

EXERCISES IN SECOND YEAR CHEMISTRY

*A Laboratory Manual of Elementary Physical-
Chemical Experiments and Quantitative
Analytical Procedures*

BY

WILLIAM H. CHAPIN

Emeritus Professor of Chemistry in Oberlin College

FOURTH EDITION

REVISED BY

WERNER H. BROMUND

Assistant Professor of Chemistry in Oberlin College

AND

LUKE E. STEINER

Professor of Chemistry in Oberlin College

NEW YORK • JOHN WILEY AND SONS, INC.
LONDON • CHAPMAN AND HALL, LTD.



THIS BOOK HAS BEEN MANUFACTURED IN
ACCORDANCE WITH THE RECOMMENDATIONS
OF THE WAR PRODUCTION BOARD IN THE
INTEREST OF THE CONSERVATION OF PAPER
AND OTHER IMPORTANT WAR MATERIALS.

COPYRIGHT, 1922, 1927, 1934

BY

WILLIAM H. CHAPIN

COPYRIGHT, 1944

BY

WILLIAM H. CHAPIN

LUKE E. STEINER

WERNER H. BROMUND

All Rights Reserved

*This book or any part thereof must not
be reproduced in any form without
the written permission of the publisher.*

PRINTED IN THE UNITED STATES OF AMERICA

PREFACE TO THE FOURTH EDITION

Although the form and general content of the material presented in the fourth edition remain substantially the same as in the third edition, much of the material has been extensively revised and rewritten.

In Part I, Experimental Physical Chemistry, the experiments which deal with the theory of ionization, homogeneous equilibrium, and heterogeneous equilibrium have been revised extensively to conform to the modern theory of electrolytes as developed by Debye and Hückel, G. N. Lewis, Brønsted, Milner and others. Although activity data, activity coefficients, etc., can be applied rigorously only on the basis of a thorough understanding of the thermodynamic principles involved, such data are applied whenever their use does not cause confusion or require involved and detailed explanations, even though this application leads to non-rigorous treatment of these data. Such treatment results in approximations, but it is justified if these concepts thereby become part of the student's working tools. The concepts of activity, activity coefficients, ionic strength, etc., tend to confuse the average student when he is first confronted with them. However, the student who has learned to apply these concepts as approximations to simple systems will find their rigorous application much easier at a later time as a result of this earlier experience.

Chapter I has been enlarged considerably by new material which is useful in the laboratory work both for the experiments in elementary physical chemistry and the procedures in quantitative analysis.

A few of the longer and more complicated analyses given in Part II of the third edition are omitted in the fourth edition since they deal with methods and analyses usually undertaken only by the advanced student in inorganic quantitative analysis. Most of the analytical experiments retained have been revised thoroughly; both the theoretical background of the analytical methods and the procedures which are involved are discussed in greater detail.

Throughout the fourth edition, more emphasis is given to the methods of calculation applied in the mathematical treatment of the fundamental theory which is discussed as background for experimental work. The mathematical treatment of experimental data and the evaluation of analytical results similarly are given more emphasis.

W. H. BROMUND
L. E. STEINER

Oberlin, Ohio
1944

PREFACE TO THE FIRST EDITION

The work outlined in this Manual is intended to accompany the author's text, "Second-Year College Chemistry." It may, according to the author's experience, be used in connection with a course in Quantitative Analysis. The general order of procedure in both classroom and laboratory has been outlined in the preface to the text.

All the experiments here presented have been carefully tested out with several classes of students and then carefully rewritten. The author feels, therefore, that careful following of directions will insure good results. In all work of a quantitative nature, however, neatness and natural aptitude are prime factors which cannot be forced upon the student. The student who is naturally sloppy and clumsy will probably emerge from any course with his original traits, and will never measure up as a real chemist. However, neatness and skill on the part of the teacher are also necessary, for even a good student may be ruined by lax supervision and a careless example.

The apparatus employed in the experiments is made as simple as possible. This has been done for two reasons: first, the author desires to make it possible to work through this entire Manual in places where the cost of more elaborate apparatus would be prohibitive; and second, he desires to emphasize principles rather than the bewildering details of refined methods and instruments. On the other hand, the aim has been constantly kept in mind to make the work accurate and truly quantitative. Careful directions have been included for the preparation of all the apparatus, although this preparatory work need not always be done by the student where the time is limited.

One of the most important parts of successful laboratory work is the careful keeping of a notebook. The teacher is, therefore, urged to insist that neat, accurate notes accompany each experiment. These notes should be taken *in the permanent notebook and in their final form, as soon as the data are obtained*. The habit of writing notes on scraps of paper and afterwards copying them off in "better form" is pernicious. Proper entry of notes should be regarded as part of every experiment, not a separate exercise. *Whether or not an experiment is going to succeed has no bearing on the recording of the notes, for the notes on a failing experiment may be more valuable than those on a successful one.*

The teacher's attention is called to the Appendix of this Manual, where suggestions are given regarding the organization of the laboratory work, and regarding apparatus, chemicals, etc. These suggestions are intended simply to give the teacher who is just taking up the course the benefit of the author's experience, and thus considerably lighten the burden.

