3.2$), then $[HA^-] \approx c(HA)$

- If $K_{a_2}c(\mathrm{HA}^-) > 20K_w$, then

$$[\mathrm{H}^+] = \sqrt{\frac{K_{a_2}c\left(\mathrm{HA}^-\right)}{1 + c\left(\mathrm{HA}^-\right)/K_{a_1}}}$$

- If $c(\mathrm{HA}^-)/K_{a_1} > 20$, then "1" is negligible,

$$[\mathrm{H}^+] = \sqrt{\frac{K_{a_2}c\left(\mathrm{HA}^-\right) + K_w}{c\left(\mathrm{HA}^-\right)/K_{a_1}}}$$

- If $K_{a_2}c(\mathrm{HA}^-) > 20K_w$ and $c(\mathrm{HA}^-)/K_{a_1} > 20$

$$[\mathrm{H}^+] = \sqrt{K_{a_1}K_{a_2}}$$

Example 2: 0.033mol·L^{-1} Na_2HPO_4

(disodium hydrogen phosphate)

pK_{a_1} ~ pK_{a_3}: 2.16, 7.21, 12.33

$K_{a_3}c = 10^{-12.32} \times 0.033 = 10^{-13.80} \approx K_w$

$c/K_{a_2} = 0.033/10^{-7.21} = 10^{5.73} >> 20$

$$[H^+] = \sqrt{\frac{K_{a_3}c + K_w}{c/K_{a_2}}} = 10^{-9.66}$$

pH = 9.66

glycine氨基乙酸(甘氨酸)

$$\overset{\curvearrowleft}{NH_2CH_2COOH}$$

$$\downarrow$$

$$NH_3^+CH_2COOH \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} NH_3^+CH_2COO^- \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} NH_2CH_2COO^-$$

$pK_{a_1}=2.35$ $pK_{a_2}=9.78$

H_2A^+	H^+A^-	A^-
cation	zwitterion	anion
阳离子	双极离子	阴离子

Isoelectric Point等电点 (pI): $[H_2A^+] = [A^-]$

等电点(pI)-一定pH下,氨基乙酸所有形态电荷之和为零,此时的pH即为pI.

Question: Is pH value of glycine solution the same as its pI?

氨基乙酸溶液的pH与其等电点的pH是否相等?

Polyprotic Acids多元酸-H_2A as an Example

PCE: $[H^+] = [HA^-] + 2[A^{2-}] + [OH^-]$

$$[H^+] = \frac{K_{a_1}[H_2A]}{[H^+]} + \frac{2K_{a_1}K_{a_2}[H_2A]}{[H^+]^2}$$

Rigorous Expression $[H^+] = \sqrt{K_{a_1}[H_2A](1 + \frac{2K_{a_2}}{[H^+]})}$

When $2K_{a_2}/[H^+] \le 0.05$, negligible $[H^+] = \sqrt{K_{a_1}[H_2A]}$

Then the case of monoprotic acid (HA) 一元酸的情形

In reality实际计算中,

1. **Using HA model模型**
2. **Recalculate $2K_a/[H^+]$ to check validity**

Strong Base+Weak Base: NaOH + A^-

PCE $[H^+] + [HA] + c(NaOH) = [OH^-]$

$$[OH^-] = c(NaOH) + \frac{K_b(A^-)c(A^-)}{K_b(A^-) + [OH^-]} + \cancel{\frac{K_w}{[OH^-]}}$$

1. **Calculate $[OH^-] \approx c(NaOH)$**
2. **Check validity to see of the weak base contribution can be neglected.**
3. **In the case of HCl + HA, the same procedure**

Example 20.00 mL HA (pK_a=7.00) + 20.04 mLNaOH, c(HA) = c(NaOH) =0.1000 mol·L^{-1}, calculate pH.

$$c_{A^-} = \frac{0.1000 \times 20.00}{20.00 + 20.04} = 10^{-1.30}\,\text{mol} \cdot \text{L}^{-1} \quad c_{\text{NaOH}} = \frac{0.1000 \times 0.04}{20.00 + 20.04} = 10^{-4.00}\,\text{mol} \cdot \text{L}^{-1}$$

PCE: c_{NaOH} + [HA] + $\cancel{[H^+]}$= [OH]

Simplest approach first $$[\text{OH}^-] = c_{\text{NaOH}} = 10^{-4.00}\,\text{mol} \cdot \text{L}^{-1}$$

Checking validity

$$[\text{HA}] = \frac{c_{A^-} K_b}{K_b + [\text{OH}^-]} = \frac{10^{-1.30} \times 10^{-7.00}}{10^{-7.00} + 10^{-4.00}} = 10^{-4.30}\,\text{mol} \cdot \text{L}^{-1}$$

[HA] in the PCE can not be neglected.

Back to less simplified approach

$$[\text{OH}^-] = \frac{10^{-1.30} \times 10^{-7.00}}{10^{-7.00} + [\text{OH}^-]} + 10^{-4.00} = 10^{-3.86}\,\text{mol} \cdot \text{L}^{-1},\ \text{pH} = 10.14$$

Weak Acid and Its Conjugate Base: $HA+A^-$

e.g. HAc+NaAc

MBE: $$[HA] + \cancel{[A^-]} = c(H\cancel{A)} + c(A^-)$$

CBE: $$+)\quad [H^+] + [\cancel{Na}^+] = [OH^-] + [\cancel{A^-}]$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$[HA] = c(HA) - [H^+] + [OH^-] \qquad (1)$$

ॐ$[A^-] = c(HA) + c(A^-) - [HA] = c(A^-) + [H^+] - [OH^-] \qquad (2)$

Substitute (1) and (2) for [HA] and $[A^-]$ in equilibrium

将（1）和（2）带入平衡表达式

$$[H^+] = \frac{[HA]}{[A^-]}K_a = \frac{c(HA) - [H^+] + [OH^-]}{c(A^-) + [H^+] - [OH^-]}K_a$$

In acidic pH, $$[\mathrm{H}^+] = \frac{c(\mathrm{HA}) - [\mathrm{H}^+]}{c(\mathrm{A}^-) + [\mathrm{H}^+]} K_\mathrm{a}$$

Simplified Expression

In basic pH, $$[\mathrm{H}^+] = \frac{c(\mathrm{HA}) + [\mathrm{OH}^-]}{c(\mathrm{A}^-) - [\mathrm{OH}^-]} K_\mathrm{a}$$

$$[\mathrm{H}^+] = \frac{c_\mathrm{a}}{c_\mathrm{b}} K_\mathrm{a}$$

Henderson-Hasselbalch Equation

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{c(\mathrm{A}^-)}{c(\mathrm{HA})}$$

pH

$$\frac{c(\mathrm{A}^-)}{c(\mathrm{HA})}$$ **Ratio dependant**

Dilution independant

Procedure:

1. Using Simplified Expression
2. Compare $[\mathrm{H}^+]$ or $[\mathrm{OH}^-]$ with $c(\mathrm{HA})$ and $c(\mathrm{A}^-)$ to check the validity.

Example:

For dichloroacetic acid (pK_a=1.26),
calculate pH when 0.080 mol·L^{-1} HA–0.12 mol·L^{-1} A$^-$

$$[H^+]=\frac{0.080}{0.12}\times10^{-1.26}=10^{-1.44}=0.037$$

$$[H^+]=\frac{c(HA)-[H^+]}{c(A^-)\ +[H^+]}K_a$$

$$[H^+]=10^{-1.65}\ mol\cdot L^{-1},\ pH=1.65$$

Example 20.00mLHA(pK_a=7.00) + 19.96mLNaOH
c(HA)=c(NaOH)= 0.1000mol·L^{-1}

$$[\mathrm{H}^+]=\frac{c(\mathrm{HA})}{c(\mathrm{A}^-)}K_\mathrm{a}=10^{-9.70}\ \mathrm{mol}\cdot\mathrm{L}^{-1}$$

$[\mathrm{OH}^-] = 10^{-4.30}$ mol·L^{-1} (c(HA) = $10^{-4.00}$)

$$\boxed{[\mathrm{OH}^-]=\frac{c(\mathrm{A}^-)\cancel{-[\mathrm{OH}^-]}}{c(\mathrm{HA})+[\mathrm{OH}^-]}K_\mathrm{b}}$$

$[\mathrm{OH}^-] = 10^{-4.44}$ mol·L^{-1}, pH = 9.56

Example

10mL of 0.20mol·L^{-1} HCl is mixed with 10mL of 0.50mol·L^{-1} HCOONa and 2.0×10^{-4} mol·L^{-1} $Na_2C_2O_4$, calculate [$C_2O_4^{2-}$] after mixing. [pK_a(HCOOH) = 3.77]

Comments

- **Neutralization reaction happened upon mixing混合时发生中和反应**
- **Concentration of $Na_2C_2O_4$ is much too small to affect 影响 reaction and pH of solution**

c(HCOOH) = 0.10 mol·L^{-1}, c(HCOO$^-$) = 0.15 mol·L^{-1}

$$[\mathrm{H}^+] = \frac{c(\mathrm{HA})}{c(\mathrm{A}^-)} K_\mathrm{a} = 10^{-3.95}\,\mathrm{mol}\cdot\mathrm{L}^{-1}$$

Validity check?

$$[\mathrm{C_2O_4}^{2-}] = \mathrm{c}(\mathrm{C_2O_4}^{2-})\ \ x(\mathrm{C_2O_4}^{2-})$$

$$= \frac{c(\mathrm{C_2O_4}^{2-})\cdot K_{\mathrm{a}_1} K_{\mathrm{a}_2}}{[\mathrm{H}^+]^2 + [\mathrm{H}^+]K_{\mathrm{a}_1} + K_{\mathrm{a}_1} K_{\mathrm{a}_2}} = 3.2\times10^{-5}\mathrm{mol}\cdot\mathrm{L}^{-1}$$

How to Calculate pH?

- 确定溶液组成 Identify the composition
- 零水准Zero Level or Reference level
- PCE, 以及MBE, CBE, 和平衡表达式

  PCE, MBE, CBE, equilibrium expression
- 基于5%的原则简化 Simplify based on 5%
- Check validity

You have to practice in order to do it quickly!

Buffer Capacity 缓冲容量/Buffer Index缓冲指数

$$\boxed{\beta = \frac{\mathrm{d}b}{\mathrm{dpH}} = -\frac{\mathrm{d}a}{\mathrm{dpH}}}$$

使1L溶液的pH增加dpH单位时所需强碱db mol

or

使1L溶液的pH减少dpH单位时所需强酸da mol

The number of moles of a strong acid or a strong base that causes 1.00 L of the buffer to undergo a 1.00 unit change in pH.

Buffer Capacity

$$HA + NaOH\ (c_b) \rightarrow HA(c_a) + NaA\ (c_b)\ (c = c_a + c_b)$$

CBE: $[H^+] + c_b = [A^-] + [OH^-]$

$$c_b = [A^-] + [OH^-] - [H^+] = \frac{cK_a}{[H^+] + K_a} + \frac{K_w}{[H^+]} - [H^+]$$

$$\beta = \frac{dc_b}{d\mathrm{pH}} = 2.3\left\{\left[H^+\right] + \left[OH^-\right] + \frac{c \cdot K_a\left[H^+\right]}{\left(\left[H^+\right] + K_a\right)^2}\right\}$$

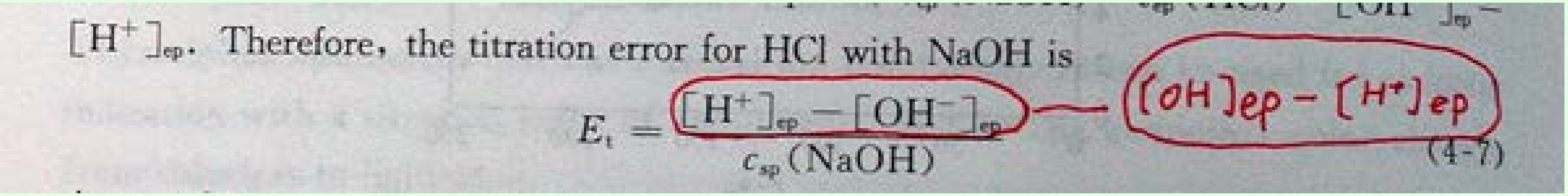
$$= 2.3\left\{\left[H^+\right] + \left[OH^-\right] + c x_0 x_1\right\}$$

$$\beta = \beta_{H^+} + \beta_{OH^-} + \beta_{HA\text{-}A^-}$$

***Quantitative Chemical Analysis* 4th ed.**

I.M. Kolthoff, et al, The Macmillan Company, 1969, pp89-90

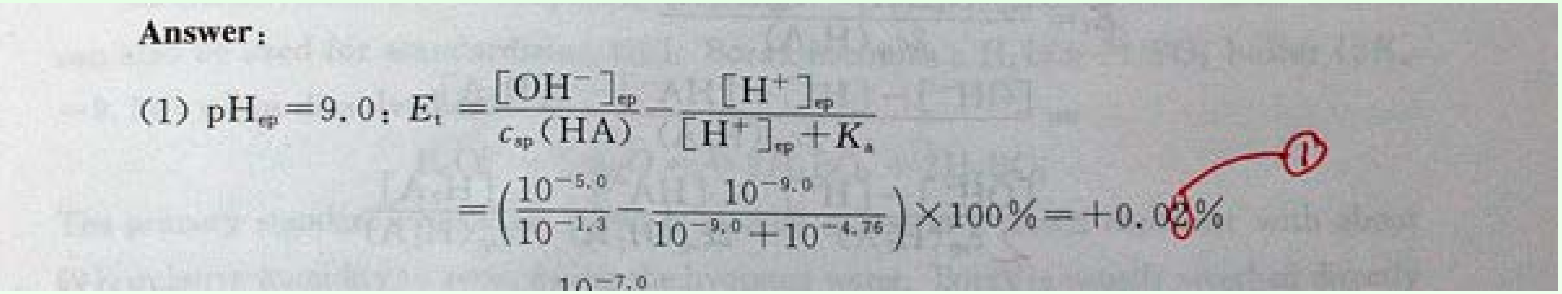
- P96



$[H^+]_{ep}$. Therefore, the titration error for HCl with NaOH is

$$E_t = \frac{\boxed{[H^+]_{ep} - [OH^-]_{ep}}}{c_{sp}(NaOH)} \text{ — } \boxed{[OH^-]_{ep} - [H^+]_{ep}} \qquad (4\text{-}7)$$

