Solving Problems in Analytical Chemistry

Brewer

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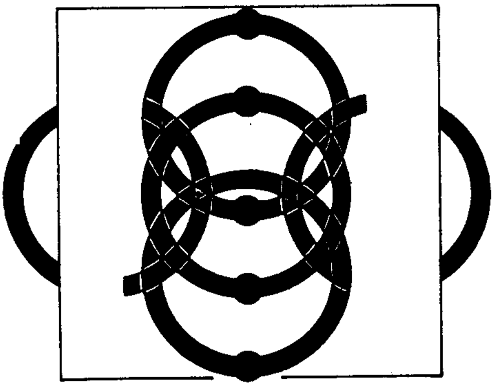

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Preface

A knowledge of analytical chemistry is important to students of many different disciplines. Thus in a typical class there will not only be students majoring in chemistry and chemical engineering but also those who are studying soil science, poultry science, dietetics, medical technology, and biology. Often, the biggest difficulty that these students, chemistry majors included, encounter is that of doing the necessary calculations in laboratory and classroom work.

The purpose of this book is to give students a readable, detailed, and useful guide to the calculations required in a beginning analytical chemistry course. Some knowledge of algebra and graphing is assumed, but no knowledge of calculus is required. Moreover, no calculus is introduced, although many topics in algebra and graphing are reviewed.

Generally, the best way to learn how to solve problems in any discipline is to work through detailed examples and then to try to solve similar problems, whose solutions are available in instances where difficulty is encountered. Thus I divided each section of almost every chapter into three parts: (1) a presentation with some descriptive material of typical calculations, which are worked out in detail; (2) a number of problems for the student; and (3) detailed solutions to those problems.

The student using the book should first buy a hand calculator, preferably one featuring scientific notation, logarithms, and a y^x key. Next he or she should get plenty of paper and sharp pencils. Each one of the calculations in the first part of a given section should be worked out with pencil, paper, and calculator. (Marking the text with a yellow pen almost never does any good.) Then the student should do each of the problems at the end of the section. An earnest attempt of at least five minutes' duration should be made on any given problem. If *no* progress is made after this attempt, the student should turn to the detailed solutions that follow the problems and learn enough at least to get a start. Once the student has worked all of the problems, he or she should try to work them once again, to determine whether the knowledge just acquired has been retained. Finally, two or more people can usually secure a quiet classroom with a blackboard and quiz each other on the problems. The process requires time, it is true, but these detailed examples and solutions should make learning how to calculate a less fearsome task.

This book may be assigned as a supplementary text by an instructor, or it may, in combination with a detailed laboratory manual, be used as the lecture text for a course. I have followed the latter course of action, perhaps because calculations are very heavily stressed in my own lectures. There are many correct ways to teach analytical chemistry, and therefore each instructor in the discipline should make his or her own choice.

In this book, I cover the calculations most frequently encountered in most beginning analytical chemistry courses. There are six chapters in the book: Chapter 1 on basic material, covering basic graphing, statistics, and stoichiometry; Chapter 2 on acid-base chemistry, in which solutions by approximation methods are stressed, and in which polyprotic acids with closely spaced dissociation constants are given their just due; Chapter 3 on solubility control, with approximation methods and a stress on complexation and acid dissolution; Chapter 4 on spectrophotometry, which includes, after basic analytical material, calculations of physical constants; Chapter 5 on potentiometry, ranging from simple cells through titrations, to physical constants and activities to ion-selective electrodes; and Chapter 6 on separations, beginning with separatory funnel extractions, going through multistage (Craig) separations, to liquid-liquid chromatography, through gas chromatography to sorption chromatography.

It would be best if the chapters were taken in the order just listed. However, it is possible to study each of the first five chapters independently. The sixth chapter, that on separations, *does* require knowledge of topics covered in Chapters 1, 2, and 4.

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Acknowledgments

I acknowledge first the generous contribution of Professor John Walters, of the Department of Chemistry at the University of Wisconsin-Madison. Professor Walters was my mentor during my graduate school days at Madison, and thus made a great contribution to the shaping of this book, although neither of us had such a project in mind at that time. In later years, Professor Walters wrote a set of highly detailed notes, which he then distributed to his classes in analytical chemistry. He very kindly sent me sets of these massive notes and urged me to use his material freely, which I was pleased to do.

