

59073

The Geochemistry of Natural Waters

SECOND EDITION

James I. Drever

University of Wyoming



Prentice Hall
Englewood Cliffs, New Jersey 07632



7181

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

ISBN 0-13-351396-3

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 International (UK) Limited, *London*
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*
Editora Prentice-Hall do Brasil, Ltda., *Rio de Janeiro*

1

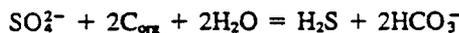
2

3

or, from (4-19),

$$\frac{a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-}}{P_{\text{CO}_2}} = \frac{K_{\text{cal}} K_1 K_{\text{CO}_2}}{K_2} \quad (4-25)$$

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 $m_{\text{HCO}_3^-}$. 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



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} ?

$$a_{\text{H}_2\text{CO}_3} = K_{\text{CO}_2} P_{\text{CO}_2} \quad (4-26)$$

$$K_1 = \frac{a_{\text{H}^+} a_{\text{HCO}_3^-}}{a_{\text{H}_2\text{CO}_3}} \quad (4-27)$$

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

$$a_{\text{HCO}_3^-} = \frac{K_1 K_{\text{CO}_2} P_{\text{CO}_2}}{a_{\text{H}^+}} \quad (4-28)$$

$$K_2 = \frac{a_{\text{H}^+} a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} \quad (4-29)$$

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

$$a_{\text{CO}_3^{2-}} = \frac{K_1 K_2 K_{\text{CO}_2} P_{\text{CO}_2}}{a_{\text{H}^+}} \quad (4-30)$$

$$K_{\text{cal}} = a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} \quad (4-31)$$

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

$$K_{\text{cal}} = \frac{a_{\text{Ca}^{2+}} K_1 K_2 K_{\text{CO}_2} P_{\text{CO}_2}}{a_{\text{H}^+}} \quad (4-32)$$

The charge balance equation is

$$m_{\text{H}^+} + 2m_{\text{Ca}^{2+}} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-} \quad (4-33)$$

If we restrict our attention to the pH region below 9, m_{H^+} , m_{OH^-} , and $2m_{\text{CO}_3^{2-}}$ will be small compared to $2m_{\text{Ca}^{2+}}$ and $m_{\text{HCO}_3^-}$ 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

(4-25)

the controlling vari-
centration and pH
mple, photosynthe-
on. Respiration and
decrease saturation.
represented in a sim-

y will increase sat-
decay.

equilibrium with calcite

(4-26)

(4-27)

(4-28)

(4-29)

(4-30)

(4-31)

(4-32)

(4-33)

and $2m_{\text{CO}_3^{2-}}$ will be
on (small quantities
quantities; they may
33) then simplifies

$$2m_{\text{Ca}^{2+}} = m_{\text{HCO}_3^-} \quad (4-34)$$

or

$$\frac{2a_{\text{Ca}^{2+}}}{\gamma_{\text{Ca}^{2+}}} = \frac{a_{\text{HCO}_3^-}}{\gamma_{\text{HCO}_3^-}}$$

or

$$a_{\text{Ca}^{2+}} = \frac{1}{2} a_{\text{HCO}_3^-} \frac{\gamma_{\text{Ca}^{2+}}}{\gamma_{\text{HCO}_3^-}} \quad (4-35)$$

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

$$K_{\text{cal}} = \frac{\frac{1}{2} K_1 K_{\text{CO}_2} P_{\text{CO}_2}}{a_{\text{H}^+}} \frac{K_1 K_2 K_{\text{CO}_2} P_{\text{CO}_2}}{a_{\text{H}^+}^2} \frac{\gamma_{\text{Ca}^{2+}}}{\gamma_{\text{HCO}_3^-}}$$

which rearranges to

$$a_{\text{H}^+}^3 = P_{\text{CO}_2}^2 \frac{K_1^2 K_2 K_{\text{CO}_2}^2 \gamma_{\text{Ca}^{2+}}}{2K_{\text{cal}} \gamma_{\text{HCO}_3^-}} \quad (4-36)$$

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_{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 γ 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_{CO_2} lies between 10^{-2} atm and the atmospheric value of $10^{-3.5}$ atm. Waters with P_{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