- P97

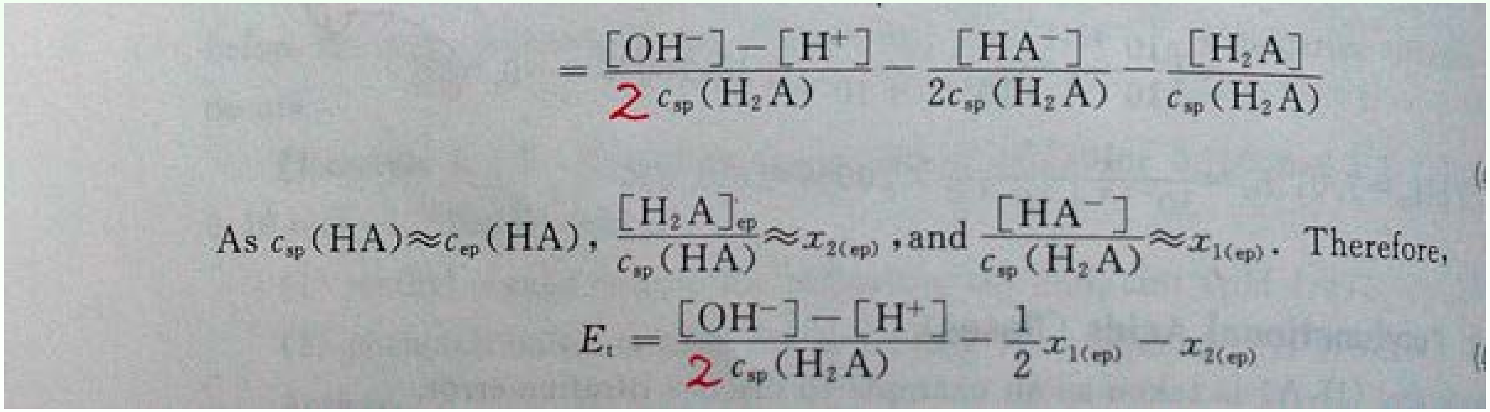


Answer:

$$(1)\ pH_{ep}=9.0:\ E_t = \frac{[OH^-]_{ep}}{c_{sp}(HA)} - \frac{[H^+]_{ep}}{[H^+]_{ep}+K_a}$$

$$= \left(\frac{10^{-5.0}}{10^{-1.3}} - \frac{10^{-9.0}}{10^{-9.0}+10^{-4.76}}\right)\times 100\% = +0.02\% \quad ①$$

- P98

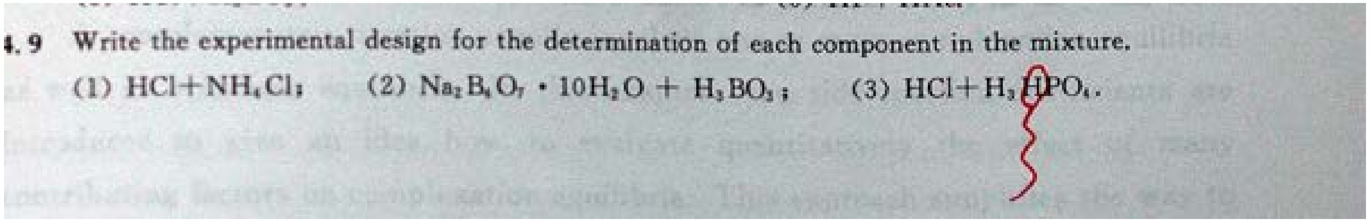


$$= \frac{[OH^-]-[H^+]}{2c_{sp}(H_2A)} - \frac{[HA^-]}{2c_{sp}(H_2A)} - \frac{[H_2A]}{c_{sp}(H_2A)}$$

As $c_{sp}(HA) \approx c_{ep}(HA)$, $\frac{[H_2A]_{ep}}{c_{sp}(HA)} \approx x_{2(ep)}$, and $\frac{[HA^-]}{c_{sp}(H_2A)} \approx x_{1(ep)}$. Therefore,

$$E_t = \frac{[OH^-]-[H^+]}{2c_{sp}(H_2A)} - \frac{1}{2}x_{1(ep)} - x_{2(ep)}$$

- p107



4.9 Write the experimental design for the determination of each component in the mixture.

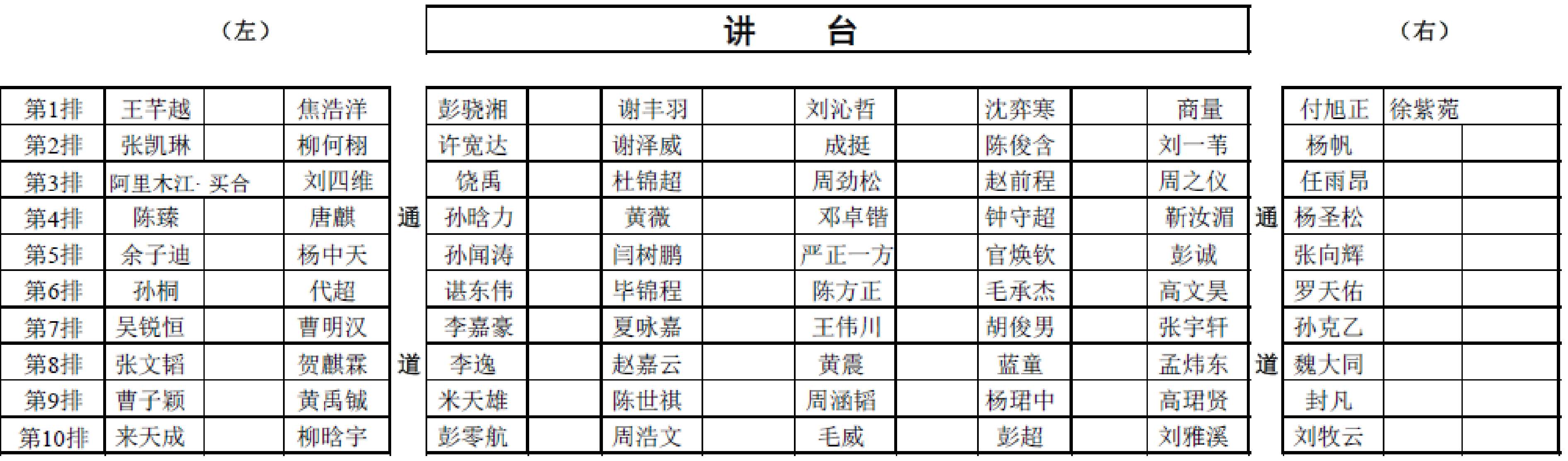
(1) $HCl+NH_4Cl$; (2) $Na_2B_4O_7 \cdot 10H_2O + H_3BO_3$; (3) $HCl+H_3HPO_4$.

期中考试安排

- 时间：2015年4月15日（周三, 8:00-9:50）
- 地点：二教411
- 考试形式：单选、填空、计算
- 请做好准备：题目多、计算量大 有效数字
  - 复习、准时、计算器
  - 答题时要有步骤、卷面要整洁
- 请提前15分钟到场
- 答疑时间：
  - 4月10日（周五）2:00-4:30 PM
  - 4月11日（周六）8:30-11:30， 2:00-4:00 PM

期中考试座次安排

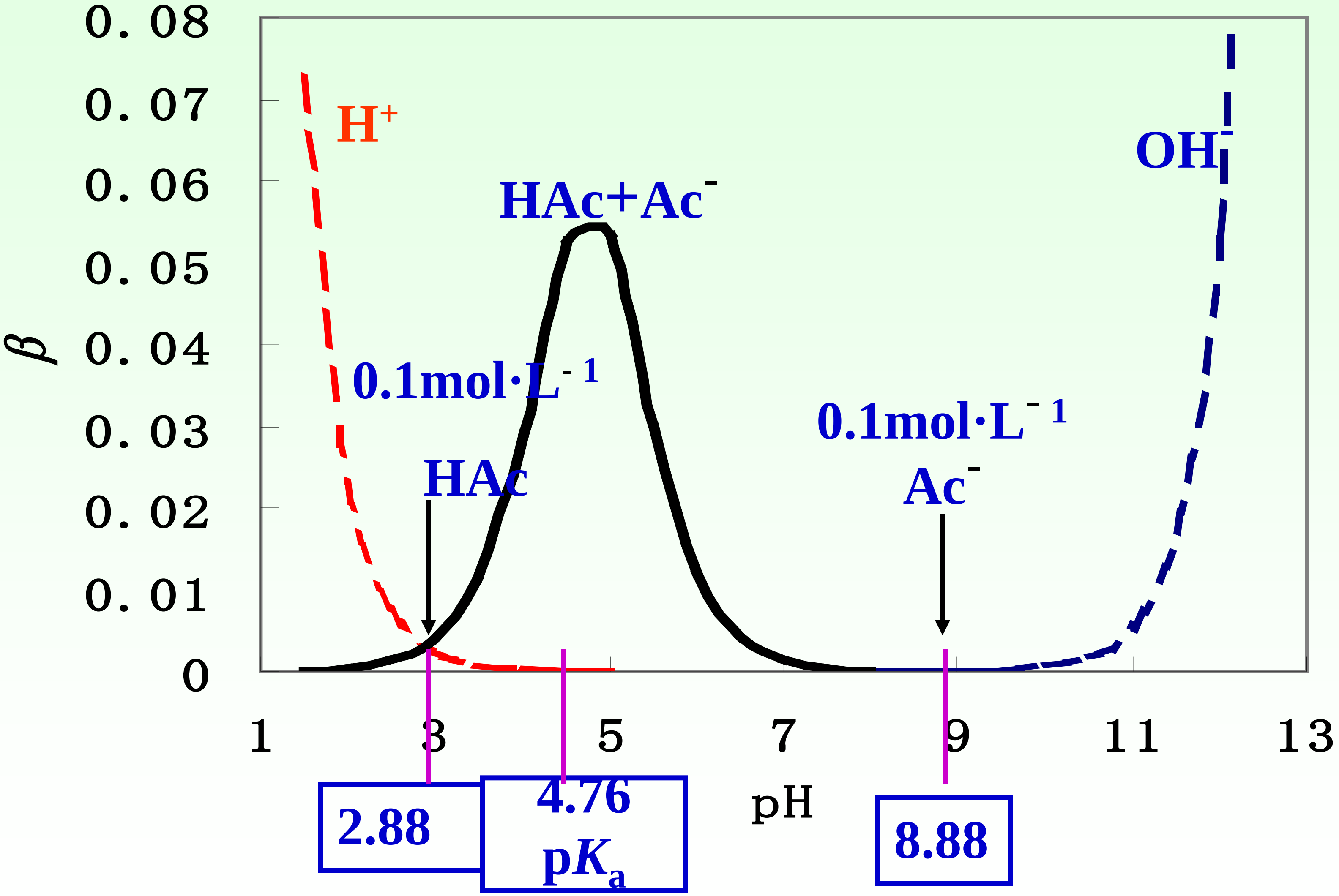
二教411



（左） **讲　　台** （右）

第1排	王芊越		焦浩洋		彭骁湘		谢丰羽		刘沁哲		沈弈寒		商量		付旭正	徐紫菀	
第2排	张凯琳		柳何栩		许宽达		谢泽威		成挺		陈俊含		刘一苇		杨帆		
第3排	阿里木江· 买合		刘四维		饶禹		杜锦超		周劲松		赵前程		周之仪		任雨昂		
第4排	陈臻		唐麒	通	孙晗力		黄薇		邓卓锴		钟守超		靳汝湄	通	杨圣松		
第5排	余子迪		杨中天		孙闻涛		闫树鹏		严正一方		官焕钦		彭诚		张向辉		
第6排	孙桐		代超		谌东伟		毕锦程		陈方正		毛承杰		高文昊		罗天佑		
第7排	吴锐恒		曹明汉		李嘉豪		夏咏嘉		王伟川		胡俊男		张宇轩		孙克乙		
第8排	张文韬		贺麒霖	道	李逸		赵嘉云		黄震		蓝童		孟炜东	道	魏大同		
第9排	曹子颖		黄禹铖		米天雄		陈世祺		周涵韬		杨珺中		高珺贤		封凡		
第10排	来天成		柳晗宇		彭零航		周浩文		毛威		彭超		刘雅溪		刘牧云		

