Chemical Principles in Calculations of IONIC EQUILIBRIA

Solution Theory for General Chemistry, Qualitative Analysis, and Quantitative Analysis

Emil J. Margolis

CHEMICAL PRINCIPLES IN CALCULATIONS OF IONIC EQUILIBRIA

Solution Theory for General Chemistry, Qualitative Analysis, and Quantitative Analysis

EMIL J. MARGOLIS

OF THE

Professorial Staff, Department of Chemistry

The City College of The City University of New York

THE MACMILLAN COMPANY · *NEW YORK*

COLLIER-MACMILLAN LIMITED · *LONDON*

First Printing

Library of Congress catalog card number: 66–19713

The Macmillan Company, New York
Collier-Macmillan Canada, Ltd., Toronto, Ontario

PRINTED IN THE UNITED STATES OF AMERICA

IONIC EQUILIBRIA

Preface

THIS BOOK represents a careful analysis of the difficulties most frequently encountered by students in the *mathematical* application of chemical principles. With perhaps-forgivable immodesty it may also be characterized as a highly experienced and confident analysis, for it represents the author's sympathetic contention with the problems of students of college chemistry during a teaching period of more than thirty-five years. The text offers no panacea for the frustrations of inadequate course preparation or lack of earnest perseverance on the part of the individual. Instead, it offers a patient and disciplined approach to the theory of ionic solution chemistry which will prepare the student to cope successfully with routine or "type" calculations and with those that require a capacity to project formulated principles imaginatively.

Frequently, the "challenge" which faces a student in the form of a mathematical exercise reduces to an eventual acknowledgment that preparation for the problem is not adequately provided in the descriptive development of the text material. The beguiling characterization of such a problem as a challenge is, then, hardly more than a euphemistic apology for an author's own oversight or lack of realism. The difficulties that such authorial deficiencies cause are especially great for the beginning student, who obviously lacks the facility born of experience, constant practice, and mathematical maturity. The almost inevitable result is the confidence-destroying frustration of extravagant time spent groping in the dark in unrequited search for something that continues to elude detection. On the other hand, the opposite extreme to "challenge" is also to be avoided. The mere availability of a simple, condensed mathematical formula for the convenient substitution of an x or a y lends nothing to the cultivation of a student's powers to analyze with facility an unconventional problem. With such a formula, the approach to a solution is made, more often than not, upon the crutch of rote memorization—which leads neither to a realistic test of chemical knowledge and understanding of principles nor to a confident ability to handle the challenges that lie in wait at examination time. The resultant personal stresses which then carry over to unrelated questions and which impair over-all performance on examinations need no elaboration here. The average student is thoroughly familiar with them.

No condensed-formula approach to problem solving is ever warranted in chemistry—even as an expedient of convenience—unless prior derivation of the formula has been carefully delineated and interpreted in terms of the chemical principles that it incorporates. The mathematics to be used in the solving of chemical problems must not be allowed to become an end in itself; it is but the means to an end—namely, the testing of one's ability to apply an absorbed and confident knowledge of principles.

Despite the sometimes attendant rigors, problem solving remains probably the very best way to learn chemistry and concomitantly constitutes a most reliable gauge of comprehension. The student may feel reassured, however, that no mathematical terrors lie await herein. The text's technical demands will not escalate beyond the normal prerequisites of satisfactory training in algebra and the use of simple logarithms.

This book is intended primarily for intensive use in the second and/or third terms of the customary college chemistry curriculum. Designed for the instructional level of the average student, it is to be carefully distinguished from the conventional "problem book" which invariably is merely a superficial condensation or extract of text material. This text will meet its planned objectives in the furtherance of chemical education by application in any of the following ways:

1. *As a supplement to the general chemistry textbook.* The general chemistry text is now in a period of transition from its traditional recitals of mere descriptive chemical facts and behavior—largely unreconciled by underlying theory—to their whys and wherefores via the denouements of quantum mechanics, thermodynamics, and kinetics. The contrasts have accentuated even further the physical limitations of the general chemistry text with respect to the time and attention it can devote to the many highly important applications of ionic solution equilibria. This limitation is particularly true where qualitative and quantitative analysis have, in response to the speed-up requirements of our technological age, disappeared from the curriculum scene and have been entrusted in an abridged fashion to the general chemistry course. The instructional compensations that consequently are now due present cogent reasons for the writing of this book, which can be keyed to any general chemistry text.

