Homework

- **1.1 ~1.3,1.6~1.8**
- **Corrections:**
  - **1.6 “assume” →“ assuming”**
  - **1.8 “KHC_2O_4-$H_2C_2O_4$” → “$KHC_2O_4 \bullet H_2C_2O_4$”**

分 析 化 学

Analytical Chemistry

Spring , 2016

分 析 化 学Analytical Chemistry

- **分析化学Ⅰ (大一下) 32 h**

  定量化学分析、仪器分析（分子光谱：紫外-可见、荧光、磷光、红外、拉曼），误差与数据处理，简单分离方法

- **分析化学Ⅱ(大二下) 32 h**

  仪器分析(原子光谱、化学发光、色谱、电化学、核磁、质谱等)

- **分析化学Ⅲ(大三上) 32 h**

  联用(hyphenated)技术和自动化(automated)方法，新进展、新技术、新方法

- **分析化学I实验课(大一下，64 h+32 h)**

- **分析化学II实验课(大二下，64 h)**

Reference Books

- **Quantitative Chemical Analysis 李娜等编 北大出版社 2009**
- **《分析化学教程》李克安 主编 北大出版社 2006**
- **《分析化学教程习题解析》，李克安主编 北大出版社， 2006**
- **Analytical Chemistry (8th ed) D. A. Skoog, Fortworth: Saunders College Pub., 2004.**

借阅:今天下午 12:00-13:00，过时不候，押金100元，助教操作完成， B309

Course Information and Requirements

- **Grading Policy:**
  - **Mid-Term 35%， Final 55%**
  - **Homework 5%， term paper 5%**
- **Homework due date:**

  随堂交上次作业

  每周三下午五点前，化学学院北门邮件室李娜（分析）信箱，过时算没交作业
- **Office hour (答疑):**
  - 固定为每周五，**2:00-4:30 PM**，或与有机化学同一时间
  - 其他时间可以预约

Term Paper & Oral Presentation

- **Topic selection:**
  - **Articles from Analytical Chemistry, American Chemical Society, 2015**
  - 两人结组，每个人都要看一篇论文，并且写详细摘要、评论以及体会， 不得相互抄袭
  - 论文长度：小四号字，单倍行距，A4纸2页，最多两幅图
  - 提交论文日期: 6月5日 24:00 教学网，过时成绩算0分
- **Who gives presentations? 3 presentations, 15 min**
- **Date: May 28 (Saturday) morning**
- **Audience: Must come!**

作业与课堂要求

请遵守！

- 作业一律使用作业本，**概不接受作业纸**。

  中英文皆可，字迹不工整者、无解题步骤视为当次作业0分

- 按时交作业：每次课到教室即交到前台来
  - 一次不交作业，扣掉作业的一半分数
  - 两次不交作业，扣掉全部作业分数
- 按时上课，迟到者，请从前门进来，三次迟到，平时分数扣5分
- 一定要预习:50 -60 slides/lecture

Challenges & Solution

- 中学与大学的区别
  - 课本与参考书
  - 题海战术与理解
  - 自我学习能力
- 教学改革
  - 内容增加
  - 学时缩短
- 普通化学 与 分析化学

  分析化学家解决问题的思路

预习 听讲 复习 总结
练习： 例题 习题
没有习题课！

Others

- 关于做题，所讲授的不仅是做题方法，而是理解化学反应本质后的解题方法
- **Be patient with**
  - **My English**
  - **Detailed explanation of basics**

  Because we are in this together!
- 考试题量

Savoir s'étonner à propos est le premier mouvement de l'esprit vers la découverte.

http://www.lmcp.jussieu.fr/~soyer/cristallo/pasteur_l.html

Knowing to be astonished by something is the mind's first step toward discovery.

