NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY

A PRELIMINARY INVESTIGATION
OF THE DISSOLUTION KINETICS
OF STRONTIANITE AND WITHERITE

by

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ABSTRACT

A preliminary investigation of the dissolution kinetics of strontianite and witherite in aqueous solutions indicates that dissolution rates are controlled by reactions at mineral surface. Dissolution rates were not effected by changes in stirring rates; activation energies calculated for strontianite and witherite are 8.4 and 10.0 kilocalories, respectively.

At pH values of less than 4.0, the dissolution rate for strontianite is a linear function of pH; the dissolution reaction is interpreted to be first order with respect to $a_{H^+}$ and to consist of the protonation of the $CO_3^{2-}$ lattice anion and desorption as $HCO_3^-$. Experiments with different partial pressures of $CO_2$ indicate that $H_2CO_3$ has a catalytic effectiveness approximately 1% of that of the hydrogen ion. The effect of $P_{CO_2}$ is interpreted to be dependent upon surface adsorption and is expressed using the Langmuir adsorption isotherm.

Forward reaction rates determined far from equilibrium are used to calculate back reaction rates. These data are consistent with a controlling mechanism which is first order with respect to $Sr^{2+}$ or $HCO_3^-$. The rate limiting step is interpreted to be the adsorption or deprotonation of $HCO_3^-$. 
LIST OF SYMBOLS

\( a \) - a constant
\( a_i \) - activity of the \( i^{th} \) species
\( \Omega_i \) - effective ion diameter of the \( i^{th} \) species
\( a \) - an empirical coefficient
\( A \) - coefficient or species
\( A_k \) - the \( k^{th} \) negatively charged species in solution
\( b \) - a constant
\( \beta \) - an empirical exponent
\( B \) - coefficient or species
\( C_i \) - concentration of the \( i^{th} \) species
\( \xi_i \) - the \( i^{th} \) positively charged species in solution
\( \delta \) - thickness of the diffusion layer
\( \delta_p \) - thickness of the product diffusion layer
\( \delta_r \) - thickness of the reactant diffusion layer
\( +\delta \) - a positive charge
\( -\delta \) - a negative charge
\( D_i \) - diffusion coefficient of the \( i^{th} \) species
\( E_a \) - activation energy
\( f_T \) - a temperature dependent function
\( F \) - a species
\( g_T \) - a temperature dependent function
\( G \) - a species
\( G_{H_2CO_3} \) - structure factor for carbonic acid
\( h_T \) - a temperature dependent function
\( i \) - integer index for chemical species
\( I \) - stoichiometric ionic strength
I - true ionic strength
j - integer index for reactant species
k_1 - a rate constant
k_2 - a rate constant
k - a constant or rate constant
k_f - a forward rate constant
k_b - a backward rate constant
K - equilibrium constant
l - integer index for product species
m_i - molality of the i^{th} species
M_{H_2O} - mass of water
n_i - number of moles of the i^{th} species
N_i - mole fraction of the i^{th} gas species
θ - fraction of the surface area covered by an adsorbed gas
P_i - partial pressure of the i^{th} gas species
P_{tot} - total gas pressure
R - the gas constant
R - the overall (observed) reaction rate
R_f - the forward reaction rate
R_b - the backward reaction rate
R_T - the overall reaction rate
R_T^i - the net overall reaction rate - a function of P_{CO_2}
R_i - reaction order of the i^{th} species
R_o - overall reaction order
s - subscript to denote saturation value
S - surface area
$t$ - time, or subscript to denote value at time $= t$

$T$ - absolute temperature

$v_i$ - velocity coefficient of the $i^{th}$ species

$\nu_i$ - stoichiometric coefficient of the $i^{th}$ species

$V$ - volume
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INTRODUCTION

Geochemists have been interested in the history of the elements and the paths they take in the "rock cycle" for many years (Rankama and Sahama, 1950). The growth of computer technology has facilitated this type of research (cf. Horn and Adams, 1966) and the interest in such models is evidenced by the texts of Garrels and Mackenzie (1971) and Berner (1971). At present, the models available (Helgeson, 1968; Helgeson, Garrels and Mackenzie, 1969) have outstripped available kinetic data and time is treated in arbitrary units of reaction progress. Many investigators are now involved with quantitatively describing the kinetic parameters which effect mineral dissolution and precipitation (Lagache, 1965; Wollast, 1967; Campbell and Nancollas, 1969; Luce, 1969; Bovington and Jones, 1970a, 1970b; Little and Nancollas, 1970; Bailey and Reesman, 1971; Liu and Nancollas, 1971; Sayles and Fyfe, 1973). Recent work on carbonate precipitation and dissolution (Gaines and Heffner, 1973; Mitterer and Carter, 1973; Walls, 1973; Berner and Morse, 1974; Plummer and Mackenzie, 1974) has been largely restricted to studies of calcium and magnesium carbonates.

Strontianite and witherite are not common sedimentary minerals, but their occurrence is believed to control the strontium and barium concentration of ground waters in Missouri (Carpenter and Miller, 1969). This preliminary investigation was undertaken to determine the dissolution
kinetics of these minerals so that the minerals might be included in models relating to the change of ground water composition with time. Constant and variable volume batch reactors were used to study thermodynamically open systems subjected to a constant gas flow. The dissolution of these minerals was studied at temperatures of 30, 40, and 50° C in order to determine their activation energies. Strontianite dissolution was investigated at varying pH and partial pressure of carbon dioxide conditions to determine their effect upon carbonate mineral dissolution. The experimental rate data provide information about activation energies, the extent of acid catalysis, mineral solubility products, and the rate limiting step.
REVIEW OF PRINCIPLES

Introduction

Kinetics is the branch of chemistry concerned with systems whose chemical compositions change as a function of time. The approach to a kinetic investigation is initially empirical, with the goal of describing mathematically the effect of conditions of state, namely temperature and pressure, and composition upon the rate of reaction. A mathematical representation, commonly termed the rate law, may suggest a molecular interpretation of the rate controlling process. At present there are no general models, rules, or laws which are applicable to all reactions (Benson, 1960; Gardiner, 1969; and Levenspiel, 1972). Consequently, generalizations about conditions not actually investigated are unreliable since the relative contributions of concurrent processes may differ in the regions not investigated (Gardiner, 1969).

Components, Phases, and Systems

Many chemistry texts have developed the concept of chemical equilibrium as the result of equal but opposing reaction rates, and have based the law of mass action on a theory of reaction kinetics. However, the only valid approach to derive the equilibrium relationship for a reaction is based upon thermodynamics or statistical mechanics (Frost, 1941). Because the thermodynamic definition of equilibrium
is used in this paper, the necessary conditions to define the system must be considered.

The number of components in a system may be defined as (Findlay, 1951):

"the smallest number of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation."

A phase may be defined as a physically distinct and mechanically separable portion of the system of interest (Findlay, 1951).

A system is the part of the objective world which is the subject of thermodynamic study (Lewis and Randall, 1923). Three types of systems are generally recognized and are isolated, closed, and open. An isolated system may not exchange energy or matter with regions outside the system boundaries. A closed system may exchange energy but not matter with regions outside the system boundaries. An open system may exchange both energy and matter with regions outside the system boundaries. Homogeneous systems consist of only one phase, while heterogeneous systems consist of two or more phases.

Activities and Activity Coefficients

The activity of the \( i \)th species, \( a_i \), is defined as

\[
a_i = \frac{f_i}{f_i^0}
\]

(1)

where \( f_i \) is the fugacity of the \( i \)th species and \( f_i^0 \) is the
standard or reference state fugacity of the $i^{\text{th}}$ species (Klotz, 1964). By definition, the activities of pure liquids and solids at the reference conditions have a value of unity. The activity of an ideal gas, $a_i$, is defined as

$$a_i = N_i P_{\text{tot}} / 1 \text{ atm}.$$  

(2)

where $N_i$ is the mole fraction of the $i^{\text{th}}$ gas in a gas mixture, and $P_{\text{tot}}$ is the total gas pressure in atmospheres (Garrels and Christ, 1965). For most gases in the pressure range from zero to one atmosphere, the deviation from the Ideal Gas Law is very small and activity, fugacity, and partial pressure are almost equal (Denbigh, 1966).

The activity of aqueous species is based upon a reference state of one mole of that species at infinite dilution (Klotz, 1964). This hypothetical reference state results from a linear extrapolation of the Henry's Law behavior of the species from the very dilute region to a one molal concentration. The correction for the non-ideal behavior of the aqueous species is accomplished by the use of an individual molal activity of coefficient, $\gamma_i$, such that

$$a_i = \gamma_i m_i$$  

(3)

where $a_i$ is the activity of the $i^{\text{th}}$ species and $m_i$ is the true molality of the $i^{\text{th}}$ species.

This study utilized the extended Debye-Hückel equation which was modified by the addition of an empirical term to account for short range interactions between the ions and the solvent (Robinson and Stokes, 1965) and has the form

$$\log \gamma_i = \frac{-\Lambda (z_i^2 - 1)^{1/2}}{1 + B_i (\bar{I})^{1/2}} + b I$$  

(4)
where $A$ and $B$ are the Debye-Huckel parameters, $\Theta_i$ is the effective diameter of the $i^{th}$ species, $z_i$ is the charge of the $i^{th}$ species, $b$ is an adjustable parameter for fitting experimental data, and $\bar{I}$ is the true ionic strength (Helgeson, 1969) defined as

$$\bar{I} = \frac{1}{2} \sum_i m_i (z_i)^2$$

(5)

for all species in solution. A value of 0.2 was used in equation (4) for $b$ which is the same value used by Liu and Nancollas [1971 (Liu, 1972, personal comm.)].

For neutral complexes and dissolved gases, the activity coefficient can be approximated by the relationship

$$\log \gamma_i = k_{i,s}\bar{I}$$

(6)

where $k_{i,s}$ is the salting coefficient for the $i^{th}$ species in the $s^{th}$ supporting electrolyte solution (Carrels and Christ, 1965) and $\bar{I}$ is the stoichiometric ionic strength which may be defined as

$$\bar{I} = \frac{1}{2} \sum_i C_i (z_i)^2$$

(7)

where $C_i$ is the number of moles of the $i^{th}$ species per kilogram of solvent. The stoichiometric ionic strength is calculated by assuming the absence of ion pairs (cation-anion complexes).