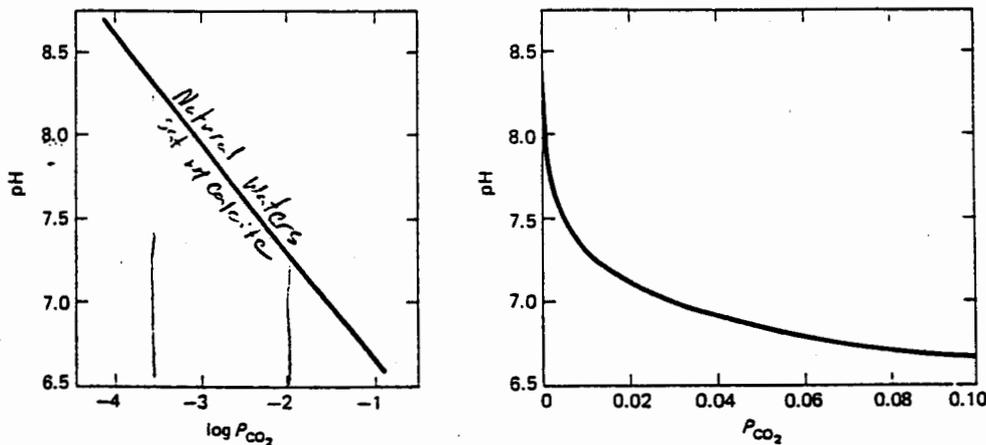


Figure 4-4 Relationship between pH and P_{CO_2} for pure water in equilibrium with calcite at 25°C and 1 atm total pressure. Note the difference of form when P_{CO_2} is plotted as a logarithm.

ADSORPTIC

The
would
ply to
tratio

surface
specie
precip
traces
dium
hand.
will b
In na
ble to
and s

minu:
The g
at hig
ent fo
is a tr
15-10

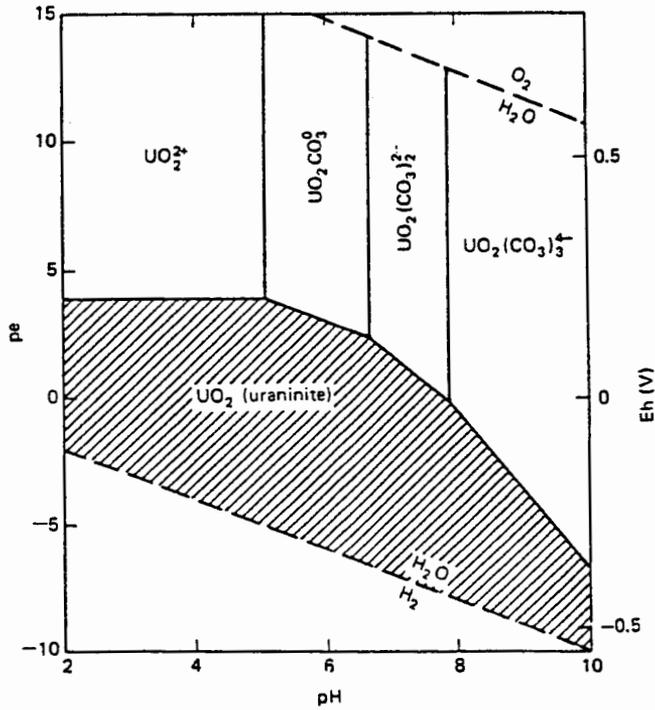


Figure 15-8 Simplified pe-pH diagram for the system U-O-H₂O-CO₂ at 25°C and P_{CO₂} = 10⁻² atm, showing the stability fields of ideal solid uraninite and dissolved species. Solubility boundaries are drawn at 10⁻⁶ m dissolved uranium species (modified from Langmuir, 1978).

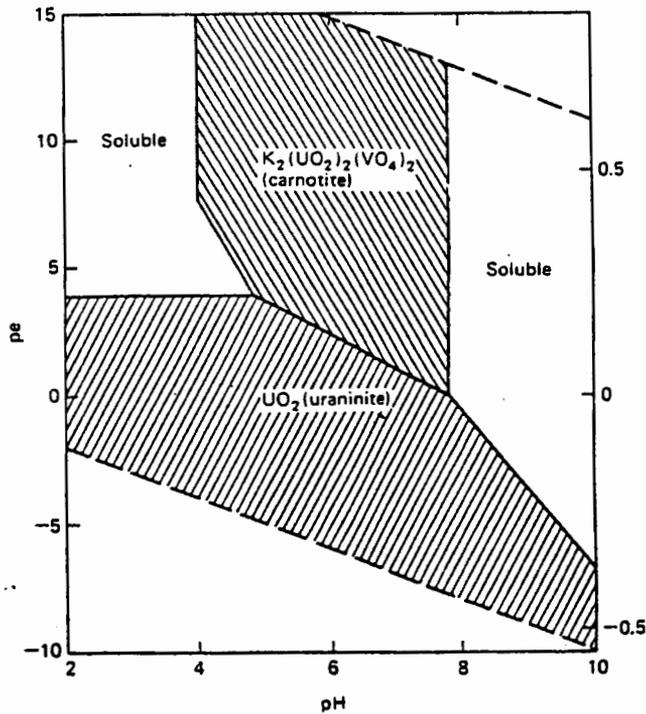


Figure 15-9 Simplified pe-pH diagram for the system U-O-H₂O-CO₂-V-K at 25°C and P_{CO₂} = 10⁻² atm, K⁺ = 10⁻³ m, V = 10⁻⁶. Solubility boundaries are drawn at 10⁻⁶ m dissolved uranium species (modified from Langmuir, 1978).