兴趣是通向发现的第一步！

Dr. Ada Yonath (right)
Insitut Weizmann, Israel

历史表明，那些取得重大科学发现的科学家，他们对研究的目标有着深刻的认识，对工作有着极大的兴趣和热忱，对结果抱有极大的希望。

一个具有创新能力的人所应具备的重要品质就是兴趣和自信心，缺乏创造力主要是由于缺乏兴趣，兴趣是创新的推动力。

兴趣的产生首先依靠对科学的了解和认识。

李克安等《分析化学教程》第1章 第一段

Chapter 1
Introduction to Analytical Chemistry

- **The Role of Analytical Chemistry分析化学的角色**
- **Steps for Analytical Chemistry步骤**
- **Methods for Quantitative Analysis定量分析方法**
- **Chemicals, Apparatus, and Unit Operations of Titration滴定分析中化学物质、仪器以及单位换算**
- **Calculations and Significant Digits计算以及有效数字**

The Definition of Analytical Chemistry

分析化学是发展和应用各种方法、仪器和策略，以获得有关物质在空间和时间方面组成和性质的信息科学。

"Analytical chemistry is a scientific discipline that develops and applies methods, instruments and strategies to obtain information on the composition and nature of matter in space and time".

by FECA

Federation of European Chemical Societies欧洲化学会联盟

What Is Analytical Chemistry?

- **With the advances of science, the questions that analytical chemists try to answer is changing.**
- **Analytical chemistry widely applies the knowledge of all the other chemical disciplines (学科), physics, biology, information theory and many other technical fields to the development of analytical methods.**

"Analytical chemistry is what analytical chemists do"

Murray, R.W., *Anal. Chem.*, 1994, *66*, 682A .

Terminology术语

- **Analyte(被)分析物:** A substance or chemical constituent 化学组分of a sample that is to be measured by an analytical method.
- **Interference干扰(物):** An interference is a species that coexists with the analyte and may affect the final measurement by enhancing增强 or attenuating减弱 the signal信号.

A Typical Quantitative Analysis Procedure

Finding a Problem

Choosing a Method

Sample Preparation

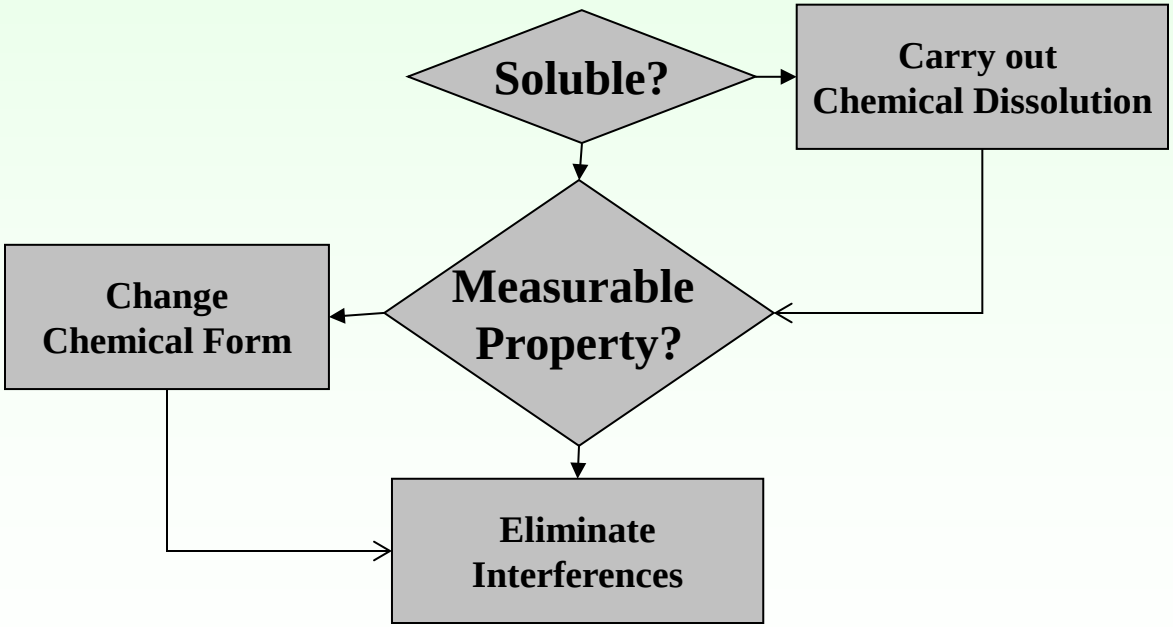
Measure Property

Sample Determination

Result Calculation & Data Analysis

Sample Preparation:

- **–Sampling取样**
- **–Dissolution溶解**
- **–Eliminating Interferences消除干扰**
- **–Enrichment & Concentration富集与浓缩**



Even today the era of modern analytical chemistry, this procedure is still followed.

