

Chapter VII

Precipitation Equilibrium, Titration & Gravimetry

沉淀滴定法与沉淀重量法

- Titration by forming precipitation
- Obtaining precipitation in order to determine sample by weighing 称量

Precipitation Equilibrium and Precipitation Titration 沉淀平衡与沉淀滴定

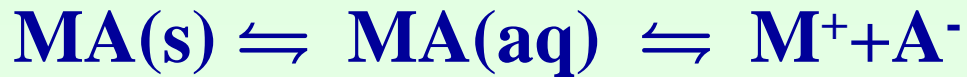
Forming Precipitation

沉淀的形成

- **The key to success**
 - To obtain precipitation without contamination
获得无污染的沉淀
 - To assure the least loss of precipitation 确保最少的沉淀损失
- **How to do**
 - Gravimetry: use excess precipitating agent
 - Titration: The solubility is small enough to assure $E_t \leq 0.1\%$.
- **Solubility (溶解度) is the key**

Solubility (S) and Solubility Product (K_{sp})

溶解度与溶度积



In a saturated 的 aqueous solution 在饱和水溶液中

- Completely dissociated (解离): S calculated from K_{sp}
- Incompletely dissociated: e.g. HgCl_2

Solubility of precipitates in molecular form ($[\text{MA}]_{\text{aq}}$), denoted as S^0 (固有溶解度或分子溶解度)

$$\text{Solubility } S = S^0 + [\text{M}^+] = S^0 + [\text{A}^-]$$

$$\text{HgCl}_2 \quad S = 0.25 \text{ mol} \cdot \text{L}^{-1}$$

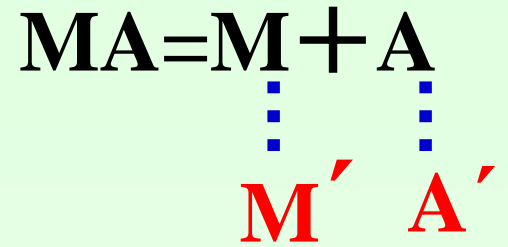
$$[\text{Hg}^{2+}] = 1.7 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$K = \frac{a(\text{M}^+) a(\text{A}^-)}{a(\text{MA})_{(\text{s})}}$$

$$K_{sp}^{\ominus} = a(\text{M}) \cdot a(\text{A})$$

thermal dynamic constant

热力学常数



$$K_{\text{sp}} = [\text{M}][\text{A}] = \frac{a(\text{M}) \cdot a(\text{A})}{\gamma(\text{M}) \cdot \gamma(\text{A})} = \frac{K_{\text{sp}}^{\ominus}}{\gamma(\text{M}) \cdot \gamma(\text{A})}$$

Conditional Solubility Product

$$K'_{\text{sp}} = [\text{M}'][\text{A}'] = [\text{M}]\alpha_{\text{M}}[\text{A}]\alpha_{\text{A}} = K_{\text{sp}} \alpha_{\text{M}} \alpha_{\text{A}}$$

$$K'_{\text{sp}} > K_{\text{sp}} > K_{\text{sp}}^{\ominus}$$

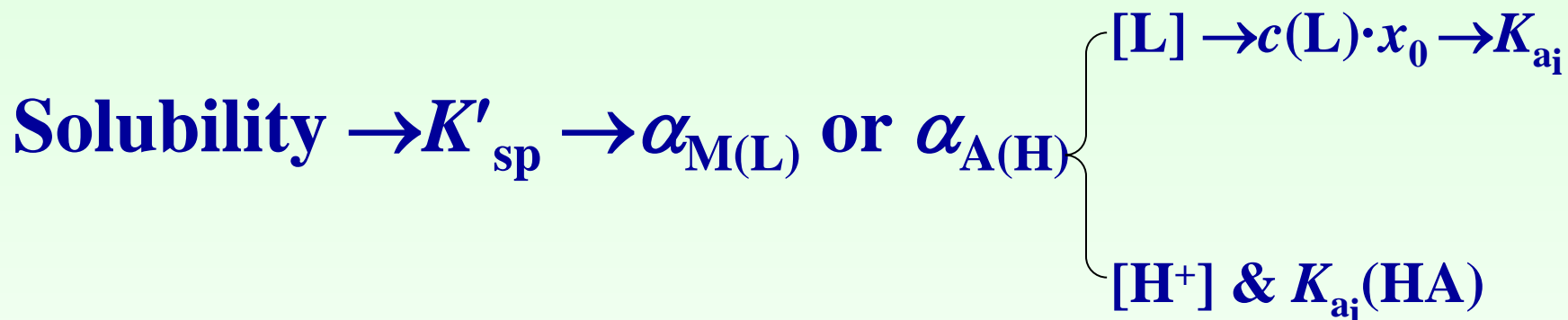
$$\text{MA} : S = \sqrt{K'_{\text{sp}}}$$

$$\text{MA}_2 : K'_{\text{sp}} = [\text{M}'][\text{A}']^2 = K_{\text{sp}} \alpha_{\text{M}} \alpha_{\text{A}}^2$$

$$S = \sqrt[3]{K'_{\text{sp}} / 4}$$

Approach to Calculate Solubility

溶解度计算方法



Without side-reaction 当没有副反应时:

