JAMES N. BUTLER
HARVARD UNIVERSITY

Carbon Dioxide Equilibria and Their Applications

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ADDISON-WESLEY PUBLISHING COMPANY
Reading, Massachusetts   Menlo Park, California
London   Amsterdam   Don Mills, Ontario
Sydney

Library of Congress Cataloging in Publication Data

Butler, James N.
Carbon dioxide equilibria and their applications.

Bibliography: p. 2
Includes index
1. Carbon dioxide. 2. Carbonates. 3. Chemical equilibrium. I. Title.
QD181.C1B87 546′.6812 81-3494
ISBN 0-201-10100-9 AACR2

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ISBN 0-201-10100-9
ABCDEFGHIJ-AL-898765432

Preface

When I wrote *Solubility and pH Calculations* nearly 20 years ago, I had in mind an audience of analytical chemistry students. Long after I finished that book, I discovered that some of my chief fans were geochemists and environmental engineers. From their point of view, the most important acid–base and solubility problems were missing from *Solubility and pH*. These were the equilibria of carbon dioxide and the solubility of carbonates, which in 1963 I considered too complicated for an elementary course. This book is an attempt to remedy that omission and to provide enough detail from this important cluster of equilibrium problems so that a diligent student can master its complexities.

Carbon dioxide occupies a central place in the biosphere and in many of the geological processes that create and erode rocks. Plants, from trees to phytoplankton, absorb CO_2 from the atmosphere and convert it into biomass; respiration by terrestrial and aquatic plants and animals returns carbon dioxide to the atmosphere. Many marine plants and animals convert CO_2 into calcium carbonate, and when they die the mineral portions of their bodies become reefs, sediment, and limestone. Thus a full understanding of the natural environment involves a quantitative understanding of the transformations of carbon dioxide and carbonate minerals. Recent concern has centered on how rapidly the the excess CO_2 produced by humans burning coal and other fossil fuels can be assimilated by biological and geochemical processes.

Almost all natural waters contain carbonate and carbon dioxide. Water conditioning and wastewater treatment must therefore include processes involving acid–base equilibria of CO_2 and precipitation or dissolution of $CaCO_3$. These topics are considered an essential part of the environmental engineering curriculum, but often are not given a very detailed treatment in engineering textbooks.

This book is about the details of carbonate equilibrium calculations and how they are applied to oceanography, geochemistry, and environmental engineering. It begins at a level accessible to most students with a sound quantitative course in general chemistry and a reasonable mastery of algebra at the high-school level. As the book proceeds, more and more complicated examples are considered, but I have tried to give correspondingly more detailed discussion.

My intent was to provide a textbook monograph that would be useful in a variety of courses. These would certainly include the aquatic chemistry courses of the environmental engineering curriculum, courses in geochemistry and chemical oceanography, and quite possibly other courses I have not yet imagined. It is not meant to substitute for a textbook in any of these subjects, but ought to provide enough supplementary material to satisfy the curiosity (and perhaps alleviate the confusion) of all but the most advanced students. Indeed, I hope this book will be useful to students who would find the introductory chapters far too elementary, but who need to understand the details of ionic strength corrections or the quantitative theory behind the lime–soda water softening process.

I have taught much of this material since 1970 in advanced undergraduate and graduate courses at Harvard. Every year, my lectures metamorphosed as I learned new perspectives on what seemed at first to be a straightforward topic. I hope some of that sense of adventure remains in this book.

I would probably not have considered writing this book if it had not been for the encouragement of Tom Robbins at Addison-Wesley, and would not have completed it except for the inspiration given by my colleagues Robert Garrels, H. D. Holland, Fred Mackenzie, James J. Morgan, Raymond Siever, the late Lars Gunnar Sillen, Werner Stumm, and Roland Wollast. Christine Lawton and Cora Bennett typed the manuscript with unusual skill and patience. A lot of my thinking and writing was done at the Bermuda Biological Station, where carbonate geochemistry has a long tradition. My wife Rosamond has given me moral support when no one else could.