Partial Equilibrium

Partial equilibrium describes a system which is in equilibrium with respect to at least one process and is out of equilibrium with respect to at least one process (Barton,
Bethke, and Toulmin, 1963). Garrels (1959) noted that reactions among dissolved species are generally quite rapid relative to reactions between dissolved and solid species. Consequently, for irreversible geochemical reactions such as mineral dissolution, partial equilibrium has commonly been assumed to consist of equilibrium within the aqueous phase and between the aqueous phase and the solid product phases, combined with heterogeneous disequilibrium between the aqueous phase and reacting solid phases. This assumption of partial equilibrium has been used with success by several investigators (Helgeson, 1968; Helgeson, Garrels and Mackenzie, 1969; Brown, 1970; Helgeson, 1971) to model the dissolution of various silicate minerals.

Nomenclature

For a reaction such as

\[ aA + bB = fF + gG \]  

the reaction rate, \( \dot{R} \), is traditionally defined as

\[
\dot{R} = \frac{dC_A}{-adt} = \frac{dC_B}{-bdt} = \frac{dC_F}{fdt} = \frac{dC_G}{gdt}
\]  

where \( C_A, C_B, C_F, \) and \( C_G \) are the concentrations of the subscripted species, \( -a, -b, f, \) and \( g \) are the stoichiometric coefficients, and \( t \) is time (Benson, 1960). The stoichiometric coefficients of the \( i^{th} \) species, \( v_i \), is the number of moles of species \( i \) in the equation as written and is negative for reactants and positive for products.

The rate limiting step of a reaction may be controlled
by only some of the species involved in the overall reaction. The molecularity, or number of molecules, of a particular species involved in the rate limiting step may sometimes be determined by expressing the reaction rate as

$$R = \frac{dC_A}{-adt} = k(C_A)^a (C_B)^\beta (C_F)^\gamma (C_G)^\delta$$

(10)

where $k$ is an empirical rate constant and $a$, $\beta$, $\gamma$, and $\delta$ are empirically determined values, usually integers, which represent the molecularity of the species $A$, $B$, $F$, and $G$ in the rate limiting step. The reaction order for the overall reaction is defined (Benson, 1960) as the sum of the exponents in equation (10) for all species which are found to effect the reaction rate. Thus, for the reaction expressed by equation (8), assuming that all species are kinetically active, the overall reaction order, $R_o$, is expressed by

$$R_o = a + \beta + \gamma + \delta$$

(11)

In homogeneous systems, the overall reaction order is rarely greater than two.

The overall reaction order should not be confused with the individual reaction order, $R_i$, with respect to the $i^{th}$ species, which is the empirical exponent for the concentration of that species (Benson, 1960) as expressed in equation (10). Thus, the reaction order with respect to $A$ is $a$ and with respect to $F$ is $\gamma$.

**Types of Reaction Vessels**

The three basic types of reaction vessels commonly employed in kinetic studies are the batch reactor, the
tubular or "plug-flow" reactor, and the backmix reactor (Levenspiel, 1972). A batch reactor contains the reaction products, and measurements are made of the concentration of one or more constituents as a function of time. Batch reactors may be divided into the subclasses of constant volume or variable volume reactors, both of which were used in this study. The reaction rate for constant volume batch reactors may be expressed as

\[ \frac{R_i}{dt} = \frac{dC_i}{dt} \]  

(12)

where \( R_i \) is the reaction rate with respect to the \( i^{th} \) species, \( C_i \) is the concentration of the \( i^{th} \) constituent, \( \nu_i \) is the stoichiometric coefficient of the \( i^{th} \) species, and \( t \) is time (Levenspiel, 1972).

The reaction rate for a variable volume batch reactor must include a term to compensate for the volume change and may be expressed as

\[ \frac{R_i}{dt} = \frac{dC_i}{dt} + \left( \frac{C_i}{V} \frac{dV}{dt} \right) \nu_i \]  

(13)

where \( V \) is the reactor volume and the other terms are as described above (Levenspiel, 1972).

**Molecular Equilibrium**

The Gibbs free energy of a solid-aqueous system with fixed temperature and pressure is, by definition, a minimum value at equilibrium. If the system is not perturbed in any manner, the activities of all species remain constant; however, the individual atoms composing the species are free
to transfer from one species to another provided that an
equal number of atoms of the same element transfer in the
opposite direction at the same rate. The molecular or
microscopic view of equilibrium is that for any equation
the rates for the forward and reverse directions of the
reaction are identical.

The Principle of Mass Action

Between 1864 and 1879, Guldberg and Waage published a
series of papers dealing with reaction kinetics and equilib-
rium conditions. Their principle or "law" of mass action,
a generalization drawn from experimental results, is that
the forward and reverse reaction rates are respectively
proportional to the concentrations of the reactant and pro-
duct species each raised to the power of the coefficient for
that species in the chemical equation. The principle of
mass action may be written

\[ R = k_f \prod_j (a_j)^{\nu_j} - k_b \prod_l (a_l)^{\nu_l} \]  (14)

where \( k_f \) is the forward rate constant, \( a_j \) is the activity of
the \( j^{th} \) reactant species, \( \nu_j \) is the stoichiometric coeffi-
cient of the \( j^{th} \) species, \( k_b \) is the backward rate constant,
\( a_l \) is the activity of the \( l^{th} \) product species, and \( \nu_l \) is the
stoichiometric coefficient of the \( l^{th} \) product species
(Anderson and Boyd, 1971). At equilibrium, the forward
reaction rate must be equal to the backward reaction rate,
\[ k_f \prod_{j}^{\nu_j} (a_j)^{-\nu_j} = k_b \prod_{1}^{\nu_1} (a_1)^{\nu_1} \]  

(15)

For the equilibrium condition, rearrangement of equation (15) yields

\[ \frac{\prod_{1}^{\nu_1} (a_1)}{\prod_{j}^{\nu_j} (a_j)} = \frac{k_f}{k_b} = K \]  

(16)

where \( K \) is the thermodynamic equilibrium constant.

Rate Laws for Mineral Dissolution

The dissolusion rate of a mineral in an aqueous solu-
tion may be expressed in terms of the rate of change of the
concentrations of species involved in the reaction. Usually
the species measured is in the aqueous phase and is derived
from the mineral. The general case for the congruent disso-
olution of a mineral, \( N_aX_b \), dissolving in water may be
represented as

\[ N_aX_b = aN^z_N + bX^z_X \]  

(17)

where \( N^z_N \) and \( X^z_X \) are ions in solution having the respective
charges of \( z_N \) and \( z_X \). The dissolution rate, \( R \), may then be
expressed as

\[ R = dm^z_N/adt = k(m^z_N^{Z_N} - m^z_N^{Z_N})^n \]  

(18)

where \( k \) is the reaction rate constant, \( m^z_N^{Z_N} \) is the molality
of \( N \) at saturation, \( m^z_N \) is the molality of \( N \) at time \( t \),
and \( n \) is an empirical constant.
For reactions such as dissolution reactions occurring at a phase boundary, the reaction rate may be controlled by either the diffusion of reactants and products to and from the phase boundary or by the reaction occurring at the interface (Benson, 1960). Diffusion controlled reactions are usually explained by the Nernst theory which may be expressed, for one dimensional transport, as

\[
\frac{dn_i}{dt} = \overline{v}_i \frac{dn_i}{dx}
\]  

(19)

in which \(n_i\) is the number of molecules of the \(i^{th}\) species in solution, \(dn_i/dx\) is the concentration gradient, and \(\overline{v}_i\) is the individual ion velocity expressed as

\[
\overline{v}_i = \frac{dx}{dt} = \frac{D_i S}{V}
\]

(20)

where \(D_i\) is the temperature dependent individual ion diffusion coefficient, \(S\) is the surface area, and \(V\) is the solution volume (Moelwyn-Hughes, 1947). The concentration gradient may be rewritten as

\[
\frac{dn_i}{dx} = \frac{(n_{is} - n_{it})}{\delta}
\]

(21)

where \(n_{is}\) is the number of moles of the \(i^{th}\) species at saturation, \(n_{it}\) is the number of moles of the \(i^{th}\) species in solution at time \(t\), and \(\delta\) is the thickness of the diffusion layer (Berner, 1971).

In geochemical literature, molality is a common basis for expressing the concentration of a species in solution.
The molality of the \( i^{th} \) species, \( m_i \), may be expressed as

\[
m_i = k'n_i/V
\]  

(22)

where \( k' \) is the temperature dependent constant for converting pure water volume to mass.

First Order Reactions

For first order reactions, the empirical constant, \( n \), is equal to unity and equation (18) reduces to

\[
dm_i/\nu_i dt = k(m_i - m_i)
\]  

(23)

where \( m_i \) is the molality of the \( i^{th} \) species at saturation, \( m_i \) is the molality of the \( i^{th} \) species at time \( t \), and \( k \) is the rate constant described by

\[
k = k'D_iS/\delta
\]  

(24)

Equation (23) is the molal rate law for the diffusion controlled reactions according to the Nernst theory and is a simple first order rate law. The assumptions involved in the formulation of the theory are (Moelwyn-Hughes, 1947; Plummer, 1972):

1) The chemical reaction at the mineral surface occurs very rapidly and creates a saturated layer of the product species at the interface.

2) The chemical composition of the aqueous phase beyond the diffusion layer is uniform and is called the "bulk solution".
3) The concentration gradients of product and reactant species are linear and restricted to thin layers. For product species, the effective diffusion layer thickness, $\delta_p$, is simply equal to the perpendicular distance between the saturated layer and the "bulk solution". Reactant species have an effective diffusion layer thickness, $\delta_r$, equal to the sum of the saturated layer and the product diffusion layer.

4) The thickness of the diffusion layer is a function of the rate of stirring and the geometry of the system.

Because the reaction rate should vary as a function of the stirring rate, a qualitative test for diffusion control of first order reactions consists of comparing the reaction rates of stirred and unstirred experiments. If the reaction rate is not effected by stirring, then the reaction must be chemically controlled.

If equation (23) is rearranged and integrated, it yields

\[ \frac{1}{\nu_i} \log \left( \frac{m_i}{m_{i0}} \right) = kt + C \]  

(25)

where $t$ is the time since the experiment started and $C$ is the integration constant. If the $i^{th}$ species is absent at $t = 0$ then $C$ must equal the logarithm of molality of the $i^{th}$ species at saturation. The molality of the $i^{th}$ species at saturation may be determined analytically from experiments
which approach equilibrium from both undersaturated and supersaturated conditions, or by calculating the equilibrium composition of the aqueous phase. Plotting \( \log (m^s_i - m^t_i) \) against time, \( t \), yields a straight line for a first order reactions and the rate constant, \( k \), is the slope of this straight line.

