

全国高等学校配套教材 • 供药学类专业用

物理化学实验指导

Experimental Physical Chemistry (双语)

主 编 崔黎丽

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本书是全国高等医药院校药学专业《物理化学》第六轮教材的配套教材,可作为 医药学院校学生的物理化学实验教材,也可供其他从事物理化学实验工作的有关人员 参考。

本书分为三个部分:①绪论,主要介绍物理化学实验课程的目的和要求、实验报告书写规则、误差理论和有效数字、实验数据的表示与处理;②实验部分,在汲取参编院校长期实验教学经验的基础上,选编了热力学、相平衡、电化学、动力学、表面和胶体化学等物理化学分支中有代表性且较成熟的实验。此外,还编写了部分设计性实验,在强化基础知识、基本技能训练的基础上,培养学生动手能力、创新思维能力和科学素养,培养学生分析问题和解决问题的能力;③附录部分,收录一些常用数据表以便查阅,以及本书编写过程中的参考文献。

为了适应现代教育发展的需要,本书采用双语体系编写,不仅为开展物理化学实验双语教学的院校提供了教材,而且对于提高学生的科技英语水平有着积极的作用。

本书的编写过程得到了药学专业《物理化学》第六轮规划教材主编侯新朴教授的 关心和支持,在此表示深深的谢意。

由于作者水平有限、书中难免存在问题和错误、恳请广大读者批评指正。

编 者 2007年4月

Preface

This textbook is attached to the textbook of Physical Chemistry, Edition Sixth. It is suitable for readers majoring in Medicine, Pharmacy or other disciplines.

The textbook is divided into three parts. The first part contains discussions of purpose and requirement of experimental physical chemistry, report writing, error theory, data processing, which is fundamental for students to finish the experiment successfully. The second part consists of a selection of some typical experiments and two comprehensive designing experiments developed not only to teach basic laboratory procedures and to reinforce basic theory, but also to encourage ability in creative consciousness cultivation, problem solving and analyzing. The experiments are in the areas of Thermodynamics, Phase Equilibrium, Electrochemistry, Kinetics, Surface and Colloid Chemistry. The third part is a list of reference data and books of experimental physical chemistry.

To keep pace with the new developments in modern education, the textbook is compiled in a bilingual system to provide a platform for the bilingual teaching of Experimental Physical Chemistry. Besides, it may help the students to learn and practice Scientific English.

This textbook owes much to many people, especially Professor Hou Xinpu, who is the editor of the Sixth Edition of Physical Chemistry. We greatly appreciate their help and suggestions.

Due to limited abilities and inexperience, errors and negligence are inevitable in the textbook, and criticisms and advice are welcomed from our readers.

> Editor Ápril 2007

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第一部分 绪 论

Part One Introduction

物理化学实验综合了化学各分支学科所需的基本研究工具和方法,在培养学生的基本实验技能、分析解决问题的能力和提高科研素质等方面占有特别重要的地位。

一、物理化学实验的目的和要求

物理化学实验的主要目的是使学生在巩固化学的基本实验技能的基础上,掌握本学科实验研究的基本方法和技能,巩固和加深对物理化学基本理论和基本概念的理解和掌握;能根据所学原理设计实验、选择和使用仪器;锻炼学生观察现象、获取实验数据、正确处理和分析实验结果的能力;培养学生严肃认真的科学态度和创新思维能力。

为了达到上述目标,必须做到以下基本要求。

- 1. 认真预习
- (1) 实验前,应认真阅读实验教材及相关的参考书目和文献资料,明确实验目的和要求,掌握实验原理和方法。
 - (2) 了解仪器的结构和操作规程,明确实验内容和操作步骤。
- (3) 根据对实验的理解,用简明扼要的方式写出预习报告,重点表述对实验原理和实验方法的理解,特别是实验操作步骤及操作过程中要注意的问题,并设计好记录原始数据的图表。
 - 2. 严格、规范操作
- (1) 进入实验室后,首先检查仪器和试剂是否符合要求,并做好实验的各项准备工作。
- (2) 在不了解仪器使用方法之前,不得擅自使用和拆卸仪器。仪器和线路安装或 连接好后,须经教师检查无误后方能接通电源开始实验。
 - (3) 在教师指导下,严格按操作规程进行操作,不得随意更改。
- (4) 仔细观察实验现象,如实、准确地记录实验数据。要善于发现和解决实验中出现的问题。
 - (5) 实验结束后,应将实验数据交指导教师审阅通过后,方能拆除实验装置。若