2. *As a self-contained, all-inclusive text for a modern course on the freshman-sophomore level devoted independently to the equilibria theory of aqueous solutions of electrolytes—ionic solutions.* In fact, the construction and orientation of this text has been guided throughout by a pedagogical recognition of, and a basic philosophical agreement with, the emergence of the second term of the college chemistry curriculum as just such a course.

3. *As an independent theory text in courses of experimental qualitative analysis.* Where a laboratory manual or more comprehensive text of analytical working procedures is being used, this book will provide a complete study of the equilibrium theory thereof. With traditional formal courses of experimental qualitative analysis undergoing continuing abridgements of allotted time and pedagogical treatment, the classical comprehensive "qual texts," with their now-excessive experimental content, have made their inexorable departures from the curriculum scene. Unhappily, with them have gone the invaluable treatments of ionic equilibria. It is to fill this void that this text of ionic equilibria has been created.

4. *As a reference adjunct for courses in quantitative analysis.*

5. *As a review book and general reference for the student in advanced chemistry courses.* The rigorous recall of many facets of solution chemistry frequently sought by chemistry students at various stages of their preparation for graduate

training will be facilitated by the integrations provided in this text of the pertinent fundamentals with searching mathematical applications.

In this book's conscientious, careful delineation of principles and terms and in its interpretative presentation of hundreds of worked-out exercises and their component parts the student will obtain an enduring comprehension rather than an ephemeral rote memorization. And in the several hundreds of supplementary assignments he will find not only opportunities for performance and satisfaction with basic tasks well learned, but also the stimulations that challenge the alertness, resourcefulness, and imagination of the thinking student.

EMIL J. MARGOLIS

New York City

Contents

Chapter

1 Principles of Mathematical Operation and Technique in Chemical Calculations 1

DEFINITIVE CONCEPTS: Exponents; Significant Figures; Logs; Quadratic Equations · 1

2 Principles of Chemical Dimensions 16

DEFINITIVE CONCEPTS: Components and Units of Concentration · 16

3 Principles of Homogeneous Phase Equilibria 33

DEFINITIVE CONCEPTS: Ionization; Hydrolysis; Acid-Base Titration; Complex-Ion Dissociation · 33

Calculations of Homogeneous Phase Equilibria 82

INTERPRETATIVE EXERCISES: Ionization; Hydrolysis; Acid-Base Titration; Complex-Ion Dissociation · 82

SUPPLEMENTARY ASSIGNMENTS: Ionization; Hydrolysis; Acid-Base Titration; Complex-Ion Dissociation · 134

4 Principles of Heterogeneous Phase Equilibria, I 146

DEFINITIVE CONCEPTS: Solid-Liquid Precipitations and Solubilizations · 146

Calculations of Heterogeneous Phase Equilibria, I 181

INTERPRETATIVE EXERCISES: Solid-Liquid Precipitations and Solubilizations · 181

SUPPLEMENTARY ASSIGNMENTS: Solid-Liquid Precipitations and Solubilizations · 231

Chapter

5 Principles of Heterogeneous Phase Equilibria, II 245

DEFINITIVE CONCEPTS: Liquid-Liquid Solubilizations and Extractions · 245

Calculations of Heterogeneous Phase Equilibria, II 253

INTERPRETATIVE EXERCISES: Liquid-Liquid Solubilizations and Extractions · 253

SUPPLEMENTARY ASSIGNMENTS: Liquid-Liquid Solubilizations and Extractions · 260

6 Principles of the Activity Function 263

DEFINITIVE CONCEPTS: Thermodynamic Concentrations and Constants · 263

Calculations of the Activity Function 274

INTERPRETATIVE EXERCISES: Thermodynamic Concentrations and Constants · 274

SUPPLEMENTARY ASSIGNMENTS: Thermodynamic Concentrations and Constants · 283

7 Principles of Electrochemistry 287

DEFINITIVE CONCEPTS: Cell Processes and Faraday's Laws · 287

Calculations of Electrochemistry 323

INTERPRETATIVE EXERCISES: Cell Processes and Faraday's Laws · 323

SUPPLEMENTARY ASSIGNMENTS: Cell Processes and Faraday's Laws · 332

8 Principles of Reactant Potential and Free Energy 339

DEFINITIVE CONCEPTS: Magnitudes of Electron Transfer; Redox Titration · 339

Calculations of Reactant Potential and Free Energy 384

INTERPRETATIVE EXERCISES: Magnitudes of Electron Transfer; Redox Titration · 384

SUPPLEMENTARY ASSIGNMENTS: Magnitudes of Electron Transfer; Redox Titration · 418

