The Geochemistry of Natural Waters

SECOND EDITION

James I. Drever
University of Wyoming

Prentice Hall
Englewood Cliffs, New Jersey 07632
Library of Congress Cataloging-in-Publication Data
Drever, James I.
The geochemistry of natural waters.
Bibliography:
Includes index.
I. Water chemistry. 2. Hydrogeology. I. Title.
GB855.D73 1988 551.48 87-17579

Editorial/production supervision and
interior design: Ann L. Mohan
Cover design: Ben Santora
Manufacturing buyer: Paula Benevento Massenaro

©1988, 1982 by Prentice Hall, Inc.
A Division of Simon & Schuster
Englewood Cliffs, New Jersey 07632

All rights reserved. No part of this book may be
reproduced, in any form or by any means,
without permission in writing from the publisher.

Printed in the United States of America
10 9 8 7 6 5

Prentice-Hall of Australia Pty. Limited, Sydney
Prentice-Hall Canada, Inc., Toronto
Prentice-Hall Hispanoamericana, S.A., Mexico
Prentice-Hall of India Private Limited, New Delhi
Prentice-Hall of Japan, Inc., Tokyo
Simon & Schuster Asia Pte. Ltd., Singapore
or, from (4-19),

\[
\frac{acal \cdot aHCO_3}{PCO_2} = \frac{Ka \cdot K_1 \cdot K_{CO_2}}{K_2}
\]  

(4-25)

Equation (4-25) is useful in understanding natural waters, since the controlling variables in many natural systems are CO_2 and HCO_3^-. Carbonate concentration and pH can often be thought of as consequences of P_{CO_2} and m_{HCO_3}. For example, photosynthesis decreases dissolved CO_2, which will increase the state of saturation. Respiration and aerobic decay, on the other hand, increase dissolved CO_2 and decrease saturation. Anaerobic decay with sulfate reduction (see Chapter 14) may be represented in a simplified way by the equation

\[
SO_4^{2-} + 2C_{org} + 2H_2O = H_2S + 2HCO_3^-
\]

Where C_{org} represents carbon in organic matter. Thus anaerobic decay will increase saturation with respect to carbonate minerals, the opposite of aerobic decay.

Example 2

How do the pH and calcium concentration of pure water in equilibrium with calcite vary as a function of P_{CO_2}?

\[
aHCO_3 = K_{CO_2} P_{CO_2}
\]  

(4-26)

\[
K_1 = \frac{aH^+ \cdot aHCO_3}{aHCO_3}
\]  

(4-27)

Rearranging Eq. (4-27) and substituting (4-26) gives

\[
aHCO_3 = \frac{K_1 \cdot K_{CO_2} \cdot P_{CO_2}}{aH^+}
\]  

(4-28)

\[
K_2 = \frac{aH^+ \cdot aCO_3^-}{aHCO_3}
\]  

(4-29)

Rearranging (4-29) and substituting (4-28) gives

\[
aCO_3^- = \frac{K_1 \cdot K_2 \cdot K_{CO_2} \cdot P_{CO_2}}{aH^+}
\]  

(4-30)

\[
K_{cal} = \frac{acal \cdot aCO_3^-}{aH^+}
\]  

(4-31)

Substituting (4-30) in (4-31) gives

\[
K_{cal} = \frac{acal \cdot K_1 \cdot K_{CO_2} \cdot P_{CO_2}}{aH^+}
\]  

(4-32)

The charge balance equation is

\[
m_{H^+} + 2m_{Ca^{2+}} = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-}
\]  

(4-33)

If we restrict our attention to the pH region below 9, m_{H^+}, m_{OH^-}, and 2m_{CO_3^{2-}} will be small compared to 2m_{Ca^{2+}} and m_{HCO_3^-} in the charge balance equation (small quantities can be neglected when they are added to or subtracted from large quantities; they may not be neglected when they multiply large quantities). Equation (4-33) then simplifies to
Calcium Carbonate Solubility

\[ 2m_{\text{CO}_2} = m_{\text{HCO}_3} \]  \hspace{1cm} \text{(4-34)}

or

\[ \frac{2a_{\text{CO}_2}}{\gamma_{\text{Ca}^{2+}}} = \frac{a_{\text{HCO}_3}}{\gamma_{\text{HCO}_3}} \]

or

\[ a_{\text{Ca}^{2+}} = \frac{1}{2} a_{\text{HCO}_3} \frac{\gamma_{\text{Ca}^{2+}}}{\gamma_{\text{HCO}_3}} \]  \hspace{1cm} \text{(4-35)}

Substituting (4-28) in (4-35) and then substituting the result in (4-32) gives

\[ K_{\text{cal}} = \frac{1}{2} K_1 K_{\text{CO}_2} P_{\text{CO}_2} K_1 K_2 K_{\text{CO}_2} P_{\text{CO}_2} \frac{\gamma_{\text{Ca}^{2+}}}{\gamma_{\text{HCO}_3}} \]

which rearranges to

\[ a_{\text{H}^+} = \frac{P_{\text{CO}_2} K_1 K_2 K_{\text{CO}_2} \gamma_{\text{Ca}^{2+}}}{2 K_{\text{cal}} \gamma_{\text{HCO}_3}} \]  \hspace{1cm} \text{(4-36)}

which is the desired relationship.

The relationship is shown graphically in Fig. 4-4, assuming 25°C and a total pressure of 1 atm. The calculation of the activity coefficients can be done by an iteration procedure similar to that used in Example 5 of Chapter 2. For each value of \( P_{\text{CO}_2} \), a preliminary calculation is made assuming that \( \gamma_{\text{Ca}^{2+}} = \gamma_{\text{HCO}_3} \); the concentrations of all species are calculated on this assumption, and these concentrations are used to calculate \( \gamma_{\text{Ca}^{2+}} \) and \( \gamma_{\text{HCO}_3} \) by the Debye-Hückel equation. These \( \gamma \) values are then used in Eq. (4-36) to give better values for pH and hence the concentrations of other dissolved species, and the cycle is repeated until consistent results are achieved.

In most surface waters, the \( P_{\text{CO}_2} \) lies between \( 10^{-2} \) atm and the atmospheric value of \( 10^{-3.5} \) atm. Waters with \( P_{\text{CO}_2} \) values in this range in equilibrium with calcite would have pH values between 7.3 and 8.4. The majority of surface waters do have

\[ \text{pH} = \text{7.7 to 7.9} \]

and \( 2m_{\text{CO}_2} \) will be

\[ \text{small quantities} \]

(small quantities; they may

\[ \text{then simplifies} \]

\[ \text{as} \]
Figure 15-8 Simplified $p$-$pH$ diagram for the system U-O-H$_2$O-CO$_2$ at 25°C and $P_{CO_2} = 10^{-2}$ atm, showing the stability fields of ideal solid uraninite and dissolved species. Solubility boundaries are drawn at $10^{-4}$ m dissolved uranium species (modified from Langmuir, 1978).

Figure 15-9 Simplified $p$-$pH$ diagram for the system U-O-H$_2$O-CO$_2$ at 25°C and $P_{CO_2} = 10^{-2}$ atm, $K^+ = 10^{-3}$ m, $V = 10^{-4}$. Solubility boundaries are drawn at $10^{-4}$ m dissolved uranium species (modified from Langmuir, 1978).