β- pH曲线



0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
β
1
3
5
7
9
11
13
pH
H^+
$HAc+Ac^-$
OH^-
$0.1mol·L^{-1}$
HAc
$0.1mol·L^{-1}$
Ac^-
2.88
4.76
pK_a
8.88

- **Strong Acid Region:**

$$\beta_{H^+}=2.3[H^+]\approx 2.3c(HCl)\quad (pH<3)$$

- **Strong Base Region:**

$$\beta_{OH^-} = 2.3[OH^-]\approx 2.3c(NaOH)\quad (pH>11)$$

- **HA – A$^-$:** $\beta_{HA-A^-} = 2.3\cdot c\cdot x_1\cdot x_0$

1. $\beta \propto c,\quad c\uparrow, \beta\uparrow$
2. $pH = pK_a,\ \beta_{max} = 0.58c$
3. **Buffering range:** $pK_a-1 < pH < pK_a+1$

Selection of Buffers

➢ Buffer with reasonably good β:

- c big enough ($0.01\sim1\,\mathrm{mol\cdot L^{-1}}$)
- $\mathrm{pH}\approx \mathrm{p}K_a$, i.e. $c_a : c_b \approx 1:1$

Examples:

$HAc - NaAc$: $\mathrm{p}K_a = 4.65$ (pH 4～5.5)

$NH_4Cl - NH_3$: $\mathrm{p}K_b = 4.63$ (pH 8～10)

$(CH_2)_6N_4 - (CH_2)_6N_4H^+$: $\mathrm{p}K_b = 8.74$(pH 4.5 ～ 6)

Hexamethylene-tetramine (urotropine)

➢ No interference with determination不干扰测定

e.g. EDTA→Pb^{2+}, HAc is not used because of the formation of $Pb(Ac)_2$

List of Reagents for Preparing Buffers
用于配制常用缓冲溶液的物质

Acid	pK_a(I=0.1)	Acid	pK_a(I=0.1)
Glysine氨基乙酸	2.5, 9.7	*Acetic acid乙酸	4.65
Chloroacetic acid氯乙酸	2.7	*Phosphoric acid 磷酸	2.0,6.9,11.7
Formic acid甲酸	3.65	•Tris(THAM) *三羟甲基甲胺	8.21
Succinic acid丁二酸	4.00, 5.28	*Borax硼砂	9.24
Bicarbonate碳酸氢盐	10.1	*AmmoniaNH_3	9.37
Citric acid柠檬酸	3.0, 4.4, 6.1	*Urotropine六次甲基四胺	8.74

Ways for Preparing Buffers配制缓冲液的方法

1. Mix HA and A^- at a desired ratio以合适比例混合
   ($NaAc + HAc$, $NH_4Cl + NH_3$);
2. To a solution with extra过量 $[H^+]$, add excess过量 A^-
   To a solution with extra $[OH^-]$, add excess HA
   $(HA+H^+) + A^- \rightarrow HA + A^-$ or
   $(A+OH^-) + HA \rightarrow HA + A^-$
3. To a solution with HA, add NaOH to neutralize partial (中和部分) HA；to a solution with A^-, add HCl to neutralize partial A^-
   $HA + OH^- \rightarrow HA + A^-$ or $A^- + HCl \rightarrow HA + A^-$

Calculation Involved in Preparing Buffer

Based on Buffer Capacity

With a Known β, calculate the acid or base or both needed.

1. Calculate β from the definition

$$\beta = -\mathrm{d}c(\mathrm{H}^+)/\mathrm{dpH} = \mathrm{d}c(\mathrm{OH}^-)/\mathrm{dpH}$$

2. Calculate c from β=2.3•c•x_0•x_1
3. Preparing buffer according to ratio of x_1 to x_0

Example

To prepare a 200 mL NH_3-NH_4Cl buffer (pH 9.4):

Δ pH $\leq$0.2 when 1.0 mmol HCl or NaOH was added,

- how many g of NH_4Cl?
- how many mL of 1.0 mol/L ammonia?

Answer

$$\beta = \frac{\mathrm{d}b}{\mathrm{dpH}} = \frac{1.0\times10^{-3} \big/ 200\times10^{-3}}{0.2} = 2.5\times10^{-2}$$

And $$\beta = 2.3\cdot c\cdot\frac{K_\mathrm{a}\cdot[\mathrm{H}^+]}{([\mathrm{H}^+]+K_\mathrm{a})^2} = 0.575c$$

$$c = \frac{2.5\times10^{-2}}{0.575} = 0.043(\mathrm{mol}\cdot\mathrm{L}^{-1})$$

$$m(\mathrm{NH_4Cl}) = c\cdot x(\mathrm{NH_4^+})\cdot V\cdot M$$

$$V(\mathrm{NH_3}) = c\cdot x(\mathrm{NH_3})\cdot V / c(\mathrm{NH_3})$$

Calibration Buffer

Buffer systems	pH (25°C)
Potassium Bitartrate (Sat.)饱和酒石酸氢钾 (0.034 $mol\cdot kg^{-1}$)	3.557
Potassium hydrogen phthalate 邻苯二甲酸氢钾 (0.050 $mol\cdot kg^{-1}$)	4.008
$0.025 mol\cdot kg^{-1}$ KH_2PO_4 $+0.025 mol\cdot kg^{-1}$ Na_2HPO_4	6.865
Borax硼砂 (0.010 $mol\cdot kg^{-1}$)	9.180
Calcium hydroxide(Sat.) 饱和氢氧化钙	12.454

The pH values in the above table is experimental data and the activity correction shall be considered when calculating the above pH.

标准缓冲溶液的pH是实验测定的,计算时应做活度校正.

Ready to Tackle Acid-base Titration?

- Construct titration curve for
  - Indicator selection
  - Titration error estimation
- Titration systems to work on:
  - Strong base (OH^-)→ strong acid (H^+)
  - Strong base (OH^-) →weak monoprotic acid (HA)
  - Strong base (OH^-) →polyprotic acid (H_nA)
  - The reversed titration of the above systems指酸滴碱

Acid/Base Indicators (pH indicators)

- 甲基橙 Methyl Orange (**MO**)
- 甲基红 Methyl Red (**MR**)
- 酚酞 Phenolphthalein (**PP**)
- Combined Indicator: **MR +BCG**

溴甲酚绿Bromocresol Green (BCG) (3.8-5.4→ Yellow to greenish blue)

$$HIn + H_2O = In^- + OH^-$$

Acid color Base color

$$K_a = \frac{[In^-][H^+]}{[HIn]} \Rightarrow \frac{[HIn]}{[In^-]} = \frac{[H^+]}{K_a}$$

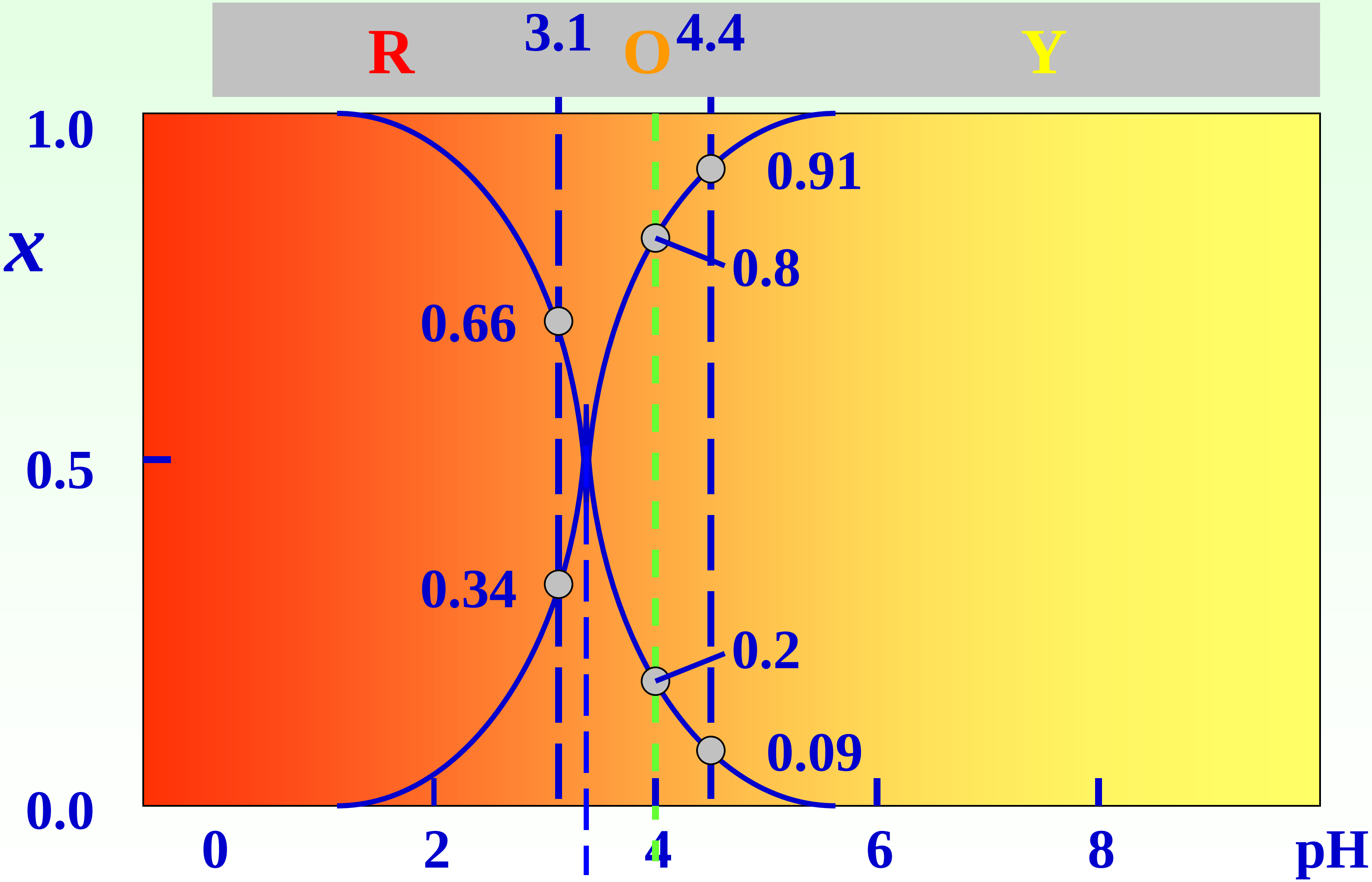
$$\frac{[HIn]}{[In^-]} \geq 10, \quad \text{acid color, pH} \leq \text{p}K_a\text{-1}$$

$$\frac{[HIn]}{[In^-]} \leq 10, \quad \text{base color, pH} \geq \text{p}K_a\text{+1}$$

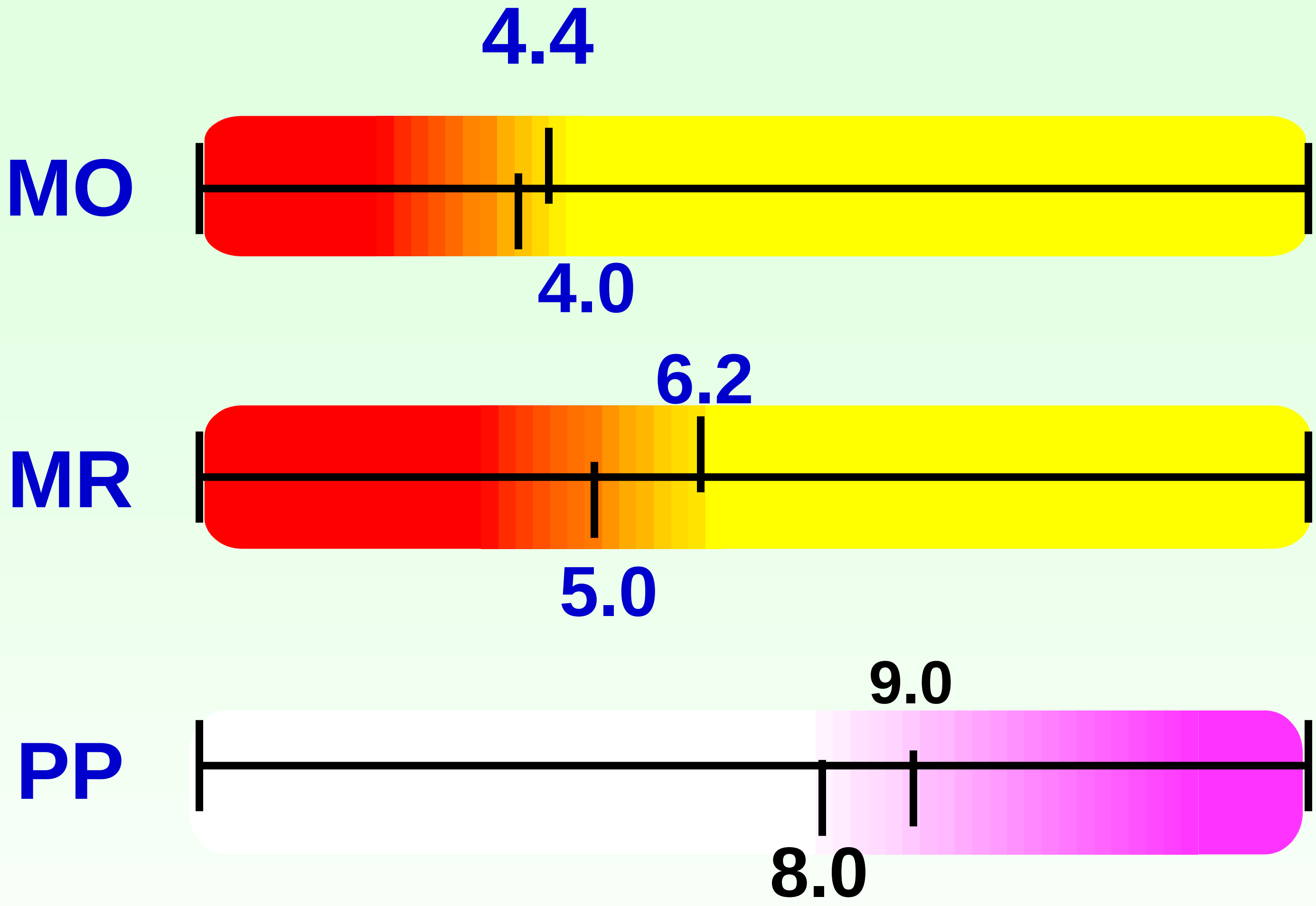
Intermediate color range过渡色范围：pK_a ±1 (theoretical)