In 1974, Professor Walters and I decided, together with Gary Carlson of Wiley, that the notes should be used as the basis for a textbook. The textbook was to emphasize problem solving for analytical chemistry, and was to contain vast numbers of solved problems.

Time went by quickly. In 1976, Professor Walters, as busy as a chemist could possibly be, generously offered me, for use in this book, any of the material contained in his notes and problem sets. The material represents a labor of several years on his part and represents an intense dedication to making complicated matters accessible to the beginning student in analytical chemistry. Indeed, the material is a symbol of his dedication to students.

Professor Walters' influence is found particularly in the section on stoichiometry and in the chapters on acids, solubility, spectrophotometry, and potentiometry. I have taken much that appears in these parts of this book directly from his notes. In the chapters on acids and solubility, his approach using approximations and α- and β-functions is closely followed. (Professor Walters has told me that Professor H. L. Laitinen, then at the University of Illinois, introduced him to the α- and β-functions) I should like, then, gratefully to acknowledge my debt to Professor Walters, without whose efforts, dedication, and generosity this book would not have appeared.

Professors J. Schrag and J. Wright, also of the Department of Chemistry at Madison, have made considerable contributions both to Professor Walters' notes and to this book. Professor D. Coleman, of Wayne State University, read the typescript and offered valuable suggestions.

Assistance in computer programming was given by Dr. A. Scheeline, then of the University of Wisconsin, who helped me write a program executed at the Madison Academic Computer Center. Also, B. Finzel, of Eastern Michigan's Chemistry Department, and R. Frownfelter, of University Computing at Eastern Michigan, made a plotting program produce the desired graphs with Eastern Michigan's instructional computer system.

Several patient and able typists helped me to prepare the typescript. They are Ms. P. Quinn, Ms. J. Wright, Ms. L. Mundt, Ms. J. Haynie, Ms. L. Myers, and Ms. C. Bashawaty.

Gary Carlson, Chemistry Editor at Wiley, gave me much help and coordinated the work of three other analytical chemists who reviewed the typescript. Nina R. West, production supervisor, gave her best efforts to the sometimes trying task of getting the book from manuscript to printed pages.

Finally, there were my student helpers—about 200 of them both at Madison and at Ypsilanti. From two of them, Vicki McGuffin and Kena Helkaa, I borrowed quires of data. Others read preliminary editions of the book, and eagerly sought and reported errors. Patrick Harrington helped proofread the galleys. (With this company of diligent proofreaders, I hope that errors are few but would be grateful to anyone who discovers and informs me of errors.)

My colleagues in the Chemistry Department at Eastern Michigan and the Eastern Michigan University administration gave me a sabbatical leave for the writing. The chemistry faculty at Madison very kindly furnished me working facilities during that leave and invited me to teach a summer session and spring term, doing everything to make me feel welcome.

S. B.

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chapter 1

Basic Material

≡ 1.1 USEFUL STATISTICS ≡

In 1954, a charming little volume entitled *How to Lie with Statistics* appeared.* The author's purpose was to educate the literate public in all the statistical ruses that could be used to influence them to buy a particular product or vote for a particular office seeker. The members of the author's high school debating team eagerly sought the book out. The purpose of *our* discussion of statistical matters is not chiefly to protect students from purveyors of snake oil, but to aid them in interpreting and evaluating their own and others' data. A rudimentary knowledge of statistics, intelligently applied, can give fairly satisfactory answers to such questions as:

¤ 1. How many figures in an answer are significant (have meaning)?

¤ 2. What do the terms *accuracy* and *precision* mean, and how do they differ?

¤ 3. What are some measures of accuracy and precision?

¤ 4. What sorts of errors plague results?

¤ 5. How may one mathematically describe distributions of random errors?

¤ 6. Can it be determined whether two averages are significantly different from each other?

¤ 7. Can a result that looks bad, or deviant, be cast out?

---

* Darrell Huff, *How to Lie with Statistics*, Norton, New York, 1954.

¤ 8. How can one draw the best straight line through points that ought to (but do not quite) line up?

1.2 Significant Figures

Let us address the first question. Modern-day computing techniques and pocket-sized calculators make it likely that workers will retain a great many more significant figures than they really should.