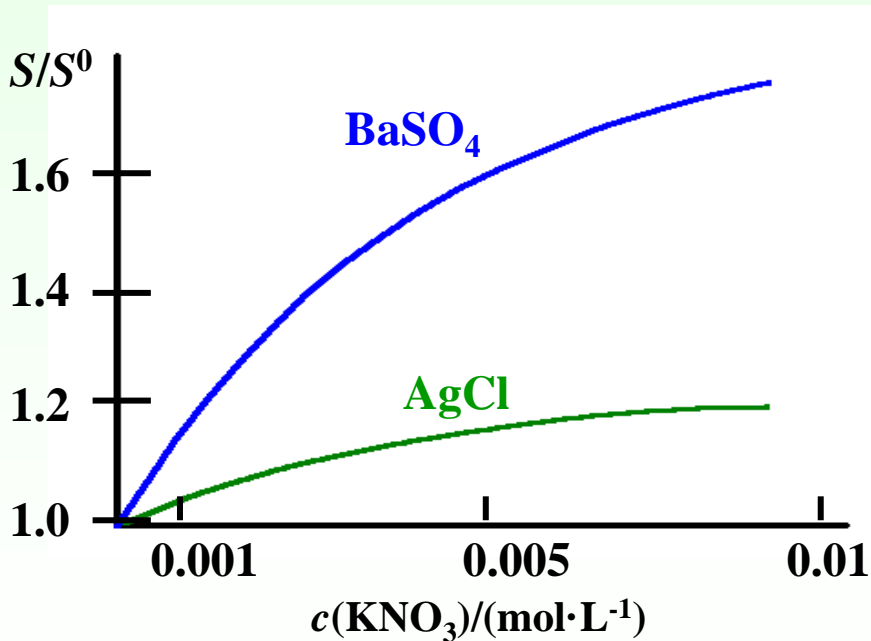


Most of the time, it is important to identify a species representing solubility.

弄清楚哪个物种的浓度表示溶解度很重要!

Salt Effect 盐效应(Electrolyte Effect电解质效应) -solubility is increased

$$K_{sp} = [M][A] = \frac{a(M) \cdot a(A)}{\gamma(M) \cdot \gamma(A)} = \frac{K_{sp}^{\ominus}}{\gamma(M) \cdot \gamma(A)}$$



$I \nearrow$, $S \nearrow$

In precipitation titration and gravimetry calculation, the K_{sp} is taken at $I=0.1$;

In solubility calculation in pure water, K_{sp} (K_{sp}^{\ominus}) is taken at pH $I=0$.

Common Ion Effect 同离子效应

Addition of excess precipitating agent is but one approach to reduce solubility

加过量沉淀剂是降低溶解度的最方便有效的办法。

Example: Determination of SO_4^{2-}

If $n(\text{Ba}^{2+})=n(\text{SO}_4^{2-})$ $V=300$ mL

$$S = \sqrt{K_{\text{sp}}} = \sqrt{6 \times 10^{-10}} = 2.4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$m(\text{BaSO}_4) = 2.4 \times 10^{-5} \times 300 \times 233.4 = \mathbf{1.7 \text{ mg}}$$

If excess Ba^{2+} is added, $[\text{Ba}^{2+}] = 0.01 \text{ mol} \cdot \text{L}^{-1}$

$$S = [\text{SO}_4^{2-}] = K_{\text{sp}} / [\text{Ba}^{2+}] = 6 \times 10^{-10} / 0.01 = 6 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$$

$$m(\text{BaSO}_4) = 6 \times 10^{-8} \times 300 \times 233.4 = \mathbf{0.004 \text{ mg}}$$

Solubility of PbSO_4 in Varied Concentration of Na_2SO_4

不同 Na_2SO_4 浓度下 PbSO_4 的溶解度

Na_2SO_4 ($\text{mol}\cdot\text{L}^{-1}$)	0	0.001	0.01	0.02	0.04	0.10	0.20	0.35
$\text{PbSO}_4 \times 10^5$ ($\text{mol}\cdot\text{L}^{-1}$)	15	2.4	1.6	1.4	1.3	1.6	1.9	2.3
	Common ion effect					Salt effect		

Game plan for addition of precipitating agent:

- Volatile挥发性agent: 50%~100% more than SR
- Non-volatile非挥发性 agent: 20%~30% more than SR

SR: stoichiometric ratio

pH Effect- for salt with weak acid as ligand (弱酸盐)

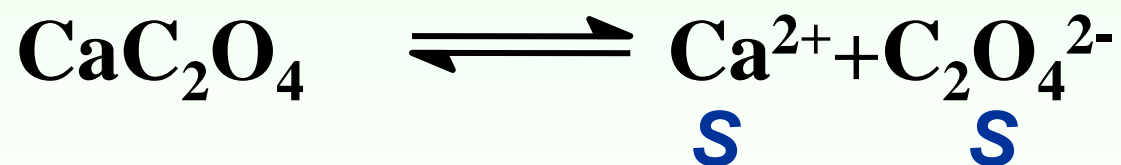
Example

Calculate Solubility of CaC_2O_4 in varied condition

(1) In Pure water

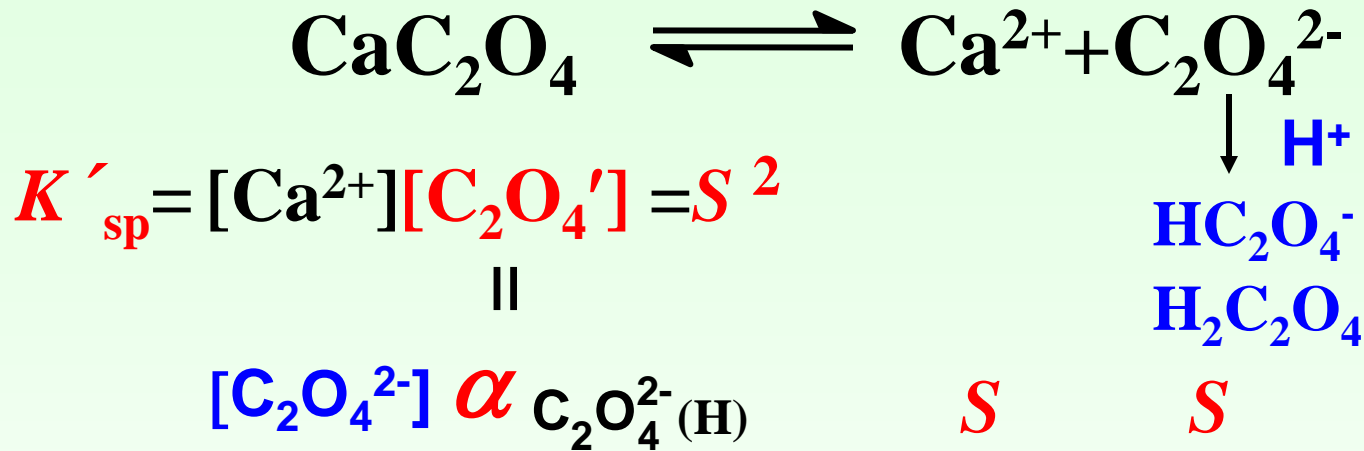
$$K_{\text{sp}}^{\ominus}(\text{CaC}_2\text{O}_4) = 10^{-8.6} \quad *(I=0)$$