Reactions Other Than First Order

For reactions which are not first order with respect to the species considered, equation (18) may be used to represent the experimental data if the value of the exponential term, \( n \), is determined empirically. The value of \( n \) may be determined by graphical analysis if equation (18) is rewritten as

\[
\log (\frac{dm^z_N}{adt}) = n \log [k(m^z_N^N - m^z_N^s_t)]
\]  

(26)

where \( n \) is defined by the slope of a straight line connecting the data points when plotted as \( \log (\frac{dm^z_N}{adt}) \) versus \( \log (m^z_N^N - m^z_N^s_t) \) (Benson, 1960; Plummer, 1972).

Other Common Empirical Rate Laws

The rate of mineral reactions with an aqueous phase can often be expressed by the general kinetic relationship

\[
\frac{dm_i}{dt} = k_i t^\omega
\]  

(27)

where \( m_i \) is the molality of the \( i^{th} \) species, \( t \) is time in arbitrary units, \( k_i \) is the rate constant for the change in molality of the \( i^{th} \) species, and \( \omega \) is an empirical exponent
(Helgeson, 1971). For the dissolution of various silicate minerals, the values $\omega = 0$, $-\frac{1}{2}$, and $-1$ provide satisfactory agreement with the experimental data (Helgeson, 1971). The rate laws for $\omega = 0$, $-\frac{1}{2}$, and $-1$ are linear, parabolic, and logarithmic and may be tested by plotting the molality of the species of interest against $t$, $t^{\frac{1}{2}}$, and $\log t$, respectively.

The affinity model, developed by Prigogine, Outer, and Herbo (1948) for gas reactions in the vicinity of equilibrium, has been successfully applied to dissolution reactions of some carbonate minerals (Sonderegger, in prep.). The model is empirical in nature and may only be applied close to equilibrium where the reaction rate is directly proportional to the Gibbs free energy of the dissolution reaction. Under this restriction, the affinity model may be used to predict the equilibrium state from the dissolution rate data (cf. Prigogine, 1967).

The Langmuir Adsorption Isotherm

Gas phase reactions catalyzed by elementary reactions occurring at an interface, such as the walls of a reaction vessel, are frequently found to have reaction rates which vary with the surface area of the vessel. Investigations of gas adsorption at solid surfaces has led to the recognition of several basic types of adsorption-pressure relationships. The mathematical relationship between the amount of a gas adsorbed by the solid phase of interest and the gas pressure
at constant temperature is called an adsorption isotherm. In cases where chemisorption occurs at the interface, the Langmuir adsorption isotherm is generally the best equation for representing the experimental data (Maron and Prutton, 1958). Figure 1 schematically represents the relationship between gas pressure and the amount of gas adsorbed at the surface for a Type I isotherm. Chemisorption reactions appear to be restricted to this type of isotherm (Maron and Prutton, 1958).

The Langmuir adsorption isotherm equation may be expressed as

\[ \theta = \frac{bP}{(1 + bP)} \]  

(28)

where \( \theta \) is the fraction of the experimental surface covered by adsorbed gas, \( b \) is an empirical constant, and \( P \) is the partial pressure of the gas (Maron and Prutton, 1958). The amount of gas adsorbed per unit area or per unit mass of absorbent, \( y \), should be proportional to the fraction of the surface covered and may be represented as

\[ y = k_1 \theta = \frac{k_1 bP}{(1 + bP)} = \frac{aP}{(1 + bP)} \]  

(29)

where \( k_1 \) is the proportionality constant and \( a = k_1 b \) (Maron and Prutton, 1958). Rearrangement of equation (29) yields:

\[ \frac{P}{y} = \frac{1}{a} + \left(\frac{b}{a}\right)P \]  

(30)

If the reaction of interest is compatible with the Langmuir adsorption isotherm, a plot of \( \frac{P}{y} \) versus \( P \) should yield a straight line with slope of \( \frac{b}{a} \) and an intercept of \( \frac{1}{a} \).
Figure 1. Diagram depicting the relationship between the amount of gas adsorbed on a solid surface versus the pressure of the gas. This is a type I adsorption isotherm and is usually related to a chemical reaction creating an activated species.
If variables such as total pressure, temperature, and pH are held constant, the change in the dissolution rate of the mineral in question may be related to the changing partial pressures of the gases in the gaseous phase. An assumption that the reaction rate is related to the fraction of the mineral surface which has adsorbed the gas phase permits the application of the Langmuir adsorption isotherm to dissolution kinetics. This assumption, a simplified approximation of the actual processes occurring at the mineral surface, allows an initial investigation of the role of specific gases on mineral dissolution. Such studies are of particular interest when the gas involved hydrates to form a weak (associated) acid, such as carbonic acid, which may catalyze the mineral dissolution reaction.

Activation Energies

For experimental data within a limited temperature range, the activation energy of a reaction may be calculated from the Arrhenius equation:

$$k_T = Ae^{-E_a/RT} \quad (31)$$

where $A$ is an empirical pre-exponential factor, $E_a$ is the activation energy, $R$ is the gas constant, $T$ is the temperature in degrees Kelvin, and $k_T$ is the temperature dependent reaction rate constant (Gardiner, 1969).

For first order dissolution reactions which may be expressed as
\[
\frac{dm_i}{\nu_i dt} = k_T m_i t
\]  
(23')

the relationship between the rate constant, \( k_T \), and the time to half saturation, \( t_{1/2} \), is (Benson, 1960; Plummer, 1972)

\[
k_T = \ln \left( \frac{2}{t_{1/2}} \right)
\]  
(32)

If equation (31) is rewritten in the form

\[
\ln (k_T) = \ln (A) - \left( \frac{E_a}{RT} \right)
\]  
(33)

it is clear that a plot of \( \ln (k_T) \) versus \( 1/T \) should yield a straight line with a slope of \(-E_a/R\) and an intercept of \( \ln (A) \) if the Arrhenius equation is applicable to the experimental data.

Activation energies provide another method of testing whether or not a dissolution reaction is diffusion controlled. The activation energy of a diffusion controlled dissolution reaction should be 4.5 kilocalories (Liu and Nancollas, 1971). Reactions having considerably larger activation energies must be controlled by some mechanism other than diffusion of the aqueous species between the bulk solution and the mineral surface.

Comparison of Graphical Data

The previous sections have briefly discussed the use of various graphic techniques. The primary purpose of these plots is screening the experimental data to determine which rate laws are most applicable.
Kinetic rate laws are based upon assumed mechanisms and the mathematical expression of these laws requires the use of small integers or ratios of small integers as the exponential factors (Benson, 1960). Consequently, the use of a high order polynomial series to regress the experimental data defeats the goal of determining a satisfactory mechanism to explain the kinetic behavior of a reaction. Instead, a general preliminary practice is to plot the logarithm of the reaction rate against the logarithm of the expression for the mechanism being tested (cf. Levenspiel, 1972). When plotted in this manner, if the experimental data approximates a straight line, the slope of the straight line defines the molecularity of the hypothetical mechanism. The next step in a data analysis is to plot the reaction rate versus the expression raised to the power of its molecularity. If this second plot yields a linear relationship, the experimental data are compatible with the proposed mechanism.
EXPERIMENTAL PROCEDURES

Introduction

The experimental apparatus and methods employed in a kinetic investigation should be designed so that all experimental parameters can be conveniently varied by the investigator. This chapter describes the apparatus and methods used in the investigation of strontianite, SrCO₃, and witherite, BaCO₃, dissolution as a function of temperature at approximately a 0.8 atmosphere partial pressure of carbon dioxide gas, P_CO₂. Strontianite dissolution was also investigated at different P_CO₂ values, and as a function of pH under an N₂ atmosphere in an attempt to evaluate the effect of P_CO₂ and pH upon the dissolution kinetics.

Sample Preparation

The samples of strontianite from the Westphalia mining district, Germany, and witherite from the Settingstones Mine, Northumberland, England, were obtained from Ward's Natural Science Establishment. Both samples were reportedly from vein deposits and were processed in the following manner:

1) All gangue minerals and a portion of the outside of the vein were removed using a hammer and chisel.

2) The sample was broken into approximately half inch pieces with a hammer.

3) The sample was crushed in a tool steel piston
style sample crusher.

4) The sample was spread on white paper and impurities, mainly galena, sphalerite, and iron hydroxide coatings, were removed by hand.

5) The sample was sieved using brass 30 mesh and nylon 100 and 200 mesh screens.

6) The -30 +100 mesh and -100 +200 mesh fractions were visually re-examined to remove impurities using a high intensity lamp and a biology pick.

7) The samples from step 6) were washed first with 0.1 N reagent grade hydrochloric acid, then with four rinses of distilled water followed by drying in a vacuum.

8) The samples were split using a small vibrating sample splitter and sealed in glassine paper packets for storage prior to use.

Reaction Vessel Design

The reaction vessel used is cylindrical in shape and was constructed from Lucite. The base is permanently attached and sealed while the top is removable and has a natural gum rubber gasket. The inside diameter is 11.3 centimeters and the height is 15.3 centimeters. A liter of water occupies about 2/3 of the available volume. The sample was added to the aqueous phase using a glass funnel inserted through a hole in the top of the reaction vessel.

Stirring was provided by an ovoid Teflon coated
magnetic spin bar within the vessel which was placed upon a variable-speed magnetic stirring unit. The ovoid shape was used to minimize grinding of the sample.

Commercially prepared nitrogen and carbon dioxide gases with purities of greater than 99% were used in this study. The gas or gas mixture was introduced into the aqueous phases through a vertical glass tube which has a sintered glass plug at the bottom. Such "bubbling tubes" greatly aid in rapidly saturating the fluid phase with the gas phase because an increased interphase contact area results from the large number of small gas bubbles produced by passage of the gas through the sintered glass. The gases were passed into a one liter Erlenmeyer flask containing 900 milliliters of water for presaturation of the gas phase with water vapor prior to introduction into the reaction vessel.

Gas mixtures of CO₂ and N₂ were provided by the use of capillary tubes and Erlenmeyer flasks (see figure 2). The capillary tubes were calibrated by the volume of water which the particular gas displaced per unit time under a fixed tank pressure. Both gases were then passed into a large Erlenmeyer flask for mixing and then introduced into the reaction vessel as discussed previously.

