Homework & Corrections

- **Chapter 5 （英文书第6章）：** 6～8
- **P163, second paragraph, line 1 & 5, and the name of the molecular structure, sulfate → sulfonate**
- **P182, line 1from the bottom, $10^{3.4} \rightarrow 10^{0.5}$**
- **P186, line 2 from the bottom, 1st paragraph, the caption in Figure 7.2, 0.1000 → 1.000,**

Chapter VI Redox Titration 氧化还原滴定

- Introduction to Electrochemistry电化学简介
  - Electrode potentials电极电位
  - Electrochemical cell potentials电池电动势
  - Redox equilibrium constant氧还平衡常数
- Redox Titration Curves and Indicators
- Applications of oxidation/reduction titrations
  - Auxiliary辅助 oxidizing and reducing reagents试剂提高选择性(selectivity)
  - Examples of Standard Reducing/Oxidizing Agents

Titration Curves

- **Acid-base titration:**
  - **Curve: pH ~ T%**
  - **Indicator: dyes with color sensitive to pH change**
- **Complexometric titration:**
  - **Curve: pM ′~ T%**
  - **Indicator: Color change between**

    Metal-dyes complex $\Leftrightarrow$ **Dye**
- **Redox titration**
  - **Curve: φ'（Potential，电极电位）~ T%**
  - **Indicator: dyes with color change upon oxidation**

Oxidation-Reduction Reactions
氧化还原反应

$$Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$$

- **An oxidizing agent has a strong affinity for electrons**
  氧化剂对电子有强的亲和性
- **A reducing agent easily donates electrons.**
  还原剂容易给出电子
- **Conservative Law:** 电子转移数守恒

The reaction unit (反应单元，基本单元）**that involves transfer of one electron.**

与一个电子的转移对应的化学式，如 Fe^{3+}, Ce^{3+}，$\frac{1}{5}KMnO_4$

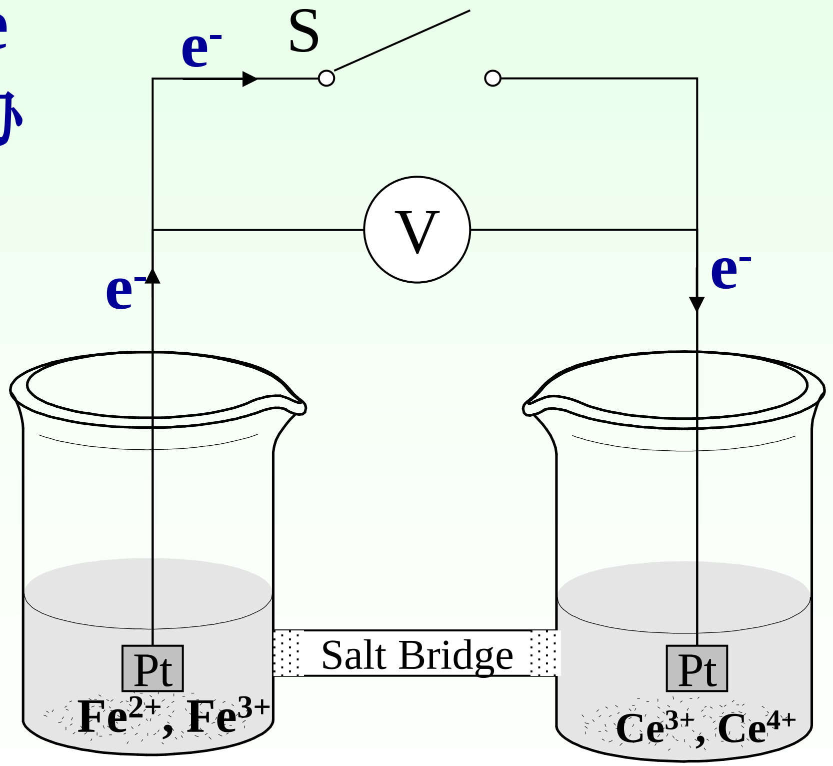
Electrochemical Cell and Half-cell Reaction
电化学池与半电池反应

Half-cell reaction: Ox + ne^- ⇋ Red **φ(Ox/Red)**

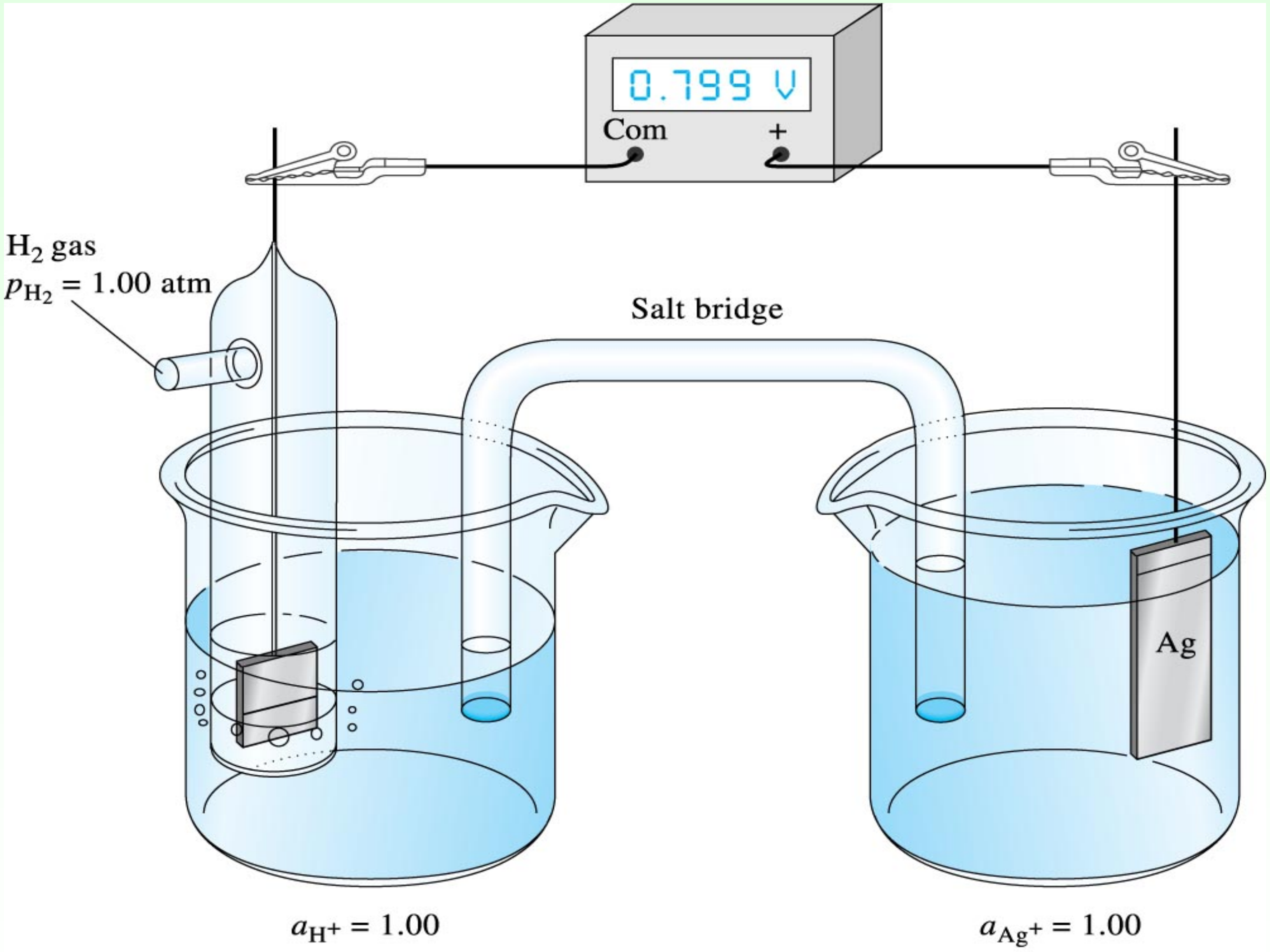
The Gibbs-Stockholm electrode potential convention电极电位协议 by IUPAC, 1953

- **Reduction Reaction 还原反应**

$\underline{E}_{cell} = E_{Ce} - E_{Fe}$



Measurement of the Electrode Potential for an Ag Electrode
银电极反应电极电位的测量



This approach is seen in everyday life!