Appendices

A Answers to Odd-Numbered Supplementary Assignments 429

B1 The Elements: Their Atomic Weights and Atomic Numbers; Electron Ground States and Oxidation States 435

B2 The Elements: Their Periodic Classifications 438

C Compendium of Solute Equilibria: Constants and Potentials of Reaction 439

INDEX 477

ENDPAPERS: Table of Common Logarithms Back Cover

CHAPTER 1

◇

PRINCIPLES OF

Mathematical Operation and Technique in Chemical Calculations

Definitive Concepts: Exponents; Significant Figures; Logs; Quadratic Equations

The following brief references to the utilization of important computative devices are intended solely as a recall to the student of material presumed to be already part of a previously acquired mathematical preparation for the work herein. A thorough familiarity with these simple arithmetical tools is indispensable. Moreover, since the student's high school training normally incorporates such preparation, it obviously will be the instructor's expectation in a second- or third-term college chemistry course in which this book will be used.

Exponents

An exponent expresses the number of times which its numerical base must be multiplied by itself in order to yield a specific digital number:

$$\underset{\text{(digital number)}}{8} = \underset{\text{(base)}}{2}^{3\,\text{(exponent)}} = 2 \times 2 \times 2$$

or

$$\underset{\text{(digital number)}}{1000} = \underset{\text{(base)}}{10}^{3\,\text{(exponent)}} = 10 \times 10 \times 10$$

Our primary interests here are in exponential powers to the base 10. These afford the entree not only to the use of common (or Briggsian) logarithms but also to the very great convenience of simplifying computations involving large numbers of zeros in numerical values which must be used in continuing sequences of ordinary multiplication, division, addition, or subtraction. The exponent to which the base 10 is raised may be either *positive* or *negative*. When the exponent is zero (i.e., 10^0) the digital value is automatically 1—in fact, any finite base exponentially raised to the zero power always equals a digital value of 1.

The essentials in the conversions of exponential powers of base 10 to non-exponential terms are simply these:

(i) The multiplication of any digital number by a *positive* power to the base 10 merely involves the shifting of the decimal point of the digital number as many places to the *right* as conforms to the numerical value of the positive exponent; thus

$$7.96 \times 10^{5} = 796000$$

(ii) The multiplication of any digital number by a *negative* power to the base 10 merely involves the shifting of the decimal point of the digital number as many places to the *left* as conforms to the numerical value of the negative exponent; thus

$$7.96 \times 10^{-5} = 0.0000796$$

The numerical illustrations used in the preceding have been modestly large and modestly small. One may readily appreciate the absurdity of writing for purposes of calculation a nonexponential expression of the Avogadro number, 6.02×10^{23}; or of the very numerous tiny values of ion concentrations and of $K_{\text{equilibrium}}$ values normally encountered in calculations of ionic solutions. In these areas of computation numerical values ranging between 10^{-10} and 10^{-50} are quite commonplace, and their frequent encounter and use commends the utilization of exponential numbers with all urgency.

It must be pointed out that positive and negative exponents need not be whole numbers by any means. However, to suggest illustratively that in the conversion of the term $1.00 \times 10^{2.5348}$ to a nonexponential expression the decimal point of the digital number 1.00 be moved 2.5348 places over to the right would obviously cause some perplexity. We shall, instead, cope with these situations conveniently by the use of logarithms—further reference to which we will temporarily defer, except to mention that the nonexponential evaluation of the cited example ($1.00 \times 10^{2.5348}$) equals 343.

Multiplication and Division of Exponential Powers to a Common Base

When multiplying, we *add* exponents; when dividing, we *subtract* exponents. Those parts of the respective numerical terms that are in digital (nonexponential) form are, of course, multiplied or divided in conventional fashion. The following examples illustrate these rules:

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^{-5}) = 8.4 \times 10^{-13}$$

$$(3.6 \times 10^{-7}) \times (2.5 \times 10^{9}) = 9.0 \times 10^{2}$$

$$10^{6.1284} \times 10^{2.3367} = 10^{8.4651}$$

$$8.8 \times 10^{-5}/2.2 \times 10^{7} = 4.0 \times 10^{-12}$$

$$9.6 \times 10^{5}/1.5 \times 10^{2} = 6.4 \times 10^{3}$$

$$10^{2.3456}/10^{1.5678} = 10^{0.7778}$$

Square roots and cube roots of exponential powers are obtained by dividing the exponent by 2 and 3 respectively; to obtain the *n*th root, divide the exponent by *n*. The nonexponential part of the numerical term takes its root in conventional fashion; thus

$$\sqrt{4.9 \times 10^{-5}} = (49 \times 10^{-6})^{1/2} = 7.0 \times 10^{-3}$$

As observed, the decimal point was conveniently moved one place to the right in order to obtain a whole number exponent fully divisible by 2 without fractional remainder. An equally valid adjustment for such purpose would be

$$\sqrt{4.9 \times 10^{-5}} = (0.49 \times 10^{-4})^{1/2} = 0.70 \times 10^{-2} = 7.0 \times 10^{-3}$$

Clearly, the identity of the total numerical term remains unaltered if for each place that the decimal point is moved to the right we compensate, in reverse, by multiplying the number by 10^{-1}. Moving the decimal point n places to the right requires, then, that we multiply by 10^{-n}. Conversely, the number likewise remains unchanged in over-all value if for each place its decimal point is moved to the left a reverse compensation is made by multiplying the number by 10^1; hence, moving the decimal point n places to the left requires that the number be multiplied by 10^n. In further illustration of extraction of a mathematical root

$$\sqrt[3]{2.7 \times 10^7} = (27 \times 10^6)^{1/3} = 3.0 \times 10^2$$

$$\sqrt[4]{10^{4.7436}} = (10^{4.7436})^{1/4} = 10^{1.1859}$$

Addition and Subtraction of Exponential Powers to a Common Base

When exponents to a common base are numerically identical, arithmetical procedures of addition and subtraction cause no change whatsoever in them; they are merely "carried through" unaltered with the results of the conventional additions or subtractions made of the nonexponential parts of the numerical terms. Illustratively,

$$(4.00 \times 10^{-6}) + (5.00 \times 10^{-6}) = 9.00 \times 10^{-6}$$

$$(8.35 \times 10^{-3}) - (7.20 \times 10^{-3}) = 1.15 \times 10^{-3}$$

When exponents to a common base differ in their magnitudes they must be transposed to identical values if any direct addition or subtraction is to be made. This is accomplished simply enough merely by shifting the decimal place of the associated digital number either to the left or to the right as required to compensate for the alteration in the exponent. This procedure for the retention of the over-all identity of the total expression has already been described. Illustratively, the addition of the terms (4.40×10^{-9}) and (3.30×10^{-8}) requires either that the former be converted validly to exponential 10^{-8}, or that the latter be converted to 10^{-9}. Obviously, any other transpositions that similarly leave an exact identity of exponents would likewise be acceptable. In response to conversions, then, the illustration yields

$$(0.440 \times 10^{-8}) + (3.30 \times 10^{-8}) = 3.74 \times 10^{-8}$$

or

$$(4.40 \times 10^{-9}) + (33.0 \times 10^{-9}) = 37.4 \times 10^{-9}$$

Of course, $3.74 \times 10^{-8} = 37.4 \times 10^{-9}$.

Significant Figures

In the preceding illustration it will be noted that we have retained in the final answer a fewer number of figures following the decimal point than appears in one of the numerical terms being added. The avoidance of 3.740×10^{-8} or of 37.40×10^{-9} as an answer has been deliberate. Scientific evaluations require that careful distinctions be made between quantities that are purely "speculative" or unprovable by measurement and those to which may be attached either the positive certainty of actual knowledge or such acceptably close proximity to other measured values as to remove much doubt. Significant figures, then, are those that provide usable information for purposes of quantitative work and that avoid implying exactitudes or near-exactitudes that do not exist or cannot be surmised. If an analytical balance capable of measurement to a sensitivity of one-tenth of a milligram (= 0.0001 gram) affords the weight of a certain object as 11.2584 grams, clearly the doubtful figure in the weight will be the very last, i.e., 4. Of all the others we are positive. But, even the 4 itself is informative, and therefore significant inasmuch as it represents a best estimate within a range of ± 0.0001 gram. Even if we cannot be certain that in absolute reality the last digit is exactly 4, nonetheless it is known to lie between a 3 (as may be modified by additional unknown decimals that follow it) and a 5 (as likewise modified by unknown decimals).