The heat source for the experiments consisted of a 100 watt standard frosted glass light bulb for 30⁰ C and a 150 watt infrared bulb for 40 and 50⁰ C. A thermistor probe extended into the aqueous phase from the top of the reaction vessel and was calibrated with an alcohol thermometer having
Figure 2. Schematic diagram of the system for delivering the gas phase to the reaction vessel: A = gas tanks; B = small flask; C = capillary tube; D = mixing flask; E = saturation flask; F = reaction vessel.
0.2 degree divisions which was inserted in the same manner.

Instrumentation

Two variables, pH and resistance, were monitored to determine the reaction progress. The pH was measured with a Beckman model 39013 combination electrode and a Corning model 12 pH meter. Buffers with pH values of 4.015 and 6.995 at 30⁰C were used to calibrate the pH meter and electrode. Instrumental drift during an experiment generally was less than ±0.02 pH units as determined using buffer solutions before and after an experimental run; however, a confidence limit of ±0.05 pH units is used to compensate for any additional errors which might have existed during the experiments.

Resistivity was measured with a conductivity cell, cell constant = 0.9828, and a Heathkit impedance bridge. Both the electrode and the conductivity cell were inserted into the reaction vessel through holes in the top of the cell with bored rubber stoppers to hold them in place.

Time Measurements

A large centrally located wall clock with a second hand was used to monitor the time.

Data Smoothing

Data smoothing was required to provide pH values for times between measurements. The data were smoothed by hand.
with a flexible curve to prevent bias of the data in the
direction of a kinetic model paralleling the mathematical
expression of a curve fitting equation.

Calculation of Partial Pressures

In experimental systems the gas phase being bubbled
through the reaction vessel must be saturated with the solv-
vent to prevent loss of the solvent to the gas phase. At
pressures of one atmosphere or less the fugacity coefficients
of most gases are very close to unity and the fugacity of
the \textit{i}th gas, \( f_i \), may be expressed by the ideal gas law

\[
f_i = N_i P_{\text{tot}} = P_i 
\]

(34)

Where \( N_i \) is the mole fraction of the \textit{i}th gas in the gas mix-
ture, \( P_{\text{tot}} \) is the total pressure, and \( P_i \) is the partial pres-
sure of the \textit{i}th gas (Denbigh, 1966). When considering a sys-
tem with a fixed overpressure, an aqueous phase, and one gas
being bubbled through the aqueous phase, the partial pressure
of the gas being bubbled through the reaction vessel may be
expressed as

\[
P_i = P_{\text{tot}} - P_{\text{H}_2\text{O}} 
\]

(35)

where \( P_{\text{H}_2\text{O}} \) is the vapor pressure of water at the tempera-
ture of interest (Maron and Prutton, 1958). Equations (34)
and (35) were used in calculating the partial pressure of
carbon dioxide in this study.

The vapor pressures of water at 30, 40, and 50\(^0\) C
are 0.0419, 0.0728, and 0.135 atmospheres, respectively.
The average barometric pressure in Socorro, New Mexico, where the experiments were conducted, is approximately 650 millimeters of mercury or 0.855 atmospheres. With a total pressure of 0.855 atmospheres, the calculated carbon dioxide partial pressures at 30, 40, and 50° C were 0.813, 0.782, and 0.720 atmospheres respectively. However, the vessel into which the gas was first bubbled to saturate it with water vapor was at the ambient room temperature which ranged from 28 to 31° C. The effective $P_{CO_2}$ for experiments run at 40 and 50° C must have ranged between 0.78 and 0.81 atmospheres and 0.72 and 0.81 atmospheres, respectively. Comparison of the calculated total strontium content with the strontium concentration determined by atomic absorption indicates that using either $P_{CO_2}$ value results in a calculated strontium content which is within the region of analytical error. The saturation values for $m_{Sr^{2+}}$ were determined from affinity plots, so corrections of $m_{Sr^{2+}}$ for differing $P_{CO_2}$ values would also shift these saturation values. Consequently, the data employed are internally consistent, with only the $K_{sp}$ value possibly being in error by more than two or three percent. A value of $P_{CO_2} = 0.81$ was used for the calculations at 30, 40, and 50° C.

Calculation of Species' Concentrations

The activities and molalities of all species in solution were calculated using the method outlined by Garrels and Christ (1965, p. 76-83) with the aid of a computer.
program, CATCALC, written for the dissolution of carbonate minerals under a fixed partial pressure of carbon dioxide (see Appendix A). The measured variable, pH, and the constraint of electrical neutrality permit an iterative solution of a series of simultaneous equations despite the fact that carbon dioxide is not conserved in the system of interest.

The equations necessary for these calculations are:

\[ K_w = a_{H^+} a_{OH^-} \]  
\[ K_0 = a_{H_2CO_3}/p_{CO_2} \]  
\[ K_1 = (a_{H^+} a_{HCO_3^-})/a_{H_2CO_3} \]  
\[ K_2 = (a_{H^+} a_{CO_3^{2-}})/a_{HCO_3^-} \]  
\[ K_\rho = (a_{Me^{2+}} a_{HCO_3^-})/a_{MeHCO_3^+} \]  
\[ K_\gamma = (a_{Me^{2+}} a_{CO_3^{2-}})/a_{MeCO_3^0} \]

and

\[ \sum_i z_i = \sum_k z_k \]

where Me is the alkaline earth of interest, \( \zeta_i \) is the \( i^{th} \) positively charged aqueous species, and \( z_k \) is the \( k^{th} \) negatively charged aqueous species. This results in a system of seven equations and nine variables of which the two independent variables, pH and \( P_{CO_2} \), are known.

The only assumptions employed in the calculations, that equilibrium is maintained by all gaseous and aqueous species and that activities of unity are assigned to the
solid phase and water, have been shown to contribute negligible error (Belgeson, 1967). The sequence of steps employed in the calculation are:

1) Calculate the activities of \( H_2CO_3 \), \( HCO_3^- \), \( CO_3^{2-} \), and \( OH^- \).
2) Assume all activity coefficients are unity.
3) Determine the molalities of the negative species and \( H^+ \).
4) Sum of the molalities of the negative species times their charge.
5) Sum of anion equivalents minus hydrogen ion molality equals sum of cation equivalents.
6) Compute the ratio of \( Me^{2+} \) to \( MeHCO_3^+ \).
7) Assign molalities to \( Me^{2+} \) and \( MeHCO_3^0 \).
8) Calculate activity and molality of \( MeCO_3^0 \).
9) Compute ionic strength and activity coefficients of all species.
10) Return to step 3) and repeat the calculations.

Calculation of Reaction Rate

The systems investigated were maintained at a fixed partial pressure of carbon dioxide. Consequently, the concentrations of carbonate species depended upon contributions to or withdrawals from the gas phase as well as the quantity resulting from carbonate mineral dissolution. Similarly, the pH was internally controlled by the carbon dioxide partial pressure (cf. Garrels and Christ, 1965, Capt. 3, cases 1 and 4),
or externally controlled by acid titration. The only component which was conserved in the aqueous phase was the respective alkaline earth oxide, SrO or BaO. The reaction rate, as used in this study is defined as

\[ \frac{dM_{\text{Me}^{2+}}}{dt} \]  

(43)

where \( \text{Me}^{2+} \) is either \( \text{Sr}^{2+} \) or \( \text{Ba}^{2+} \) depending upon the mineral being dissolved.
EXPERIMENTAL RESULTS

Introduction

The experimental data for the dissolution of strontianite and witherite may be divided into three subgroups:

1) The effect of pH on strontianite dissolution at 40\degree C with continuous removal of carbon dioxide by a stream of nitrogen.

2) The effect of various partial pressures of carbon dioxide on strontianite dissolution at 40\degree C and pH = 4.5.

3) The dissolution of strontianite and witherite at 30, 40, and 50\degree C with a fixed carbon dioxide partial pressure of 0.81.

By holding all variables except pH or $P_{CO_2}$ constant, the effect of pH and $P_{CO_2}$ upon strontianite dissolution can be determined. The laboratory dissolution of strontianite and witherite under a fixed partial pressure of carbon dioxide approximates geologic conditions where connection with the soil atmosphere is maintained or where a high $P_{CO_2}$ is maintained by connection with a gas reservoir. An example of a high $P_{CO_2}$ reservoir is the Madera Limestone aquifer in the Ladron Mountains, New Mexico (Titus, 1974, personal comm.).

The results of this study include the determination of activation energies and solubility products for strontianite and witherite dissolution and an interpretation of the mechanism which limits their dissolution rate.
The Effect of pH

The rate of strontianite dissolution was investigated under a nitrogen atmosphere at pH values of 1.5, 2.5, 3.5, 4.5, 5.5, and 6.5. In order to maintain approximately the same degree of undersaturation for each of the experiments, nitrogen gas was bubbled through the system to remove the carbonic acid resulting from strontianite dissolution. Each experiment was run for one hour and the acid consumption for the period from 20 to 40 minutes was used to calculate the rate of acid addition at the experimental pH. The reaction rate was expressed by the number of moles of HCl added per minute to maintain the predetermined pH. The reaction rate varied over three orders of magnitude while the hydrogen ion activity was varied over five orders of magnitude as shown in figure 3.