不合格,则需重做或补做。

- (6) 严格遵守实验室各项规则,保持实验室安静和整洁,尊重教师的指导。
- 3. 独立完成实验报告 实验后必须及时、认真地完成实验报告。实验报告必须独立完成,同一小组成员不得合写一份报告。实验报告要格式规范、内容完整、文字简练、表达清晰、结论明确,一般包括:①实验名称,实验日期,完成者姓名;②实验目的;③实验原理(简述);④实验内容,选用最简明扼要的方式表达每一项实验内容的操作步骤;⑤实验现象或实验数据;⑥实验结论、解释或实验数据处理、计算结果;⑦实验讨论,包括对实验中遇到的异常现象或问题的说明,分析误差的原因,并对该实验提出进一步的修改建议或意见;⑧思考题。

实验报告不仅是概括实验过程和总结实验结果的重要的文献性资料,也是提高学生思维能力、专业能力和初步科研能力的重要的训练环节,希望能高度重视。

二、误差理论和有效数字

在测量实验中,测量值和真实值不可能完全一致,其差值称为误差。分析测量结果的准确性和产生误差的主要原因,寻找减少误差的有效措施,可以提高测量结果的准确性。

(一) 误差的分类

1. 系统误差 在同一条件下对同一量进行多次测量时,误差的符号保持恒定(即多次测量中均出现正误差或负误差,具有单一方向性),其数值按某一确定的规律变化,这种误差称为系统误差。

系统误差不能依靠增加实验的次数使之消除,但可以通过改进实验方法、校正仪器、提高试剂纯度等,有针对性地使之减少到最小程度。

- 2. 偶然误差 偶然误差通常由一些不确定的因素所引起。从单次测量值看,误差的绝对值和符号的变化时大时小,时正时负,呈现随机性,但是其多次测量的结果服从概率统计规律,可采用多次测量取算术平均值的方法来减小偶然误差对测量结果的影响,使测得结果接近真实值。
- 3. 过失误差 过失误差是一种与事实不符的误差,是由于工作粗枝大叶,操作不正确引起的。例如读错刻度值,看错砝码,加错试剂,记录错误,计算错误等。此种误差只要加强责任心、工作认真细致即可避免。

(二) 准确度与精密度

准确度是指测量值与真实值符合的程度。若实验的准确度高,说明测量值与真实值之间的差值小。精密度是指测量中所测数据重复性的好坏。若所测数据重复性好,说明此实验结果的精密度高。

在分析测定过程中,由于存在误差且误差会传递,因而直接影响分析结果的精密度 和准确度。系统误差仅影响分析结果的准确度,而偶然误差既影响精密度,也影响准 确度。

评价分析结果应先看精密度再看准确度。但是,精密度高,准确度不一定高;而高准确度的数据却要足够的精密度来保证。因此,只有精密度、准确度都高的数值,才是

可取的。

(三) 实验误差的表示

表示实验误差的方法很多,下面介绍常用的几种:

1. 算术平均值与平均误差 在任何测量中,偶然误差总是存在,所以不能以任何一次的观察值作为测量结果。为了使测量结果有较大的可靠性,常取多次测量的算术平均值。设物理量 A 的每次测量值为 $x_1, x_2, x_3 \cdots x_n$,共测量 n 次,其算术平均值 \overline{x} 为:

$$\bar{x} = \frac{x_1 + x_2 + x_3 \cdots x_n}{n} \tag{1-1}$$

测定值与平均值之差称为偏差,用以衡量精密度的高低

$$\Delta x_i = x_i - \overline{x} \tag{1-2}$$

 Δx_i 值越小,测量的精度越高。又因为各次测量误差的数值可正可负,故需引入平均误差的概念:

$$\overline{\Delta x} = \frac{|\Delta x_1| + |\Delta x_2| + |\Delta x_3| \cdots + |\Delta x_n|}{n} = \frac{\sum_{i=1}^{n} |x_i - \overline{x}|}{n}$$
(1-3)