In reality, determined experimentally

x - pH Plot and Associated Color for MO (自学)



pK_a=3.4, pT=4.0



Titration Errors

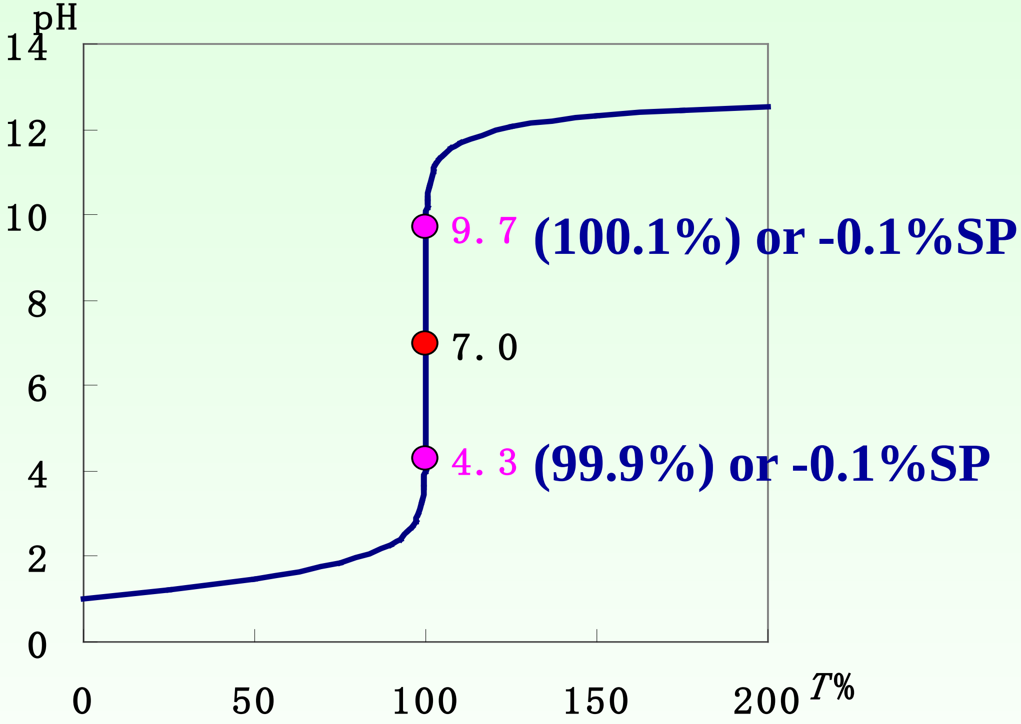
- ➢ Systematic error: EP is different from SP
- ➢ Random error: visual uncertainty, ±ΔpH

Rationale原理

NaOH

↓

HCl



(100.1%) or -0.1%SP

(99.9%) or -0.1%SP

$V(\mathrm{HCl})=20.00\ \mathrm{mL},\ c(\mathrm{NaOH})=c(\mathrm{HCl})=0.1000\ \mathrm{mol\cdot L^{-1}}$

Indicator changes color in a pH range to make sure the titration error within ±0.1%

Strong Acid – Base Titration

$0.1000\ \mathrm{mol \cdot L^{-1}}$ NaOH→ 20.00 mL $0.1000\ \mathrm{mol \cdot L^{-1}}$ HCl

Initial Point起始点: $[\mathrm{H^+}] = c(\mathrm{H^+}) = 0.1000\ \mathrm{mol \cdot L^{-1}}$

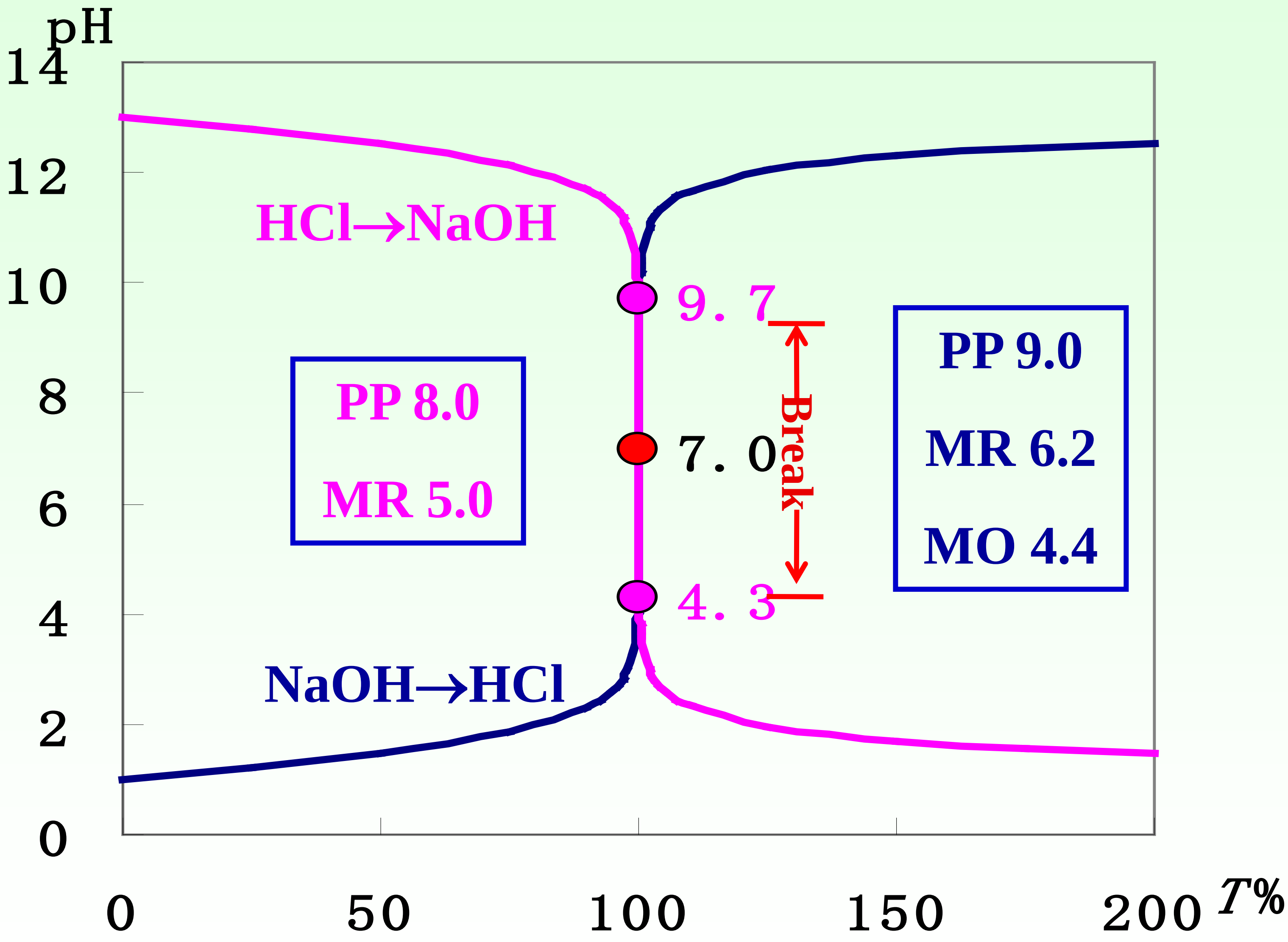
- $\mathrm{Pre\ SP:}\ [\mathrm{H^+}] = \dfrac{c(\mathrm{H^+})V(\mathrm{H^+}) - c(\mathrm{OH^-})V(\mathrm{OH^-})}{V(\mathrm{H^+}) + V(\mathrm{OH^-})}$
- SP $[\mathrm{H^+}] = [\mathrm{OH^-}] = \sqrt{K_w} = 10^{-7.00}$
- Post SP $[\mathrm{OH^-}] = \dfrac{c(\mathrm{OH^-})V(\mathrm{OH^-}) - c(\mathrm{H^+})V(\mathrm{H^+})}{V(\mathrm{H^+}) + V(\mathrm{OH^-})}$

Important: identify the system composition → pH
重要提示：先确定溶液组成，然后计算pH

$0.1000 mol \cdot L^{-1}$ NaOH → $20.00 mL$ $0.1000 mol \cdot L^{-1}$ HCl

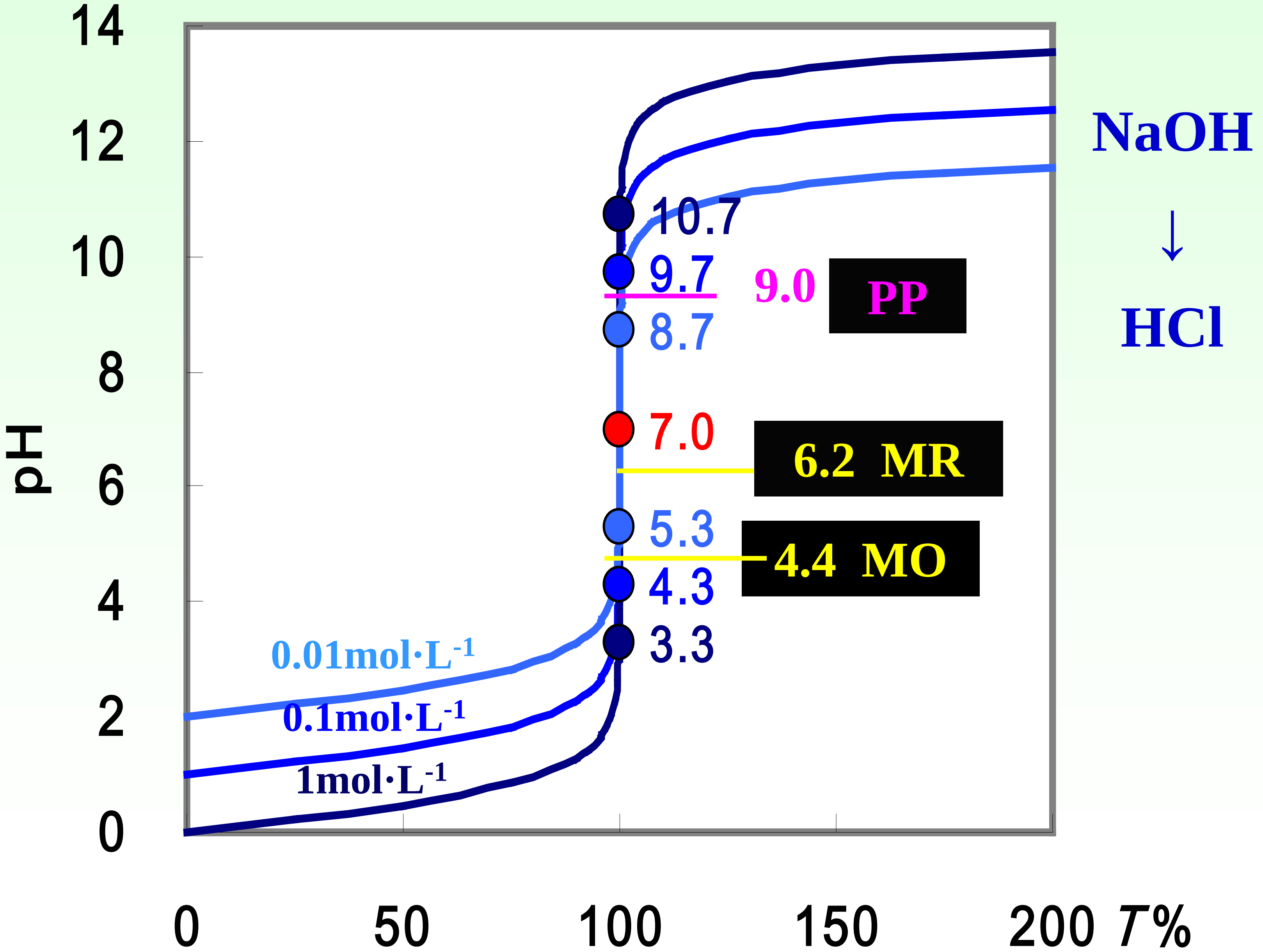
NaOH, mL added	*T*%	HCl, mL (in excess)	NaOH,mL (in excess)	pH	$[H^+]_{calc}$
0.00	0	20.00		1.00	**Initial Point: $[H^+] = c(HCl)$**
18.00	90.0	2.00		2.28	**Pre SP** $[H^+] = \frac{c(H^+)V(H^+) - c(OH^-)V(OH^-)}{V(H^+) + V(OH^-)}$
19.80	99.0	0.20		3.30	
19.98	99.9	0.02		4.30	突跃 **sp:** $[H^+] = [OH^-] = 10^{-7.00}$
20.00	100.0	0.00	0.00	7.00	
20.02	100.1		0.02	9.70	
20.20	101.0		0.20	10.70	**Post SP** $[H^+] = \frac{c(OH^-)V(OH^-) - c(H^+)V(H^+)}{V(H^+) + V(OH^-)}$
22.00	110.0		2.00	11.68	
40.00	200.0		20.00	12.52	