Selecting An Analytical Method

- **Scale of Operation**
  - The amount of sample available可用的样品量
  - The concentration of analyte in the sample分析物的浓度
  - The absolute amount of analyte needed to obtain a measurable signal.能产生信号的绝对样品量
- **Accuracy准确度**
- **Precision精密度**
- **Sensitivity灵敏度**
- **Selectivity选择性**
- **Repeatability重复性**
- **Reproducibility重现性**
- **Equipment, Time, and Cost仪器、时间和经费**

The requirements of the analysis determine the best method.

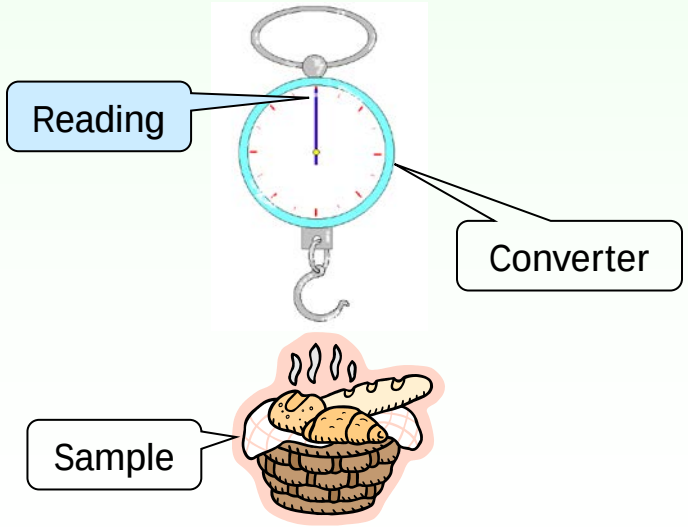
分析要求决定了哪个是最佳方案

Quantitative Analytical Chemistry

- **Chemical Analysis: 化学分析，Macroamount 常量**
  - Gravimetry重量分析: balance to measure mass用天平测量质量
  - Volumetric analysis:容量分析，根据反应分类

    Color of indicator changes based on chemical reaction
- **Instrumental Analysis仪器分析，微量(半) (semi-)micro**
  - Electric电
  - Magnetic磁
  - Optical光
  - Mass 质量
  - Mechanics力

signal change 信号变化



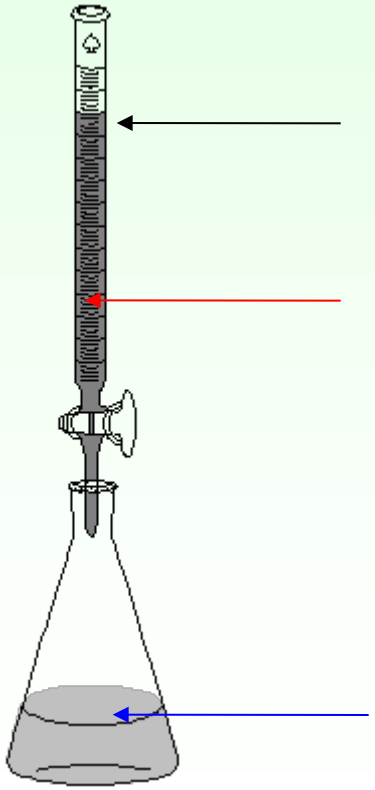
Introduction to Volumetric Titrimetry
容量(滴定)分析法简介

- **Some Terms Used in Volumetric Titrimetry**
- **Chemical Reactions Used for Titration**
- **Primary Standard基准物质and Solutions标准溶液**
- **Measuring Volume in Volumetric titrimetry**
- **Volumetric Calculations滴定分析的计算**

Titrimetry: refers to the group of analytical techniques that are based on measuring the amount of a reagent of known concentration to determine the quantity of an analyte.