而平均相对误差则为:

$$\frac{\overline{\Delta x}}{\overline{x}} = \frac{|\Delta x_1| + |\Delta x_2| + |\Delta x_3| \cdots + |\Delta x_n|}{n \, \overline{x}} \times 100 \,\% \tag{1-4}$$

2. 标准偏差 若物理量 A 的个别测量值为 x_i , n 次测量的算术平均值为 \overline{x} , 则标准偏差 S 为:

$$S = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})}{n-1}}$$
 (1-5)

3. 间接测量的误差传递 有些物理量不能直接测量(如物质的摩尔质量等),但可通过其他可以测量的数据,经过数学运算间接得到所需的结果,称为间接测量。下面讨论间接测量的误差传递。

设直接测量的数据为 x 及 y,测量误差为 Δx 和 Δy ,当误差和测量值相比很小时,可以把它们看作微分,dx、dy。已知物理量 U 是由直接测量的 x、y 经过计算而得,即 U 是 x、y 的函数,写作:

$$U = f(x, y) \tag{1-6}$$

微分之

$$dU = \left(\frac{\partial U}{\partial x}\right)_{x} dx + \left(\frac{\partial U}{\partial y}\right)_{x} dy \tag{1-7}$$

因此,在运算中,误差 dx 和 dy 将影响最后结果 U,使其产生 dU 的误差。对于各种运算过程所受影响的规律归纳于表 1-1 中:

Table 1-1 Some examples for calculation of o	Table 1-1	Some	examples	for	calculation	of	dί
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函数式	绝对误差	相对误差
Function	Absolute error	Relative error
U = x + y	$\pm (dx + dy)$	$\pm \left(\frac{\mathrm{d}x + \mathrm{d}y}{x + y}\right)$
$U = \frac{x}{y}$	$\pm \left(\frac{x dy + y dx}{y^2}\right)$	$\pm \left(\frac{\mathrm{d}x}{x} + \frac{\mathrm{d}y}{y}\right)$

例 用冰点降低法测定物质的相对分子质量时,所用计算公式为:

$$M = \frac{1000k_{\rm f} \cdot m}{m_0 \left(t_0 - t \right)} = \frac{1000k_{\rm f} \cdot m}{m_0 \cdot \theta}$$

式中: k_f 为冰点下降常数;m 为溶质质量; m_0 为溶剂质量; θ 为冰点下降度数; t_0 为溶剂冰点;t 为溶液冰点。由实验测出: $m = (0.3000 \pm 0.0002)$ g, $m_0 = (20.00 \pm 0.002)$ g, $\theta = (0.300 \pm 0.008)$ °。求物质的相对分子质量的相对误差。

解:根据表 1-1 中误差传递的计算方法,物质的相对分子质量的相对误差为:

$$\frac{\Delta M}{M} = \frac{\Delta m}{m} + \frac{\Delta m_0}{m_0} + \frac{\Delta \theta}{\theta} = \frac{0.0002}{0.3000} + \frac{0.02}{20.00} + \frac{0.008}{0.3000}$$
$$= 7 \times 10^{-4} + 1 \times 10^{-3} + 2.6 \times 10^{-2}$$
$$= 0.028 = 2.8\%$$

从以上计算可知,测量物质的相对分子质量最大相对误差为 2.8 %,因此,其误差主要来源于温度的测量,称重并不能增加测量的准确度,所以不必采取过分准确的称量。要想提高测量的准确度,应寻找更精密的测温仪器或选用其他更好的实验方法。

(四) 有效数字

实验所获得的数值,不仅表示某个量的大小,还应反映测量这个量的准确程度。记录和计算测量结果都应与测量的误差相适应,不应超过测量的精确程度,即测量和计算所表示的数字位数,除末位数字为可疑者外,其余各位数从仪器上可直接测得。通常将所有确定的数字和最后不确定数字一起称为有效数字。常用仪器的精度见表 1-2。