For example, altitude is given in meters or feet above the sea level!

The Standard Hydrogen Reference Electrode 标准氢电极

- **The standard hydrogen electrode (SHE) serves as a reference electrode参比电极**

  $$2H^+ (aq) + 2e^- \leftrightharpoons H_2 (g)$$

- **By convention根据惯例, the potential of SHE is assigned to a value of 0.000 V at all temperatures.**
- **An electrode potential is the potential of a cell that has a SHE as the reference参比.**

The Nernst Equation

Ox + *n*e$^-$ ⇋ Red   Reversible可逆

$$\varphi(\mathrm{Ox/Red}) = \varphi^{\odot\prime}\mathrm{Ox/Red}) + \frac{0.059}{n}\log\frac{a(\mathrm{Ox})}{a(\mathrm{Red})}$$

$\varphi^{\ominus}$ **(The standard electrode potential) 热力学常数**

- **The higher the $\varphi^{\ominus}$， the stronger the oxidizing agent**
- **The lower the $\varphi^{\ominus}$， the stronger the reducing agent**

Electrode Potential电极电位

$$\varphi = \varphi^{\odot} + \frac{0.059}{n}\log\frac{a(\mathrm{Ox})}{a(\mathrm{Red})}$$

↑

$\varphi=\varphi^{\ominus}$（标准电位） where a(Ox) =1 mol/M and a(Red)=1 mol/L

$$\varphi = \varphi^{\odot} + \frac{0.059}{n}\log\frac{\gamma(\mathrm{Ox})}{\gamma(\mathrm{Red})} + \frac{0.059}{n}\log\frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

$\varphi=\varphi^{\ominus c}$ (浓度电位） where [Ox]=1 mol/L and [Red]=1 mol/L

Ionic strength is considered.考虑了离子强度

$$\varphi = \varphi^{\odot C} + \frac{0.059}{n}\log\frac{\alpha_{\mathrm{Red}}}{\alpha_{\mathrm{Ox}}} + \frac{0.059}{n}\log\frac{c(\mathrm{Ox})}{c(\mathrm{Red})}$$

$\varphi^{\ominus\prime}$（条件电位）

$\varphi=\varphi^{\ominus\prime}$(条件电位/克式电位）Formal Potential where c(Ox)=1 mol/L and c(Red)=1mol/L. Side reaction occurs. 有副反应发生

Factors Affecting $\varphi^{\ominus\prime}$影响条件电极电位的因素 -Ionic Strength of Solution溶液离子强度

$$\varphi^{\ominus}(Fe(CN)_6^{3-}/Fe(CN)_6^{4-}) = 0.355V$$

I	0.00064	0.00128	0.112	1.6
$\varphi^{\ominus\prime}$	0.3619	0.3814	0.4094	0.4584

Other than pointed out, Ionic Strength is not considered in most cases, that is, $\varphi^{\ominus c} \approx \varphi^{\ominus}$

为了简化，除非另外指出，在大多数时候不考虑离子强度

Complex Formation络合物的形成

$\varphi^{\ominus}(Fe^{3+}/Fe^{2+})=0.77\ V$

Media (1 mol·L^{-1})	$HClO_4$	HCl	H_2SO_4	H_3PO_4	HF
$\varphi^{\ominus\prime}(Fe^{3+}/Fe^{2+})$ /V	0.75	0.70	0.68	0.44	0.32

→ 与Fe^{3+}的络合作用增强

Complex of Oxidizing form is more stable, which makes the electrode potential decrease. 氧化形形成的络合物更稳定，因此电极电位降低

Exceptional Example 例外, 邻二氮菲（phen),

$\log\beta(Fe(phen)_3^{3+}) = 14.1$, $\log\beta(Fe(phen)_3^{2+}) = 21.3$

$$\varphi^{\ominus\prime}(Fe^{3+}/Fe^{2+}) = 1.06\ V\ (1\ mol{\cdot}L^{-1}\ H_2SO_4)$$

Example

$I_2/Na_2S_2O_3$ titration for Cu^{2+} at pH 3.0 in trace amount of Fe^{3+} and $c(F^-)=0.1 mol\cdot L^{-1}$, $\varphi^{\ominus\prime}(Fe^{3+}/Fe^{2+})=?$

$$\varphi^{\ominus}(Fe^{3+}/Fe^{2+}) = 0.77V, \quad \varphi^{\ominus}(I_2/I^-) = 0.54V$$

For FeF_3, $\log \beta_{1\text{-}3}$=5.1, 9.2, 11.9, $\log K^H(HF)$=3.1 $^*(I=0.1)$

$S_2O_3^{2-}$

$$2Cu^{2+} + 4I^- \rightarrow 2CuI\downarrow + I_2$$

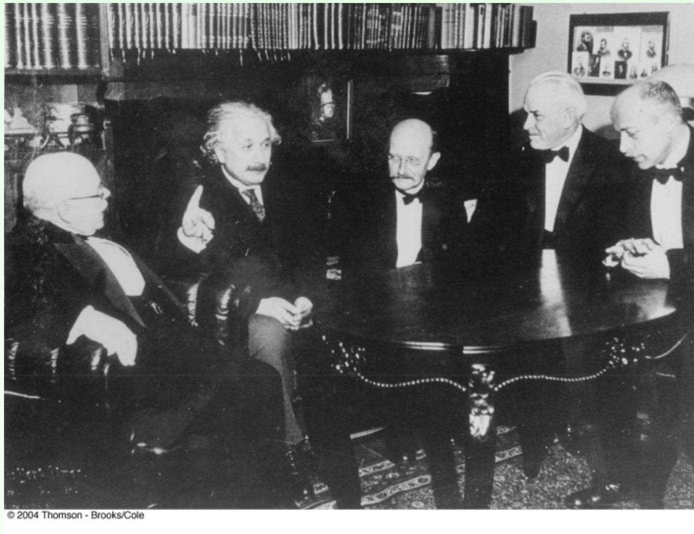
Approach

$$\varphi = \varphi^{\odot} + 0.059\log\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

$$\approx \varphi^{\odot} + 0.059\log\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$= \varphi^{\odot} + 0.059\log\frac{c(Fe^{3+})/\alpha_{Fe^{3+}}}{c(Fe^{2+})/\alpha_{Fe^{2+}}}$$

$$= \varphi^{\odot} + 0.059\log\frac{\alpha_{Fe^{2+}}}{\alpha_{Fe^{3+}}} + 0.059\lg\frac{c(Fe^{3+})}{c(Fe^{2+})}$$



L to R:

- •Walther Nernst (Chemistry, 1920)
- •Albert Einstein, (Physics 1921)
- •Max Planck (Physics 1918),
- •Robert A. Millikan (Physics 1923)),
- •Max von Laue (Physics 1914)

Sort backwards and calculate forwards:

$\alpha_{M(F)} \rightarrow [F^-] \rightarrow [H^+]$

Cont'd

$$\alpha_{F(H)} = 1 + [H^+]K^H(HF) = 10^{0.4}$$

$$[F^-] = c(F^-)/\alpha_{F(H)} = 10^{-1.4}$$

$$\alpha_{Fe^{3+}(F)} = 1 + [F^-]\beta_1 + [F^-]^2\beta_2 + [F^-]^3\beta_3 = 10^{7.7}$$

$$\alpha_{Fe^{2+}(F)} = 1$$

$$\varphi^{\odot'}(Fe^{3+}/Fe^{2+}) = \varphi^{\odot c}(Fe^{3+}/Fe^{2+}) + 0.059\log\frac{\alpha_{Fe^{2+}}}{\alpha_{Fe^{3+}}}$$

$$=0.77-0.059\times 7.7=0.32<0.54\ (\varphi^{\odot}(I_2/I^-))$$

Fe^{3+} will not oxidize I^-.