$$\text{H}_2\text{C}_2\text{O}_4 \quad \text{p}K_{\text{a}_1} = 1.3 \quad \text{p}K_{\text{a}_2} = 4.3 \quad *(I=0)$$



$$S = [\text{Ca}^{2+}] = [\text{C}_2\text{O}_4^{2-}] = \sqrt{K_{\text{sp}}^{\ominus}} = 5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

(2) In acidic medium 酸性介质中



$$S = [\text{Ca}^{2+}] = [\text{C}_2\text{O}_4'] = \sqrt{K'_{\text{sp}}} = \sqrt{K_{\text{sp}} \cdot \alpha_{\text{C}_2\text{O}_4^{2-}(\text{H})}}$$

$$\alpha_{\text{C}_2\text{O}_4^{2-}(\text{H})} = 1 + [\text{H}^+] \beta_1 + [\text{H}^+]^2 \beta_2$$

$$K_{\text{sp}}(\text{CaC}_2\text{O}_4) = 10^{-7.8} \quad *(I=0.1)$$

$$\text{H}_2\text{C}_2\text{O}_4 \quad \text{p}K_{\text{a}_1} = 1.3 \quad \text{p}K_{\text{a}_2} = 4.3 \quad *(I=0.1)$$

pH=1.0 (HCl)

$$\alpha_{\text{C}_2\text{O}_4(\text{H})} = 1 + 10^{-1.0+4.0} + 10^{-2.0+5.1} = 10^{3.4}$$

$$S^2 = [\text{Ca}^{2+}][\text{C}_2\text{O}_4'] = K'_{\text{sp}}$$

$$= K_{\text{sp}} \cdot \alpha_{\text{C}_2\text{O}_4^{2-}(\text{H})} = 10^{-7.8+3.4} = 10^{-4.4}$$

$$S = 10^{-2.2} = 6 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

Barely precipitate

几乎不沉淀

In H₂O $5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$

pH = 1.0 with excess $\text{H}_2\text{C}_2\text{O}_4$ ($c = 0.10 \text{ mol}\cdot\text{L}^{-1}$)

$$[\text{Ca}^{2+}] = S, [\text{C}_2\text{O}_4'] = S + c \approx c = 0.10 \text{ mol}\cdot\text{L}^{-1}$$

$$S = [\text{Ca}^{2+}] = \frac{K'_{\text{sp}}}{[\text{C}_2\text{O}_4']} = 10^{-4.4+1.0} = 10^{-3.4} = 4 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$$

pH = 4.4 with excess $\text{H}_2\text{C}_2\text{O}_4$ ($c = 0.10 \text{ mol}\cdot\text{L}^{-1}$)

$$\alpha_{\text{C}_2\text{O}_4(\text{H})} = 10^{0.15} \quad K'_{\text{sp}} = K_{\text{sp}} \alpha_{\text{C}_2\text{O}_4^{2-}(\text{H})} = 10^{-7.7}$$

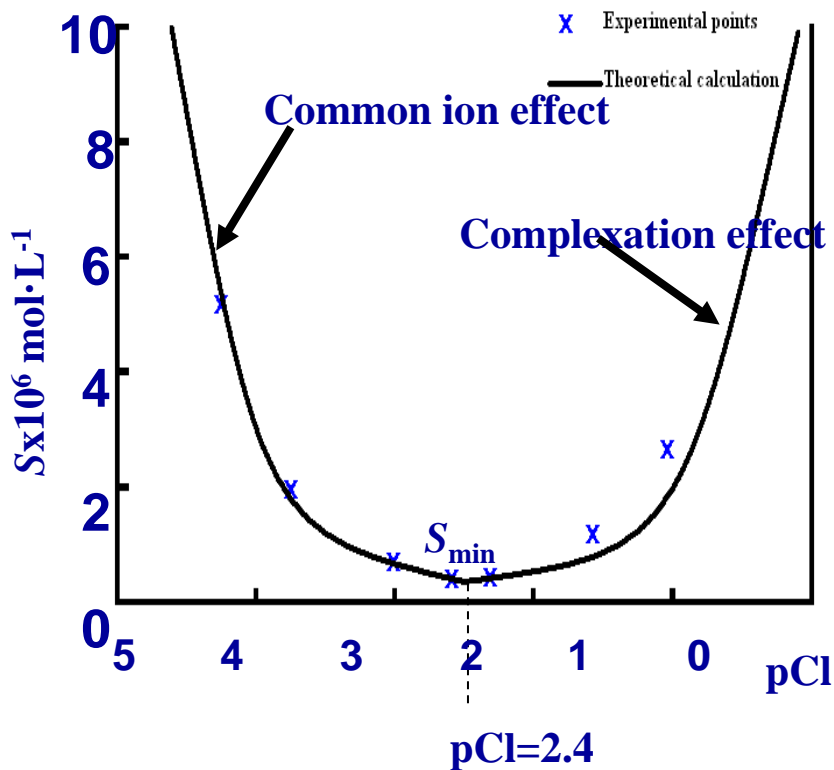
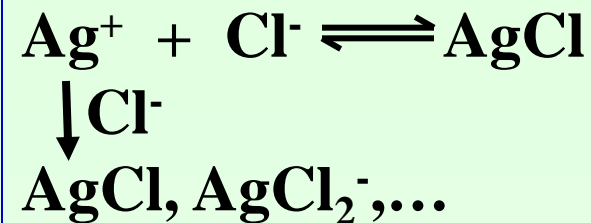
$$S = \frac{K'_{\text{sp}}}{[\text{C}_2\text{O}_4']} = 10^{-7.7+1.0} = 10^{-6.7} = 2 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}$$