Terminologies术语 for Volumetric Analysis容量分析

$HCl + NaOH \leftrightharpoons NaCl + H_2O$



滴定管 (Buret)

滴定剂 (Titrant)

被滴定溶液 (Titrand)

化学计量点(sp) **Stoichiometric point**

滴定终点(ep) **Endpoint**

终点误差(E_t) **Endpoint error**

指示剂 (In) **Indicators**

基准物质(Primary Standard)

- **Compound used to prepare standard solution or standardize standard solution**

  用以直接配制标准溶液或标定溶液浓度的物质

  $H_2C_2O_4 \cdot 2H_2O$, NaCl
- **High Purity 试剂纯度 > 99.9%;**
- **High chemical and physical stability 稳定**

  Na_2CO_3, $CaCO_3$, $Na_2C_2O_4$, $K_2Cr_2O_7$, etc.
- **Source标准物质的来源**

  The National Institute of Standard and Technology (NIST) (USA);

  National Research Center for CRM's 国家标准物质研究中心

  CRM: Certified Reference Materials

标准溶液Standard Solution

Solution with known concentration

具有准确浓度的溶液

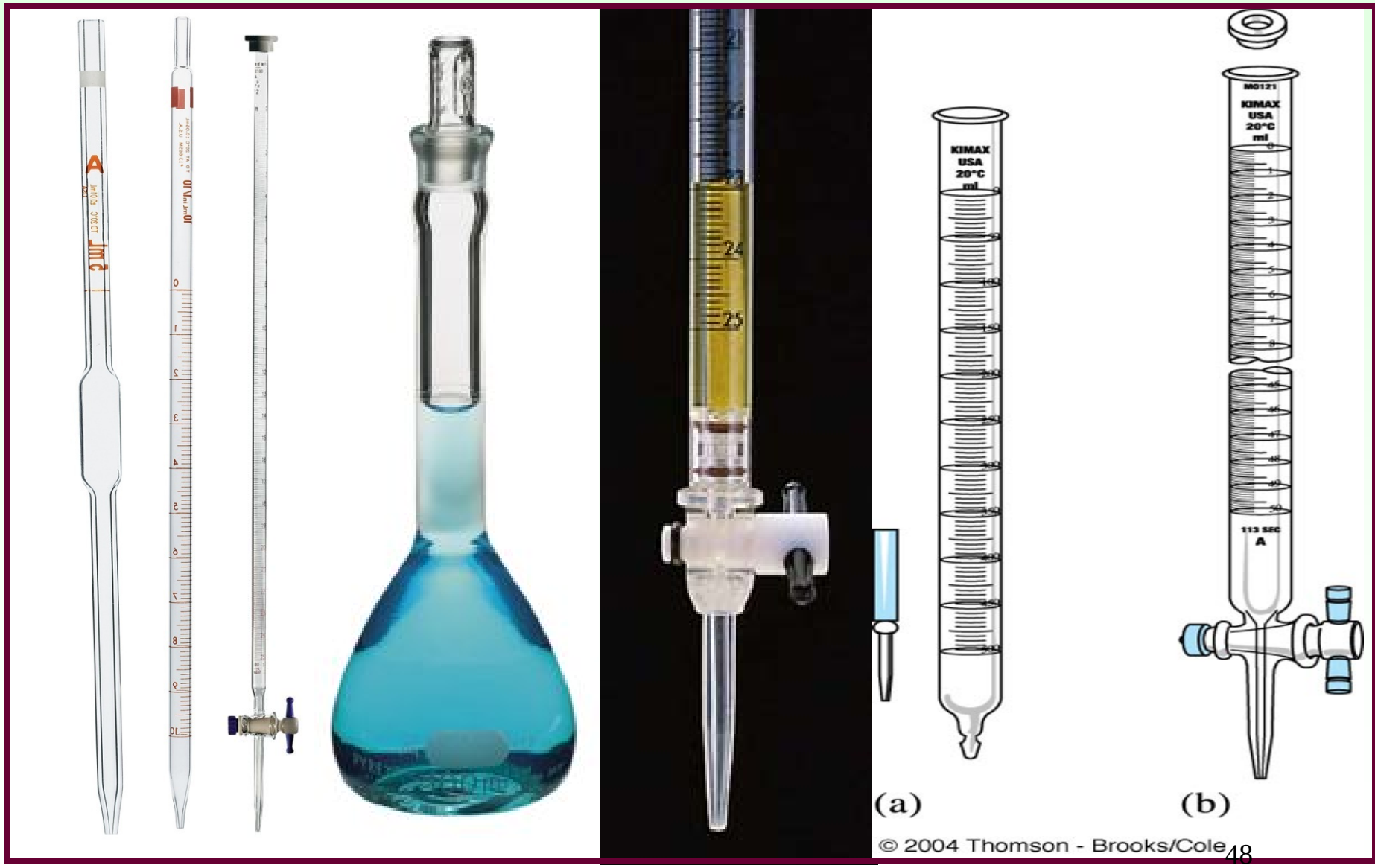
- **Directly or determinately prepared from primary standard直接配制**