Effect of Precipitation沉淀的影响

Example:

At 25℃, [KI] = 1mol·L^{-1}, $\varphi^{\ominus}_{Cu^{2+}/Cu^{+}} = ?$
(Disregard effect of ionic strength.)

忽略离子强度的影响

$$\varphi^{\ominus}(Cu^{2+}/Cu^{+}) = 0.17\,V,\quad \varphi^{\ominus}(I_2/I^{-}) = 0.54\,V$$

$S_2O_3^{2-}$

$$2Cu^{2+} + 4I^{-} \rightarrow 2CuI\downarrow + I_2$$

（Principle for Iodine/Thiosulfate Titration)

$$\varphi = \varphi^{\odot} + 0.059\log\frac{a_{Cu^{2+}}}{a_{Cu^{+}}}$$

$$\approx \varphi^{\odot} + 0.059\log\frac{[Cu^{2+}]}{[Cu^{+}]}$$

$$= \varphi^{\odot} + 0.059\log\frac{[Cu^{2+}]}{K_{sp}(CuI)/[I^{-}]}$$

$$= \underbrace{\varphi^{\odot} + 0.059\log\frac{1}{K_{sp}(CuI)/[I^{-}]}}_{\varphi^{\odot\prime}(Cu^{2+}/Cu^{+})} + 0.059\lg[Cu^{2+}]$$

$$\| \alpha_{Cu^{2+}} = 1$$

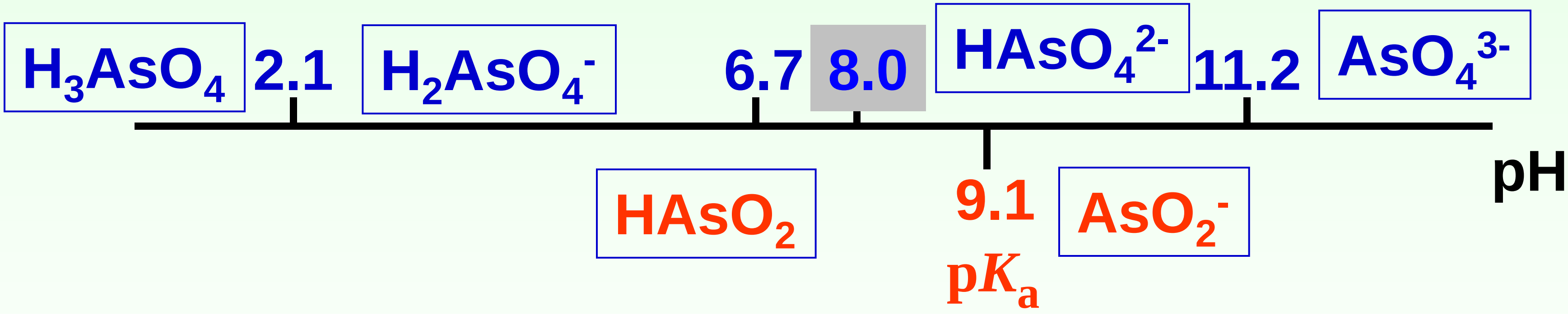
$$c(Cu^{2+})$$

$$K_{sp}(CuI) = 2.0\times10^{-12} (I = 0.1), [I^{-}]=1.0\ mol\cdot L^{-1}$$

$$\varphi^{\odot\prime} = 0.17 + 0.69 = 0.86V > \varphi^{\odot}(I_2/I^{-})$$

Example: pH effect

$$pH = 8.0,\ \varphi^{\odot\prime}(As(V)/As(III)) = ?$$



Half reaction

$$H_3AsO_4 + 2H^+ + 2e^- \leftrightharpoons HAsO_2 + 2H_2O$$

When H^+ or OH^- are in involved in the half-cell reaction, Nernst Equation will include $[H^+]$ or $[OH^-]$

$$\varphi = \varphi^{\ominus}(\mathrm{As(V)/As(III)}) + \frac{0.059}{2}\log\frac{[\mathrm{H}^+]^2[\mathrm{H_3AsO_4}]}{[\mathrm{HAsO_2}]}$$

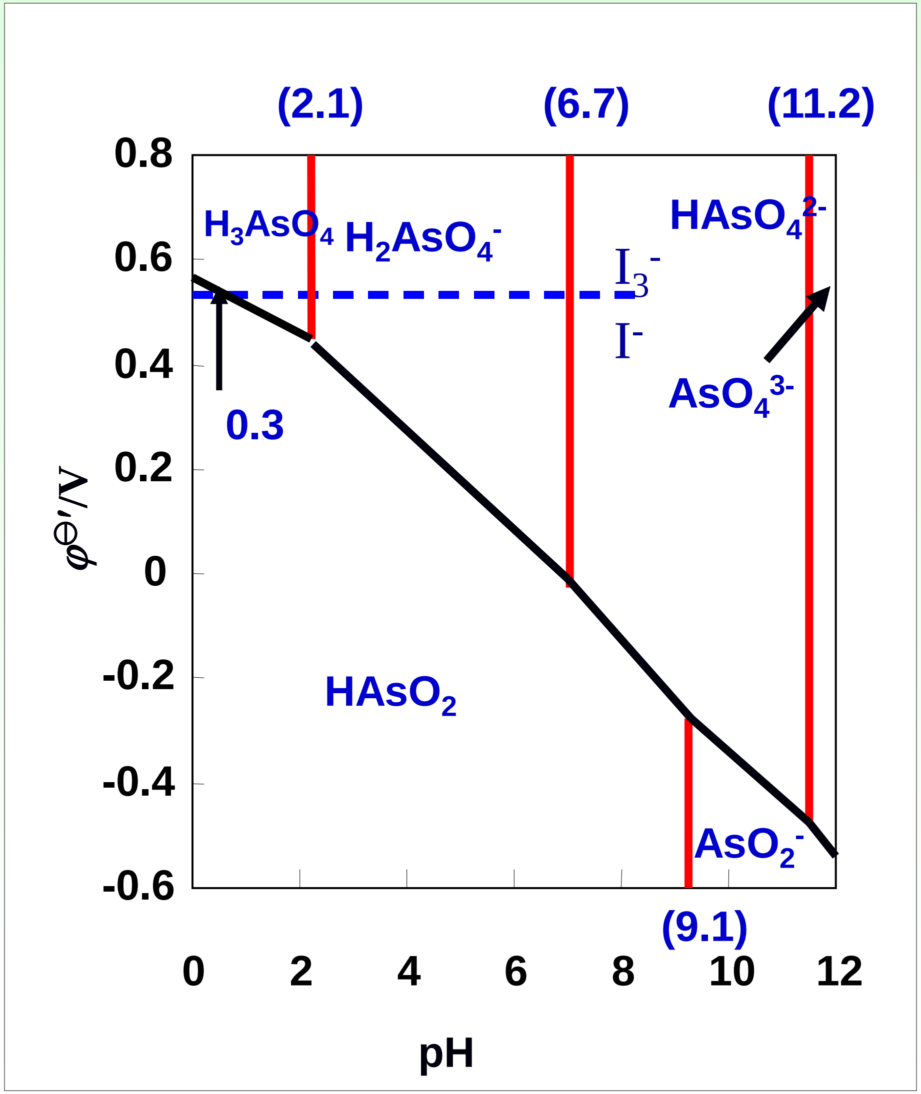
$$= \underbrace{\varphi^{\ominus}(\mathrm{As(V)/As(III)}) + \frac{0.059}{2}\log\frac{[\mathrm{H}^+]^2 x(\mathrm{H_3AsO_4})}{x(\mathrm{HAsO_2})}}_{\varphi^{\ominus\prime}(\mathrm{As(V)/As(III)})} + \frac{0.059}{2}\log\frac{c(\mathrm{As(V)})}{c(\mathrm{As(III)})}$$