We observe in the accepted weight, 11.2584, *six* significant figures. A common error among the uninitiated is to "assume" that because a digit is not given that it may be accepted as a zero. Obviously, since the weighing instrument which we have selected is incapable of weighing to the *fifth* decimal place it would be absurd to assume that a zero necessarily follows the figure 4 and that the weight could accurately be cited as 11.25840. We have no knowledge whatsoever of the value of the integer in the fifth decimal place; this may be anything from zero to nine—a number incapable of determination by the instrument. However, if we had been able to measure to the fifth decimal place and this had come out to be 0, then the weight of the object would be expressed correctly by *seven* significant figures—the zero being significant here. Again, we stress that a zero does not signify "unknown." It offers information that is acceptable as a result of careful measurement, and like any other numeral in the weight it is therefore significant—although being the last number of the weight, it will therefore be the most doubtful. We must not now jump to the other extreme and assume that all zeros are necessarily significant. A zero used solely to locate the decimal point, whether it precedes or follows, is not significant; thus, in 0.0163 or in 0.0000163 none of the zeros is significant. Were we, however, to write

(a) 0.01630 or (b) 0.000016300

each of the zeros following the figure 3 in both terms is definitely significant, since our purpose in placing it in the respective expressions is to reveal that the actual value of term (a) is best estimated between 0.01629 and 0.01631 and that of (b) between 0.000016299 and 0.000016301. We thus observe four significant figures in (a) and five in (b). Zeros between any other significant numerals are, of course, always significant. Sometimes doubt arises as to whether a zero that is stated in a mathematical term is or is not significant. Let us take the value 100, illustratively. A valid question here is whether the zeros are intended solely to locate the decimal point in a roughly "rounded-off" approximation of about one hundred or to convey the certainty of exact numbers (as in counting one hundred discrete objects) or the near-certainty of some sensitivity-limited instrument measurement which puts the best value between 99 and 101. Informational perplexities such as these may conveniently be avoided by transposing all nonsignificant zeros to powers of 10, and retaining all significant zeros in the digital part of the term. Thus, if in the term 100 both zeros are merely locating the decimal point then appropriately and informatively it should be expressed as 1×10^2. If only the first zero is known to be significant, then 1.0×10^2 would be the correct designation of the term; if both zeros are significant, then 1.00×10^2 would be the proper representation. An exact value—that is, one completely immune from variabilities due to instrument "sensitivities," or one arbitrarily assumed or actually conforming to reality—of which there cannot be the slightest doubt must of course be considered to possess an *infinite* number of significant zeros following the last digit in the decimal part of the term. If the term possesses no fractional remainder, then an infinite number of zeros will follow the decimal point. Thus, six discrete and separately discernible objects will certainly conform to the expression 6.0000 . . . *ad infinitum* numbers of zeros in unbroken sequence.

Just as a chain cannot be any stronger than its weakest link, the result of a computational process cannot be any more reliable than the least reliable of the quantities from whence that result was derived. Therefore, lest the information which the result purports to convey be factually unwarranted or actually misleading, the final answer to any process of addition, subtraction, multiplication, or division—or any combination thereof—must be reduced to the level of sensitivity of the least sensitive of the computational factors involved, if not already at such a level. The following interpretations will then apply.

Significant Figures in Addition and Subtraction

Reduce the final result to the number of decimal places conforming to that of the quantity or term possessing the smallest number of decimal places. Thus, addition

$$\begin{array}{r} 3.172 \\ 4.06 \\ 5.9158 \\ \hline 13.1478 \end{array}$$

produces not 13.1478 as an answer, but 13.15 in conformity with the sensitivity restrictions imposed upon the final sum by the component term 4.06. Note the convention of increasing by one unit the last significant figure retained in the result when the following digit subject to discard is a 5 or larger. Parenthetically, practice varies somewhat arbitrarily here when the digit determining this "rounding off" of the last significant figure to be retained is, itself, actually 5. A rounded-off increase of one unit in the last significant figure to be retained may then be "directed" by digit 5 only if such significant figure is already an odd number. On the assumption that the laws of probability are better served, mathematically, thereby, no alteration is "directed" by a 5 when the last numeral to be affected is already even. These slight differences in conventional practice remain rather arbitrary and hardly of critical concern.