Finally, I want to dedicate this book to my friend Conrad D. Gebelein (1944–1978), who taught me much of what I know about the real world of carbonate geochemistry. His untimely death was a great loss to his friend and to science.

J. N. B.

Cambridge, Mass.
December, 1981

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CHAPTER ONE

Review of Solubility and pH Calculations

This book is intended to be self-contained, but of course it depends on knowledge of some chemistry and mathematics. The topics reviewed in this chapter are presented in more detail, with more examples, in my other books.* My intent here is only to give a catalog of what you ought to be familiar with for the rest of this book.

CONVERTING CHEMICAL MODELS TO MATHEMATICAL PROBLEMS

If you are going to calculate the equilibrium composition of an aqueous solution, you must have in mind a "chemical model" of the system. A chemical model consists of a set of chemical species and the equilibria relating them. This information may not be explicitly stated in a problem, and a successful attack on the problem may require some prior chemical knowledge on your part. Part of the model, of course, is the set of numerical values for the appropriate equilibrium constants. In this book, I have tried to make my chemical models explicit.

Equilibrium constant expressions alone are not enough to provide an answer to most problems, and additional relations between the concentrations of species are needed. I feel that the method of mass and charge balances is easiest to understand and to generalize, even though it may lead to a little more algebra than other methods† in some of the simplest examples. The combination of equilibria with mass and charge balances will give you as many independent equations as you have unknown species, and you can then solve this set of simultaneous mathematical equations.

---

* See Butler, J. N. 1964. *Solubility and pH Calculations* or *Ionic Equilibrium.* Reading, Mass: Addison-Wesley. I refer to these books throughout; for brevity, they will be cited by their titles only.

† You may have learned a method normally limited to those relations that can be derived from one balanced chemical reaction. There is also a method that involves minimization of total free energy, which is the basis of some computer programs but is not feasible for hand calculation.

LOGARITHMIC AND EXPONENTIAL FUNCTIONS

Because the numerical values of concentrations in aqueous solutions range from 10 M down to less than 10^{-15} M, logarithmic functions of the variables are common and graphical representations are usually made on a logarithmic scale. The function you are probably most familiar with is

$$\mathrm{pH} = -\log_{10}[\mathrm{H}^+]\gamma_+,$$

where $[\mathrm{H}^+]$ is the concentration of hydrogen ion in moles per liter and γ_+ is its activity coefficient, a correction for non-ideality which is usually between 0.7 and 1.2 but depends on the concentrations of other ions in the solution.*

For some examples in this book, the activity coefficient is approximated by $\gamma_+ = 1.0$ for simplicity, and

$$\mathrm{pH} = -\log_{10}[\mathrm{H}^+].$$

For other examples, I will show you how to make numerical estimates of the activity coefficients.

A NOTE ON CALCULATORS

In the numerical work presented in my examples, concentrations are sometimes written as $z = 5.28 \cdot 10^{-4}$, and sometimes as $10^{\log z}$ or $z = 10^{-3.28}$. (These are numerically equal, as you can verify.) You should have a calculator that has both "$\log_{10}x$" and "10^x" function keys for the most efficient use of these notations. Practice by doing numerical examples like this:

$$z = 10^{-3.28} + 10^{-3.55} - 10^{-4.20} = 10^{-3.13}.$$

Regardless of your calculator's logical system, you should be able to evaluate such expressions without writing down any intermediate answers.

Note that, if only two decimal places are retained in the logarithms, any terms at least two orders of magnitude less than the largest can be neglected without calculation. For example:

$$10^{-3.28} + 10^{-5.28} = 10^{-3.276} \cong 10^{-3.28}.$$

You can see that addition of the second term affected the answer only in the third decimal place of the logarithm.

---

* See Chapter 2; see also *Ionic Equilibrium*, Chapter 12, or Bates, R. G. *Determination of pH: Theory and Practice*, ed. 2. 1973. New York: John Wiley Interscience.