At pH = 8.0, $x(\mathrm{HAsO_2}) = 1.0$, $x(\mathrm{H_3AsO_4}) = 10^{-6.8}$

$$\varphi^{\ominus\prime}(\mathrm{As(V)/As(III)}) = 0.56 + \frac{0.059}{2}\log\frac{10^{-8.0\times 2}\times 10^{-6.8}}{1.0}$$

$$= -0.11\,\mathrm{V}$$

$\varphi^{\ominus\prime}$ (As(V)/As(III)) ~ pH



- **pH 8-9, I_3^- oxidizes As(III)**
- **4 mol/L HCl, As(V) oxidizes $I^- \rightarrow I_3^-$**

$Na_2S_2O_3$

Conditional Constant, K'

Half-cell reactions:

$$Ox_1 + n_1e^- \leftrightharpoons Red_1,\quad \varphi_1 = \varphi_1^{\odot'} + \frac{0.059}{n_1}\log\frac{c(Ox_1)}{c(Red_1)}$$

$$Ox_2 + n_2e^- \leftrightharpoons Red_2,\quad \varphi_2 = \varphi_2^{\odot'} + \frac{0.059}{n_2}\log\frac{c(Ox_2)}{c(Red_2)}$$

Balanced equation配平方程式:

$$n_2Ox_1 + n_1Red_2 \leftrightharpoons n_2Red_1 + n_1Ox_2 \qquad K' = \left(\frac{c(Red_1)}{c(Ox_1)}\right)^{n_2}\left(\frac{c(Ox_2)}{c(Red_2)}\right)^{n_1}$$

$$\log K' = \frac{n(\varphi_1^{\odot'} - \varphi_2^{\odot'})}{0.059}$$

At equilibrium平衡时, $\varphi_1 = \varphi_2$

n

—数学上为n_1 与 n_2 的最小公倍数

Mathematically, the lease common multiple

—物理意义，电子转移数

Physically the total number of electrons transferred

Criteria for Redox Titration

$$n_1 = n_2 = 1, \quad \Delta\varphi = \varphi_1^{\odot'} - \varphi_2^{\odot'} = 0.35\text{v}$$

$$n_1 = 1, n_2 = 2, \quad \Delta\varphi = \varphi_1^{\odot'} - \varphi_2^{\odot'} = 0.27\text{v(why?)}$$

$$n_1 = n_2 = 2, \quad \Delta\varphi = \varphi_1^{\odot'} - \varphi_2^{\odot'} = 0.18\text{v(why?)}$$

$$\log K' = \frac{(\varphi_1^{\odot'} - \varphi_2^{\odot'})n}{0.059}$$

在氧还滴定中，一般滴定反应常数都比较大，大多数时候反应速率起关键性作用。因此滴定误差在本章不做讨论。

Reaction Rate (反应速率) of Redox Reaction (自学)

Concentration浓度
Temperature温度
Catalysts催化剂
Induced Reaction诱导反应

The reaction below is slow in the beginning and accelerates加速 after Mn(II) is generated in the solution. Why?

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ = 2Mn^{2+} + 10CO_2 + 8H_2O$$

General Redox Indicator通用型氧化还原指示剂

$$\text{In(Ox)} + n\text{e}^- \rightleftharpoons \text{In(Red)}$$

O color　　　　　　R color

$$\varphi = \varphi^{\ominus'} \pm \frac{0.059}{n} \log \frac{c(\text{In(Ox)})}{c(\text{In(Red)})}$$

Transition potential for indicator $\varphi_t(\text{In})$

$$\varphi^{\ominus'}(\text{In}) \pm \frac{0.059}{n} \text{(Transition potential range)}$$

General Redox Indicators

$$\mathrm{In(Ox)} + ne^- \rightleftharpoons \mathrm{In(Red)} \qquad \varphi = \varphi^{\ominus'} \pm \frac{0.059}{n}\log\frac{c(\mathrm{In(Ox)})}{c(\mathrm{In(Red)})}$$

	Indicator	$\varphi^{\ominus'}$ ([H^+]=1mol·L^{-1})	Red Form	Ox form
	Methylene Blue 次甲基蓝	**0.52**	**Colorless**	**Blue**
√	**Sodium diphenylamine sulfonate** 二苯胺磺酸钠	**0.85**	**Colorless**	**Mauve**
	O-phenylamine carboxylic acid 邻苯氨基苯甲酸	**0.89**	**Colorless**	**Mauve**
√	**Ferroin** 邻二氮菲亚铁	**1.06**	**Red**	**Light blue**

Indicators for Redox Titration

- Self-indicators: $KMnO_4$
- Specific Indicator: Starch淀粉 for I_3^-
- Potassium thiocyanate (KSCN) for Fe^{3+}
- Redox Indicators: based on redox reaction

Every way leads to Rome !

Titration Curve for Redox Titration

$Ce^{4+} \rightarrow Fe^{2+}$ （c=0.1000 mol·L^{-1}, 1mol·L^{-1}H_2SO_4）

Through the titration:

$$\varphi(Fe^{3+}/Fe^{2+}) = \varphi(Ce^{4+}/Ce^{3+}) = \varphi_{system}$$

- **Initial point, no enough information for calculation**
- **Pre-sp，Fe^{3+}/Fe^{2+}**
- **Post-sp，Ce^{4+}/Ce^{3+}**

Redox systems at equilibrium, φ of all half reactions are equal, that is the cell potential is zero.
在氧还体系的反应达到平衡，所有点对的电极电位相等，电池电动势为0.

Electrode Potential Calculation at sp

$$\varphi_{sp} = \varphi^{\ominus\prime}(Fe^{3+}/Fe^{2+}) + 0.059\log\frac{c(Fe^{3+})}{c(Fe^{2+})}$$

$$\varphi_{sp} = \varphi^{\ominus\prime}(Ce^{4+}/Ce^{3+}) + 0.059\log\frac{c(Ce^{4+})}{c(Ce^{3+})}$$

$$2\varphi_{sp} = \varphi^{\ominus\prime}(Fe^{3+}/Fe^{2+}) + \varphi^{\ominus\prime}(Ce^{4+}/Ce^{3+})$$

$$+0.059\log\frac{c(Fe^{3+})}{c(Fe^{2+})}\frac{c(Ce^{4+})}{c(Ce^{3+})}$$

$$\because \text{ at sp}，\; c(\mathrm{Fe}^{3+}) = c(\mathrm{Ce}^{3+}), \quad c(\mathrm{Fe}^{2+}) = c(\mathrm{Ce}^{4+})$$

$$\therefore \log \frac{c\left(\mathrm{Fe}^{3+}\right) \cdot c\left(\mathrm{Ce}^{4+}\right)}{c\left(\mathrm{Fe}^{2+}\right) \cdot c\left(\mathrm{Ce}^{3+}\right)} = 0$$

$$\varphi_{\mathrm{sp}} = \frac{\varphi^{\odot}{}'(\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}) + \varphi^{\odot}{}'(\mathrm{Ce}^{4+}/\mathrm{Ce}^{3+})}{2} = \frac{0.68 + 1.44}{2} = 1.06$$

$$\varphi_{\mathrm{sp}} = \frac{n_1 \varphi_1^{\odot}{}' + n_2 \varphi_2^{\odot}{}'}{n_1 + n_2}$$

$$\log K' = \frac{(\varphi_1^{\odot}{}' - \varphi_2^{\odot}{}')n}{0.059}$$

Ce^{4+}

↓

Fe^{2+}

$$Ce^{4+} + Fe^{2+} \xrightleftharpoons{1\,mol \cdot L^{-1} H_2SO_4} Ce^{3+} + Fe^{3+}$$

$$\varphi^{\odot\prime}(Ce^{4+}/Ce^{3+}) = 1.44\ V,\ \varphi^{\odot\prime}(Fe^{3+}/Fe^{2+}) = 0.68\ V$$