Titration Curve



突跃：**Titration Break/Titration Jump**

Effect of Concentration on Titration Break
浓度对滴定突跃的影响



Titrating a Weak Acid with a Strong Base

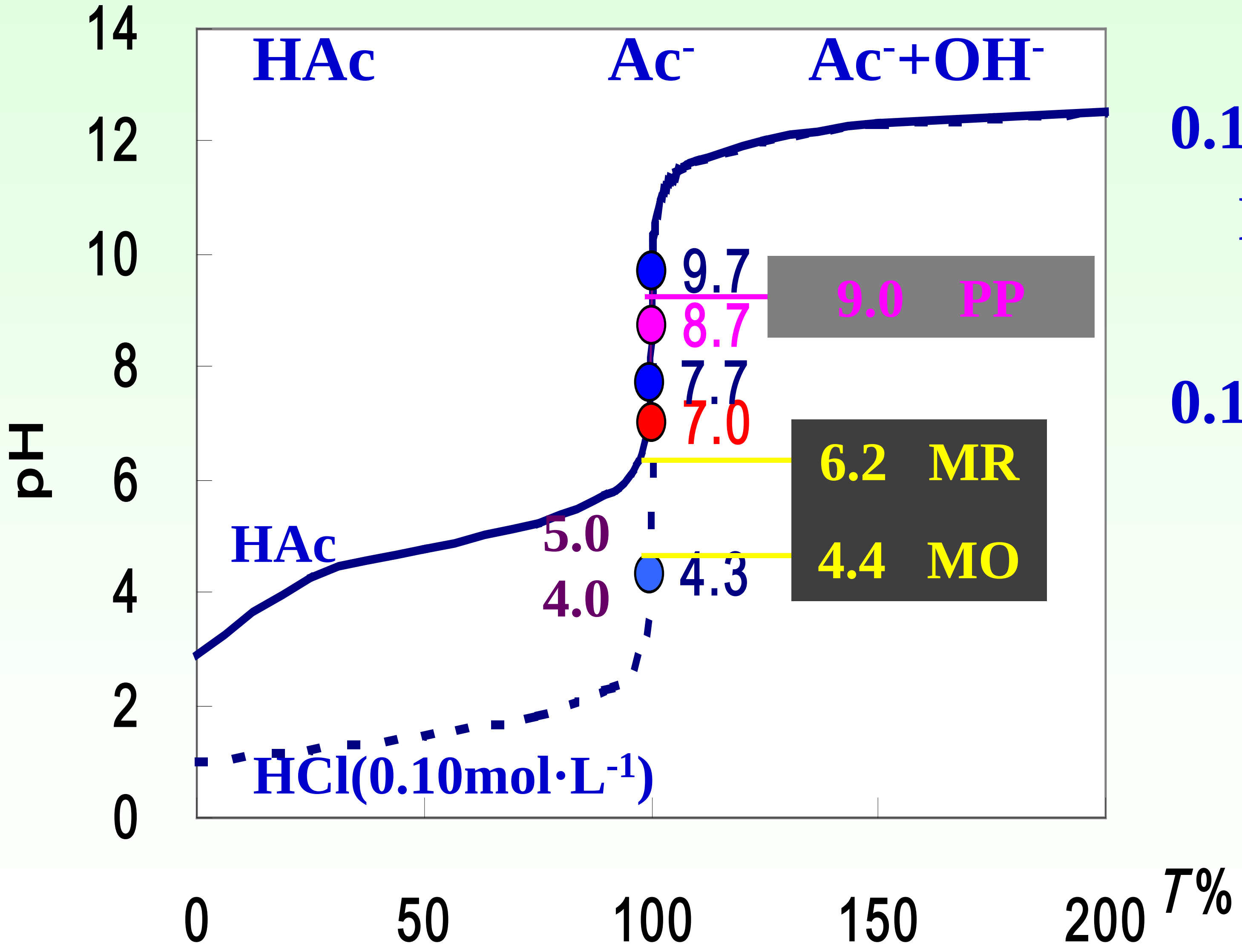
0.1000 mol·L^{-1} NaOH → 20.00 mL 0.1000 mol·L^{-1} HAc

- Initial Point $[\mathrm{H}^{+}]=\sqrt{K_{\mathrm{a}}c_{\mathrm{a}}}=10^{-2.88}$
- Pre SP $[\mathrm{H}^{+}]=\dfrac{[\mathrm{HA}]}{[\mathrm{A}^{-}]}K_{\mathrm{a}}$
- SP $[\mathrm{OH}^{-}]=\sqrt{K_{\mathrm{b}}c(\mathrm{A}^{-})}$
- Post SP $[\mathrm{OH}^{-}]=c(\mathrm{NaOH})+[\mathrm{HA}]$

0.1000 $mol \cdot L^{-1}$ NaOH → 20.00 mL 0.1000 $mol \cdot L^{-1}$ HAc $K_a(HAc) = 10^{-4.76}$, $K_a(HA) = 10^{-7.00}$)

NaOH, mL added	*T*%	Composition	pH (HAc)	pH (HA)	$[H^+]_{calc}$
0	0	HA	2.88	4.00	$[H^+] = \sqrt{K_a c_a}$
10.00	50.0	$HA+A^-$	4.76	7.00	
18.00	90.0	$HA+A^-$	5.71	7.95	$[H^+] = \frac{[HA]}{[A^-]} K_a$
19.80	99.0	$HA+A^-$	6.67	9.00	
19.96	99.8	$HA+A^-$	7.46	9.56	
19.98	99.9	$HA+A^-$	7.76	9.70	
20.00	100.0	A^-	8.73	9.85	$[OH^-] = \sqrt{K_b c(A^-)}$
20.02	100.1	A^-+OH^-	9.70	10.00	$[OH^-]=c(NaOH)+[HA]$ **The same as titrating strong acid**
20.04	100.2	A^-+OH^-	10.00	10.13	
20.20	101.0	A^-+OH^-	10.70	10.70	
22.00	110.0	A^-+OH^-	11.68	11.68	