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STRONG ACIDS AND BASES

When water ionizes, a proton (hydrogen ion) is transferred from one water molecule to another, resulting in a hydrated hydrogen ion and a hydroxyl ion:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-.$$

Actually, H_3O^+ is further hydrated by at least three additional water molecules, and the complexity of the structure increases at lower temperatures. Because this hydration structure is not normally part of the chemical models discussed in this book, I write the hydrated proton as H^+ (a common simplification); but you should keep the complexities in the back of your mind.

The equilibrium constant expression for the ionization of water in its most general form would be written

$$[H^+][OH^-]\gamma_+\gamma_- = K^0[H_2O]\gamma_0,$$

but in dilute solutions the activity coefficients are close to 1.0 (see Chapter 2) and the concentration of water is nearly constant at $[H_2O] = 55.5$ mole/L. Therefore, the concentration ion product

$$[H^+][OH^-] = K_w = \frac{K^0[H_2O]\gamma_0}{\gamma_+\gamma_-} \qquad \textbf{(1.1)}$$

is commonly used.* Both the activity of undissociated water and the activity coefficients of the ions can be included in the equilibrium constant K_w. In dilute aqueous solutions at 25°C, $K_w = 10^{-14.0}$. In more concentrated solutions, K_w depends on the concentrations of other ions (see Fig. 2.8 for more details).

The second equation required to solve for pH is a *charge balance* between H^+ and OH^-, which states that all positive ions formed must be balanced by an equal number of negative charges. In pure water,

$$[H^+] = [OH^-]. \qquad \textbf{(1.2)}$$

Substitute the ion product of water (1.1) and you get

$$[H^+]^2 = K_w.$$

Taking the negative logarithm of both sides and setting $K_w = 10^{-14.0}$ and $\gamma_+ = 1.0$, you get:†

$$\mathrm{pH} = -\log[H^+] = -\frac{1}{2}\log K_w = 7.0.$$

---

* In some books K_w is used for the activity product $a_H a_{OH} = [H^+][OH^-]\gamma_+\gamma_-$. I use K_w for the concentration product at finite ionic strength and K_w^0 for the activity product, since K_w^0 is equal to the concentration product K_w extrapolated to zero ionic strength. At 25°C, $K_w^0 = 10^{-13.999}$.

† Note that if you set $\mathrm{pH} = -\log([H^+]\gamma_+)$ and $\gamma_+ = \gamma_-$, you will find $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_w^0$ even if γ_+ or γ_- is not 1.0.

Addition of acid to pure water will increase $[H^+]$; addition of base will decrease $[H^+]$ and increase $[OH^-]$. If an acid is fully dissociated into ions it is called *strong*; an example is HCl, which yields only H^+ and Cl^- in aqueous solution.

For a solution containing some constant C molar HCl, two equations are required besides the ion product of water—a *mass balance* on chloride (all the chloride in solution comes from HCl):

$$[Cl^-] = C; \tag{1.3}$$

and a *charge balance*, including chloride as well as hydroxyl ion:

$$[H^+] = [OH^-] + [Cl^-]. \tag{1.4}$$

Equations (1.1), (1.3), and (1.4) can be solved without approximation. Substitute from the mass balance (1.3) into the charge balance (1.4) to eliminate $[Cl^-]$, then solve the resulting equation for $[OH^-]$:

$$[OH^-] = [H^+] - C. \tag{1.5}$$

Substitute Eq. (1.5) in the ion product (1.1) to obtain a quadratic equation:

$$[H^+]([H^+] - C) = K_w = 10^{-14.0}. \tag{1.6}$$

Normally, C is large compared to 10^{-7}, and this should encourage you to neglect $[OH^-]$ compared to $[Cl^-]$ in the charge balance (1.4) and to try the approximation*

$$[H^+] = [Cl^-] + \cdots = C + \cdots. \tag{1.7}$$

EXAMPLE Find pH for 10^{-4} M HCl. With $C = 10^{-4}$, approximation (1.7) gives pH = 4.0. Substitution in the full quadratic (1.6) gives

$$[H^+]([H^+] - 10^{-4.0}) = 10^{-14.0}$$

$$[H^+] = 10^{-4.0} + \frac{10^{-14.0}}{[H^+]} = 10^{-4.0} - 10^{-10} = 10^{-4.0}.$$

Here I have substituted the approximate value in the second term on the right, to show that it was negligible. ■

You will notice, of course, that when C is small compared to 10^{-7}, the result is pH = 7.0, the same as in pure water.