W. H. C.

Oberlin, Ohio,
March 10, 1922

CONTENTS

PART I

EXPERIMENTAL PHYSICAL CHEMISTRY

CHAPTER	PAGE
1. Introduction	
1. Honesty	1
2. Intelligent Work	1
3. Skill and Neatness	2
4. Precision and Accuracy	2
5. Errors	3
6. Notation of Error and Deviation	4
7. Choice of Results in a Series; Rejection of Observations	5
8. Significant Figures	6
9. The Laboratory Record	7
10. Report of an Analysis	8
11. The Analytical Balance and Its Manipulation	9
12. Cleaning of Glass and Porcelain Ware	16
13. Calibration of Volumetric Apparatus	17
14. Handbooks and Apparatus Catalogs	22
2. Kinetic Theory	
Exp. 1. Brownian Movement	23
Exp. 2. Change of the Rate of Evaporation with Pressure	23
3. The Gas Laws	
Exp. 3. Boyle's Law	25
Exp. 4. Partial Volumes and Pressures of the Gases in the Air	26
Exp. 5. The Coefficient of Expansion of a Gas	27
Exp. 6. Graham's Law of Diffusion	30
Exp. 7. Graham's Law and Molecular Weights	31
4. Laws Governing Change of Phase	
Exp. 8. Vapor Pressure of Water	33
Exp. 9. Heat of Evaporation (Vaporization) of Water	35
5. Molecular Weights. The Avogadro Number	
Exp. 10. Molecular Weight of Carbon Dioxide	37
Exp. 11. Molecular Weight of Ether	38
Exp. 12. The Avogadro Number	39
6. The Laws of Combination	
Exp. 13. The Composition of Silver Oxide	42
Exp. 14. The Composition of Silver Chloride	44
Exp. 15. The Law of Multiple Proportions. Determination of Chlorine in the Chlorides of Mercury	47
Exp. 16. The Law of Volumes from the Analysis of Ammonia	49
7. Atomic Weights	
Exp. 17. Heat Capacity and Atomic Weight of Nickel	51

CHAPTER	PAGE
8. Valence	
Exp. 18. Valence of Sodium, Magnesium, and Aluminum	53
Exp. 19. Oxidation and Reduction Valence	54
Exp. 20. Zinc as a Reducing Agent. (The Jones Reductor.)	58
9. Solutions	
Exp. 21. Solubility of Sodium Chloride	60
Exp. 22. Supersaturated Solutions of the Hydrates of Sodium Sulfate	61
Exp. 23. The Test for Potassium Ion	62
Exp. 24. Preparation of Approximately Normal Solutions of Acids and Bases	62
Exp. 25. Preparation of a Solution of an Exactly Specified Concentration	68
Exp. 26. Analysis of an Unknown Acid or Base Solution	70
10. Freezing Points and Molecular Weights	
Exp. 27. Molar Lowering of the Freezing Point of Water	72
Exp. 28. Molecular Weight of Methyl Acetate	73
11. Acids, Bases, and Salts	
Exp. 29. Salt Effect	74
Exp. 30. Qualitative Tests for Differences in Ionization	74
Exp. 31. Speed of Catalysis as an Approximate Measure of Ionization	75
Exp. 32. Heat of Neutralization	76
12. Homogeneous Equilibrium	
Exp. 33. Velocity of Reaction and the Velocity Constant	78
Exp. 34. Determination of an Equilibrium Constant	79
Exp. 35. Common Ion Effect. Buffer Solutions	82
Exp. 36. Neutralization Effect	84
13. Neutralization Indicators	
Exp. 37. Color Range of Methyl Orange Indicator and Its End-point Correction	86
Exp. 38. The Color Range of Phenolphthalein	88
Exp. 39. Choice of an Indicator	90
Exp. 40. Titration of a Polybasic Acid and of a Salt of a Polybasic Acid	91
14. Heterogeneous Equilibrium	
Exp. 41. Decomposition of the Hydrates of Cupric Sulfate	95
Exp. 42. Distribution of Succinic Acid between Water and Ether	96
Exp. 43. The Cooling Curve of Sodium Sulfate; Application of the Phase Rule	97
Exp. 44. The Solubility Product Principle; the Precipitation of Silver Acetate	98
Exp. 45. Precipitation by Means of Hydrogen Sulfide and Its Salts	102
Exp. 46. Precipitation of Magnesium Ions by Hydroxyl Ions (to Form Magnesium Hydroxide) in Aqueous Ammonia Solutions	103
Exp. 47. The Silver Diammine Complex Ion	104
Exp. 48. The Ferric-oxalate Complex Ion	108
Exp. 49. Amphoteric Nature of the Aluminum Group	108
15. Colloids	
Exp. 50. Typical Methods of Preparing Colloidal Suspensions	110
Exp. 51. Coagulation of Colloids	110
Exp. 52. Protective Colloids	111
Exp. 53. Solvated Colloids	111
Exp. 54. Emulsions	112
Exp. 55. Adsorption	113