To compare these results with the results of the temperature dependent strontianite dissolution, the reaction rate must be expressed in terms of \( \frac{dm_{Sr^{2+}}}{dt} \). These strontianite dissolution reactions were conducted by titrating hydrochloric acid into the system to maintain the desired pH and carbon dioxide was removed by the stream of nitrogen gas. Therefore, the reaction may be written as

\[
SrCO_3 + 2 H^+ = Sr^{2+} + CO_2(g) + H_2O
\]  \hspace{1cm} (44)

and the reaction rate, \( \mathbb{R} \) is
Figure 3. Plot of the logarithm of the number of moles of hydrochloric acid added per minute to maintain the desired pH for strontianite dissolution. For pH values of 1.5, 2.5, and 3.5, the data are linear. At higher pH values, the change in the rate of acid addition is much less. Nitrogen gas was continuously bubbled through the reaction vessel.
\[ R = \frac{\text{d}m_{\text{Sr}^{2+}}}{\text{d}t} = \frac{1}{2} \left( \frac{\text{d}m_{\text{H}^{+}}}{\text{d}t} \right) \] (45)

Figure 4 is a plot of the calculated \( \log R \) versus pH for strontianite dissolution at \( 40^\circ \text{C} \) under a continuously renewed \( N_2 \) atmosphere. The hydrogen ion activity decreases away from the origin, a common convention for presenting pH dependent data in the geologic literature. The data suggest that two separate contributions to the dissolution rate exist. Under low pH conditions, the dissolution rate appears to be controlled by a process which is approximately first order with respect to hydrogen ion activity because the slope of a line connecting the first three data points is approximately minus one (-0.92). At higher pH conditions, pH greater than 4.0, some other condition becomes the rate limiting factor. This second concurrent mechanism does not appear to be independent of pH, but has a small empirical exponential coefficient which is shown by the slope of a line connecting the data points at pH's of 5.5 and 6.5. The data may be represented by an equation of the form

\[ R = k_1 (a_{\text{H}^{+}})^{0.92} + k_2 (a_{\text{H}^{+}})^{0.13} \] (46)

where \( k_1 = 2.05 \times 10^{-2} \) and \( k_2 = 8.65 \times 10^{-6} \) and the exponents come from the slopes of the straight lines in figure 4. However, the last term may only be applicable to pH values up to 6.5.

While the nature of the second term in equation (46) has not been determined, two regions characterized by different rate limiting mechanisms have been shown to exist.
Figure 4. Plot of the logarithm of the reaction rate versus pH for strontianite dissolution. The reaction rate was calculated using equation (45). The slope for the low pH region is -0.92. This may be interpreted as the rate controlling step being first order with respect to $a_{H^+}$. Carbonate species were removed by a continuous stream of nitrogen gas.
The strontianite dissolution rate is, within experimental error, a first order function of hydrogen ion activity at pH values less than 4.0; however, at higher pH values another mechanism, possibly a reaction involving water at the mineral surface, controls the reaction rate. Because this aspect of the experimental work was conducted under a continuously renewed nitrogen atmosphere, carbon dioxide resulting from mineral dissolution was removed from the system. Consequently, the system remained extremely undersaturated.

The extent of undersaturation is demonstrated by the molality product, \( m_{\text{Sr}^{2+}} \cdot m_{\text{CO}_3^{2-}} \), of strontianite at the end of 40 minutes. Assuming a \( P_{\text{CO}_2} \) value of 0.81, the molality product ranged from a low of \( 10^{-13.6} \) at a pH of 1.5 to a high of \( 10^{-11.2} \) at a pH of 6.5. Thus, neglecting activity coefficients and assuming the maximum \( P_{\text{CO}_2} \) rather than a value very close to zero, the molality product still yields a value which is only 1.3% of the solubility product. At the termination point of these experimental runs, the dissolution of strontianite was less than 2% completed. Therefore, it is reasonable to assume that any back reaction has not yet become significant (Benson, 1950; Gardiner, 1969).

**Effect of \( P_{\text{CO}_2} \)**

The effect of carbon dioxide partial pressure upon strontianite dissolution was investigated by streaming mixtures of carbon dioxide and nitrogen gases at 40° C.
The $P_{CO_2}$ conditions studied were 0.0, 0.2, 0.4, and 0.8 atmospheres. Each experimental run had an initial pH of 4.02 to provide identical starting pH values which required acid addition for the $P_{CO_2}$ values of 0.0, 0.2, and 0.4 atmospheres. The pH was maintained at 4.50 ± 0.03 by titrating 0.094 normal hydrochloric acid into the reaction vessel. The time period from 20 to 40 minutes after the start of the experiment was used to calculate the rate of acid addition. At a pH of 4.5, $H_2CO_3$ is the dominant carbonate species in solution and the dissolution reaction may be written as

$$SrCO_3 + 2 H^+ = Sr^{2+} + H_2CO_3$$ (47)

for the experimental conditions. Once the pH of 4.5 has been established, the reaction rate may be expressed as

$$R = \left(\frac{dm_{Sr^{2+}}}{dt}\right) + \left(\frac{m_{Sr^{2+}}}{M_{H_2O}}\right)\left(\frac{dM_{H_2O}}{dt}\right)$$

$$= \frac{1}{2}\left[\left(\frac{dm_{H^+}}{dt}\right) + \left(\frac{m_{H^+}}{M_{H_2O}}\right)\left(\frac{dM_{H_2O}}{dt}\right)\right]$$ (48)

where $M_{H_2O}$ is the mass of liquid water.

Figure 5 is a plot of the amount of acid added per minute to maintain a pH of 4.5 as a function of the mole percent of carbon dioxide in the gas phase being introduced into the system. Figure 6 is a plot of $P_{CO_2}$ versus the reaction rate calculated from equation (48). The partial pressure of carbon dioxide was calculated from the relationship
Figure 5. Plot of the raw data for strontianite dissolution at 40°C and pH = 4.5. The rate is the number of milliliters of 0.094 N hydrochloric acid added per minute to maintain the pH. The term % CO₂ is the percentage of carbon dioxide in the CO₂-N₂ gas mixture.
Figure 6. Plot of the dissolution rate of strontianite, calculated using equation (48), versus $P_{CO_2}$ for strontianite dissolution at 400°C and pH = 4.5.
\[ P_{CO_2} = N_{CO_2} (P_{tot} - P_{H_2O}) \]  \quad (49)

where \( N_{CO_2} \) is the mole fraction of carbon dioxide in the \( CO_2-N_2 \) mixture. It can be seen from figure 6 that the relationship between the dissolution rate of strontianite and \( P_{CO_2} \) is definitely non-linear. Therefore, it was assumed that the reaction rate was dependent upon the degree of surface adsorption of either \( CO_2^{(aq)} \) or \( H_2CO_3 \) and the data were analyzed to see if an adsorption isotherm was compatible with the experimental values.

Application of the Langmuir adsorption isotherm to this study was accomplished by evaluating the change in reaction rate as a function of \( P_{CO_2} \), assuming concurrent contributions to the reaction rate, using the relationship

\[ R_T = f_T(a_{H^+}) + g_T(P_{CO_2}) + h_T \]  \quad (50)

where, at the temperature of interest, \( R_T \) is the observed reaction rate, \( f_T \) is a rate function describing the effect of hydrogen ion activity, \( g_T \) is a rate function describing the effect of carbon dioxide pressure, and \( h_T \) is a rate function of any additional unknown variables. If all known variables except the partial pressure of carbon dioxide are held constant, the function \( g_T \) may be expressed as

\[ g_T(P_{CO_2}) = R_T - R_T', P_{CO_2} = 0 = R_T' \]  \quad (51)

where \( R_T, P_{CO_2} = 0 \) is the experimental reaction rate determined by bubbling 100% nitrogen gas through the reaction
vessel. Setting y in equation (30) equal to \( R_T' \) permitted a test of the hypothesis that the reaction rate might be controlled by an adsorption mechanism.

Figure 7 is a plot of \( P_{CO_2}/R_T' \) versus \( P_{CO_2} \). The linearity of the points demonstrates that the kinetic effect of the partial pressure of carbon dioxide on strontianite dissolution is satisfactorily represented by the Langmuir adsorption isotherm, a Type I isotherm. This strongly suggests, but does not prove conclusively, that the rate limiting step is related to an adsorption mechanism.

The dissolution of strontianite with \( P_{CO_2} \) values of 0.0, 0.2, 0.4, and 0.8 atmospheres was conducted at an artificially maintained pH of 4.5. For this reason, none of the reactions proceeded as far as one percent of completion. Consequently, the reaction rate is only applicable to conditions far from equilibrium where the back reaction should be insignificant (Gardiner, 1969).

Effect of Temperature

Strontianite Dissolution

Strontianite dissolution with a carbon dioxide partial pressure of 0.81 atmosphere, was investigated at temperatures of 30, 40, and 50° C to determine the activation energy of the dissolution reaction and to investigate the kinetics as the reaction proceeds toward equilibrium. Minor fluctuations in barometric pressure were not considered
Figure 7. Plot of $P_{CO_2}/E_T'$ versus $P_{CO_2}$ for strontianite dissolution at 40$^\circ$ C and pH = 4.5. This plot is used to test the applicability of the Langmuir adsorption isotherm. The linearity of the data points demonstrates that $R_T'$, the $CO_2$ contribution to the reaction rate, is proportional to $\theta$, the fraction of the mineral surface covered by the adsorbed gas.
significant (cf. Garrels, Thompson, and Siever, 1960) and were not monitored. The experimental system was left open to the atmosphere to provide a fixed overpressure on the system.

The research required a fairly large amount of stronti- nite and the only size fraction used was the -30 +100 mesh split (sample between mesh sizes 0.589 mm and 0.149 mm). The sample was homogenized and passed repeatedly through a sample splitter to provide 16 aliquots. Fourteen of the splits were used for these experiments. The mean sample weight was 18.716 grams with a standard deviation of 0.208 grams.

The experimentally determined parameters, pH and specific resistivity, were monitored to define the reaction progress. Empirical resistivity values were obtained by titrating a 0.0841 molal solution of strontium hydroxide into distilled water under a carbon dioxide partial pressure within the range of 0.78 to 0.81 atmospheres at 40° C. The break in the slope of a plot of resistivity against volume of titrant added suggests saturation with respect to SrCO₃ was achieved when 3.46 x 10⁻³ moles of Sr(OH)₂ had been added (pH = 5.81), but a definite precipitate was not formed until 4.44 x 10⁻³ moles had been added (pH = 5.91).

The molal solubility and solubility product values used for subsequent calculations were estimated by the affinity method of Prigogine, Outer, and Herbo (1948) to be: 3.42 x 10⁻³ moles of Sr²⁺ per kilogram H₂O at 30° C (pK_{sp} =
9.37, equilibrium pH = 5.75); 3.22 \times 10^{-3} \text{ moles of } \text{Sr}^{2+} \text{ per kilogram H}_2\text{O at 40}^\circ \text{C (pK}_{\text{sp}} = 9.32, \text{ equilibrium pH} = 5.81); and 3.05 \times 10^{-3} \text{ moles of } \text{Sr}^{2+} \text{ per kilogram H}_2\text{O at 50}^\circ \text{C (pK}_{\text{sp}} = 9.28, \text{ equilibrium pH} = 5.83).}

The reproducibility of the experimental data is demonstrated in figure 8 where four experimental runs at 40^\circ \text{C are plotted. Agreement during the first 200 minutes is excellent. From 200 to 400 minutes the divergence of experimental points is greater but well within the range of experimental error discussed earlier. Stirred and unstirred experiments proceeded at the same rate.}

The molalities of all aqueous species and the activities of all aqueous species other than H^+ were calculated using the computer program CATCALC as discussed on pages 29 and 30. Appendix B contains a listing of the equilibrium constants used in the calculations. Comparison of the calculated strontium concentrations with atomic absorption analyses of samples taken at the end of the experiment are in complete agreement within the analytical limits of the equipment (± 10%) under routine conditions. The atomic absorption analyses are not consistently higher or lower than the values determined from CATCALC; thus, systematic error in the program constants is probably minimal or compensating.