---

* The missing term $[OH^-]$ is represented by three dots to remind you that this result is an approximation. In other examples or approximate equations the quantity represented by "$+\cdots$" may be much more complicated, and may be either positive or negative. In the example, you see that "$+\cdots$" is -10^{-10}, which is negligible compared to $10^{-4.0}$.

A strong base (such as NaOH) is completely ionized in solution, and the charge balance for a solution containing both strong base and strong acid is

$$[\mathrm{H^+}] + [\mathrm{Na^+}] = [\mathrm{OH^-}] + [\mathrm{Cl^-}], \tag{1.8}$$

and the mass balances are

$$C_a = [\mathrm{Cl^-}] \tag{1.9}$$

$$C_b = [\mathrm{Na^+}], \tag{1.10}$$

where C_a and C_b are the molar concentrations of acid and base respectively. Proceeding as above, you can combine Eqs. (1.8), (1.9), and (1.10) with the ion product (1.1) to give the quadratic

$$[\mathrm{H^+}]([\mathrm{H^+}] + C_b - C_a) = K_w. \tag{1.11}$$

The same sort of approximations apply. When there is excess strong acid,

$$[\mathrm{H^+}] = C_a - C_b + \cdots. \tag{1.12}$$

When there is excess strong base ($C_b > C_a \gg [\mathrm{H^+}]$), Eq. (1.11) reduces to

$$[\mathrm{H^+}] = \frac{K_w}{C_b - C_a} + \cdots, \tag{1.13}$$

which is what you would derive by setting the hydroxyl ion concentration equal to the excess of strong base:

$$[\mathrm{OH^-}] = C_b - C_a + \cdots \tag{1.14}$$

and substituting in the ion product (1.1).*

WEAK ACIDS

When an acid does not fully dissociate in solution, it is called "weak," and description of such solutions requires the use of the familiar equilibrium between the undissociated (HA) and dissociated forms:

$$\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-},$$

which gives the following equilibrium expression:

$$[\mathrm{H^+}][\mathrm{A^-}] = K_a[\mathrm{HA}]$$

or

$$10^{-\mathrm{pH}}[\mathrm{A^-}] = K_a'[\mathrm{HA}], \tag{1.15}$$

---

* The titration of a strong acid with a strong base, or vice versa, is discussed briefly in Chapter 3 of this book, and in *Ionic Equilibrium*, Chapter 4.

where again the activity coefficients have been included in the equilibrium constant.* The mass balance for total weak-acid concentration C is

$$C = [\mathrm{HA}] + [\mathrm{A}^-] \tag{1.16}$$

and the charge balance for pure water containing only the weak acid is

$$[\mathrm{H}^+] = [\mathrm{A}^-] + [\mathrm{OH}^-]. \tag{1.17}$$

Equations (1.15), (1.16), and (1.17), together with the ion product of water (1.1), comprise four equations in four unknowns, and their general solution is straightforward (see *Solubility and pH Calculations*, pp. 46–47 or *Ionic Equilibrium*, pp. 116–120).

These equations are easily represented by a logarithmic concentration diagram, such as shown in Fig. 1.1. This is a plot of the various concentrations as a function of pH (in the figure, I have set $\gamma_+ = \gamma_- = 1.0$):

$$[\mathrm{H}^+] = \frac{10^{-\mathrm{pH}}}{\gamma_+} = 10^{-\mathrm{pH}} + \cdots, \tag{1.18}$$

$$[\mathrm{OH}^-] = \frac{K_w 10^{+\mathrm{pH}}}{\gamma_-} = K_w 10^{+\mathrm{pH}} + \cdots, \tag{1.19}$$

$$[\mathrm{A}^-] = \frac{CK'_a}{10^{-\mathrm{pH}} + K'_a}, \tag{1.20}$$

$$[\mathrm{HA}] = \frac{C(10^{-\mathrm{pH}})}{10^{-\mathrm{pH}} + K'_a}. \tag{1.21}$$