It is noted that rounding-off adjustments are occasionally made of each of the separate and individual terms prior to their addition or subtraction. This practice by no means leads to necessarily the same result. While here again the deviations are hardly critical inasmuch as an approximation is all that can be expected in any event, convention predominantly avoids such repetitive adjustments—despite the greater simplicity or convenience that may be invited when a truly long column of figures is being added. Compare the results 16.6 and 16.8 respectively in the following addition illustrating the rounding-off contrasts of these different approaches:

1.26	1.3
2.351	2.4
3.4602	3.5
4.573	4.6
5.0	5.0
16.6442	16.8

yields

16.6 (*Ans.*)

Significant Figures in Multiplication and Division

The final result is reduced to the *number of significant figures* present in the quantity possessing the *smallest* thereof. The multiplication of a term possessing five significant figures by a term possessing two significant figures yields a result that must be limited to two significant figures. Thus, the multiplication

$$6.7093 \times 1.2$$

produces not the value 8.05116 that is obtained without benefit of sensitivity refinements, but correctly 8.1, conforming to the limitations imposed upon the product by the two significant figures in the term 1.2. Again, the last significant figure to be retained in the final answer is increased by one unit when the following digit that is being discarded in the rounding-off process is a 5 or larger.

Identical considerations apply, of course, in the process of division.

Logarithms

The logarithm (or "log") of a number is the exponential power to which a given base must be raised in order to yield that number. *Common* logs utilize the base 10 (i.e., $\log_{10}$); *natural* logs utilize the parameter e as a base (symbolized either as $\log_e$ or ln). The parameter e is a constant having the value 2.71828 (derived as the cumulative sum of the sequence $1 + 1/1 + 1/(1 \times 2) + 1/(1 \times 2 \times 3) + 1/(1 \times 2 \times 3 \times 4) + 1/(1 \times 2 \times 3 \times 4 \times 5) + \cdots$, etc. Since the logarithm of the number 10 to the base e (i.e., $\log_e 10$) equals 2.303, interconversions of natural and common logs of the number N may always be accomplished conveniently via the formula

$$\log_e N = 2.303 \log_{10} N$$

Inasmuch as common logs are invariably used in this book, the four-place table of values provided (end pages, inside back cover) thus represents in each instance the exponential power to which the base 10 is being raised in order to produce the number marginally indicated. Conversely, if the log of a number is an exponent, then the antilog of that exponential power to which the base is being raised is the number itself. Illustratively, we validly express

$$\log_{10} N = 0.6990$$

and

$$N = 10^{0.6990} = \text{antilog } 0.6990 = 5.0$$

A logarithm is itself the sum of two component parts; a "characteristic" and a "mantissa." The characteristic of a number is determined solely by inspection of the number, and for a number larger than 1 the characteristic is always a positive value that is one less than the number of digits to the left of the decimal point. The characteristic of a number smaller than 1, that is, a decimal fraction, is always negative and is represented by a value that is one more than the number of zeros between the decimal point and the very first significant (nonzero) figure to the right. The characteristic may also be described by the number of places that the decimal point must be shifted in order to produce a numerical quantity between 1 and 10, algebraically qualified by a positive sign if the decimal point is being moved to the left, and by a negative sign if the decimal point is being moved to the right. Thus, the characteristic of the number 12000 is 4, since

$$12000 = 1.2 \times 10^4$$

and the characteristic of the number 0.00012 is −4, since

$$0.00012 = 1.2 \times 10^{-4}$$

The mantissa of any number is obtained by direct reference to the log table, and represents the decimal part of the logarithm of the number. The mantissa is thus *added* to the characteristic. It is vital to correct mathematics to bear always in mind that the mantissa represents a positive value, since antilogs of entirely negative numbers are frequently sought, as well. Correct conversion of an all-negative number (and hence of a negative mantissa) for the purpose of employing the always-positive mantissa of the log table is accomplished easily enough merely by a *concurrent* addition and compensating subtraction of an appropriate number. Thus, in the following illustration we may "add and subtract" the number 4 to obtain the positive decimal (mantissa) usable with the log table:

$$10^{-3.7082} = 10^{0.2918-4}$$

The use of the "proportional parts" of the table of logarithms may require some refreshing. For example, let us find the log of 8.215. The characteristic is, of course, zero, in conformity with the rules already expounded. We determine the mantissa (without regard for the decimal point) by locating in the side-marginal column the first two digits (82) of the given number—as a first step. We then locate the third digit (1) by carrying our reference over on this same line to the vertical column denoted by the upper-marginal heading 1. The value of the log indicated to this point is 0.9143. However, we seek the log not of 8.21