CHAPTER

16. Electrochemistry	
Exp. 56. Determination of the Faraday	114
Exp. 57. Electrode Reactions	115
Exp. 58. Migration Velocity of Hydrogen and Hydroxyl Ions	116
Exp. 59. The Daniell Cell	117
Exp. 60. Decomposition Voltage	118
Exp. 61. Displacement Reactions	118

*PART II**QUANTITATIVE ANALYSIS*

17. Measurement of Acids and Bases	
Exp. 62. Colorimetric Determination of pH	121
Exp. 63. Standard Hydrochloric Acid Solution	126
Exp. 64. Standard Sodium Hydroxide Solution	132
Exp. 65. Analysis of a Carbonate-hydroxide Mixture	134
18. Gravimetric Analysis	
Exp. 66. Iron in an Iron Ore	139
Exp. 67. Sulfur in a Sulfide Ore	146
Exp. 68. Determination of Calcium and Magnesium in Limestone	152
Exp. 69. Determination of Carbon Dioxide in a Carbonate	157
19. Volumetric Precipitations	
Exp. 70. Mohr's Method for the Analysis of Chloride or Bromide Ion	160
Exp. 71. Adsorption Indicators. Fajans' Method for the Volumetric Determination of Chloride Ion	165
Exp. 72. Determination of Cyanide Ion with Standard Silver-ion Solution	168
20. Volumetric Oxidation-reduction Reactions	
Exp. 73. Standard Potassium Permanganate Solution	174
Exp. 74. Determination of Iron in an Iron Ore by Titration with Standard Potassium Permanganate Solution	178
Exp. 75. Preparation of a Standard Potassium Dichromate Solution	182
Exp. 76. Determination of Iron in an Iron Ore by Titration with a Standard Solution of Potassium Dichromate	187
Exp. 77. Preparation of a Standard Solution of Iodine	189
Exp. 78. Preparation of a Standard Solution of Sodium Thiosulfate	192
Exp. 79. Iodometric Analysis of a Solution Containing Cupric Ion	197
Exp. 80. Determination of Arsenic and Copper in Paris Green	198
21. Electrolytic Deposition and Electrolytic Separations	
Exp. 81. Deposition of Metals from Acid Solutions	200
Exp. 82. Deposition of Metals from Alkaline Solutions	208
Exp. 83. Separation of Metals by Electrolysis	209
Appendix	
Apparatus	212
Logarithms	214
International Atomic Weights	216

I. EXPERIMENTAL PHYSICAL CHEMISTRY

CHAPTER 1

INTRODUCTION

The laboratory exercises which constitute Part I of this manual may be described generally as elementary experiments in physical chemistry. Their purpose is twofold: they are intended to illustrate and clarify physical-chemical principles for the student, and to give him some of the knowledge and skills required in analytical chemistry. Part II of this manual consists of a number of analytical procedures of various types. The experiments in this part are based on the experiments in Part I. Thus the theoretical discussions which precede the laboratory directions, and the laboratory directions themselves, are based on the physical-chemical principles illustrated at some length by the experiments in Part I.

Before we discuss the experiments in detail, we shall review some of the essential requirements for reliable experimental work in science. It is obvious that trustworthy conclusions can be drawn from experimental data only if the experiments and the data are reliable.

1. Honesty. The personal habits of the experimenter are as important in chemistry as they are in other sciences. Students sometimes feel mistakenly that the experimenter should have no interest in an experiment other than in the final results; these are often the students who work for an answer primarily to turn it in as a report to the instructor. Scientific endeavor should be objective, but the student must be interested in the whole procedure leading to the final result if he wishes to obtain reliable results. His interest, however, should not be of the persuasive kind which colors his interpretation of data and results so that he records values which he thinks or hopes he obtained rather than those he actually obtained. Scientific work demands a high degree of integrity and honesty from the scientist; anything less than absolute honesty detracts from the value of scientific work.

Be absolutely honest in your work. Your instructor will not expect you to obtain results more accurate than the experimental methods described are capable of giving. An experienced teacher can frequently uncover evidence of dishonesty in a reported result (derived from "adjusted" data) which appears to be much more accurate than the method described can give. On the other hand, occasional honest results that are apparently more precise than those produced by the experimental method need no further explanation than that errors in a given method sometimes tend to cancel each other.