Ca^{2+} is completely precipitated

Determination of Ca^{2+} using KMnO_4 titrimetry (MO is used to indicate pH for precipitation)

Complexation effect

—Increase Solubility



$S(\text{AgCl})$ - pCl plots

$$K_{\text{sp}}' = [\text{Ag}'] [\text{Cl}^-]$$

$$= [\text{Ag}^+] [\text{Cl}^-] \alpha_{\text{Ag}(\text{Cl})}$$

$$= K_{\text{sp}} (1 + [\text{Cl}] \beta_1 + [\text{Cl}]^2 \beta_2 + \dots)$$

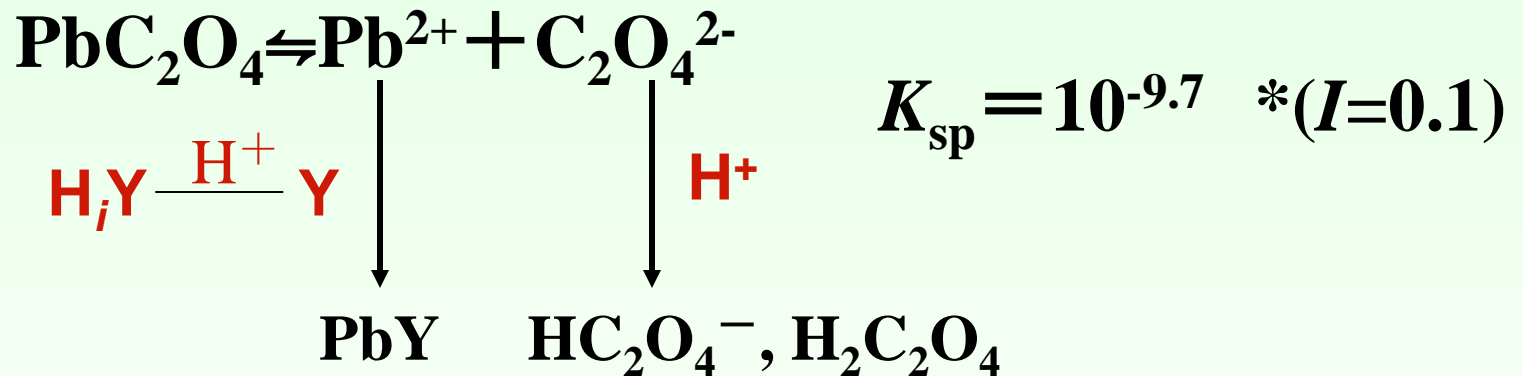
$$S = [\text{Ag}'] = K_{\text{sp}}' / [\text{Cl}^-]$$

$$= K_{\text{sp}} \left(\frac{1}{[\text{Cl}^-]} + \beta_1 + [\text{Cl}] \beta_2 + \dots \right)$$

Or $S = [\text{Ag}'] = [\text{AgCl}(\text{aq})] + [\text{Ag}^+] + [\text{AgCl}_2^-] + \dots$ 19

pH & Complexation Effects

Example: Solubility of PbC_2O_4 when $\text{pH}=4.0$,
 $[\text{C}_2\text{O}_4'] = 0.1 \text{ mol}\cdot\text{L}^{-1}$, and $[\text{Y}'] = 0.01 \text{ mol}\cdot\text{L}^{-1}$



$$\text{pH}=4.0: \alpha_{\text{C}_2\text{O}_4(\text{H})} = 10^{0.3} ; \alpha_{\text{Y}(\text{H})} = 10^{8.6}$$

$$[\text{Y}] = [\text{Y}'] / \alpha_{\text{Y}(\text{H})} = 10^{-10.6}$$

$$\alpha_{\text{Pb}(\text{Y})} = 1 + 10^{-10.6+18.0} = 10^{7.4}$$

$$K'_{sp} = K_{sp} \alpha_{\text{Pb(Y)}} \alpha_{\text{C}_2\text{O}_4(\text{H})} = 10^{-9.7+7.4+0.3} = 10^{-2.0}$$

$$S = [\text{Pb}'] = \frac{K'_{sp}}{[\text{C}_2\text{O}_4'] } = 10^{-2.0} / 0.1 = 0.1 \text{ mol} \cdot \text{L}^{-1}$$

$\therefore \text{PbC}_2\text{O}_4$ does not precipitate at this condition

Will CaC_2O_4 precipitates at this condition?

$$\alpha_{\text{Ca(Y)}} = 1 + 10^{-10.6+10.7} = 10^{0.4}$$

$$K'_{sp} = K_{sp} \alpha_{\text{Ca(Y)}} \alpha_{\text{C}_2\text{O}_4(\text{H})} = 10^{-7.8+0.4+0.3} = 10^{-7.1}$$

$$S = [\text{Ca}'] = \frac{K'_{sp}}{[\text{C}_2\text{O}_4'] } = 10^{-7.1} / 0.1 = 10^{-6.1} \text{ mol} \cdot \text{L}^{-1}$$

Ca^{2+} is completely precipitated. That is, Ca^{2+} can be completely separated from Pb^{2+} .