表 1-2 常用仪器的精度

Table 1-2 Precision of some commonly used instruments

仪器名称	仪器的精度	举例	有效数字位数
Instrument	Precision	Example	Number of significant figure
托盘天平(scale)	0. 1g	15. 6g	3 位
1/100 天平(balance)	0. 01 g	15. 61g	4 位
电光天平(photoelectric balance)	0.0001g	15. 6068g	6 位
10ml 量筒(measuring cylinder)	0. 1 ml	8.5ml	2 位
100ml 量筒(measuring cylinder)	1 ml	96ml	2 位
移液管(pipette)	0. 01 ml	25.00ml	4 位
滴定管(burette)	0. 01 ml	50.00ml	4 位
容量瓶(volumetric flask)	0. 01 ml	100.00ml	5 位

任何超出或低于仪器精度的数字都是不恰当的。例如上述滴定管的读数为50.00ml,不能当作50ml,也不能当作50.000ml,因为前者降低了实验的精确度,后者则夸大了实验的精确度。

现列出有效数字的一些规则和概念。

(1) 根据 0 在数字中的位置,确定其是否包括在有效数字的位数中。若 0 在数字前面,只表示小数点的位置(仅起定位作用),不包括在有效数字中;若 0 在数字的中间或在小数的末端,则表示一定的数值,应包括在有效数字的位数中。例如:

数值	0. 68	6.80×10^{-3}	0. 02350	6. 08
有效数字位数	2 位	3 位	4 位	3 位

但在另一种情况下,例如 1480 这个数值就无法判断后面一个 0 究竟是用来表示有效数字的,还是用以标志小数点位置的。为了避免这种困惑,常采用指数表示法。例如, 137000 表示三位有效数字,则可写成 1.37×10^5 ;若表示四位有效数字,则写成 1.370×10^5 。

- (2) 对数值有效数字位数,仅由小数部分的位数决定,首数(整数部分)只起定位作用,不是有效数字。对数运算时,对数小数部分的有效数字位数应与相应的真数的有效数字位数相同。例如,pH = 7.68,其相应的真数为 $c_{\rm H^+}$ = 2.1 × 10 $^{-8}$ mol·L $^{-1}$,即有效数字为二位,而不是三位。
- (3) 记录和计算结果所得的数值,均只能保留一位可疑数字。当有效数字的位数确定后,其余的尾数应根据"四舍五人"的方法取舍。
- (4) 若第一位的数值等于或大于 8,则有效数字的总位数可以多算一位。例如 9.15,虽然实际上只有三位有效数字,但在运算时可以看做四位。
- (5) 加减法运算时,各数值小数点后面所取的位数与其中最少者相同。乘除运算时,所得的积或商的有效数字,应以各值中有效数字位数最少的值为标准。

三、实验数据的表示法和处理

物理化学实验数据的表达方式主要有列表法、作图法和方程式法。

(一) 列表法

实验结束后,将测得的一系列数据按自变量和因变量的对应关系用表格列出,这种表达方式称为列表法。列表时应注意以下几点:

- (1) 每一个表都应有简明而又完备的名称。
- (2) 在表的每一行或每一栏要详细地写出名称和单位。
- (3) 表中的数据应化为最简单的形式,公共的乘方因子应在第一栏的名称中注明。
- (4) 在每一行中数值要排列整齐,通常将位数和小数点对齐。
- (5) 实验条件和环境条件应在表中或表外注明,如室温、大气压、测定日期和时间等。

列表法简单易行,便于参考比较,实验的原始数据记录一般采用列表法。

(二) 作图法

用几何图形来表示实验数据的方法称为作图法。作图法有很多优点,如能清晰显示数据的变化规律;能直观看出数据之间所显示的特点,如直线、曲线、极大、极小和转折点等;能利用直线求斜率,由曲线求切线;还能用内插、外推等方法对数据作进一步处理。