  $K_2Cr_2O_7$, $KBrO_3$

- **Standardization 标定法配制**

  NaOH, HCl, EDTA, $KMnO_4$, I_3^-

Apparatus for Titrimetric Analysis 常用滴定分析仪器



Measuring Volume
滴定分析中的体积测量

Apparatus for Precisely Measuring Volume

常用容量分析仪器:

- **Volumetric Flask 容量瓶(To Contain, TC 量入式)**
- **Pipets 移液管(To Deliver, TD 量出式)**
- **Buret 滴定管(TD, 量出式)**

Skoog book 2G-2H pp39-51

Calibration of Volumetric Glassware
容量仪器校准方法

- **Absolute Calibration绝对校准:**
  - Volumetric Pipet 移液管
  - Buret 滴定管
  - Volumetric Flask容量瓶

请自学
这一节

- **Relative Calibration相对校准:**
  - A volumetric flask relative to a pipet

Skoog book 2G-2H pp39-51

Preparation of Standard Solution from Primary Standard

Example 1

Describe the Preparation of 250.0 mL of 0.02000 mol·L^{-1} $K_2Cr_2O_7$ from Solid $K_2Cr_2O_7$.

配制0.02000 mol·L^{-1} $K_2Cr_2O_7$标准溶液250.0mL,求*m* = ?

$$m(K_2Cr_2O_7) = n \cdot M = c \cdot V \cdot M$$

$$= 0.02000 \times 0.2500 \times 294.2 = 1.471(g)$$

One Example:

Generally titration is carried out at 0.02 mol·L^{-1}. The appropriate manipulation is to make a 250 mL solution by weighing 1.47 g (±10%) $K_2Cr_2O_7$ to 0.1 mg.

通常仅需要溶液浓度为0.02 mol·L^{-1}左右, 做法是:

准确称量1.47g(±10%) $K_2Cr_2O_7$基准物质, 于容量瓶中定容, 再计算出其准确浓度:

$$c(K_2Cr_2O_7) = \frac{m(K_2Cr_2O_7)}{M(K_2Cr_2O_7)\cdot V(K_2Cr_2O_7)}$$

Number of Reaction Unit Conservation Principles
反应单元数守恒（等物质的量规则）

The number of Reaction Unit of A equals the number of Reaction Unit of B in one reaction.

- **Precipitation沉淀 reaction: Charges电荷**
- **Acid-base reaction: protons质子**
- **Complexation络合reaction: coordination bonds 配位数**
- **Redox氧化还原 reaction: electrons电子**

$$n(\frac{1}{Z_A}\mathrm{A}) = n(\frac{1}{Z_B}\mathrm{B})$$

Z_A and Z_B denote number of reaction unit of A molecule and B molecule, respectively.