Part VI Precipitation Titrimetry 沉淀滴定法

考试要求，请自学！

- Titration Curves
- Mohr Method—chromate ion $\text{K}_2\text{Cr}_2\text{O}_7$ as the indicator
- Volhard Method—Iron (III) $\text{FeNH}_4(\text{SO}_4)_2$ 铁铵矾 as the indicator
- Fajans Method—adsorption indicators

Homework

- Chapter 6 (英文讲义第7章): 1, 2, 11

Based on reactions that yield ionic compounds of limited solubility

银量法 Argentometric Methods



Analytes分析物:

- Halides卤化物: Cl^- 、 Br^- 、 I^-
- Halide-like anions: SCN^- 、 CN^- and CNO^-
- Ag^+

Titration Curves

$$pK_{sp}(\text{AgCl})=9.5 \quad (I=0.1)$$

<i>T</i> %	pCl	pAg
0.0	1.0	
90.0	2.3	7.2
99.0	3.3	6.2
99.9	4.3	5.2
100.0	4.75	4.75
100.1	5.2	4.3
101.0	6.2	3.3
110.0	7.2	2.3
200.0	8.0	1.5

AgNO₃ (0.10 mol/L)



NaCl (0.10 mol/L)



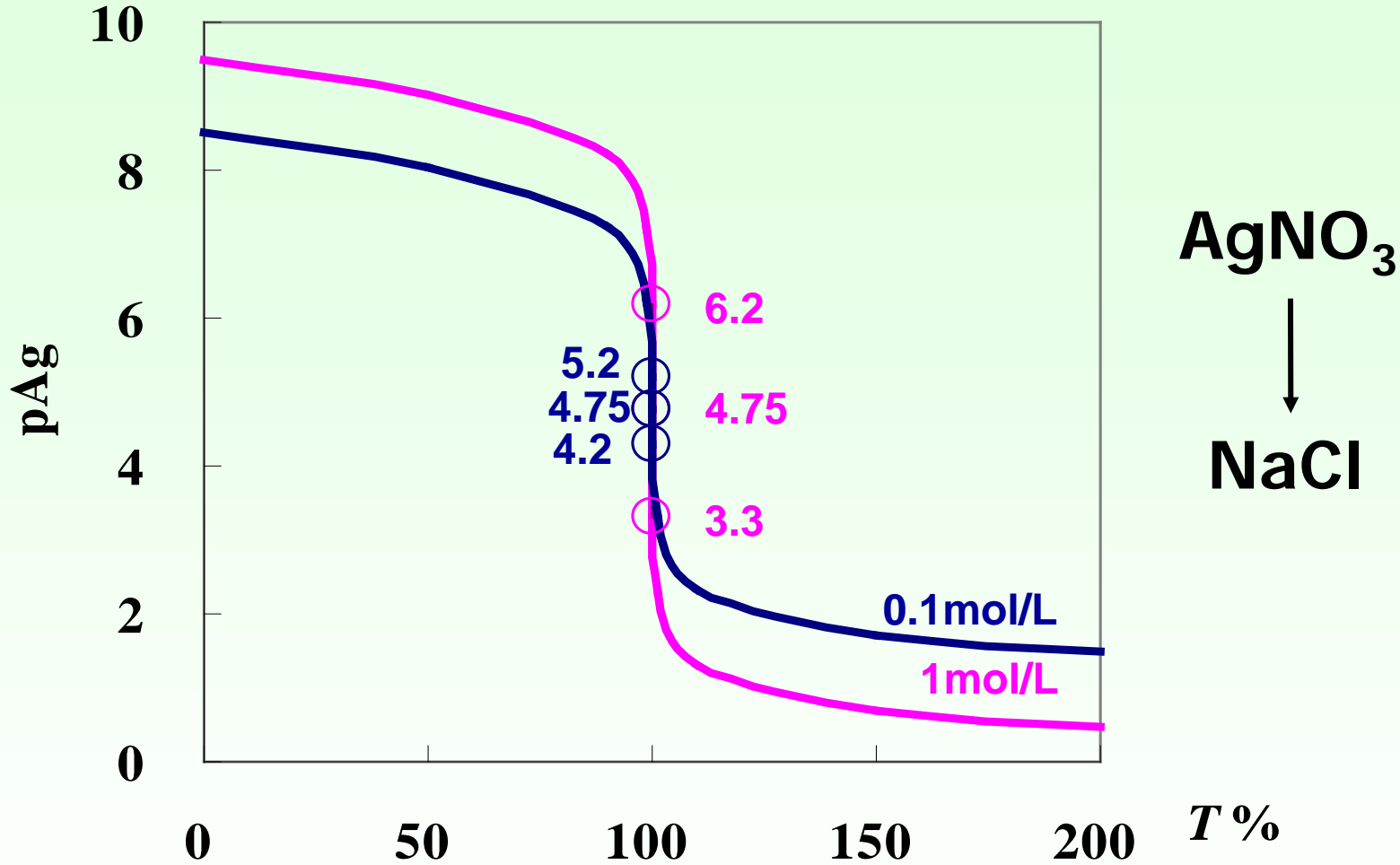
Pre-sp: Cl⁻

⇒ sp: $\sqrt{K_{sp}}$



Post-sp: Ag⁺

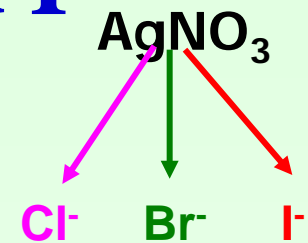
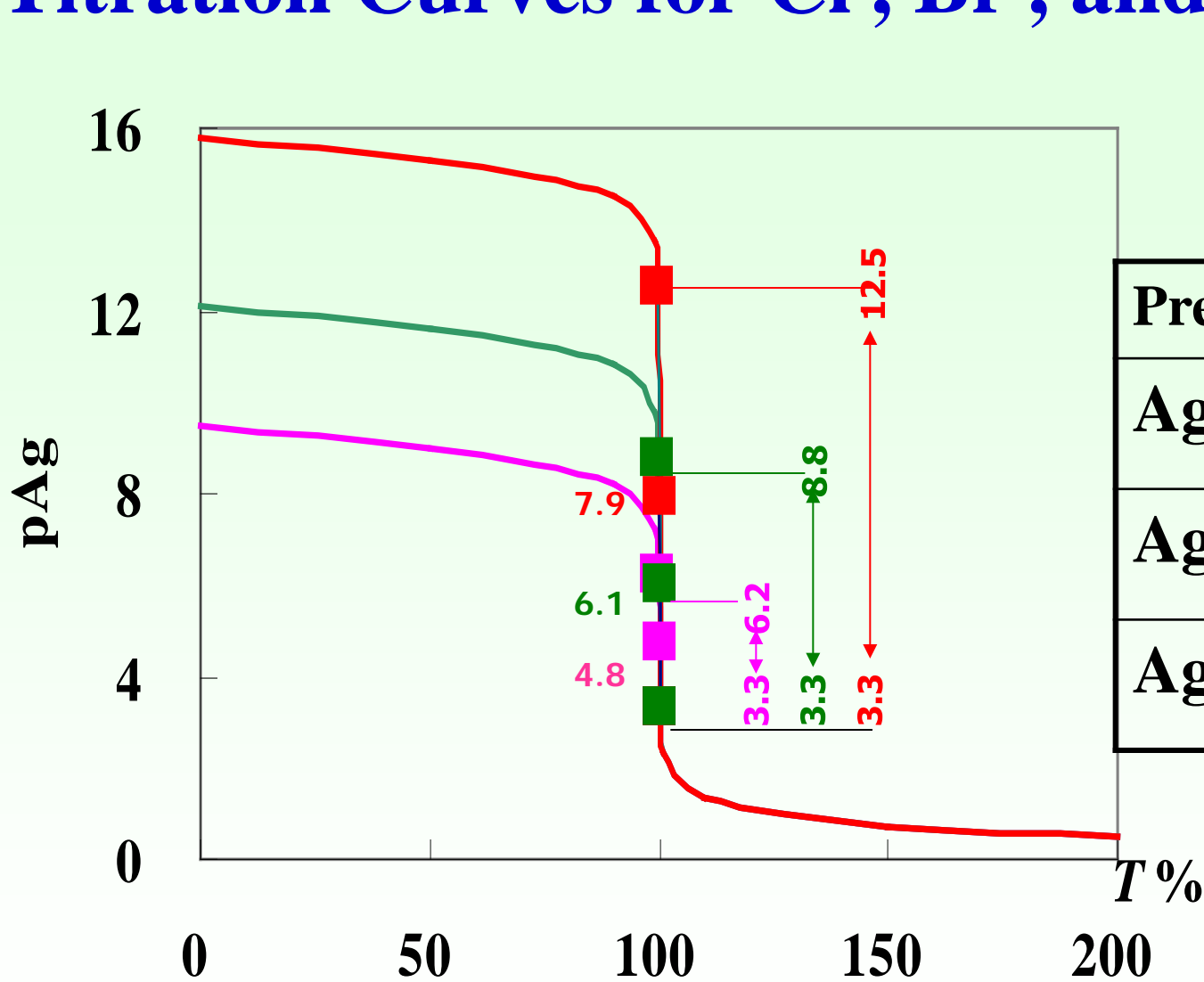
Titration Curve



Jump range expands by 2 pAg units when concentration increases by 10 folds.