- (1) 求内插值:根据实验所得数据,作出函数间相互关系的曲线,然后找出与某函数相应的物理量的数值。
- (2) 求外推值:在某种情况下,测量数据间的线性关系可以外推到测量范围之外, 求某一函数的极限值,这种方法称为外推法。很多情况下,外推法可以推广到无法用实 验方法测量的范围中。
- (3) 求任何一点函数的导数:过曲线上的已知点作切线,求出切线的斜率即为该点函数的导数,是物理化学实验数据处理中常用的方法。如反应物浓度对时间作图,在不同时间下求曲线切线的斜率即为该时间的反应速率。
- (4) 求经验方程式:若函数和自变量有线性关系:y = mx + b,则以相应的 x 和 y 的 实验值作图,得到一条尽可能连接各实验点的直线,由直线的斜率和截距可求出方程式中 m 和 b 的数值,代入上述方程即得所求经验方程。

下面为作图法的一般步骤和规则:

1. 坐标纸和比例尺的选择 直角坐标纸最常用,有时也用单对数坐标纸或对数坐标纸,在表达三组分物系相图时,常用三角坐标纸。

在直角坐标图上,习惯用横坐标表示自变量,以纵坐标表示因变量,横、纵坐标读数不一定从零开始,但应充分合理地利用坐标纸的全部面积。

为了能从图上迅速读出任一点的坐标值,坐标分度宜选 1、2、4、5 的倍数。直角坐标的两个变量的全部变化范围在两个坐标轴上表示的长度要相近,否则图形会扁平或细长。若所作图形为直线,则两坐标轴标度的选择应使直线的斜率值在 1 附近。

2. 描绘实验点及连线 习惯上用 ●、○、△等符号表示实验各点。在同一张图纸上,不同的物理量应选用不同的符号表示,以示区别,并在图中注明。

作曲线时,应根据所描的数据点,将曲线光滑、连续地描出。通常曲线并不能通过 所有数据点,应使数据点平均地分布在曲线两旁,或使所有的实验点离开曲线距离的平 方和最小,此即"最小二乘法原理"。

3. 写图名 每个图都应写上简明的图题、横纵坐标表示的物理量名称、标度和单位。与列表法相同的是横纵坐标的标注应是纯数,物理量和单位之间用斜线"/"隔开。

用计算机作图给数据处理带来了极大的方便,但是应用计算机作图时,也要遵循以上规则。

(三) 方程式法

用数学方程式表示实验数据的方法称为方程式法。该法不但表达方式简单,记录方便,而且能在实验范围内计算与自变量相对应的函数值,并能对所得方程式进行微分、积分和内插求值。

通常情况下,两个变量间的关系是已知的。但是,当两个变量间存在的具体关系未知时,可以先作图,由图形的形状与已知方程式相对应的图形比较,判断曲线的类型。

由于直线关系式最简单而又容易直接检验,因此,对所得的函数关系式要尽量通过函数变化将其直线化,用图解法求出该直线的斜率和截距,即直线方程式 y=a+bx 中的 a 和 b 两常数。但是,在很多情况下,变量之间的关系为 $y=a+bx+cx^2+dx^3+\cdots$ 的多项式。

通常用作图法、平均值法和最小二乘法三种方法求线性方程中的常数 a 和 b。图解法最简便,常用于实验数据较少、比较精密的情况下;平均法较麻烦,但在有六个以上比较精密的数据时,结果比作图法好;最小二乘法处理较繁,但结果可靠,它需要 7 个以上的数据。

Experimental physical chemistry is of great importance in training in basic experimentation and encouraging ability in problem solving and research.

1 Objective and requirement

The purpose of the experimental physical chemistry is to amplify and make more meaningful of the abstract concepts, principles and equations treated in the textbook, to reinforce the skills in fundamental experiment methodology in other chemistry laboratory courses, to train the students in the methods and techniques of physical chemistry, to train the students in the processes of obtaining and interpreting experimental data, and to encourage their ability in research.

To achieve the above objectives, there are some remarks for the students as follows.