T%	Electrode Reaction	Electrode Potential
9.0	Fe^{3+}/Fe^{2+}	φ=0.68+0.059lg(9/91)=0.62
*50.0	Fe^{3+}/Fe^{2+}	φ=0.68
91.0	Fe^{3+}/Fe^{2+}	φ=0.68+0.059=0.74
*99.9	Fe^{3+}/Fe^{2+}	φ=0.68+0.059x3=0.86
*100.0		φ=(0.68+1.44)/2=1.06
*100.1	Ce^{4+}/Ce^{3+}	φ=1.44+0.059x(-3)=1.26
110.0	Ce^{4+}/Ce^{3+}	φ=1.44+0.059x(-1)=1.38
*200.0	Ce^{4+}/Ce^{3+}	φ=1.44

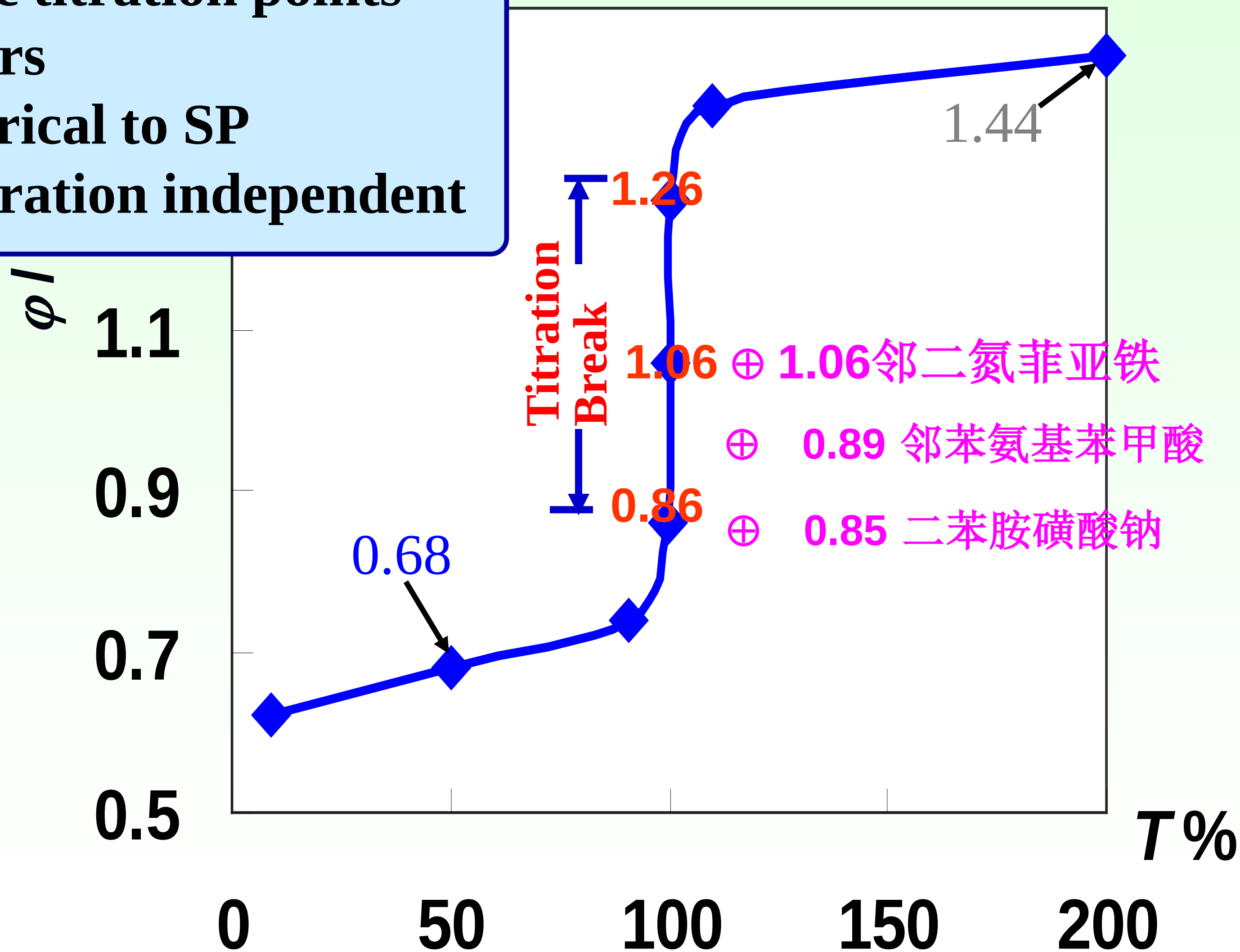
Titration curve for $Ce^{4+} \rightarrow Fe^{2+}$

$\varphi^{\ominus\prime}(Fe^{3+}/Fe^{2+}) = 0.68V$

$\varphi^{\ominus\prime}(Ce^{4+}/Ce^{3+}) = 1.44V$

Major points to Make:

- ✓ 5 specific titration points
- ✓ Indicators
- ✓ Symmetrical to SP
- ✓ Concentration independent



$Fe^{3+} \rightarrow Sn^{2+}$:

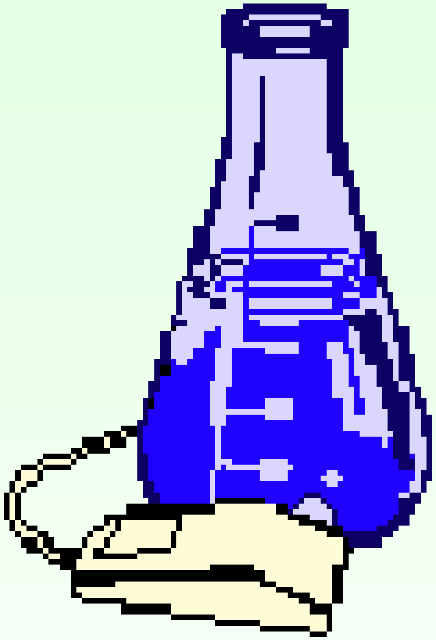
$$2Fe^{3+} + Sn^{2+} = 2Fe^{2+} + Sn^{4+}$$