The rate of mineral reaction with an aqueous phase can often be expressed by the general kinetic relationship

\[
\frac{dm_i}{dt} = k_1 t^\omega
\]  
(27)
Figure 8. Plot of pH versus time in minutes for strontianite dissolution at 40° C and 0.81 atmosphere $P_{CO_2}$. The purpose of the plot is to demonstrate the reproducibility of the data.
Figures 9, 10, and 11 are plots of linear ($\omega = 0$), parabolic ($\omega = -\frac{1}{2}$), and logarithmic ($\omega = -1$) rate laws for strontiante dissolution at 30, 40, and 50° C. If a rate law is applicable, its figure should show a linear relationship between $m_{Sr}^{2+}$ and time, the square root of time, or the logarithm of time. The plot of $m_{Sr}^{2+}$ versus time, figure 9, is obviously non-linear so the linear rate law need not be considered further. The plot of $m_{Sr}^{2+}$ versus the square root of time, figure 10, approximates a straight line relationship, especially at 30° C; therefore, the parabolic rate law requires additional evaluation. The plot of $m_{Sr}^{2+}$ versus the logarithm of time, figure 11, shows distinct curvature so the logarithmic rate law is not applicable.

The data were next tested to determine if equation (26) could adequately represent the experimental data. Figure 12 is a plot of $\log R$ versus $\log (m_{Sr}^{2+} - m_{Sr}^{2+})$ and shows that the experimental data for 30° C deviates excessively and possibly systematically from the expected behavior. The data for 40 and 50° C approximate a first order reaction having an average value for $\bar{n}$ of 1.1. Consequently, equation (25) should be used to evaluate a possible first order reaction mechanism.

Figure 13, a plot of $\log (m_{Sr}^{2+} - m_{Sr}^{2+})$ versus time since the start of the experiment, provides a test of the first order hypothesis. Because the experimental data plot in nearly straight lines, it is apparent that the experimental data are essentially compatible with a first order
Figure 9. Plot of the molality of $\text{Sr}^{2+}$ in solution versus time for strontianite dissolution under 0.81 atmosphere $P_{\text{CO}_2}$. The experimental temperatures are 30, 40, and 50$^\circ$C. The time since the start of the reaction is expressed in minutes. A reaction obeying the linear rate law would be represented by a straight line.
Figure 10. Plot of the molality of Sr$^{2+}$ in solution versus the square root of time for strontianite dissolution under 0.81 atmosphere P$_{O_2}$. The experimental temperatures are 30, 40, and 50°C. Time, t, is in minutes since the start of the reaction. A reaction obeying the parabolic rate law would be represented by a straight line. The lines marked A, B, and C result from regression of all of the 30°C data, the first 200 minutes of the 50°C data, and all of the 50°C data, respectively.
Figure 11. Semilog plot of the molality of $\text{Sr}^{2+}$ in solution versus time, in minutes, since the reaction started. The dissolution of strontianite was studied under 0.31 atmosphere of $P_{\text{CO}_2}$ at temperatures of 30, 40, and 50°C. A dissolution reaction which obeys the logarithmic rate law would be represented by a straight line.
Figure 12. Plot of \( \log \frac{R}{t} \) versus \( \log (m_{\text{Sr}^{2+}}) \) for strontianite dissolution under 0.81 atm \( P_{\text{CO}_2} \) at temperatures of 30, 40, and 50° C. This type of plot is used to graphically evaluate \( n \) in equation (18). The values of \( n \) are 1.28 at 30° C, 1.05 at 40° C, and 1.16 at 50° C. The best fit between the experimental data and the postulated kinetic equation is obtained at 50° C.
Figure 13. Plot of $\log (m_{\text{Sr}^{2+}} - m_{\text{Sr}^{2+}})$ versus $t$ for strontianite dissolution under a 0.81 atmosphere $P_{\text{CO}_2}$ at temperatures of 30, 40, and 50° C. This plot is based upon the assumption that the overall reaction is first order ($n = 1.0$) and obeys the first order rate law. Under the experimental conditions the integration constant, $C$, from equation (25) must equal the molality of $\text{Sr}^{2+}$ at saturation, $m_{\text{Sr}^{2+}}$. 
rate controlling process which is dependent upon the concentration of the Sr\textsuperscript{2+} ion. The systematic curvature in the 50\textdegree C data may result from either an erroneous estimate of the solubility at this temperature or from a change of the rate limiting mechanism at later stages. The convex upper surface of the 50\textdegree C data plot could be altered by slightly decreasing the molality of Sr\textsuperscript{2+} at equilibrium. Nevertheless, the results shown in figure 13 constitute a good empirical fit.

Comparison of the molality of the Sr\textsuperscript{2+} ion predicted by the parabolic and first order rate laws provides a method of determining which of these rate laws best fits the experimental data. If the parabolic rate law applies, \( m_{\text{Sr}^{2+}} \) should plot as a straight line as a function of \( t^{\frac{1}{2}} \); the equation used to regress the data for the parabolic rate law was

\[
m_{\text{Sr}^{2+}} = a + bt^{\frac{1}{2}}
\]

(52)

where \( a \) and \( b \) are empirical constants. These values were determined to be \(-0.27 \times 10^{-3}\) and \(0.153 \times 10^{-3}\), respectively. Regression of the 30\textdegree C data for the first order rate law used the equation

\[
\log (m_{\text{Sr}^{2+}} - m_{\text{Sr}^{2+}}) = a + bt
\]

(53)

where the empirical coefficients \( a \) and \( b \) were determined to be \(-2.49\) and \(-1.7 \times 10^{-3}\), respectively. Equations (52) and (53) were used to calculate values of \( m_{\text{Sr}^{2+}} \) at various times as shown in Table 1. These calculated values show that the
<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Experimental $m_{Sr^{2+}}$ x $10^3$</th>
<th>First order rate law $m_{Sr^{2+}}$ x $10^3$</th>
<th>$\Delta (m - m_{exp})$ x $10^3$</th>
<th>Parabolic rate law $m_{Sr^{2+}}$ x $10^3$</th>
<th>$\Delta (m - m_{exp})$ x $10^3$</th>
</tr>
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<tr>
<td>10</td>
<td>0.229</td>
<td>0.31</td>
<td>+0.08</td>
<td>0.21</td>
<td>-0.02</td>
</tr>
<tr>
<td>25</td>
<td>0.455</td>
<td>0.48</td>
<td>+0.03</td>
<td>0.49</td>
<td>+0.04</td>
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<td>50</td>
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<td>0.76</td>
<td>-0.01</td>
<td>0.81</td>
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<td>75</td>
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<td>-0.02</td>
<td>1.05</td>
<td>+0.02</td>
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<td>100</td>
<td>1.272</td>
<td>1.24</td>
<td>-0.03</td>
<td>1.26</td>
<td>-0.01</td>
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<td>150</td>
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<td>+0.00</td>
<td>1.89</td>
<td>-0.05</td>
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<tr>
<td>250</td>
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<td>2.19</td>
<td>+0.01</td>
<td>2.15</td>
<td>-0.04</td>
</tr>
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<td>300</td>
<td>2.391</td>
<td>2.42</td>
<td>+0.03</td>
<td>2.38</td>
<td>-0.01</td>
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</table>
first order and parabolic rate laws provide equally valid equations to express the experimental dissolution of strontianite at 30° C. However, for reactions which approach equilibrium, the parabolic rate law alone cannot be expected to remain valid (cf. Helgeson, 1971, p. 432). This failure of the parabolic rate law is demonstrated in Table 2 by the $m_{\text{Sr}^2+}$ values calculated for strontianite dissolution at 50° C; the departure from the parabolic rate law of the 40° C data is not as great. The parabolic rate law, fitted to the 50° C data for the first 200 minutes of reaction progress (line B, figure 10) with $a = -0.35 \times 10^{-3}$ and $b = 0.217 \times 10^{-3}$, provides a good predictive model for the early dissolution stage; but it is not applicable beyond $t = 200$ minutes. The regressed line for the entire experimental period (line C, figure 10), with $a = -0.07 \times 10^{-3}$ and $b = 0.166 \times 10^{-3}$, does not yield a satisfactory predictive model because of the large systematic errors which it introduces, up to 16% at 100 minutes. The first order rate law was chosen to represent strontianite dissolution because it provides a better fit over the investigated experimental conditions and allows for a molecular interpretation of the rate limiting step.