浓度增大10倍，突跃增加2个pAg单位

Titration Curves for Cl⁻, Br⁻, and I⁻



Precipitates	pK _{sp}
AgCl	9.75
AgBr	12.31
AgI	16.08

When K_{sp} decreases by 10^n , jump range decreases by n folds of pAg

K_{sp} 减小 10^n , 突跃增加 n 个 pAg 单位

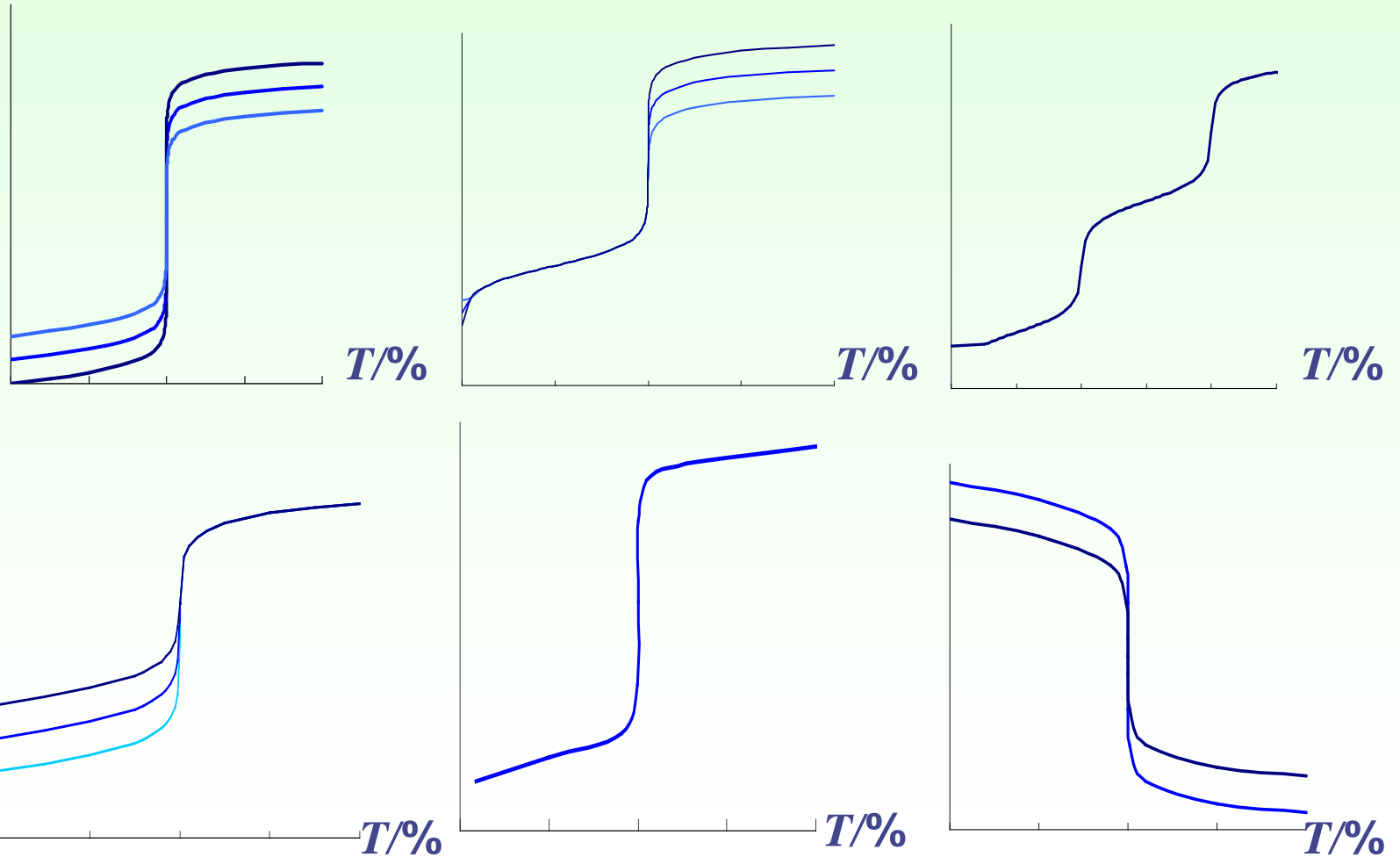
Argentometric Methods (银量法) Using Different Indicator (Learn by Yourself)

- Methods named by the name of inventor:
 - Mohr
 - Volhard
 - Fajans
- Titrations:
 - Titrand
 - Titrant
 - pH
 - Indicator

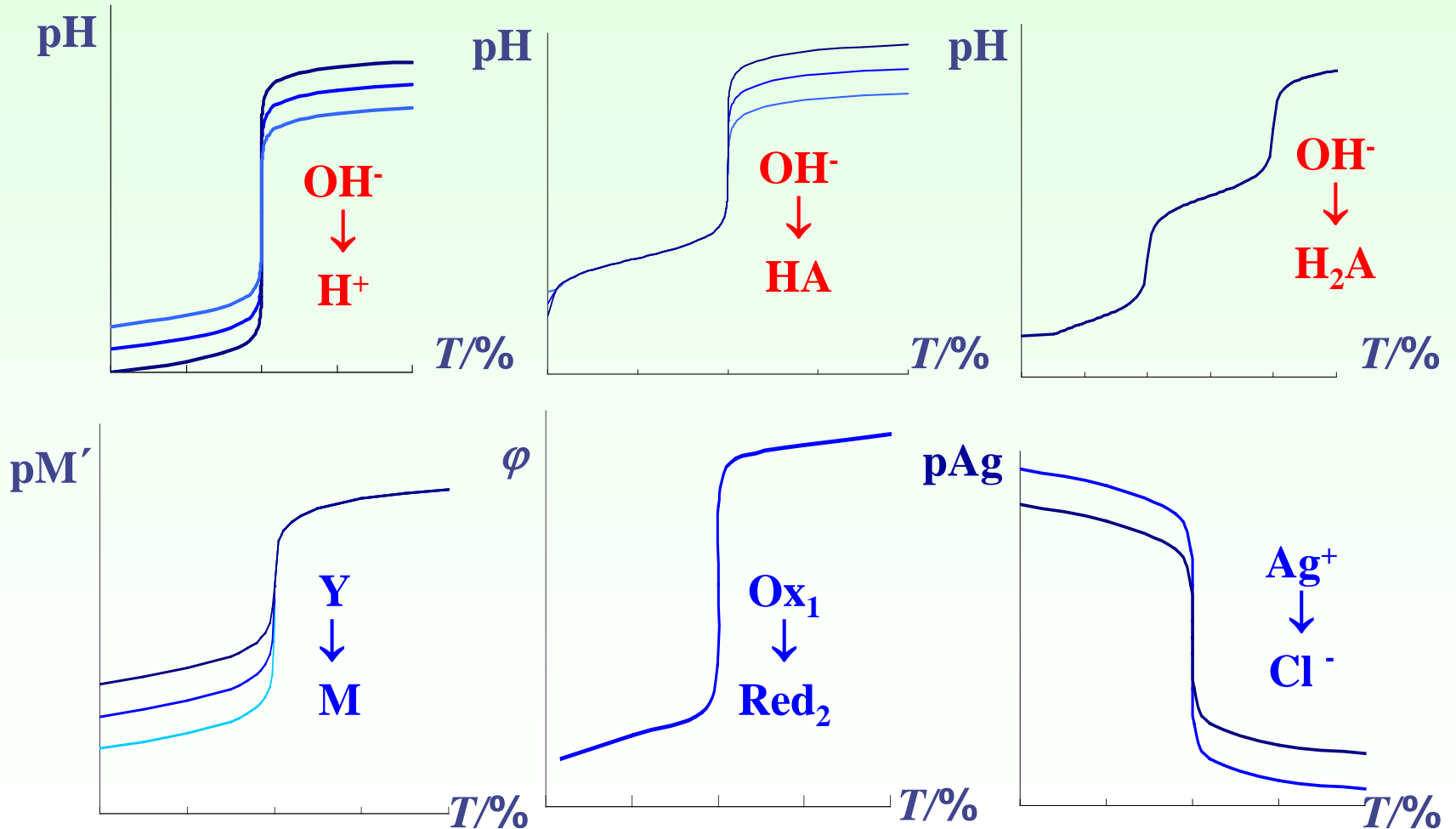
Goal-A Successful Titration, $E_t \leq \pm 0.1\%$