- 1. 1 Read the text carefully before coming to the laboratory.
- 1. 1. 1 Make a careful study of the experiment for that day before coming to the laboratory. Familiarize yourself with the objective, principle and technique of the experiment.
- 1. 1. 2 Familiarize yourself with the structure and operation method of the instrument. Make a good understanding of the experimental content and procedure.
- 1. 1. 3 According to your advance reading, write down briefly the principle and procedure, especially questions concerning the experiment, draw in your laboratory notebook columns or tables that will allow you to record the data.
- 1. 2 Do the experiment seriously
- 1. 2. 1 Make sure that the instruments and chemicals are of experimental requirement after entering the laboratory, otherwise change them with your instructor. Get everything ready before starting the experiment.
- 1. 2. 2 Do not use the instruments or unload the apparatus before a well understanding of them. Do not experiment unless the circuit connection or apparatus setting is examined by your instructor.
- 1.2.3 Do the experiment as instructed. Do not change the procedure at will unless a permission is obtained from the instructor.
- 1. 2. 4 Always observe carefully during the experiment, and record the experimental data as it is read.
- 1.2.5 When all the necessary measurements have been completed, hand in your notebook

to have your instructor sign on the data sheet. If the measurement is not qualified, repeat the experiment.

- 1. 2. 6 Obey the laboratory rule strictly, keep quiet in laboratory and have high regard to instructor's guidance.
- 1. 3 Write the report independently After finishing the experiment, make suitable data processing and write the report independently. A shared report is not allowed among the group members. The report should includes; ①title of the experiment, the date on which the experiment is done, the name of the accomplisher; ②experimental objective; ③brief introduction of principle; ④a description of experiment procedure; ⑤experiment output or data; ⑥ results, explanation and calculations; ⑦a discussion, especially the explanation of the abnormal phenomena observed during the experiment, cause of error, and some suggestions for the experiment; ⑧key to questions.

Experiment report is not only the summary of the experiment procedure and results, but also an important way to encourage the student's ability in thoughts, knowledge and research.

2 Error theory and significant figures

We can never measure the true value of any quantity but only an approximation to it. The difference between the observed value and true value is called the error of a measurement. To analyze the precision of the measurement and the cause of the errors can help us to take the steps in errors reducing, and to improve the measurement precision.

- 2. 1 Types of errors
- 2. 1. 1 Systemic errors Systemic errors refer to the errors which persist during a series of experiments of a given type, i. e., the value of the measurement will always be greater (or less) than the real value. They most commonly arise from defects in the instrument or from using improper experiment design. Systemic errors cannot, in general, be eliminated by any process of averaging, but can be avoided by methodological improvement, proper calibration and adjustment of the instruments, and upgrading the chemical purity and so on.
- 2. 1. 2 Random errors Random errors usually arise from some indeterminate causes and manifest themselves in variations in successive readings of a magnitude by the same observer under the same set of conditions. However, they can be treated by the methods of statistics. Random errors can be eliminated by taking the procedures in which a large number of readings are used for arriving at a best value.
- 2. 1. 3 Mistake Mistake is an error which can be traced to carelessness, inattention, and various negative attitudes.

Mistakes can be reduced in most cases by developing the measurer in a way that he or she learns to be more careful, attentive, conscientious and proud of the work being done.

2. 2 Precision and accuracy Accuracy is the degree of conformity with a true value. The higher the accuracy, the less the difference between the measured value and true value is. Precision is the degree of reproducibility of the measurement. If a little divergence among the readings is shown, the method of measurement is one of high precision.

The measurement of a physical quantity can never be made with perfect accuracy and precision, because of some errors or uncertainty present, and because of the propagation of errors. In general, systemic errors may only affect the accuracy of the measurement. On the other hand, random error may affect both the accuracy and precision.

A precise measurement is not necessarily accurate, though we should concern the precision first other than accuracy in judging the quality of the measurement. However, an accurate measurement is guaranteed by a high degree of precision. A result of both precision and accuracy is valuable.

- 2. 3 Error analysis
- 2. 3. 1 Arithmetic mean and average error The existence of random errors makes the result of a single measurement be not reliable in principle. Only with frequent repetition of the measurement do we get the validity of a measurement result. If one makes a series of n measurements with the results $x_1, x_2, x_3 \cdots x_n$, the arithmetic mean or average value \overline{x} of the measurements is defined as

$$\bar{x} = \frac{x_1 + x_2 + x_3 \cdots x_n}{n}$$
 (1-1)