Z_A和Z_B分别为一分子的A物质和B物质在反应中的基本单元数量。

Examples

$$H_2SO_4 + 2NaOH \leftrightharpoons Na_2SO_4 + 2H_2O$$

Reaction Unit for H_2SO_4 : $\frac{1}{2}H_2SO_4$

Reaction Unit for NaOH : **NaOH**

$$n(\frac{1}{2}H_2SO_4) = n(NaOH)$$

Examples

$$MnO_4^- + 5Fe^{2+} + 8H^+ \leftrightharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Reaction Unit for MnO_4^-: $\frac{1}{5}MnO_4^-$

Reaction Unit for Fe^{2+}: Fe^{2+}

$$n(\frac{1}{5}MnO_4^-) = n(Fe^{2+})$$

One Example

To standardize concentration of 0.020mol·L^{-1}$Na_2S_2O_3$ via the following reaction, how to prepare $K_2Cr_2O_7$ standard solution to meet the requirement that weighing error is less than 0.1%?

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightleftharpoons 2Cr^{3+} + 3I_2 + 7H_2O$$

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

$$Cr_2O_7^{2-} \xrightarrow{+6e} 2Cr^{3+} \qquad 2S_2O_3^{2-} \xrightarrow{-2e} S_4O_6^{2-}$$

$$n(\tfrac{1}{6}\ K_2Cr_2O_7) = n(Na_2S_2O_3)$$

One Example (*Cont'd*)

$$m(K_2Cr_2O_7) = n(\tfrac{1}{6}K_2Cr_2O_7)\,M(\tfrac{1}{6}K_2Cr_2O_7)$$

$$= c(Na_2S_2O_3)\,V(Na_2S_2O_3)\,\tfrac{1}{6}\,M(K_2Cr_2O_7)$$

$$= 0.020 \times 0.025 \times 294.18/6 = 0.025(g)\ (?)$$

By weighing 0.025 g directly,

$$E_r = \frac{\pm 0.0002}{0.025} \times 100\% \approx \pm 1\%$$

How to weigh such that weighing error is less than 0.1%?

称大样 (Weighing Big Mass of a Sample)
—One way to reduce weighing error

Procedure:

- Weigh about 0.25 g $K_2Cr_2O_7$ to 0.1 mg
- Dissolve $K_2Cr_2O_7$ in a 100 mL beaker
- Quantitatively transfer the solution into a 250 mL volumetric flask and dilute to the mark with water.
- After homogenizing 均匀化 by gently shaking, 3 aliquots等份 of 25 mL was transferred into Erlenmeyer flasks to be titrated with $Na_2S_2O_3$.

准确称取0.25g左右$K_2Cr_2O_7$,于小烧杯中溶后定量转移到250mL容量瓶中定容,用25mL移液管移取3等份溶液于锥形瓶中,分别用$Na_2S_2O_3$滴定。

$$E_r = \frac{0.0002}{0.25} = 0.08\% < 0.1\%$$

How to standardize 0.10mol·L^{-1}NaOH using the following primary standards:

$H_2C_2O_4 \cdot 2H_2O$ (Oxalic Acid草酸）

$KHC_8H_4O_4$

(potassium acid phthalate (KHP, 邻苯二甲酸氢钾）

The advantages and disadvantages for using these two primary standard

比较“称大样”、“称小样”两种方法的优劣

For you to think about after class!

Significant Figures有效数字

The number of digits necessary to express the results of a measurement consistent with the measured precision

包括全部可靠数字及一位不确定数字在内

Learning the rule by yourself!

自学有效数字修约规则！

Error in Titration and Sample Weighing
滴定误差与称量误差

V	E_a	E_r
20.00 mL	±0.02 mL	±0.1%
2.00 mL	±0.02 mL	±1%

m	E_a	E_r
0.2000 g	±0.2 mg	±0.1%
0.0200 g	±0.2 mg	±1%

Errors from measuring volume and mass come from the two time measurements of volume and mass before and after delivery of liquid or solid.

Homework

- **1.1 ~1.3,1.6~1.8**
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  - **1.6 “assume” →“ assuming”**
  - **1.8 “KHC_2O_4-$H_2C_2O_4$” → “$KHC_2O_4 \bullet H_2C_2O_4$”**