Witherite Dissolution

Witherite dissolution was investigated using the same experimental conditions and size fraction as employed for strontianite dissolution. The sample weights resulting
<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Experimental $m_{Sr^{2+}} \times 10^3$</th>
<th>First order rate law $m_{Sr^{2+}} \times 10^3$</th>
<th>$\Delta (m - m_{exp})$ $\times 10^3$</th>
<th>Parabolic rate law (line B) $m_{Sr^{2+}} \times 10^3$</th>
<th>$\Delta (m - m_{exp})$ $\times 10^3$</th>
<th>Parabolic rate law (line C) $m_{Sr^{2+}} \times 10^3$</th>
<th>$\Delta (m - m_{exp})$ $\times 10^3$</th>
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<tr>
<td>10</td>
<td>0.313</td>
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<td>+0.14</td>
<td>0.336</td>
<td>+0.02</td>
<td>0.455</td>
<td>+0.14</td>
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<tr>
<td>20</td>
<td>0.589</td>
<td>0.65</td>
<td>+0.06</td>
<td>0.625</td>
<td>+0.04</td>
<td>0.642</td>
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<tr>
<td>40</td>
<td>1.016</td>
<td>1.01</td>
<td>-0.01</td>
<td>1.022</td>
<td>+0.01</td>
<td>0.980</td>
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<td>60</td>
<td>1.353</td>
<td>1.31</td>
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<td>1.331</td>
<td>-0.02</td>
<td>1.216</td>
<td>-0.14</td>
</tr>
<tr>
<td>100</td>
<td>1.885</td>
<td>1.79</td>
<td>-0.10</td>
<td>1.820</td>
<td>-0.05</td>
<td>1.590</td>
<td>-0.30</td>
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<td>150</td>
<td>2.275</td>
<td>2.21</td>
<td>-0.07</td>
<td>2.308</td>
<td>+0.03</td>
<td>1.963</td>
<td>-0.31</td>
</tr>
<tr>
<td>200</td>
<td>2.510</td>
<td>2.49</td>
<td>-0.02</td>
<td>2.719</td>
<td>+0.21</td>
<td>2.278</td>
<td>-0.33</td>
</tr>
<tr>
<td>250</td>
<td>2.672</td>
<td>2.67</td>
<td>+0.00</td>
<td>3.081</td>
<td>+0.41</td>
<td>2.555</td>
<td>-0.12</td>
</tr>
<tr>
<td>300</td>
<td>2.790</td>
<td>2.80</td>
<td>+0.01</td>
<td>3.408</td>
<td>+0.62</td>
<td>2.805</td>
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<tr>
<td>350</td>
<td>2.859</td>
<td>2.88</td>
<td>+0.02</td>
<td>3.036</td>
<td>+0.18</td>
<td>3.250</td>
<td>+0.36</td>
</tr>
<tr>
<td>400</td>
<td>2.890</td>
<td>2.93</td>
<td>+0.04</td>
<td>3.250</td>
<td>+0.36</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
from the splitting procedure, ranging between 25.75 and 26.97 grams, were not as consistent as those for strontianite. However, for the experiments discussed, the maximum deviation from the mean weight was less than 2.12% and the effect is within the analytical tolerances of the pH determinations.

The experimentally determined parameters, pH and specific resistivity, were monitored to determine the reaction progress. Empirical resistivity values were obtained by titrating a 0.116 molal barium hydroxide solution into distilled water under a constant carbon dioxide partial pressure; the $P_{CO_2}$ value was between 0.78 and 0.81 atmospheres at 40°C. A pH reversal and a resistivity break mark the saturation point at a pH of 6.075 with a total barium concentration of $6.62 \times 10^{-3}$ moles per kilogram H$_2$O. A permanent precipitate was formed by further addition of the base (pH = 6.081).

The molalities of all aqueous species and the activities of all aqueous species other than $H^+$ were calculated using the computer program CATCALC as discussed on pages 29 and 30. Appendix B contains a listing of the equilibrium constants used in this study. Figure 14 is a plot of the calculated molality of Ba$^{2+}$ against time for the dissolution of witherite at 30, 40, and 50°C. Stirred and unstirred reactions proceeded at the same rate.

Atomic absorption determinations of the barium concentration were not satisfactory. The sensitivity claimed for the Perkin-Elmer 403 could not be obtained (Billings, 1973,
Figure 14. Plot of the molality of $\text{Ba}^{2+}$ in solution versus time for witherite dissolution under 0.81 atmosphere $P_{\text{CO}_2}$ at temperatures of 30, 40, and 50°C. The time since the start of the reaction, t, is expressed in minutes. A reaction obeying the linear rate law would be represented by a straight line.
personal comm.). This problem of poor precision with barium is common with all atomic absorption equipment according to the U. S. Geological Survey Water Quality Laboratory in Atlanta, Georgia (Liefeste, 1974, personal comm.).

The molal solubility values used for subsequent calculations were estimated by the affinity method of Prigogine, Outer, and Herbo (1948) to be: $7.23 \times 10^{-3}$ moles of $\text{Ba}^{2+}$ per kilogram $\text{H}_2\text{O}$ at $30^\circ\text{C}$ ($\text{pK}_{sp} = 8.48$; equilibrium $\text{pH} = 6.07$); $6.03 \times 10^{-3}$ moles of $\text{Ba}^{2+}$ per kilogram $\text{H}_2\text{O}$ at $40^\circ\text{C}$ ($\text{pK}_{sp} = 8.55$; equilibrium $\text{pH} = 6.07$); and $5.24 \times 10^{-3}$ moles of $\text{Ba}^{2+}$ per kilogram $\text{H}_2\text{O}$ at $50^\circ\text{C}$ ($\text{pK}_{sp} = 8.62$; equilibrium $\text{pH} = 6.07$).

The linear, parabolic, and logarithmic rate laws were graphically tested by plotting the molality of $\text{Ba}^{2+}$ against the appropriate function of time as shown in figures 14, 15, and 16. As was the case with strontianite dissolution, the linear and logarithmic rate laws do not provide a satisfactory fit for the witherite dissolution data. The parabolic rate law provides a good data fit at $30^\circ\text{C}$, but shows increased deviations from linearity at 40 and $50^\circ\text{C}$.

The data were next tested to determine if equation (26) could adequately represent the experimental data. Figure 17 is a plot of $\log R$ versus $\log (m_{\text{Ba}^{2+}} - m_{\text{Ba}^{2+}})$ for witherite dissolution under a 0.81 atmosphere $P_{\text{CO}_2}$ at temperatures of 30, 40, and $50^\circ\text{C}$. The linear portion of the plot is used to graphically determine the value of $n$ in equation (26). The slopes decrease with increasing
Figure 15. Plot of the molality of $\text{Ba}^{2+}$ in solution versus the square root of time for witherite dissolution under $0.81$ atmosphere $P_{\text{O}_2}$ at temperatures of $30$, $40$, and $50^\circ \text{C}$. Time, $t$, is in minutes since the start of the reaction. A reaction obeying the parabolic rate law would be represented by a straight line. The lines marked A, B, and C result from regression of all of the $30^\circ \text{C}$ data, the first $200$ minutes of the $50^\circ \text{C}$ data, and all of the $50^\circ \text{C}$ data, respectively.
Figure 16. Semilog plot of the molality of Ba$^{2+}$ in solution versus time, $t$, in minutes since the reaction started under 0.81 atmosphere of P$\ce{CO_2}$ at temperatures of 30, 40, and 50$^\circ$ C. A dissolution reaction which obeys the logarithmic rate law would be represented by a straight line.
Figure 17. Plot of \( \log R \) versus \( \log (m_{Ba_2^+}^s - m_{Ba_2^+}^t) \) for withite dissolution under 0.81 atmosphere \( P_{CO_2} \) at temperatures of 30, 40, and 50° C. This type of plot is used to graphically evaluate \( n \) in equation (18). The values of \( n \) are 1.3, 1.04, and 0.87 at 30, 40, and 50° C, respectively. There appears to be a systematic decrease in the value of \( n \) with increasing temperature.
temperature, being 1.30, 1.04, and 0.87 at 30, 40, and 50°C, respectively. At all three temperatures, the witherite dissolution data for the first 5 minutes depart from the experimental slope. Since the experimental slopes are approximately 1.0, the data were plotted on a log (m_{\text{Ba}^{2+}}_{s} - m_{\text{Ba}^{2+}}_{t}) versus time diagram, figure 18. The linearity of the data points shows that the first order reaction, as expressed by equation (25), provides a good data fit.

The parabolic and first order rate laws were tested by predicting m_{\text{Ba}^{2+}} as a function of time. As with strontianite dissolution, both rate laws yield adequate results at 30°C for witherite dissolution; however, at 40 and 50°C the first order rate law predicts values of m_{\text{Ba}^{2+}} much closer to the experimental data than does the parabolic rate law. Consequently, the first order rate law was chosen to mathematically express witherite dissolution.

Discussion

Activation Energies

For reactions which obey the first order kinetic rate law, the activation energy of the reaction may be calculated by the time to half saturation method, i.e.

$$\ln (k_T) = \ln (A) - \left( \frac{E_a}{RT} \right)$$  \hspace{1cm} (33)

where $k_T$ is the appropriate rate constant in sec^{-1}, $A$ is an empirical constant, $E_a$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature. The
Figure 18. Plot of $\log \left( m_{Ba^{2+}}^s - m_{Ba^{2+}}^t \right)$ versus $t$ for witherite dissolution under 0.81 atmosphere $P_{CO_2}$ at temperatures of 30, 40, and 50$^0$C. This plot is based upon the assumption that the overall reaction obeys the first order rate law. Under the experimental conditions the integration constant, $C$, in equation (25) must equal the molality of $Ba^{2+}$ at saturation, $m_{Ba^{2+}}^s$. 
empirical reaction orders of strontianite and witherite dissolution are not precisely 1.0 as shown in figures 12 and 17. However, because the first order rate law provides a satisfactory data fit, the time to half saturation method may be employed with sufficient precision to determine whether or not the dissolution reactions are diffusion controlled \([E_a = 4.5 \text{ kilocalories} \ (\text{Liu and Nancollas, 1971})]\).

Figure 19, a plot of \(\ln (k_T)\) versus \(1/T\) (discussed on pages 19 and 20), was constructed for the experimental temperatures of 303, 313, and 323° K. The calculated activation energies, using equation (33), are 8.4 kilocalories per mole for strontianite dissolution and 10.0 kilocalories per mole for witherite dissolution. These activation energies should be accurate to within 10% according to Benson's (1960) error estimating procedure; however, a confidence limit of 15% is preferred to account for any additional errors. This second value is approximately the same as that used by Liu and Nancollas (1971) for the dissolution of gypsum.

Controlling Process Far From Equilibrium

Strontianite dissolution was investigated far from equilibrium at various constant pH values and at various partial pressures of carbon dioxide at a fixed pH. The first series of experiments resulted in data which described the effect of a dissociated acid on the dissolution rate. Under the experimental conditions the dissolution
Figure 19. Plot of the natural logarithm of the overall rate constant versus 1/T. The rate constant, from equation (23) is expressed in reciprocal seconds and is temperature dependent. The temperature, T, is in degrees Kelvin. Use of the Arrhenius equation (33) permits evaluation of the activation energy, $E_a$, from the slope of the best fit lines for the experimental data. The slope, $E_a/R$, for witherite dissolution is $5.0 \times 10^3$ which yields an activation energy of 10.0 kilocalories. The slope for strontianite dissolution is $4.2 \times 10^3$ which yields an activation energy of 8.4 kilocalories.
rate may be expressed as

\[ R = k_1(a_{H^+})^{0.92} + k_2(a_{H^+})^{0.13} \]  \hspace{1cm} (46)

The investigation of the effect of the partial pressure of carbon dioxide showed that the rate of reaction did not increase proportionally with the increase in associated acid (figure 6) and that the data were compatible with the Langmuir adsorption isotherm. The assumption necessary to reach the second conclusion was that the corrected reaction rate, \( \frac{R}{T} \) in equation (51), could be attributed to the change in the partial pressure of carbon dioxide. Combining the separate experiments results in a rate equation of the form

\[ R = k_1(a_{H^+})^{0.92} + k_2(a_{H^+})^{0.13} + \frac{a_F}{1 + b_F P_{CO_2}} \]  \hspace{1cm} (54)

This equation is experimentally valid at 40°C, at pH values ranging from 1.5 to 6.5 when \( P_{CO_2} = 0 \), and at pH = 4.5 when \( P_{CO_2} \) ranges from 0.0 to 0.81 atmosphere.