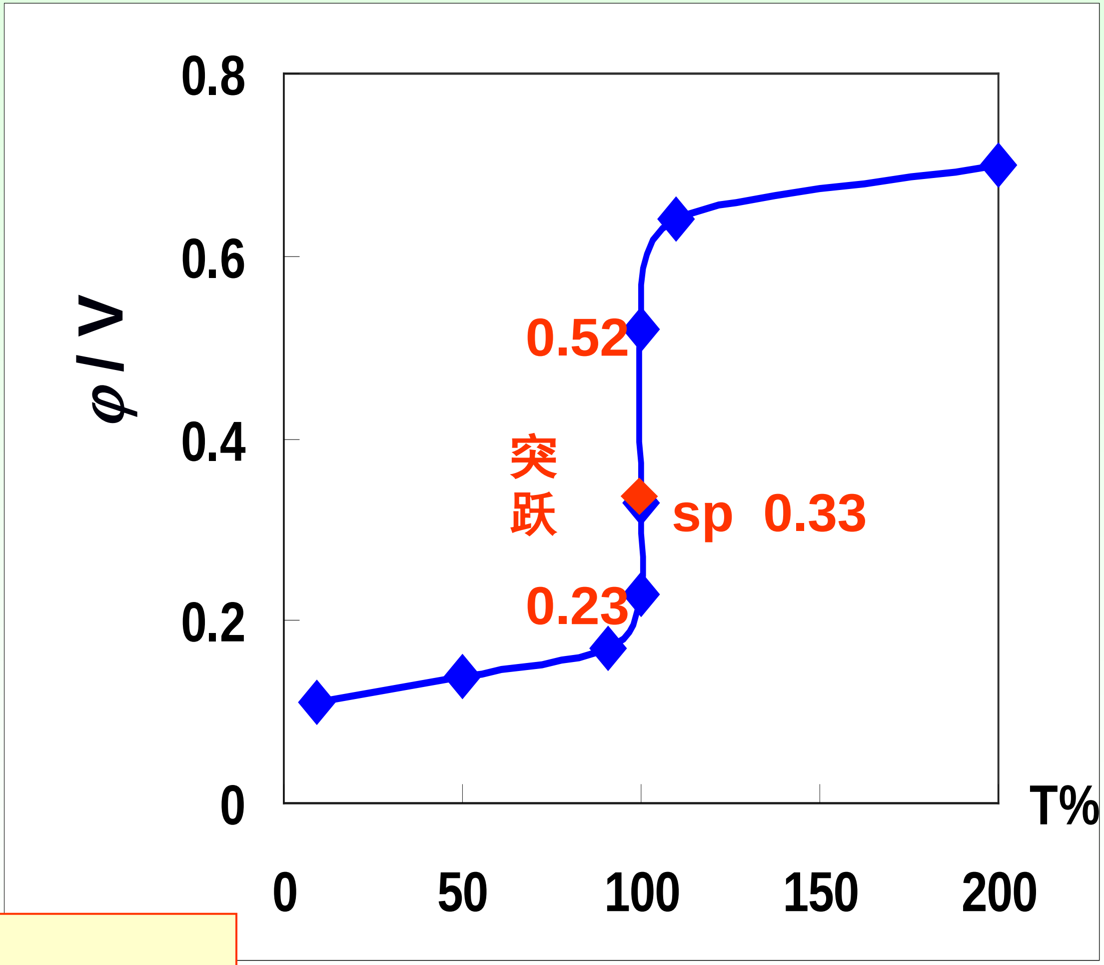
T%	Electrode Reaction	Potential of the system
9.0	Sn^{4+}/Sn^{2+}	$\varphi=0.14+(0.059/2)\times(-1)=0.11$
50.0	Sn^{4+}/Sn^{2+}	$\varphi=0.14$
91.0	Sn^{4+}/Sn^{2+}	$\varphi=0.14+(0.059/2)=0.17$
99.9	Sn^{4+}/Sn^{2+}	$\varphi=0.14+(0.059/2)\times 3=0.23$
100.0		$\varphi=(0.14x2+0.70)/(2+1)=0.33$
100.1	Fe^{3+}/Fe^{2+}	$\varphi=0.70+0.059\times(-3)=0.52$
110.0	Fe^{3+}/Fe^{2+}	$\varphi=0.70+0.059\times(-1)=0.64$
200.0	Fe^{3+}/Fe^{2+}	$\varphi=0.70$

in 1 $mol\cdot L^{-1}$ HCl

$$\varphi^{\ominus\prime}(Fe^{3+}/Fe^{2+}) = 0.70V, \qquad \varphi^{\ominus\prime}(Sn^{4+}/Sn^{2+}) = 0.14V$$

Titration Curve for $Fe^{3+} \rightarrow Sn^{2+}$





Indicator： SCN$^-$
Red color developed after SP
$Fe(SCN)^{2+}=1x10^{-5}$ mol·L^{-1}

$$\varphi^{\odot\prime}(Fe^{3+}/Fe^{2+}) = 0.70V$$

$$\varphi^{\odot\prime}(Sn^{4+}/Sn^{2+}) = 0.14V$$

Ox_1

$\downarrow$

Red_2

$$n_2Ox_1 + n_1Red_2 \rightleftharpoons n_2Red_1 + n_1Ox_2$$

$$-0.1\%: \quad \varphi = \varphi_2^{\ominus\prime} + \frac{3\times 0.059}{n_2}$$

$$sp: \quad \varphi = \frac{n_1\varphi_1^{\ominus\prime} + n_2\varphi_2^{\ominus\prime}}{n_1 + n_2}$$

$$+0.1\%: \quad \varphi = \varphi_1^{\ominus\prime} - \frac{3\times 0.059}{n_1}$$

$$50\%: \quad \varphi = \varphi_2^{\ominus\prime} (\varphi \text{ for reducing agent})$$

$$200\%: \quad \varphi = \varphi_1^{\ominus\prime} (\varphi \text{ for oxidizing agent})$$

Concentration effect on titration Curve?

Homework

- Chapter 5(英文讲义第六章)：12,13,15
- 2015年5月30日论文口头报告: 3个报告

Applying Standard Oxidizing/Reducing Agents

常用的氧化还原滴定法 （自学）

- **Potassium permanganate高锰酸钾法**
- **Potassium dichromate重铬酸钾法**
- **Sodium thiosulfate/iodine碘量法**
- **Potassium bromate溴酸钾法**
- **Iodine 碘量法**

Basic Rules for $KMnO_4$ Titration

1. Mn(III) exists in extremely strong acidic solution;
2. MnO_4^{2-} exists in strong basic solution (pH>14);
3. MnO_4^- can not exist in the presence of Mn^{2+}, *vice versa*反之亦然.

$$MnO_4^- \xrightarrow{?} Fe^{2+} \qquad Fe^{2+} \xrightarrow{?} MnO_4^-$$

Most Applied Electrode Reactions for $KMnO_4$

1. Acidic (pH≤1)

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O \quad \varphi^{\ominus} = 1.51$$

For: H_2O_2, $H_2C_2O_4$, Fe^{2+}, Sn^{2+}, NO_2^-, As(III), K^+

2. Basic with pH>14

$$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$$

For determination of organics, such as glycerine甘油

Number of reaction unit in each situation?

Preparation and Standardization of $KMnO_4$ Standard Solution

Rough weighing粗称 $\xrightarrow[\text{Boiling gently 0.5-1h}]{\text{Dissolved in } H_2O}$ **filtering $MnO_2\downarrow$**

→Brown Bottle棕色瓶 → Standardizing before titration

What filtering crucibles滤器to choose?
sintered-glass filter crucible，#P16 (10-16 μm porosity孔径）

Potassium dichromate重铬酸钾法

$$Cr_2O_7^{2-}+14H^{+}+6e=2Cr^{3+}+7H_2O \quad \varphi^{\ominus}=1.33\ V$$

Advantages:

high purity and stability, a primary standard with a moderate redox potential to facilitate a good selectivity