Titration Curve



$0.10 mol\cdot L^{-1}$

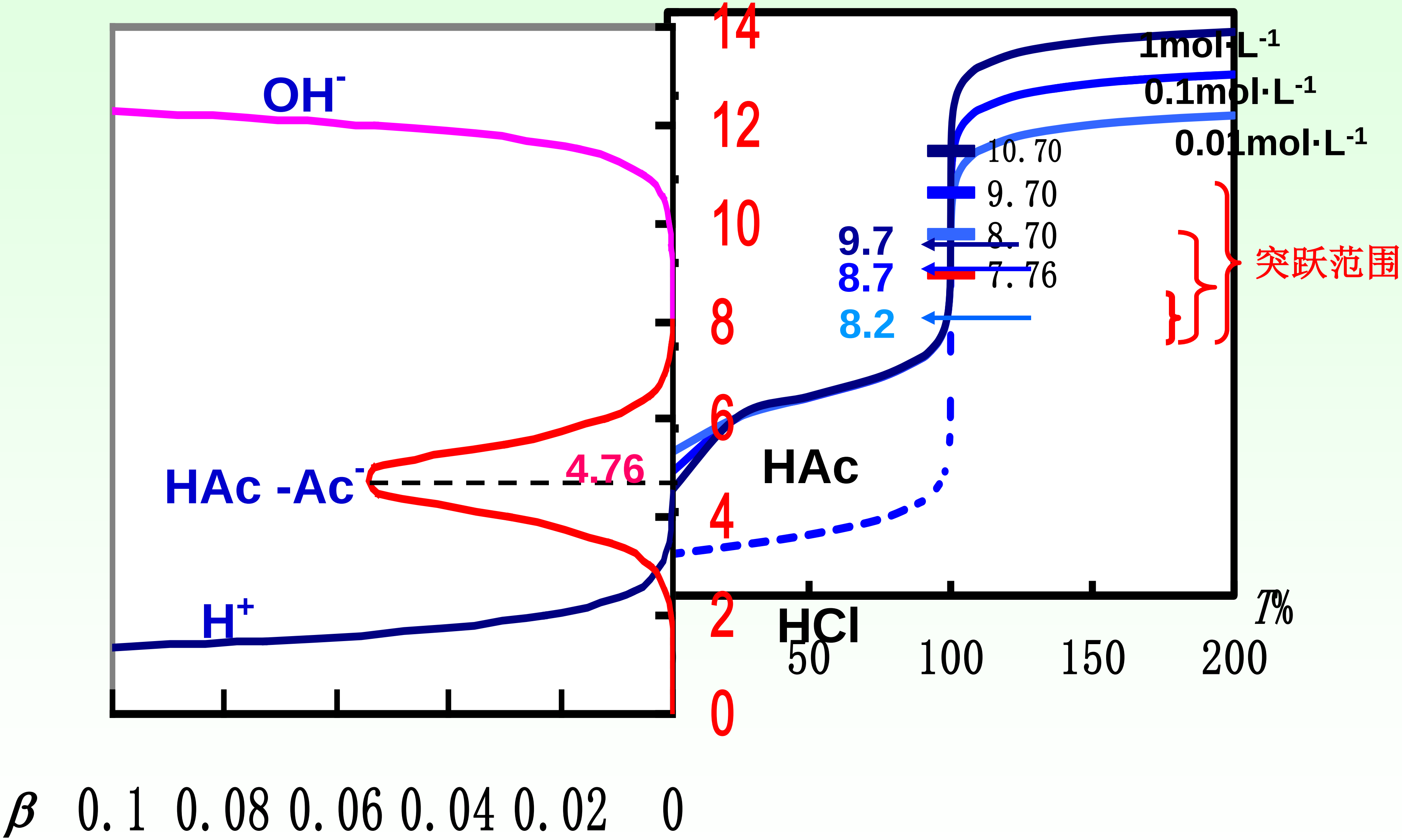
NaOH

↓

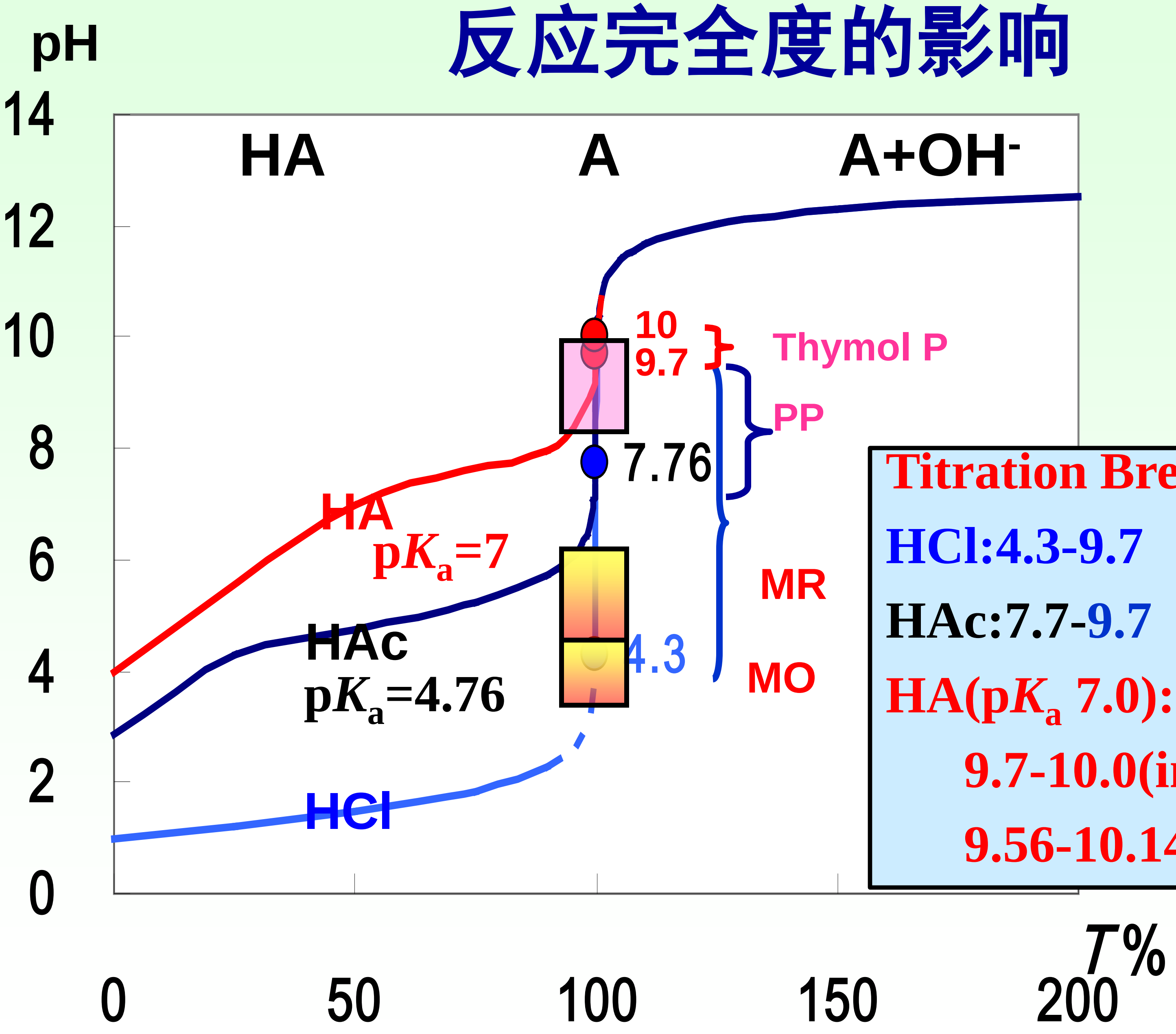
$0.10 mol\cdot L^{-1}$

HAc

Effect of Concentration浓度的影响



Effect of Reaction Completeness (pK_a)
反应完全度的影响



0.10 mol·L^{-1}
NaOH
↓
HA
0.10 mol·L^{-1}

Titration Break

HCl:4.3-9.7

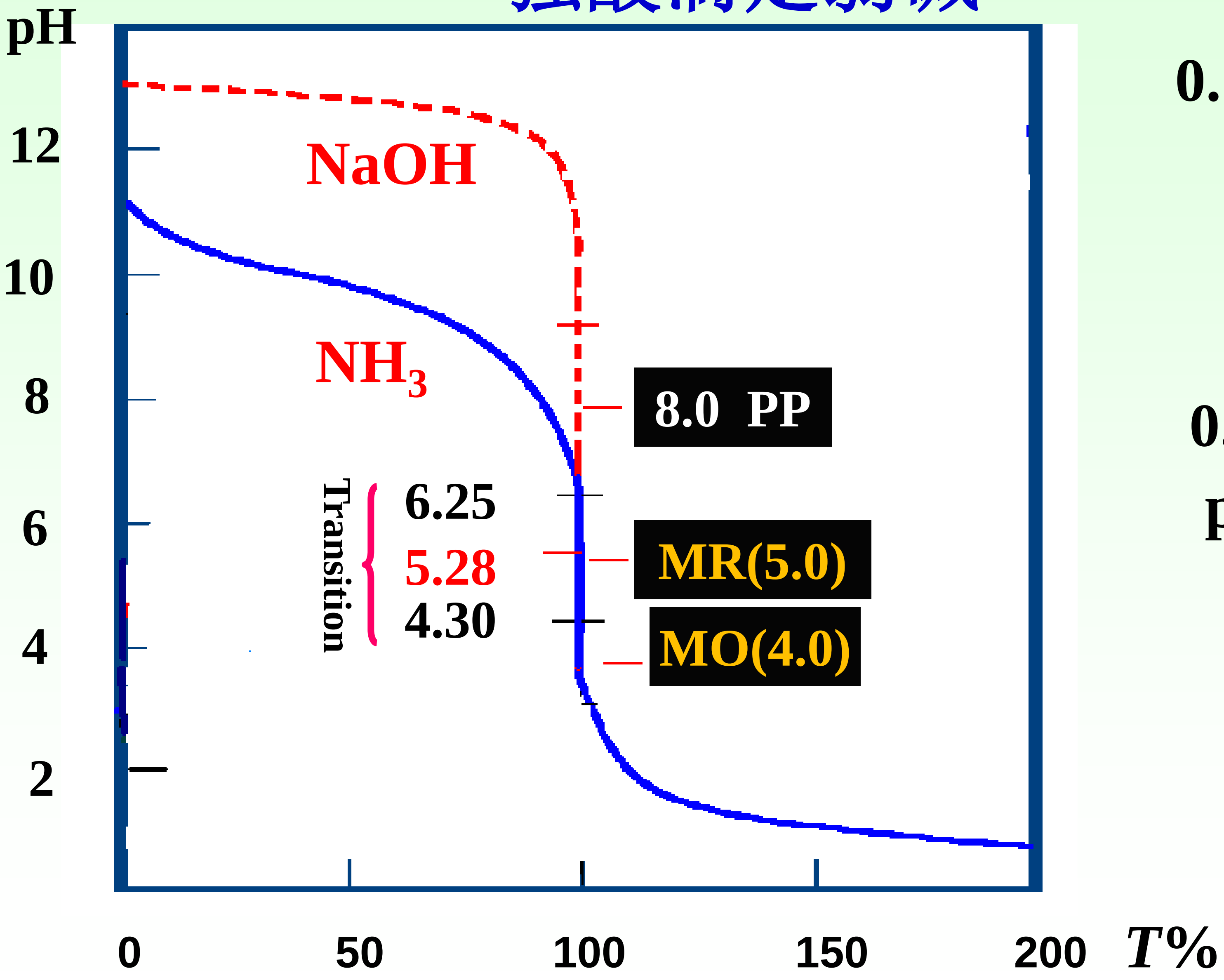
HAc:7.7-9.7

HA(pK_a 7.0):

9.7-10.0(infeasible)

9.56-10.14 (±0.2%)

Titration of Weak Bases with Strong Acids
强酸滴定弱碱



$0.1 mol \cdot L^{-1}$

HCl

↓

NH_3

$0.1 mol \cdot L^{-1}$

$pK_b = 4.75$

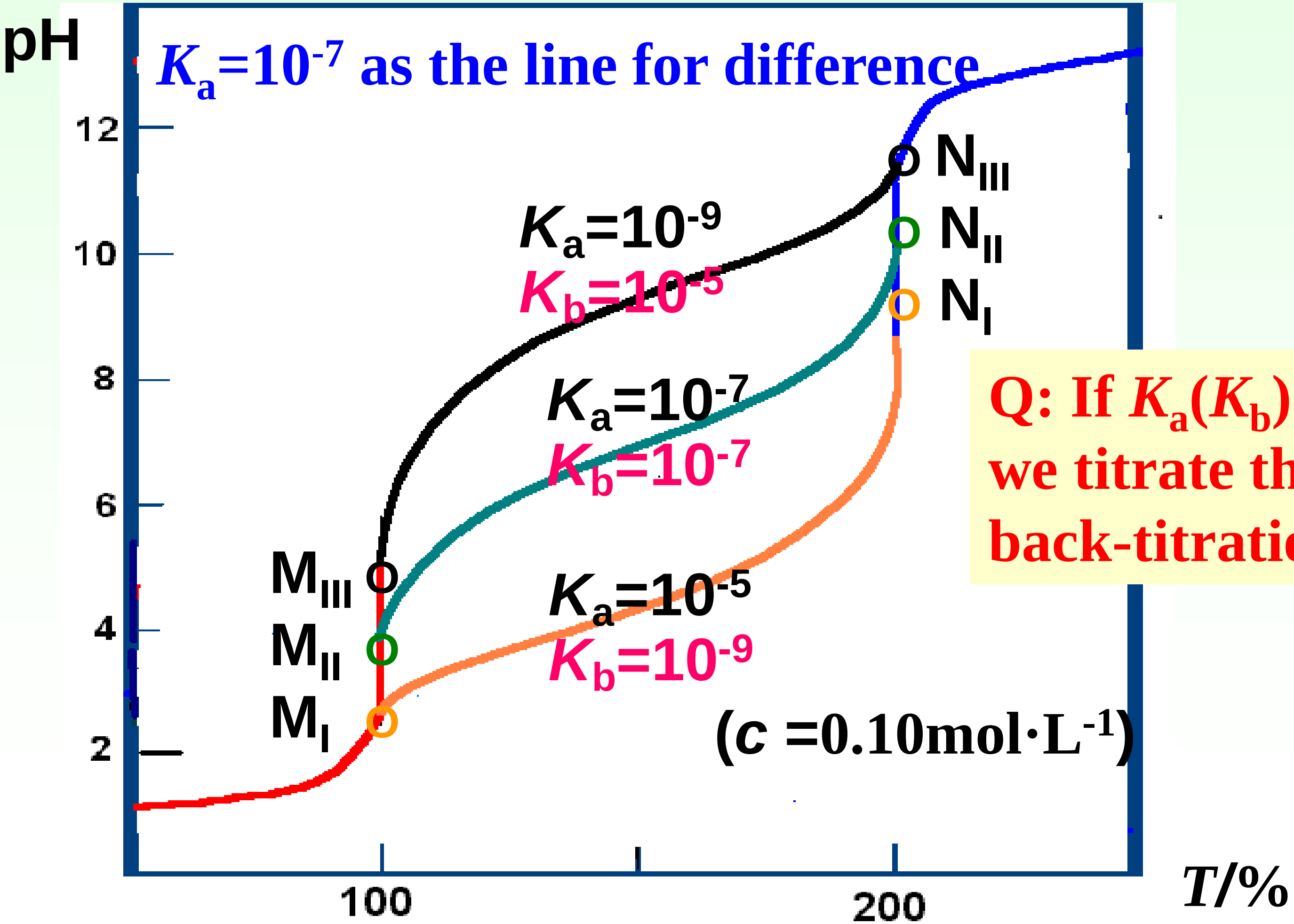
Acid-base Titration Summary Table

Concentration	**Pre-0.1% SP**	**SP**	**Post-0.1% SP**	**Indicators**
Strong Acid-base Titration (NaOH – HCl)				
1.0 mol/L				
0.1 mol/L				
0.01 mol/L				
Weak Acid-base Titration (NaOH →HAc, pK_a 4.76)				
1.0 mol/L				
0.1 mol/L				
0.01 mol/L				
Weak Acid-base Titration (HCl →NH_4^+, pK_b 4.75)				
0.1 mol/L				

强酸（碱）-弱酸（碱）混合体系的滴定

$$\mathrm{H^+ + HA \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} HA \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} A^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} A^- + OH}$$

（Q）（R）（S）（T）

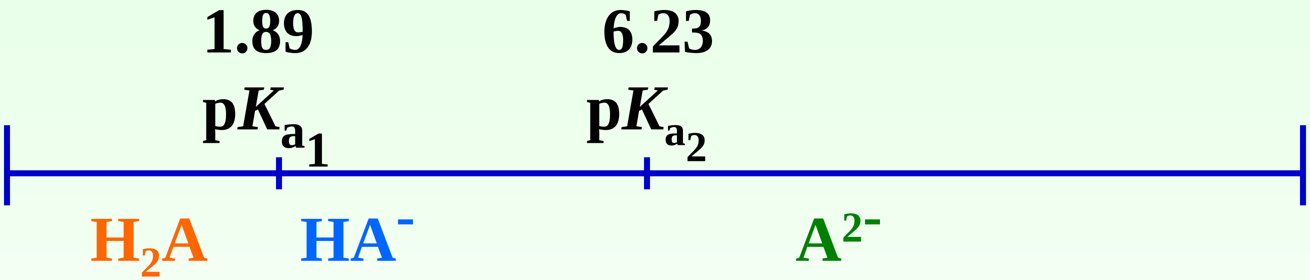


Q: If $K_a(K_b)<10^{-7}$, can we titrate the acid via back-titration?