2. Intelligent Work. To do intelligent work in the laboratory, you must know exactly **what** you are going to do and **why** you are to do it. In this way you learn to judge the reliability of your data. If you follow laboratory directions in the same frame of mind with which you might follow directions given in a cook-book, you will derive little benefit, even though your experimental results may be excellent. Furthermore, you may often be tempted to "substitute the data in the appropriate mathematical formula" in calculating your results. However, avoid the blind use of a formula which someone else has told you gives the right answer. Make an effort to know why that formula is used and how it is derived.

The student can do intelligent work in the laboratory only if he has studied the theory underlying the experiment before he begins any laboratory work. Such study often requires reference to the Textbook;¹ it is therefore helpful to have a copy of this available for reference in the laboratory. When the pressure of work increases, or whenever extra-curricular activities tend to absorb your interest, you may neglect the discipline in thinking required by intelligent laboratory work unless you remember that work done without a purpose is a useless expenditure of energy. One of the fundamental purposes of laboratory work is to illustrate theoretical principles and thereby to aid your understanding of them. If you understand **why** and **how** any procedure is carried out, you will derive benefits from your laboratory work which are much more important than your increase in skill in handling apparatus.

The proper understanding of any subject demands mental concentration which can be achieved most readily in orderly surroundings undisturbed by unnecessary foreign noises. You are expected to work as quietly as possible at your own desk and to attend strictly to your own work.

3. Skill and Neatness. The proper performance of a quantitative analytical procedure of average difficulty demands not only a knowledge of the reasons for the various steps but also a rather high degree of manual dexterity and skill on the part of the analyst. Most of the laboratory work is done with the hands or with simple manually operated equipment. The skill required for these manipulations can be developed by most persons who have the determination to learn and to improve. One of the best indications of the skill with which an operator works is the neatness of his tools and equipment and the neatness of his immediate surroundings. An ill-kept desk or laboratory bench is indicative of his attitude toward analytical work; a littered floor and side-shelf show the same poor attitude, and in addition they show an antisocial attitude by the individuals who are responsible.

The laboratory and all the equipment in it are yours for your use. You must keep them clean and orderly if you wish to do the best work of which you are capable.

4. Precision and Accuracy. Although the student may perform an analysis or an experiment with great skill and without any known errors, it does not follow that the results will be accurate; nor is it necessarily true that the results are accurate when duplicate analyses or experiments show exact checks. Errors in quantitative analysis or in laboratory measurements also arise from other causes than through fault of the student. Experimental (and sometimes theoretical) errors are inherent in every method, so that it is virtually impossible to avoid them entirely. One experimental method may have a higher degree of accuracy than another designed to achieve the same result because the magnitude of the errors can be reduced more extensively, but absolute accuracy is unobtainable. An absolutely accurate measurement would be one which gives the **true value** (or **absolute value**) of a physical quantity. When we speak of the "accuracy" of an analytical result, we usually mean the agreement between the observed value of the analytical result and the true value of the physical quantity being measured. Since the absolute value of any physical quantity cannot be determined, the agreement between the analytical result and the true value likewise cannot be determined. However, as we eliminate or compensate for more and more of the errors in an experiment, we feel that our experimental results become more and more accurate even though we can do no more than approximate the desired true value.

¹ Chapin and Steiner, *Second Year College Chemistry*. John Wiley and Sons, Inc., New York, 1943. Fifth Edition. All future references to the "Textbook" will be to this edition.

Students too often assume that duplicate analyses which they obtained by following an accepted procedure and which agree closely with each other constitute an acceptable analytical report. Such a report may have a high degree of precision, but it may still be relatively inaccurate. *Precision means the reproducibility of a result; accuracy means the agreement between the measured value and the true value of any quantity.* A series of analyses may be very precise and still be very inaccurate, for an error committed in an analysis is a primary cause of inaccuracy, but the same error repeated in the duplicate runs might lead to the precise results. The most desirable analytical methods for the estimation of any quantity are those which give results with a high degree of accuracy and precision; if less accurate methods must be used, their relative accuracy and the degree of precision should be known and stated.

5. Errors. The errors to which all experimental measurements are subject can be grouped conveniently into two classes, determinate errors and indeterminate errors.

Determinate errors (often called constant errors) may be divided into (a) errors of method, (b) instrumental errors, and (c) personal errors.

(a) Errors of method may arise from a number of sources. The fundamental theory on which an analytical method is based may be unsound; a precipitate may be contaminated by impurities introduced at some step of the procedure; a sample taken for analysis may not be representative of the whole mass of material. In general these errors can be eliminated by a change in analytical procedure.