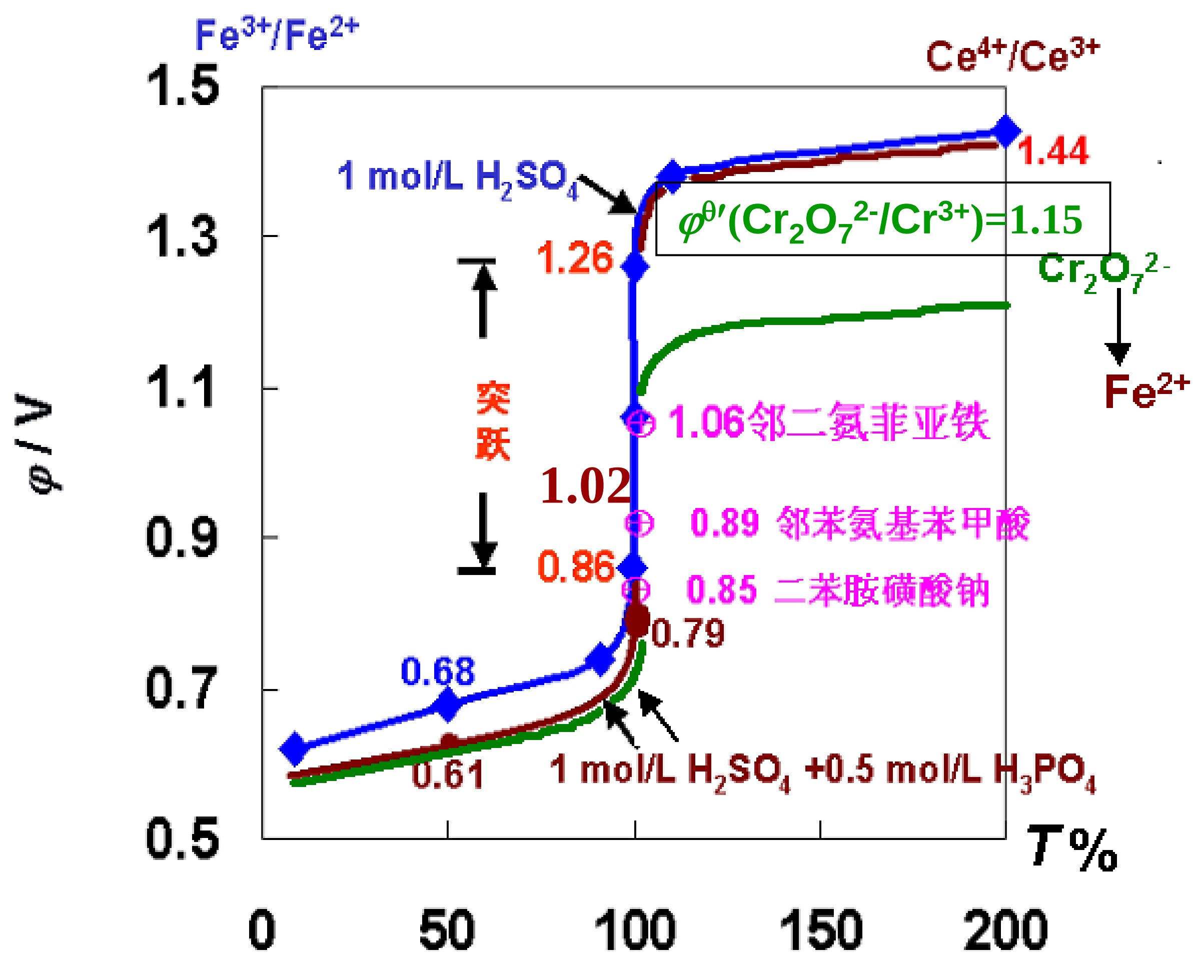
Disadvantages: toxicity and needs to calibrate the reagent background

Indicator: 二苯胺磺酸钠, 邻苯氨基苯甲酸.

Applications:

1. Iron (representative applications)
2. Other analytes via $Cr_2O_7^{2-}$ – Fe^{2+} reaction

Redox Titration Curves



$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightleftharpoons 2\,Cr^{3+} + 6Fe^{3+} + 7H_2O$$

$$Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$$

Iodine碘量法

$$I_3^- + 2e \rightleftharpoons 3I^- \quad \varphi^{\ominus}(I_3^-/I^-) = 0.54V$$

↑ Weak Oxidizing Agent ↑ Strong Reducing Agent

Direct (Iodine as titrant, Iodimetry): **titrant 滴定剂 I_3^-**

Indirect（Sodium thiosulfate, Iodometry）: $Na_2S_2O_3$

Indicator: Starch淀粉

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$

1 : 2

Preparation and Standardization of Standard Iodine

Preparation配制：I_2 dissolved in KI and stored in brown bottle

Standardization标定：Primary reference As_2O_3 or standardized $Na_2S_2O_3$（**How to prepare?**）

pH8~9

$$\varphi^{\ominus'}\left(HAsO_4^{2-}/HAsO_2\right)$$

$$\varphi^{\ominus'} = 0.84 - 0.12pH$$

$$-0.1 \sim -0.2V$$

$$\varphi^{\ominus}\left(S_4O_6^{2-}/S_2O_3^{2-}\right) = 0.09V$$

$$\left(\begin{array}{l}\left[H^+\right] = 4mol \cdot L^{-1} \\ As(V) \xrightarrow{I^-} I_2\end{array}\right) \leftarrow S_2O_3^{2-}$$

Preparation of $Na_2S_2O_3$ Standard Solution

Distilled H_2O —boiling→ Dissolve $Na_2S_2O_3 \cdot 5H_2O$ —Adding small amount Na_2CO_3→ Dark bottle → Standardization

- The purpose to boil water:
  - Kill bacterial to avoid degradation of $S_2O_3^{2-}$
  - Remove CO_2-Generate acid, $S_2O_3^{2-} \rightarrow HSO_3^-$
  - Remove O_2 to avoid oxidation of $S_2O_3^{2-}$

- The purpose for adding Na_2CO_3
  - Stabilize $S_2O_3^{2-}$
  - Maintain pH to be weak basic
  - Prevent putrefying变质 of solution

Standardization of $Na_2S_2O_3$

$$Cr_2O_7^{2-} + 6I^-(ex) + 14H^+ \xrightarrow[\text{in dark}]{\text{Reaction}} 2Cr^{3+} + 3I_2 + 7H_2O$$

$[H^+] \sim 0.4\ mol \cdot L^{-1}$

$3I_2 + S_2O_3^{2-} \rightarrow I^- + S_4O_6^{2-}$

$Na_2S_2O_3$ is not stable in either strong acidic or strong basic solutions.

KIO_3 can also be used to standardize $Na_2S_2O_3$

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

Titration of Cu^{2+} by Iodine/dithiosulfate Method

Cu^{2+} (Fe^{3+}) $\xrightarrow[\text{Till a flocculent mass}\downarrow \text{ pH} \sim 3]{NH_3 \text{ to adjust pH}}$ Adjust pH $\xrightarrow[\text{pH3\textasciitilde4 masking}]{NH_4HF_2}$ Cu^{2+} $\xrightarrow{\text{KI(ex)}}$

$CuI\downarrow + I_2$ $\xrightarrow{S_2O_3^{2-}\text{titraion}}$ yellow $\xrightarrow{\text{Starch}}$ Dark blue

$\xrightarrow{S_2O_3^{2-}\text{titration}}$ Light blue $\xrightarrow{\text{KSCN}}$ blue

$CuI\downarrow \rightarrow CuSCN\downarrow$

$\xrightarrow{S_2O_3^{2-}\text{titration}}$ Blue fades away (white precipitation)

Sample Preparation in Redox Titration

Objectives and Criteria目的与要求:

To prepare the analyte to be in a mono-oxidation state.

To be useful as a peroxidation预氧化 or a prereductant与还原, a reagent must react quantitatively with the analyte and any reagent excess must be easily removable除掉.