(Construction of the diagram without numerical work is described in *Solubility and pH Calculations*, pp. 48–53 or *Ionic Equilibrium*, pp. 122–127.) The pH of the pure weak acid is the pH where the charge balance (1.17) is satisfied, or approximately

$$[\mathrm{H}^+] = [\mathrm{A}^-] + \cdots. \tag{1.22}$$

On the diagram, this point is given by the intersection of the $[\mathrm{H}^+]$ and $[\mathrm{A}^-]$ lines at pH = 3.0. (You can see from the diagram that at pH = 3.0 you get $[\mathrm{OH}^-] = 10^{-11}$, which is indeed small compared to $[\mathrm{A}^-] = 10^{-3}$.)

To obtain pH algebraically, substitute (1.18) and (1.20) in (1.22) and note that since pH is a full unit smaller than pK_a, $10^{-\mathrm{pH}}$ is large compared to K'_a in the denominator of (1.20). This gives

$$\mathrm{pH} = \frac{1}{2}(\mathrm{p}K'_a - \log C\gamma_+) + \cdots = \frac{1}{2}(\mathrm{p}K^0_a - \log C) + \cdots, \tag{1.23}$$

---

* Some books use K_a for the activity combination $[\mathrm{H}^+][\mathrm{A}^-]\gamma_+\gamma_-/[\mathrm{HA}]\gamma_0$, but I use K_a for the concentration combination at finite ionic strength and K^0_a for the activity combination, which is numerically equal to K_a extrapolated to zero ionic strength. A third notation is the "hybrid" constant $K'_a = K_a\gamma_+ = K^0_a\gamma_0/\gamma_-$, so that $K'_a = 10^{-\mathrm{pH}}[\mathrm{A}^-]/[\mathrm{HA}]$, where $10^{-\mathrm{pH}} = [\mathrm{H}^+]\gamma_+$ (see pp. 34–38).

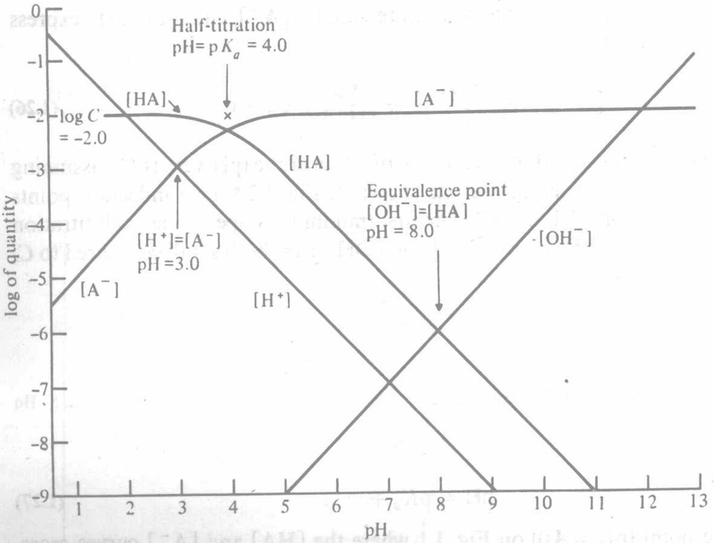

Fig. 1.1. Logarithmic concentration diagram for a weak acid with $K_a = 10^{-4}$ and total concentration $C = 10^{-2}$.

where the approximations $\gamma_0 = 1.0$ and $\gamma_+ = \gamma_-$ were made to simplify the result. Note, however, that (1.23) applies even if γ_+ and γ_- are significantly different from 1.0, so long as they are equal.