- Calculate solubility
- Construct a titration curve
- How to select an indicator
- Application examples
 - 《教程》思考题与习题6.11 and 6.12.
- Standard solution preparation

Summary of Titration Curves



Summary of Titration Curves



Summary of Titrimetry

- **Transition range as affected by**
 - **Concentration**
 - **Titration constant**
- **Criteria for a successful titration**
- **Selection of Indicator**
- **Preparation and standardization of standard solution**
- **Application examples**

Analytical Chemistry

- **Chemical Analysis**

化学分析

Chemical Reaction, macro-amount 化学反应, 常量分析

- **Titrimetry**

滴定分析法、容量分析法

Visual Indication 视觉指示

- **Gravimetry** 重量分析法

- **Instrumental analysis:**

仪器分析

Properties of compounds that can be transferred into detectable signals, micro and trace amount 化合物的性质转变成可测信号, 微量与痕量分析

可测信号:

- **Light** 光

- **Mass** 质量 - **mass spectroscopy**

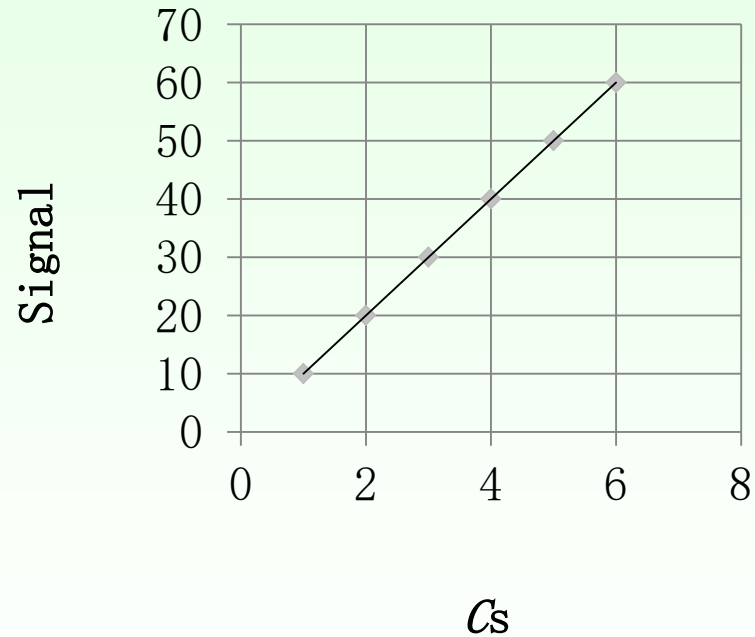
- **Magnetic** 磁性 - **NMR (C, H, P, etc.)**

- **Electric signal: charge** 电荷, **voltage** 电压, **current** 电流

Chemical Analysis versus Instrumental Analysis

化学分析与仪器分析

$$c_x = \frac{c_s V_s}{25.00}$$



单点定量 与

校准曲线

Range of Analysis

- Based on sample size 样品的绝对量

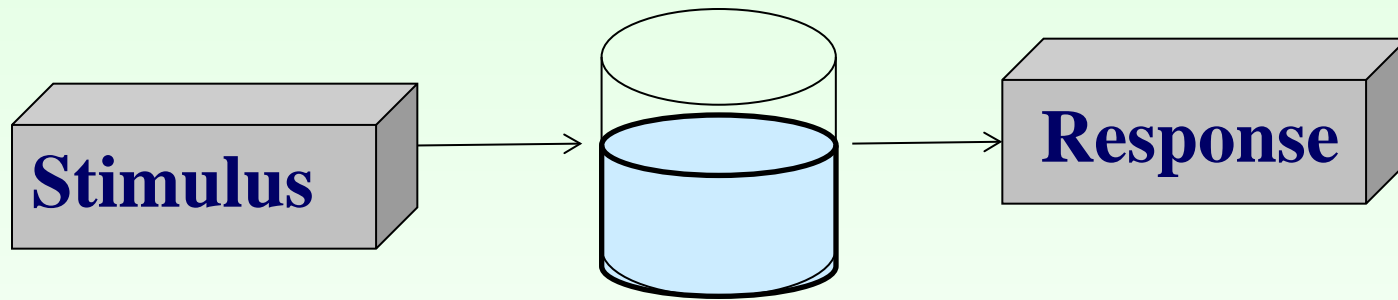
Sample Form 样品形态	Solid (mg)	Liquid (mL)
Macro (or Meso) 常量	>100	>10
Semi-micro 半微量	10~100	1~10
Micro 微量	<10	<1

- Based on content of constituents 组分含量

Constituents	Concentration Level
Major 常量	> 1%
Minor 微量	0.1 - 1%
Trace 痕量	<0.1%

Instrumental Analysis

仪器分析



Energy source
能量源

System under study
研究的系统

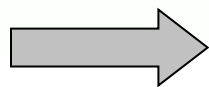
Analytical information
分析化学信息

Basic Elements for Instrumental Analysis

仪器分析方法的基本要素

- Properties of compounds that can be transferred into detectable signals
化合物的性质能够被转换成可测信号
- Detector that can detect such signals
可以检测这样的信号的检测器
- Signal to concentration transformation
信号与浓度关系的转换

The Fundamental Law of Chemistry and Physics



Now, spectrochemical analysis
光化学分析