(b) Instrumental errors arise from inaccuracies in the instruments and apparatus used in the experiment. For example, a 25.00-ml pipet may deliver 24.92 ml of liquid; or the same pipet may deliver different volumes of different liquids because of the difference in viscosity of the two liquids. Or, as frequently happens in quantitative analysis, there may be a difference between the actual value for an analytical weight and the value marked on it; thus a 10.0000-gram weight may actually weigh 9.9982 grams. Instrumental errors can be avoided if calibrated apparatus is used. When an instrument is calibrated the corrective factors, which should be applied to the data collected with the instrument, are evaluated.

(c) Personal errors are those which result from some defect, peculiarity, or sensitivity of the individual observer. The most common example is the inability of some individuals, because of slight color blindness, to make proper use of indicators involving a change of color. A person who is totally color-blind rarely makes a mistake unwittingly because he probably already knows of his inability to distinguish colors. A person who is slightly color-blind but is unaware of it may easily make a considerable error in determining the end point of a titration when he uses a colored indicator to mark the end point.

One can usually compensate for personal errors by running a blank determination. In such a determination, the entire experimental procedure is carried through with the omission of no step, reagent, or substance, other than the material for which the sample is being analyzed. If one knows that his observations may be in error because of a slight color blindness, he may often remove the source of error by using indicators with different color combinations; or he may use another method of analysis, or a different instrumental aid such as a photoelectric colorimeter.

Indeterminate (or casual) errors are those over which the observer has no control; they may occur whenever measurements are taken or judgments are made. They may be due to slight changes in instruments, changes that are too small to detect by calibration, or they may occur because of the very slight undetectable erratic behavior of the instruments. Slight differences in judgment of an observer are a common source of indeterminate errors.

The magnitude and sign of indeterminate errors follow the law of chance. If a very large number of careful measurements of a physical quantity are made, and the determinate errors are avoided as much as possible, we find that very large errors are unlikely to occur, small errors occur much more frequently than large ones, and positive and negative errors of the same numerical size are equally likely to occur. Since in a great number of measurements the number of positive errors will be equal to the number of negative errors of the same numerical magnitude it is easily seen that one method of getting the best value for such a series of measurements is to take the **arithmetical average** of the series.

6. Notation of Error and Deviation. The results of a chemical analysis for the amount of a given constituent in a sample are most often expressed in terms of percentage. It is therefore confusing and ambiguous to express the error in the determination or the observed deviation between two analyses in terms of percentage. For measurements such as those in physical chemistry and in physics in which the percentage of the constituents are not involved, the difference between the accepted value of a measurement and the experimental value may be expressed in percentage without confusion. If, for example, the best experimental value for the Avogadro number be taken as 6.023×10^{23} , and the value obtained by a student in the laboratory is 6.002×10^{23} , the error when stated in per cent becomes

$$\frac{(6.002 \times 10^{23} - 6.023 \times 10^{23})(100)}{6.023 \times 10^{23}} = -0.35\%$$

This value -0.35 per cent is not ambiguous. On the other hand, if the correct value for the percentage of iron in an ore be taken as 29.36 per cent, and if a student finds 29.19 per cent iron in the sample as the average of a series of analyses, he may state his error in one of two ways: (a) he may say his analysis was in error by $(29.19 - 29.36)$ or -0.17 per cent, or (b) he may say his analysis was in error by

$$\frac{(29.19 - 29.36)(100)}{29.36} = -0.58\%$$

His expression of the percentage error, therefore, is ambiguous unless he states also the basis on which it was calculated.

To avoid such ambiguity, analysts customarily indicate error and deviation in **parts per thousand**. If the accepted value of the percentage of iron in a sample is 29.36 per cent and the experimental value is 29.19 per cent, the analyst has made an error of $29.36 - 29.19$ or 0.17 parts in every 29.36 parts. This amounts to 17 parts per 2936 or 5.8 parts per 1000. Since the analysis shows less iron present than the accepted value, the error is expressed as -5.8 parts per 1000.

One method of stating the precision of a series of analytical results is to indicate the deviation in parts per thousand between the two results most widely separated in numerical value. Consider a series of analytical results for the analysis of iron in an ore stated in percentage figures as 29.12, 29.18, 29.23, and 29.23. In this series, the deviation in parts per thousand for the two results which show the greatest deviation is

$$\frac{29.23 - 29.12}{\frac{1}{2}(29.23 + 29.12)} = 3.8 \text{ parts per 1000}$$

A more comprehensive method of stating the precision of a series of results is to indicate the average of the individual deviations (without regard to sign) from the arithmetical average of the members of the series. An example will make this clear. The arithmetical

average of the above series is 29.19 per cent. The individual deviations from the arithmetical average without regard to sign are 0.07, 0.01, 0.04, and 0.04. The average of these individual deviations is 0.04 and the average deviation from the arithmetical average is 4 parts per 2919 or 1.4 parts per 1000.