The difference between measured value and average value is the deviation which represents the precision of the measurement and can be expressed as

$$\Delta x_i = x_i - \overline{x} \tag{1-2}$$

The smaller the deviation is, the more precision the measurement is. Since the magnitude of the random errors is different for every repetition of the experiment, average error is defined and can be calculated using the equation

$$\overline{\Delta x} = \frac{|\Delta x_1| + |\Delta x_2| + |\Delta x_3| \cdots + |\Delta x_n|}{n} = \frac{\sum_{i=1}^{n} |x_i - \overline{x}|}{n}$$
 (1-3)

Then the percent relative error is given by

$$\frac{\overline{\Delta x}}{\overline{x}} = \frac{|\Delta x_1| + |\Delta x_2| + |\Delta x_3| \cdots + |\Delta x_n|}{n \, \overline{x}} \times 100 \,\% \tag{1-4}$$

2. 3. 2 Standard deviation The data $x_1, x_2, x_3 \cdots x_n$ are dispersed around average. A measure of this dispersion is called the standard deviation and is given by

$$S = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})}{n-1}}$$
 (1-5)

2. 3. 3 Propagation of errors Some quantities, such as molar mass of substance, cannot be measured directly through experiment, but you can calculate it depending on some other quantities which you can measure. This is called indirect measurements. The error propagation in indirect measurement is discussed as follows.

Suppose the numerical property is symbolized by U and is the function of x and y

$$U = f(x, y) \tag{1-6}$$

The measurement of quantities x and y yields uncertainties of Δx and Δy . If the errors are small, then Δx and Δy can be taken as dx and dy. The total differential of U is given by

$$dU = \left(\frac{\partial U}{\partial x}\right)_{x} dx + \left(\frac{\partial U}{\partial y}\right)_{x} dy \tag{1-7}$$

Therefore, the errors for x and y will have an effect dU for the calculation quantity U. Several examples for calculation of dU are listed in Table 1-1.

Example. The molar mass can be measured by the depression of freezing point method and is calculated using the equation

$$M = \frac{1000k_{\rm f} \cdot m}{m_0 (t_0 - t)} = \frac{1000k_{\rm f} \cdot m}{m_0 \cdot \theta}$$

where k_f is the constant of depression of freezing point, m the mass of solute, m_0 the mass of solvent, θ the degree of freezing point depression, t_0 the freezing point of solute, t the freezing point of solution. The measurements give that $m = (0.3000 \pm 0.0002) \, \text{g}$, $m_0 = (20.00 \pm 0.08) \, \text{g}$, $\theta = (0.300 \pm 0.008) \, \text{C}$. (1) Where does the error arise from? (2) Is it a proper selection of the instruments?

Solution. From equation (1-7)

$$\frac{\Delta M}{M} = \frac{\Delta m}{m} + \frac{\Delta m_0}{m_0} + \frac{\Delta \theta}{\theta} = \frac{0.0002}{0.3000} + \frac{0.02}{20.00} + \frac{0.008}{0.3000}$$
$$= 7 \times 10^{-4} + 1 \times 10^{-3} + 2.6 \times 10^{-2}$$
$$= 0.028 = 2.8\%$$

From the above calculation we see that the maximum relative error of M is 2.8×10^{-2} , which indicates a main cause of error from temperature measurement. Too much attention to accurate mass measurement is not necessary. A higher degree of accuracy can be obtained if a more precision apparatus for temperature measurement is used.

2. 4 Significant figures The data obtained in measurement reflect both the magnitude of the quantity and the degree of accuracy. It means that digits recorded or reported should be related only to the precision of the observation. The number of digits expressed in a measurement should be read directly from the instrument except for the end doubtful one. Significant figure often been defined as "those that are read directly, plus the first doubtful one". The precision of some commonly used instruments are listed in Table 1-2.

Any figure that under or beyond the precision of instrument is considered inappropriate. A recorded measurement viewed with burette as 50.00ml does not mean the same thing as 50ml or 50.000ml. The former lowers the precision of the experiment, while the latter enlarges the precision of the experiment.

There are some rules in dealing with the significant figures.

2. 4. 1 Whether zeroes are included in number of significant figures or not depends on their positions in the figure. Zeroes at the beginning (either to left or right of the decimal point) are not significant. Such zeroes merely indicate the position of the decimal point. Any zeroes between two significant digits or a final zero in the decimal portion only are significant. Here