If strong acid (with concentration C_a) is added, pH decreases, and a term in $[Cl^-]$ is added to the charge balance:

$$[H^+] = [A^-] + [OH^-] + [Cl^-]$$

or

$$[H^+] = [A^-] + [OH^-] + C_a. \tag{1.24}$$

As soon as C_a is large compared with $[A^-]$, it dominates the right-hand side of Eq. (1.24), which becomes simply $[H^+] = C_a$. ($[OH^-]$ is negligible unless C_a and $[A^-]$ are both less than 10^{-7}.) Looking at the diagram, you can see that, because $[A^-]$ decreases as $[H^+]$ increases, this approximation is good to 1% when pH has decreased by only one unit, from pH = 3.0 to pH = 2.0.

TITRATION WITH STRONG BASE

If strong base is added to a weak acid, pH increases, and a term $[Na^+] = C_b$ is added to the charge balance:

$$[H^+] + [Na^+] = [A^-] + [OH^-] + [Cl^-]. \tag{1.25}$$

Combine (1.15) and (1.16) to obtain an expression for $[\mathrm{A}^-]$, and use (1.1) to express $[\mathrm{OH}^-]$ as a function of $[\mathrm{H}^+]$:

$$[\mathrm{H}^+] = \frac{CK_a}{[\mathrm{H}^+] + K_a} + \frac{K_w}{[\mathrm{H}^+]} + C_a - C_b. \qquad \textbf{(1.26)}$$

Equation (1.26) can be used to calculate a titration curve (pH versus C_b, assuming $\gamma_+ = 1.0$ and $C_a = 0$), such as the one shown in Fig. 1.2.* Two inflection points may be noted on Figs. 1.1 and 1.2. The first (minimum slope) is the "half titration point," when $C_b = \frac{1}{2}C$. Provided $[\mathrm{H}^+]$ and $[\mathrm{OH}^-]$ are both small compared to C, Eq. (1.26) simplifies to

$$\frac{CK_a}{[\mathrm{H}^+] + K_a} = \frac{1}{2}C + \cdots,$$

which can be further simplified to give

$$[\mathrm{H}^+] = K_a + \cdots$$

or

$$\mathrm{pH} = \mathrm{p}K_a' + \cdots. \qquad \textbf{(1.27)}$$

This is the point (pH = 4.0) on Fig. 1.1 where the [HA] and $[\mathrm{A}^-]$ curves cross, at a point equal to $\frac{1}{2}C$ (-2.3 log units if $C = 10^{-2}$), or 0.3 logarithmic units below the horizontal lines at log C.

The second inflection point (maximum slope on Fig. 1.2) is the *equivalence point*, where $C_b = C$. Here $[\mathrm{OH}^-]$ can no longer be neglected, but $[\mathrm{H}^+]$ is normally small compared with both K_a and $[\mathrm{OH}^-]$. This assumption, applied to (1.26), yields

$$[\mathrm{H}^+] = 0 = \frac{K_w}{[\mathrm{H}^+]} + \frac{CK_a}{[\mathrm{H}^+] + K_a} - C + \cdots$$

or

$$\frac{K_w}{[\mathrm{H}^+]} = \frac{C[\mathrm{H}^+]}{[\mathrm{H}^+] + K_a} + \cdots. \qquad \textbf{(1.28)}$$

Equation (1.28) is equivalent to $[\mathrm{OH}^-] = [\mathrm{HA}]$. If $[\mathrm{H}^+] \ll K_a$, it reduces to

$$[\mathrm{H}^+]^2 = \frac{K_w K_a}{C} + \cdots \qquad \textbf{(1.29)}$$

---

* Given $C_a = 0$ and constant values of $C = 10^{-2}$ and $K_a = 10^{-4}$, choose a series of values for pH, calculate $[\mathrm{H}^+] = 10^{-\mathrm{pH}}$ and from Eq. (1.26) obtain

$$C_b = \frac{CK_a}{[\mathrm{H}^+] + K_a} + \frac{K_w}{[\mathrm{H}^+]} - [\mathrm{H}^+].$$

If C_a is not zero, replace C_b by $C_b - C_a$. The slightly more complicated version in terms of titrant volumes is presented in *Ionic Equilibrium*, pp. 154–157 (see also Chapter 3).

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