7. Choice of Results in a Series; Rejection of Observations. Whenever a series of observations (or analyses) is completed, the observer (or analyst) usually finds that the observations do not agree exactly. This is no cause for concern, since the indeterminate errors in each observation may be large enough to cause the variation. We have seen that the arithmetical mean represents the best value for a very large number of observations. If an observation is very easily made, this method of obtaining one value as representative of a very large number of values is not too difficult. In quantitative analysis, however, the increase in accuracy obtained by running more and more analyses soon reaches the point where the law of diminishing returns becomes operative.

The actual number of determinations that should be run depends of course on a number of factors, such as the degree of accuracy demanded, the amount of sample available, and the time available for more analyses (this also depends on the length of time the procedure may take and on the difficulty of the procedure). For ordinary gravimetric determinations two duplicate analyses which agree within limits dependent on the precision expected of the method usually are acceptable. Until the student has developed sufficient laboratory skill to make it reasonably certain that he will commit no large determinate error on any single analysis, it is advisable that he run three determinations concurrently. If two determinations are run concurrently and one is spoiled well along in the procedure, or if the desired precision is not obtained, another determination must then be started. It takes only a little more time to run three determinations instead of two, and the spoiling of one out of three does not make it absolutely necessary to repeat the whole procedure. For ordinary volumetric analyses it is also advisable to run at least three concurrent determinations if two acceptable results are desired. The procedures of the volumetric analyses usually assigned to students are easy enough so that three acceptable determinations are often required for a report.

Two rules are available for choosing the acceptable results from a series of results. They are (a) an empirical rule, and (b) a mathematical rule. However, the student should understand very definitely that any result **known** to be in error because of some mistake committed in the procedure is not to be considered as acceptable on any basis. To continue any determination beyond the point where an irremediable error was made is a waste of time. On the other hand, in a series of observations, it occasionally happens that one result differs very widely from the others even though no apparent or known error was made. Under these conditions, one of the following rules may be applied.

(a) An empirical rule may be applied to as few as two or three results. It is based upon some knowledge of the degree of precision to be expected of the method of analysis used. The rule is usually stated in terms of the largest deviation (expressed in parts per thousand) that is allowed between any two acceptable results. For example, consider the results of three determinations in an analysis for iron by a gravimetric method, the values for the per cent of iron being 24.37, 24.44, and 24.48. If the upper limits of deviation were set at 3 parts per 1000, the first result given above would probably be omitted since its deviation from the third is 4.5 parts per 1000. The deviation between the second and third results is only 1.6 parts per 1000 whereas that between the first and second is 2.9 parts per 1000. If it were known that the procedure used tends to give results that are too high, the average

of the first two results may be accepted as the best report since the deviation between these results is still less than the allowable deviation. If no general characteristics of the procedure are known, the average of the second and third results is taken for the report since the precision of these two results is better than the precision of the first two.

The empirical rule may also be stated in various other ways, such as in terms of the largest average deviation of the various members of the series from the arithmetical average, or in terms of the largest absolute deviation of any one result from the arithmetical average of the results which are considered acceptable.

(b) The mathematical rule can be applied only if four or more results are obtained. If only three results are available, and the analyst wishes to use the mathematical rule, he must make another determination. If one result of the four or more results appears to be doubtful, its inclusion or exclusion in the average to be reported may be determined by application of the following rule:

- (1) Omit the doubtful result and compute the arithmetical average of the others.

- (2) Calculate the average deviation of the results (other than the doubtful one) from the arithmetical average calculated in (1).

- (3) Calculate the deviation of the doubtful result from the arithmetical average calculated in (1). If this deviation is greater than four times the average deviation calculated in (2), reject the doubtful result since the chances are about 99 in 100 that the result is in error because of some mistake.

As an example of the application of this rule, let us consider the following series of results obtained by a volumetric method for the per cent of chloride ion present in an unknown: 38.68, 38.74, 38.70, 38.57, 38.67. We see by inspection that 38.57 is a rather doubtful result. If we omit this value, the average of the other four results is 38.70, and the average deviation of the four results from this average is 0.023. The difference between the doubtful result and the average is 0.13, and this is greater than 4×0.023 . Therefore the doubtful result is not acceptable, and the analysis is reported as 38.70 per cent.