Titration Curves of Polyprotic Acids
多元酸的滴定曲线

0.1000 mol·L^{-1} NaOH →25.00 mL 0.1000 mol·L^{-1} H_2A

pK_{a_1}=1.89, pK_{a_2} =6.23



1. **Initial Point: H_2A**

$[H^+]=$⌧$K_{a_1}(c- [H^+])$, $[H^+]=10^{-1.52}$

Cont’d

1st SP: HA^-(majority 主要成分)

$$[H^+]=\sqrt{\frac{K_{a_2}c\left(HA^-\right)+Kw}{1+c\left(HA^-\right)/K_{a_1}}}=10^{-4.11}$$

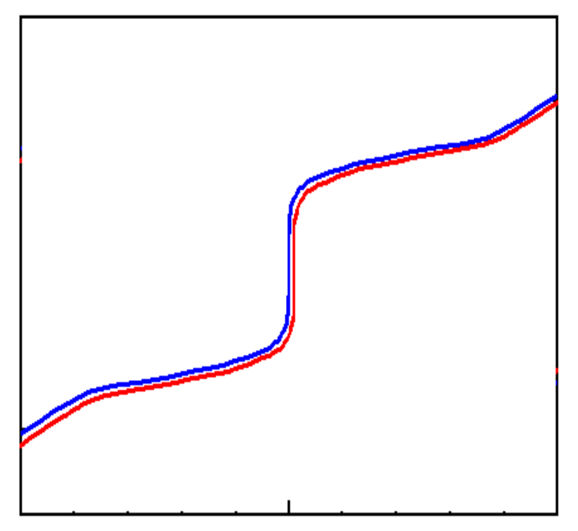
2nd SP: A^{2-}(majority)

$$[OH^-]=\sqrt{K_{b_2}c\left(A^{2-}\right)+K_w}=10^{-4.62}$$

$$pH=14-4.62=9.38$$

Titration of H_2A to HA^-

- **Titration Break does not change with concentration but increases with ΔpK_a. Why?**
  滴定图跃与ΔpK_a有关，与浓度无关。



Titration curve construction:

- **Pre sp: H_2A-HA^-**
- **Post sp: HA^-- A^{2-}**
- **SP: HA^-**

Fun reading:

Skoog book: Example 15-9, p408

终点误差–代数法
Calculation of Titration Error

Definition:

$$E_{\mathrm{t}} = \frac{n\text{(过量或不足的滴定剂）}}{n\text{（在化学计量点时应加入的滴定剂）}}$$

$$= \frac{n\ \textbf{(titrant in shortage or in excess)}}{n\ \textbf{(titrant at stoichiometric point)}}$$

以质子转移数量为计量比

Be careful: E_{t} bears a sign.

E_t for Titration of Strong Acid with Strong Base

$$E_{\mathrm{t}} = \frac{c(\mathrm{NaOH})_{\mathrm{ep}} \cdot V(\mathrm{NaOH})_{\mathrm{ep}} - c(\mathrm{HCl})_{\mathrm{ep}} \cdot V(\mathrm{HCl})_{\mathrm{ep}}}{c(\mathrm{HCl})_{\mathrm{sp}} \cdot V(\mathrm{HCl})_{\mathrm{sp}}}$$

At a point Close to SP：

$$\because\ V(\mathrm{NaOH})_{\mathrm{ep}} = V(\mathrm{HCl})_{\mathrm{ep}} \approx V(\mathrm{HCl})_{\mathrm{sp}}$$

$$\therefore\ E_{\mathrm{t}} = \frac{c(\mathrm{NaOH})_{\mathrm{ep}} - c(\mathrm{HCl})_{\mathrm{ep}}}{c(\mathrm{HCl})_{\mathrm{sp}}}$$

Zero Level: NaOH, HCl, H_2O

$$\text{PCE}: c(\text{NaOH}) + [\text{H}^+] = c(\text{HCl}) + [\text{OH}^-]$$

i.e. $$c(\text{NaOH}) - c(\text{HCl}) = [\text{OH}^-] - [\text{H}^+]$$

$$\therefore E_t = \frac{c(\text{NaOH})_{ep} - c(\text{HCl})_{ep}}{c(\text{HCl})_{sp}} = \frac{[\text{OH}^-]_{ep} - [\text{H}^+]_{ep}}{c(\text{HCl})_{sp}}$$

strong acid → strong base

$$E_t = \frac{[\text{H}^+]_{ep} - [\text{OH}^-]_{ep}}{c(\text{NaOH})_{sp}}$$

$0.10\,\mathrm{mol\cdot L^{-1}\,NaOH} \rightarrow 0.10\,\mathrm{mol\cdot L^{-1}\,HCl}$,

Calculate E_t with MO and PP as Indicator, respectively.

分别计算用MO和PP指示终点时的滴定误差

（1）$\mathrm{pH_{ep}} = 4.4$

$$E_{\mathrm{t}} = \frac{[\mathrm{OH^-}]_{\mathrm{ep}} - [\mathrm{H^+}]_{\mathrm{ep}}}{c(\mathrm{HCl})_{\mathrm{sp}}} = \frac{10^{-9.6}-10^{-4.4}}{0.10/2} \times 100\% = -0.08\%$$

（2）$\mathrm{pH_{ep}} = 9.0$

$$E_{\mathrm{t}} = \frac{10^{-5.0}-10^{-9.0}}{0.10/2} \times 100\% = +0.02\%$$

How to calculate E_t when a back titration is carried out?

反滴定的误差如何计算？

E_t for Titration of Weak acid with Strong Base

$$E_t = (c(\mathrm{NaOH})_{ep} - c(\mathrm{HA})_{ep})/c(\mathrm{HA})_{sp}$$

Zero Level: **HA, NaOH, H_2O**

PCE $$c(\mathrm{NaOH}) + [\mathrm{H}^+] = [\mathrm{A}^-] + [\mathrm{OH}^-]$$

MBE $$-)\quad c(\mathrm{HA}) = [\mathrm{HA}] + [\mathrm{A}^-]$$

$$c(\mathrm{NaOH}) - c(\mathrm{HA}) = [\mathrm{OH}^-] - [\mathrm{H}^+] - [\mathrm{HA}]$$

$$E_t = \frac{[\mathrm{OH}^-]_{ep} - [\mathrm{H}^+]_{ep}}{c(\mathrm{HA})_{sp}} - x(\mathrm{HA})_{ep}$$

E_t for titration of A with Strong acid?

0.100 mol·L^{-1}NaOH→0.100 mol·L^{-1} HAc, Indicator PP, E_t=?

$$E_t = \left[\frac{10^{-5.0} - 10^{-9.0}}{0.100/2} - \frac{10^{-9.0}}{10^{-9.0} + 10^{-4.76}} \right] \times 100\%$$

$$= +0.01\%$$

If titration ends at pH7.0, [H$^+$]=[OH$^-$]

$$E_t = -x(\mathrm{HA}) = \frac{10^{-7.0}}{10^{-7.0} + 10^{-4.76}} = -0.6\%$$

$0.10\,\mathrm{mol\cdot L^{-1}}$ NaOH→$0.050\,\mathrm{mol\cdot L^{-1}}$ $H_2C_2O_4$ using PP as indicator (pH = 9.0) , E_t=? pK_{a_1}=1.25, pK_{a_2}=4.29)

$$E_t = \frac{c(\mathrm{NaOH})V(\mathrm{NaOH})(\mathrm{ep}) - 2c(\mathrm{H_2A})V(\mathrm{H_2A})(\mathrm{ep})}{2c(\mathrm{H_2A})V(\mathrm{H_2A})(\mathrm{sp})}$$

$$E_t = \frac{[\mathrm{OH^-}]_{ep} - [\mathrm{H^+}]_{ep}}{2c(\mathrm{H_2A})_{sp}} - \frac{x_{1(ep)}}{2} - x_{2(ep)}$$

$$E_t = \left(\frac{10^{-5.0}}{2\times\frac{0.05}{2}} - \frac{10^{-9.0}}{2\times\left(10^{-9.0}+10^{-4.29}\right)} \right)\times 100\% = +0.02\%$$

Stepwise Titration for Polyprotic Acid

NaOH

$$\big\downarrow$$

$$H_2A \longrightarrow HA^-$$

Zero Level: NaOH, H_2A, H_2O

PCE: $$c(\mathrm{NaOH})+[H^+]=[HA^-]+2[A^{2-}]+[OH^-]$$

MBE: -) $$c(H_2A)=[H_2A]+[HA^-]+[A^{2-}]$$

$$c(\mathrm{NaOH})-c(H_2A)=[A^{2-}]-[H_2A]+\cancel{[OH^-]}-\cancel{[H^+]}$$

$$E_t=\frac{c_{ep}(\mathrm{NaOH})-c_{ep}(H_2A)}{c_{sp}(H_2A)}=\frac{[A^{2-}]_{ep}-[H_2A]_{ep}}{c_{sp}(H_2A)}$$

$$E_t = \frac{c(\mathrm{NaOH})_{ep} - c(\mathrm{H_2A})_{ep}}{c(\mathrm{H_2A})_{sp}} = \frac{[\mathrm{A}^{2-}]_{ep} - [\mathrm{H_2A}]_{ep}}{c(\mathrm{H_2A})_{sp}}$$

$$= \left(\frac{K_{a_2}[\cancel{\mathrm{HA}^-}]_{ep}}{[\mathrm{H}^+]_{ep}} - \frac{[\mathrm{H}^+]_{ep}[\cancel{\mathrm{HA}^-}]_{ep}}{K_{a_1}}\right)/c\cancel{(\mathrm{H_2A})}_{sp}$$

$$[\mathrm{H}^+]_{ep} = [\mathrm{H}^+]_{sp} \cdot 10^{-\Delta\mathrm{pH}} = \sqrt{K_{a_1} \cdot K_{a_2}} \cdot 10^{-\Delta\mathrm{pH}}$$

$$E_t = \frac{10^{\Delta\mathrm{pH}} - 10^{-\Delta\mathrm{pH}}}{(K_{a_1}/K_{a_2})^{1/2}}$$

E_t for two week acids in solution ? 混合酸如何计算?

Criteria for Stepwise Titration of Polyprotic Acid
多元酸分步滴定的标准

1. $cK_{a_1} \geq 10^{-8}$
2. **Δ p*K*$_a$: big enough to assure an significant break**

   Δ p*K*$_a$足够大保证明显的突跃

   ΔpH=±0.3 random errors for visual observation of pH

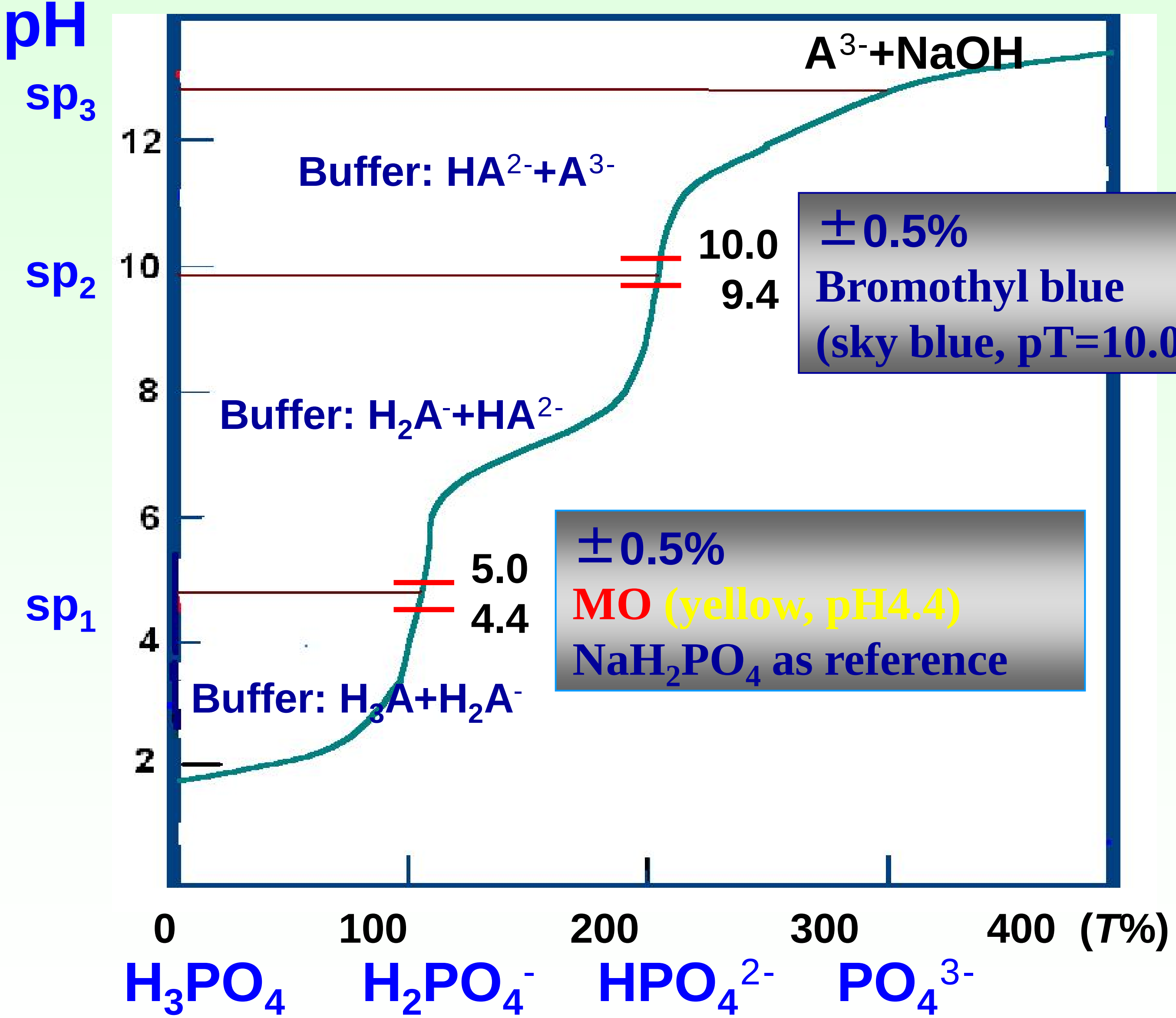
ΔpK_a	≥ 4	≥ 5	≥ 6
E_t	±1%	±0.5%	±0.1%

Criteria for stepwise titration with ($E_t \leq 0.5\%$):