1. Auxiliary Oxidizing辅助氧化剂
2. Auxiliary Reducing辅助还原剂

Examples for Auxiliary Oxidizing

Ammonium peroxydisulfate
过硫酸铵

1. Mn^{2+} (Cr^{3+}) $\xrightarrow{S_2O_8^{2-}} \xrightarrow{Ag^+} \xrightarrow{\Delta}$ MnO_4^- ($Cr_2O_7^{2-}$) $\leftarrow$? Fe^{2+}

Auxiliary oxidizing

$\varphi^{\ominus}(S_2O_8^{2-}/SO_4^{2-})=2.0$

2. Chromium in chromium-iron alloy

$$\begin{matrix} Cr_2O_3 \\ Fe_2O_3 \end{matrix} \xrightarrow[H_2O_2\text{(预氧化)}]{NaOH} CrO_4^{2-} + Fe(OH)_3\downarrow \xrightarrow{H^+} Cr_2O_7^{2-}$$

Separate by filtration

Fe^{2+} $\downarrow$? $Cr_2O_7^{2-}$

Back Titration: $Cr_2O_7^{2-}$ $\uparrow$? Fe^{2+} $\uparrow$ $Cr_2O_7^{2-}$

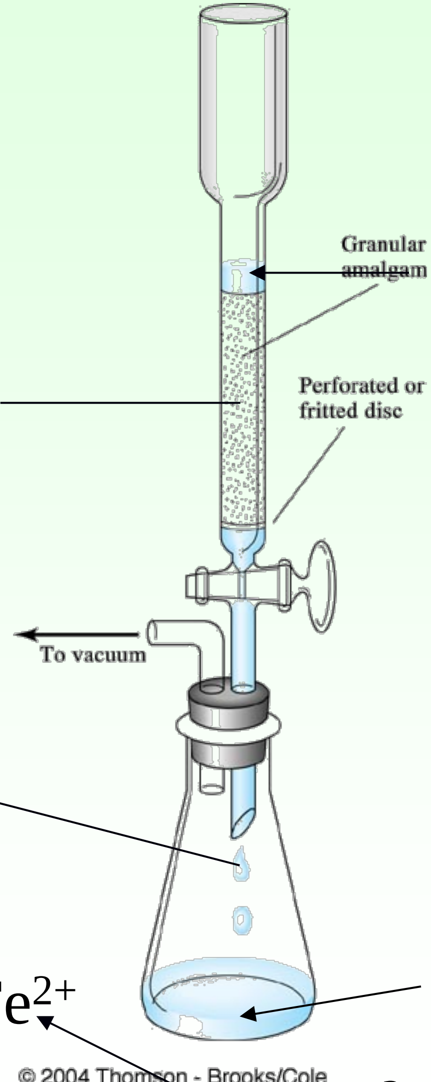
Indicator?

3. $Sn^{4+} \xrightarrow{Zn} Sn^{2+} \leftarrow I_2$

4. Iron ore铁矿

$$\begin{matrix} Fe^{3+} \\ Fe^{2+} \end{matrix} \xrightarrow[\triangle]{SnCl_2} Fe^{2+} \leftarrow Cr_2O_7^{2-}$$

Auxiliary Reducing Agents
—Jones Reductor 还原器



Ti^{4+}+HCl

Zinc Amalgam
锌-汞齐

Ti^{3+}

Fe^{3+} ↓

Ti^{4+}+Fe^{2+}

Fe^{3+}

$Cr_2O_7^{2-}$

$$\varphi^{\odot}(Zn^{2+}/Zn) = 0.76$$

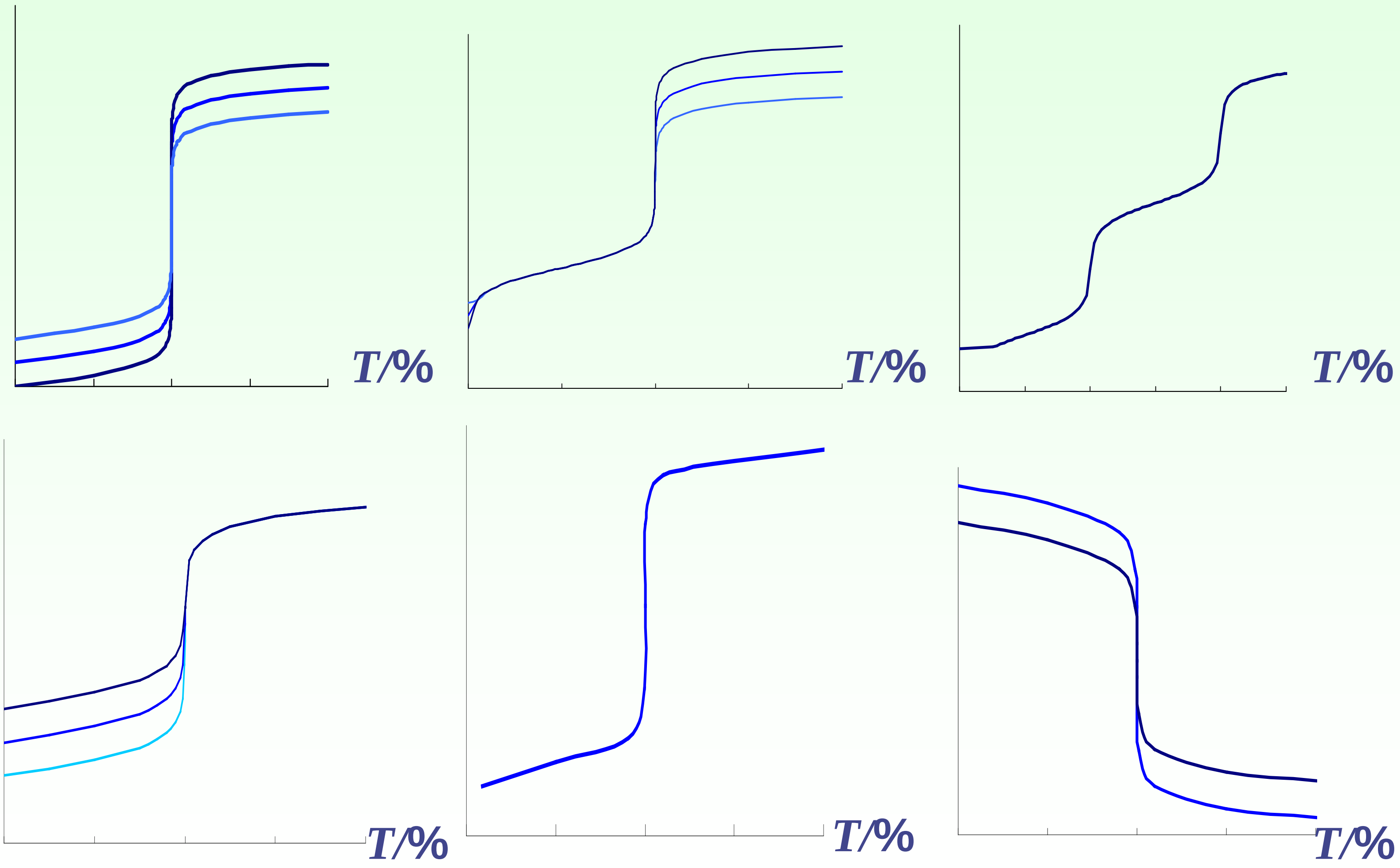
$$\varphi^{\odot}(Ti^{4+}/Ti^{3+}) = 0.10$$

$$3\ mol \cdot L^{-1}\ HCl$$

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

- Calculate electrode reaction potential
- Select an indicator for we need to know where to stop
  - Specific indicators
  - General redox indicators
- Construct a titration curve for we need to know how to select an indicator
- Application examples of redox titration
  - $KMnO_4$, $K_2Cr_2O_7$, $I_3^-/Na_2S_2O_3$, $KBrO_3$
- Sample preparation

Summary of Titration Curves



Summary of Titration Curves