8. Significant Figures. Results of experimental measurement are always expressed in numbers. In scientific work numbers are most useful if they include only enough digits to show the precision of the measurement clearly. In any number the digits whose values are clearly known are called significant figures. In addition to these digits known with certainty, the first digit about which any doubt exists is also included among the significant figures. For example, a good analytical balance can be used to weigh an object with a precision of 0.1 mg. If the weight of an object is determined as 0.5463 gram, the last figure, 3, is in doubt, since it may actually be 4 or 2. The number 0.5463 has four significant figures. The digit 0 has no significance since it serves only to place the decimal point. This placement of the decimal point is necessary only because of the units that we have chosen for our measurement. We may say just as truthfully that the object weighs 546.3 mg; in this number the digit 0 does not appear.

Zeros are often used rather loosely as digits, especially for very large numbers which are approximations. As an example, the population of Europe has been given in population tables as 500,000,000 inhabitants. If each zero were significant, it could mean that there may be only several persons more or several persons less than five hundred million. Actually, however, the population might be known only to the nearest one hundred thousand inhabitants, so the number should be stated as 500.0 million or 500.0×10^6 or 5.000×10^8 . In any of these last three numbers there are only four significant figures.

Analytical determinations described in Part II of this manual should be carried to four significant figures. Many of the measurements in the physical-chemical experiments described in Part I are to be made only to two or three significant figures. Any result based by multiplication or division on a figure having only two or three significant figures is not precise to more than two or three figures; the statement of such a result to four significant figures is therefore misleading and incorrect. In other words, no result calculated by multiplication or division from experimental data is more precise than the least precise datum used in the calculation.

9. The Laboratory Record. One of the most important operations in good laboratory work is the proper recording of data and calculations. Many an experiment which would otherwise be entirely lost can be saved by a review of the recorded data and a correction of errors in calculation. Moreover, no experiment can be considered complete unless it is accompanied by a faithful record. This record should be prepared **as the experiment proceeds**, not after it is completed. One of the most pernicious habits is that of writing down data and calculations on loose scraps of paper and later transferring them to a permanent book just to turn in to the instructor. Remember the record is not for use of the teacher, but for the student. The record book should be permanently bound, not of the loose-leaf type, and should be taken to the laboratory at the time of the first exercise.

The material should be written **in ink** and should be arranged according to the following directions:

1. Write down the title of the experiment.
2. Prepare a short outline such as is usually found in the description of the experiment; this is simply a résumé of the method by which the determination is made. To do this one must study the procedure beforehand and know what he is about to do. It scarcely needs to be said that it would be foolish to begin an experiment until this is done.
3. Perform the experiment according to the procedure as given in the manual. As the data are obtained record them **immediately**, with proper designation, in the record book. Remember that data mean **all quantitative measurements**, such as temperatures, pressures, weights, volumes, and dimensions, obtained by the student himself or obtained from reference books, etc. The order in which the data are recorded is of no importance, but the natural thing to do is to put them down in the order obtained. Above all, do not forget to designate what each entry represents.
4. When the data are all recorded, proceed with the calculation as directed. Here again everything must be properly designated. It is not necessary, however, to put down all the operations of multiplication, division, etc.; all that is necessary is to indicate what numbers are multiplied or divided and then give the result.
5. If a more accurate value of the experimental measurement is known, calculate the deviation in parts per thousand between your experimental value and the more accurate value. If the accepted value has a high degree of accuracy, the deviation may be taken as the error of your result.
6. Conclude your record of the experiment with some statement of the result you obtained and its error in parts per thousand. If possible, the conclusion should contain some discussion of the sources of error.

If an experiment fails at any stage do not cross out the data or calculations and thus mutilate the record; simply note the failure and give the reason if you know what it is, and then start with a new set of data. The impression you make on the instructor will not be injured by your repetition of an experiment, but it will be by mutilated or untidy notes.

To help in understanding the above directions the following sample record is included.

Exp. 11. Molecular Weight of Ether.

The weight of a known volume of ether vapor at a known temperature and pressure is found. From these data the weight of 22.4 liters of the vapor under standard conditions is calculated; this weight is the molar weight.

Weight of bulb + air = 57.9200 grams.

Temp. of balance room = 23° C = 276° K.

Barometer reading = 740.5 mm at 21° C.

Atmospheric pressure = 740.5 - 2.5 = 738 mm.

Temp. of bath = 88° C = 361° K.

Wt. of bulb + ether vapor = 58.297 grams.

Wt. of bulb + water = 342.2 grams.

Wt. of 1 ml air at 23° C and 738 mm = 0.001161 gram.

Wt. of water in bulb = (342.2 - 57.92) = 284.3 grams.

Approximate volume of bulb = 284.3 ml.

Wt. of 284.3 ml air at 23° C and 738 mm = $284.3 \times 0.001161 = 0.3302$ gram.

Wt. of evacuated bulb = (57.9200 - 0.3302) = 57.5898 grams.

Wt. of ether in bulb = (58.297 - 57.590) = 0.707 gram.