$\Delta pK_a \geq 5$ and $cK_{a_{n-1}} \geq 10^{-8}$

Titration of total polyprotic acid: $cK_{a_n} \geq 10^{-8}$

NaOH → $0.1 mol\cdot L^{-1}$ H_3PO_4



±0.5%
Bromothyl blue
(sky blue, pT=10.0)

±0.5%
MO (yellow, pH4.4)
NaH_2PO_4 as reference

pK_a	ΔpK_a
2.16	
	5.05
7.21	
	5.11
12.32	

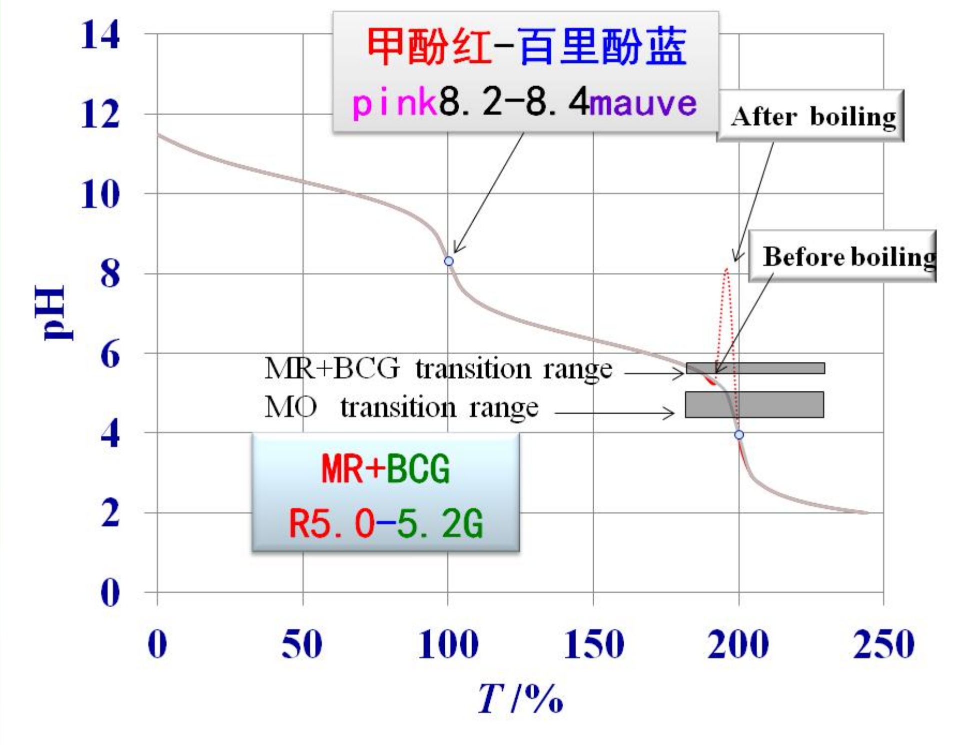
pH_{sp_1}= 4.7

pH_{sp_2}= 9.7

Required!

sp_3: $2HPO_4^{2-} + 3Ca^{2+} \rightleftharpoons Ca_3(PO_4)_2 + 2H^+$

$HCl \rightarrow 0.1 mol \cdot L^{-1}\ Na_2CO_3$



H_2CO_3

$pK_{a_1}=6.4$

$pK_{a_2}=10.3$

$\Delta pK_a=3.9$

CO_3^{2-}

$pK_{b_1}=3.7$

$pK_{b_2}=7.6$

$\Delta pK_b=3.9$

**c* does not affect the 1st titration break, but the 2nd titration break

*MR+BCG, red at pH 5.0, $x(HCO_3^-)\approx 4\%$; △to expel CO_2, the solution is then $NaHCO_3$ system with pH≈8, R→G. after cooling , 1 or 2 drops of HCl was added till pH 5.0, $x_1 \approx 0.16\%$; repeat the above procedure one more time.

1. CO_2 Is Existing in Either NaOH or in H_2O

Standardization using organic acid: PP, $CO_3^{2}\rightarrow HCO_3^{-}$

- **Determination of organic acid:**

  PP, $CO_3^{2-} \rightarrow HCO_3^{-}$ no effect on results

- **Determination of HCl in HCl+NH_4^{+} mixture**

  MO or MR, $CO_3^{2-} \rightarrow H_2CO_3$, less NaOH consumed

  ***c*(HCl) determined↓**

$$\boldsymbol{c}(\mathrm{HCl})\cdot \boldsymbol{V}(\mathrm{HCl})=\boldsymbol{c}(\mathrm{NaOH})\cdot \boldsymbol{V}(\mathrm{NaOH})$$

↘

25 mL set

不变

As calculated from standardization

不变

↘

2. NaOH Solution Properly Prepared and Standardized Previously but Absorbed CO_2 During Storage

- **MO, MR：** $Na_2CO_3 + 2H^+ \rightarrow H_2CO_3$

  no effect on results

- **PP：** $Na_2CO_3 + H^+ \rightarrow HCO_3^-$

  ***c*(HCl) Determined ↑**

$$c(\mathrm{HCl})\cdot V(\mathrm{HCl}) = c(\mathrm{NaOH})\cdot V(\mathrm{NaOH})$$

↗

25 mL set
不变

As calculated from standardization
不变

↗

Nitrogen in Organic Compounds

kjeldahl method (凯氏定氮法)

$$N \xrightarrow[CuSO_4]{\text{cont. } H_2SO_4} NH_4^+ \xrightarrow[\triangle]{NaOH} NH_3$$

Absorbed in

$$\xrightarrow{HCl(\text{stand.})} NH_4^+ + \underset{\overset{\uparrow}{NaOH(\text{stand.})}}{HCl(\text{excess})} \longrightarrow NH_4^+ \qquad In \xrightarrow[MR?]{MO?}$$

$$\xrightarrow[\text{in excess}]{H_3BO_3} NH_4^+ + H_3BO_3(\text{excess})\,{}^{+}\underset{\overset{\uparrow}{HCl(\text{stand.})}}{H_2BO_3^-} \longrightarrow NH_4^+ + H_3BO_3$$

$$In \xrightarrow{MR}$$

pH_{sp}~5

Always work for solution!

Real Example for Kjeldahl method (Home work: Chapter 4, 4-6)

- Distilled sample was collected in 100 mL of 0.3 mol·L^{-1} HCl in excess amount.
- The acidic ammonium solution is then back-titrated with 0.2 mol·L^{-1} NaOH.
- Assuming $c_{NH_4^+}$= 0.2 mol·L^{-1}in the solution (NH_3: pK_b=4.75)
- Calculate:
  - pH at SP
  - Titration error at pH 4.0
  - Titration error at pH 7.0

- **In reality, it is titration of NH_3 using HCl. Why back titration?**

  A back titration was conducted as excess standardized HCl was added to absorb gaseous NH_3.
- **After absorbing NH_3， c(HCl) remained is 0.3-0.2=0.1(mol·L^{-1}).**
- **The volume of NaOH used for the back titration was calculated as**

$$\frac{0.1\times100}{0.2}=50（mL）$$

- **At the endpoint, the total volume will be 150 mL**

At sp, it was a solution of NH_4^+

$$c(\mathrm{NH_4^+})_{\mathrm{sp}} = \frac{0.2\times100}{100+50} = 0.13(\mathrm{mol\cdot L^{-1}})$$

$K_a \bullet c$? K_a/c?

$$[\mathrm{H^+}]_{\mathrm{sp}} = \sqrt{K_a c(\mathrm{NH_4^+})_{\mathrm{sp}}} = \sqrt{10^{-9.25}\times0.13} = 10^{-5.1},\ \mathrm{pH_{sp}} = 5.1$$

Titration Error Calculation

$$E_{\mathrm{t}} = \frac{n(\text{HCl in excess or shortage})_{\mathrm{ep}}}{n(\mathrm{NH_3})_{\mathrm{sp}}}$$

$$= \frac{(n(\mathrm{HCl})_{\mathrm{ep}} - n(\mathrm{NaOH})_{\mathrm{ep}}) - n(\mathrm{NH_3})_{\mathrm{ep}}}{n(\mathrm{NH_3})_{\mathrm{sp}}}$$

$$= \frac{(c(\mathrm{HCl})_{\mathrm{ep}} \cancel{V_{\mathrm{ep}}} - c(\mathrm{NaOH})_{\mathrm{ep}} \cancel{V_{\mathrm{ep}}}) - c(\mathrm{NH_3})_{\mathrm{ep}} \cancel{V_{\mathrm{ep}}}}{c(\mathrm{NH_3})_{\mathrm{sp}} \cancel{V_{\mathrm{ep}}}}$$

$$= \frac{c(\mathrm{HCl})_{\mathrm{ep}} - c(\mathrm{NaOH})_{\mathrm{ep}} - c(\mathrm{NH_3})_{\mathrm{ep}}}{c(\mathrm{NH_3})_{\mathrm{sp}}}$$

Zero Level：HCl，NH_3，$NaOH$，H_2O

PCE：　$[H^+] + [NH_4^+] + c(NaOH) = c(HCl) + [OH^-]$

We have: $c(HCl) - c(NaOH) = [H^+] + [NH_4^+] - [OH^-]$

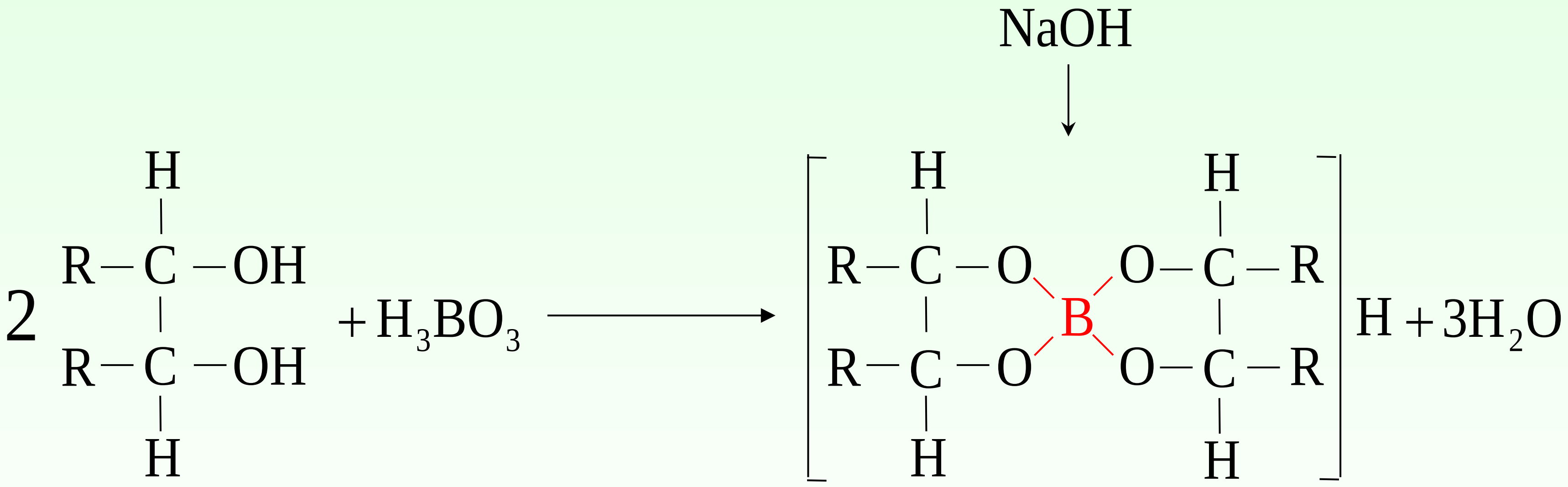
Combine with MBE：　$c(NH_3) = [NH_4^+] + [NH_3]$

We have: $c(HCl) - c(NaOH) - c(NH_3) = [H^+] - [OH^-] - [NH_3]$

$$E_t = \frac{c(HCl)_{ep} - c(NaOH)_{ep} - c(NH_3)_{ep}}{c(NH_3)_{sp}}$$

$$= \frac{[H^+]_{ep} - [OH^-]_{ep} - [NH_3]_{ep}}{c(NH_3)_{sp}} = \left(\frac{[H^+]_{ep} - [OH^-]_{ep}}{c(NH_3)_{sp}} - x_0 \right) \times 100\%$$

Boric acid H_3BO_3 $pK_a = 9.24$



$pKa = 4.26$

络合酸

indicator? **PP**

It is better to light the candle instead of cursing the darkness!

Goal-A Successful Titration, $E_t \leq \pm 0.1\%$

- Select an indicator for we need to know where to stop
- Construct a titration curve for we need to know how to select an indicator
- Calculate pH
- K_a, fractions of forms in the solution at a specific pH
- There is one thing having practical application – buffer solution
- Selectivity? Solution(解决办法)?