EXAMPLE:

Multiply

$$(1.236) \cdot (4.859)$$

on a pocket calculator.

$$(1.236) \cdot (4.859) = 6.005724$$

The multiplier and multiplicand each contain four digits. The product, displayed on the dial of a calculator, contains 7. If numbers are simply being multiplied together, this is all right, but what happens when each number is part of a measurement? Is the area of a square 1.236 in. by 4.859 in. exactly 6.005724 in.^2? Can one start with four-figure numbers, and finish with a seven-figure number, all of whose digits are significant? Of course not! The following rules will help the student avoid at least the sillier mistakes in manipulation.

RULE 1 / Retain *no* digits beyond the first uncertain one.

EXAMPLE:

On a balance, you might read a mass as 21.4238 grams. This number means, in practice, 21.4238 ± 0.0002 grams because ± 0.0002 grams is the uncertainty stated by the manufacturer. The last figure, 8, is uncertain.

You should not guess one more figure. In a number such as 21.4238$\underline{7}$ grams, guessed on the same balance, the 7 would be meaningless.

RULE 2 / Rounding off. The *residue* is the digit to be dropped. If the residue > 5, increase the digit to the left of the residue by 1.

$$\boxed{11.48\underset{\uparrow\,\text{residue}}{6} \rightarrow 11.49}$$

If the residue < 5, do not change the digit to the left of the residue.

$$11.39\underset{\uparrow\,\text{residue}}{2} \rightarrow 11.39$$

If the residue = 5, and the digit to the left of the residue is even, do not change the digit to the left of the residue. If

$$41.28\underset{\uparrow\,\text{residue}}{5} \rightarrow 41.28$$

the digit to left of residue is odd, increase the digit to the left of the residue by 1.

$$37.13\underset{\uparrow\,\text{residue}}{5} \rightarrow 37.14$$

RULE 3 / In addition or subtraction, one may safely retain only as many digits to the right of the decimal as there are in addend or subtrahend with the smallest number of digits to the right of the decimal point.

EXAMPLE:

$$\begin{array}{r} 48.7 \\ 2.941 \\ \underline{33.13} \\ 84.771 \rightarrow 84.8 \end{array}$$

RULE 4 / In multiplication and division, the relative uncertainty in the product or quotient must be the same as the relative uncertainty in the factor with the lowest number of significant figures. In simple terms, this means roughly that the number of significant figures in the answer may not exceed the number of significant figures in the factor with the lowest number of significant figures.

EXAMPLES:

$(1.0923)(2.07) = 2.261061 \rightarrow 2.26$

three significant figures also three significant figures

$(1.0923)(207) = 226.1061 \rightarrow 226$

CAUTION:

What is the average of these four replicates done on one chloride sample?

% Cl
14.68
14.66
14.70
14.68

$$\text{average} = \frac{14.68 + 14.66 + 14.70 + 14.68}{4}$$

Is this "4" only *one* significant figure?

ANSWER:

The 4 is like 4.00000000 ad infinitum. There is *no* uncertainty in the number of samples. Who, for example, ever heard of 3.9 or 4.1 samples?

$$\text{average} = 14.68\%\ \text{Cl}$$

RULE 5 / Sometimes it is not altogether clear which zeros in a number are significant and which are not. Exponential notation makes the task of assigning significance easier.

Example: In 0.000250, the leftmost four zeros are not significant. The rightmost zero *is* significant. This is more easily seen with exponential notation

$$0.000250 = 2.50 \times 10^{-4}$$

The zero to the right of the five is there for a reason—namely, because some other number is not. The number is 0.000250, *not* 0.000251 nor 0.000252.

In a number written like this

$$420$$

it is not clear whether

$$4.2 \times 10^2 \quad \text{or} \quad 4.20 \times 10^2$$

is the correct representation. A decimal point after the last zero would indicate that the last zero is significant. For example,

$$220. = 2.20 \times 10^2$$

In a number like

$$340.0$$

the zero after the decimal point is significant.

$$340.0 = 3.400 \times 10^2$$

RULE 6 / There should be as many significant figures in the mantissa of the logarithm of a number as there are in the number. The characteristic of the logarithm does not count in enumerating significant figures.

In logarithms, the numbers to the left of the decimal are called the characteristic, and those to the right the mantissa.

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