Vol. of ether at standard conditions = $\frac{284.3 \times 273 \times 738}{361 \times 760} = 209$ ml. This is the volume of 0.707 gram.

Wt. of 22,400 ml ether vapor at standard conditions = $\frac{0.707 \times 22,400}{209} = 75.8$ grams.

Accepted molar weight of ether = 74.12 grams.

Error in parts per thousand = $\frac{75.8 - 74.1}{74.1} (1000) = +23$ parts per 1000.

The molecular weight of ether was determined to be 75.8. This result is in error by 23 parts per thousand. The major source of error probably results from the assumption that ether vapor behaves as an ideal gas. Instrumental errors undoubtedly contributed somewhat to the total error since uncalibrated apparatus was used.

Note that there are five divisions in this record. (1) **The outline:** a clear and concise statement of the method. (2) **Data:** weights, volumes, etc., as they were obtained during the course of the experiment. (3) **Calculations:** note that all the results obtained here are calculated from the data recorded in (2). (4) **Error:** the error of the result is calculated by comparing it with an experimental result of a high degree of accuracy. (5) **Conclusion:** a statement of the experimental result, the error, and the possible sources of error.

10. Report of an Analysis. The formal report of the quantitative analysis of an unknown should be as informative and yet as brief as possible. The report may be submitted to the instructor either by turning in the laboratory record book with a suitable report on a page by itself, or the report may be made on a filing card of a size designated by the instructor. A standard 4 in. by 6 in. filing card is a convenient size. If the report is submitted on a card, the data entered on it **must** be a copy of the same data entered in permanent form in the laboratory record.

The report should contain the following data: the title of the analysis, the number of determinations attempted, an outline of the calculation used in obtaining the final results, a list of acceptable results (with the highest result listed first), a list of unacceptable results (with reasons for their non-acceptance), average of the acceptable results, the deviation in parts per thousand between the two acceptable results showing the greatest deviation, the average deviation from the average of the acceptable results, the date, and the signature of the analyst. The following report is given as an example.

Report of Gravimetric Iron Analysis.

Five determinations were started. Number 2 was discarded at the point of reprecipitation of the ferric hydroxide because of loss of material.

Calculation:

$$\% \text{ Fe} = \frac{\left(\frac{2\text{Fe}}{\text{Fe}_2\text{O}_3} \right) (\text{grams of ferric oxide weighed}) (100)}{\text{Grams of sample}}$$

Acceptable Results		Unacceptable Results	
No. 5	% Fe = 25.67	No. 3	% Fe = 25.04
No. 1	25.63	Result not accepted because deviation is greater than four times the average deviation from the average of the other results shown.	
No. 4	25.60		
	$3 \overline{)76.90}$		

Average: 25.63% Fe

Deviation between the two acceptable results showing greatest deviation = 2.7 parts per 1000.

Average deviation of acceptable results from the arithmetical average = 0.90 parts per 1000.

Date:

Signed:

11. The Analytical Balance and Its Manipulation. Any good analytical balance can be relied upon to give the weight of an object to within one- or two-tenths of a milligram (0.0001 or 0.0002 gram). This is scarcely more than the weight of a barely visible particle of sand. To maintain such precision, however, the balance must have the best of treatment. To show what such treatment really is, the following rules are given for the use of the balance.

1. Each student will be assigned to a certain balance and should use only this one, never any other. Weighings of the same object made on different balances are not necessarily identical, partly because the arms of a balance are scarcely ever of exactly the same length, and partly because different weights may vary somewhat. Furthermore, use of a balance assigned to another student often causes him inconvenience.

2. No chemical is ever placed directly on the pan of a balance. Such a procedure will almost certainly result in corrosion and speedy ruin of the pan. Chemicals should be weighed in weighing bottles or crucibles, or on watch glasses, and the greatest care should be taken to avoid spilling any of the material on the pan. To prevent possible spilling on the pan, form the habit of removing the crucible or watch glass from the pan before putting anything into it. It is advisable to protect the balance pans by accurately balanced disks of black Bakelite $1\frac{1}{2}$ mm thick and 9 cm in diameter. Anything spilled on one of these is easily seen, and cleaning is very easily accomplished for the disk may be removed and brushed off.

3. Brush the pans frequently with a camel's-hair brush. Never allow dust or anything else to accumulate on the floor or case of the balance.

4. Always place the weights on the right-hand pan of the balance, and the object to be weighed on the left-hand pan.

5. Never place anything on the balance pans or remove anything from them without first arresting the beam. This rule applies also to the rider.

6. All movement of the parts of a balance should be slow and deliberate. The beam should never be arrested while it is swinging far to one side. Open and close the balance door gently.

7. Any irregularities in the working of the balance should be reported to the instructor. Do not attempt adjustment yourself.