The observed kinetic phenomena may be interpreted as the reactions of a dissociated acid, \( H^+ \), and an associated acid, \( H_2CO_3 \), at the mineral surface. The mineral surface must have alternating zones of opposite charge because the lattice is not complete at the surface. If the mineral surface is represented symbolically as
where a residual positive charge, +, is associated with the lattice cation, M, and a residual negative charge, -, is associated with the lattice anion group, X. For experiments run under a nitrogen atmosphere, the value of \( \frac{m_{\text{Me}^2+}}{m_{\text{Me}^+}} \) is infinite with respect to strontianite saturation if \( \text{H}_2\text{CO}_3 \) is removed from the system. Therefore, the rate limiting step is interpreted to be the interaction of a hydrogen ion at an anion position on the surface.

\[
\begin{align*}
+ &+ \\
M & M \\
X & X
\end{align*}
+ H^+ \rightarrow \begin{align*}
+ &+ \\
M & M \\
X & X
\end{align*} \rightarrow \begin{align*}
+ &+ \\
M & M \\
X & X
\end{align*} + HX^-
\]

This process should result in a weakening of the ionic lattice bonds and should be followed by removal of the lattice cation, which would result in a layered or stepwise dissolution of the mineral surface. At pH values less than 4.0 hydrogen ion penetration beyond the surface layer probably occurs. Photomicrographs of calcite grains dissolved at varying pH values (Berner and Morse, 1974, p. 118-119) show rounding and pitting of calcite grains immersed in an aqueous solution with was maintained at a pH of 3.9. This hydrogen ion mechanism is associated with the linear region (low pH) of figure 4 which is a plot of reaction rate
reaction rate versus pH.

Similarly, the electrically neutral carbonic acid molecule may be attracted to the mineral surface because of the electrical asymmetry of the molecule. The deprotonation reaction would require the breaking of an O-H bond and the formation of a new O-H bond at the mineral surface, represented as

\[
\begin{align*}
\text{+} & \quad \text{+} \\
\text{M} & \quad \text{M} \\
\text{+H}_2\text{X} & \quad \text{+H}_2\text{X} \\
\text{M} & \quad \text{M} \\
\text{X} & \quad \text{X} \\
\text{M} & \quad \text{M} \\
\text{+} & \quad \text{+} \\
\text{X} & \quad \text{X} \\
\text{M} & \quad \text{M} \\
\text{+} & \quad \text{+} \\
\text{X} & \quad \text{X} \\
\text{M} & \quad \text{M} \\
\text{M} & \quad \text{M} \\
\text{M} & \quad \text{M} \\
\text{M} & \quad \text{M} \\
\text{M} & \quad \text{M} \\
\end{align*}
\]

where \( \text{H}_2\text{X} \) is \( \text{H}_2\text{CO}_3 \) and \( \text{HX}^- \) is \( \text{HCO}_3^- \). With the carbonate ion removed from the lattice, the lattice cation would be less strongly bonded to the mineral surface.

The relative effectiveness of free acid, \( \text{H}^+ \), and associated acid, \( \text{H}_2\text{CO}_3 \), can be compared in terms of reaction rate constants from the experimental data. The rate of acid addition at \( \text{pH} = 4.5 \) under a nitrogen atmosphere was \( 0.109 \text{ ml/min} \) and with \( \text{p}_{\text{CO}_2} = 0.81 \) atmosphere was \( 0.869 \text{ ml/min} \). Assuming a first order reaction for hydrogen ion catalysis yields

\[
0.109 \text{ ml/min} = k_1(a_{\text{H}^+})
\]

for which \( k_1 = 10^{+3.54} \text{ ml/min} \). Subtracting the contribution for this reaction and assuming a first order reaction for \( \text{H}_2\text{CO}_3 \) catalysis yields

\[
0.76 \text{ ml/min} = k_2(a_{\text{H}_2\text{CO}_3})
\]
for which \( k_2 = 10^{+1.61} \) ml/min. Thus the ratio of \( k_1/k_2 \) is approximately 100 to 1 under these conditions.

The normal approach to general acid catalysis for reactions which do not consume the hydrogen ion suggests that the reaction rate shift should be proportional to the activity of the associated acid multiplied by its acid dissociation constant (Benson, 1960). This may be expressed as

\[
R_T\frac{1}{G_{H_2CO_3}} = \frac{G_{H_2CO_3}}{K_{H_2CO_3}^a} a_{H_2CO_3} = k_a(a_{H_2CO_3})
\]  

(55)

where \( G_{H_2CO_3} \) is a constant for acids with the \( H_2CO_3 \) structure, \( K_{H_2CO_3} \) is the first dissociation constant for carbonic acid, \( a_{H_2CO_3} \) is the activity of carbonic acid, \( a \) is an empirical constant such that \( 0 < a < 1 \), and \( k_a \) is the general acid catalysis constant. This constant, \( k_a \), is usually at least two orders of magnitude less than the unassociated acid catalysis rate constant (Laidler, 1950; Hammett, 1970). For \( H^+ \) and \( H_2CO_3 \), \( k_1 \approx 100 k_2 \).

The structure constant, \( G \), is usually close to unity, so for carbonic acid catalysis \( a \) is about 0.31. The standard interpretation of the \( a \) value is that it represents the fractional degree of proton transfer in the transition state. The transition state is thought to consist of the formation of an activated complex such as

\[
\text{CO}_3^{2-} -H-O-C-OH
\]

at the lattice anion position.

The available data imply that for dissolution far from
equilibrium adsorption reactions with two aqueous species, H\(^+\) and H\(_2\)CO\(_3\), limit the dissolution rate. Methods applicable for reactions which do not consume hydrogen ions, true catalytic reactions, suggest that the free hydrogen ion is about 100 times more effective than carbonic acid as a dissolution catalyst.

Controlling Process Approaching Equilibrium

Interpretation of the rate controlling processes from mathematical expressions is an inductive process (Gardiner, 1969). The model proposed to explain experimental data may be completely invalid yet its equation may describe the system investigated with good precision. The following discussion uses the principle of employing the least complicated model consistent with the available experimental data and uses data for the mean experimental temperature of 40\(^\circ\)C. Kinetic expressions compatible with the observed overall reaction rate are discussed, tested against the calculated back reaction, and interpreted with respect to the dissolution mechanism.

Investigations by Plummer (1972) and Berner and Morse (1974) of calcite dissolution in the vicinity of equilibrium have shown that the dissolution rate can be expressed in terms of the activity of hydrogen ion at the time of interest minus the activity of hydrogen ion at saturation, \(a_{H^+}^t - a_{H^+}^s\). Figure 20 shows the relationship between hydrogen ion activity as \(\log (a_{H^+}^t - a_{H^+}^s)\) and \(\log R\) for
Figure 20. Plot of \( \log R \) versus \( \log (a_{H^+} - a_{H^+}) \) for strontianite dissolution at 40° C under 0.81 atmosphere \( P_{CO_2} \). The slopes, which are interpreted to represent molecularities of 2/3, 1/3, and 1/6, are 0.71, 0.31, and 0.14 for lines A, B, and C respectively.
strontianite dissolution. The first order rate law requires that the data as plotted behave linearly and have a slope of approximately one. The data for strontianite dissolution do not fulfill these requirements. By dividing the data into three groups, the linear relationships A, B, and C with slopes of 0.71, 0.31, and 0.14 may be defined. Line C, defined by only four data points, may not be necessary. Each of these linear relationships represent different stages of the reaction progress and are compatible with equation (26) which is used with reactions other than first order where the slope of the line, n, is the assumed molecularity. A plot of the witherite dissolution data, figure 21, lines A, B, and C have slopes of approximately 1, $\frac{1}{2}$, and $\frac{1}{4}$, respectively. The data for strontianite and witherite may be interpreted as having different stages, with different molecularities of the rate limiting mechanisms, related to the adsorption of $H^+$ at the mineral surface.

The linearity of the data and slope of approximately one shown in figures 22 and 23 indicate that the dissolution of strontianite and witherite can be more simply interpreted in terms of reactant removal from the mineral surface. Only one reaction mechanism is required to explain the kinetic behavior over most or all of the experimental range. Furthermore, plots of $\log (m_{Me}^{2+} - m_{Me}^{2+})$ versus time, figures 24 and 25, show that the experimental data are compatible with equation (25) for first order kinetics.
Figure 21. Plot of $\log R$ versus $\log (a_{H^+} - a_{H^+_s})$ for wetherite dissolution at 40°C under 0.81 atmosphere $P_{CO_2}$. The slopes, which are interpreted to represent molecularities of 1, 1/2, and 1/4, are 1.01, 0.52, and 0.26 for lines A, B, and C, respectively.
Figure 22. Plot of log $R$ versus log $(m_{Sr}^{2+}_s - m_{Sr}^{2+}_t)$ for strontianite dissolution at 40° C and $P_{CO_2} = 0.81$ atmosphere. The slope is 1.05.
\[ \log \left( \frac{m_{Sr^{2+}}}{s} - \frac{m_{Sr^{2+}}}{t} \right) \]
Figure 23. Plot of $\log R$ versus $\log (m_{Ba}^{2+}\text{ss} - m_{Ba}^{2+}\text{t})$ for witherite dissolution at 400°C and $P_{CO_2} = 0.81$ atmosphere. The slope is 1.0.
\[ y = \frac{s + a_{\text{ag}} \mu_{\text{ag}}}{(s + a_{\text{ag}})} \log(\frac{E}{d}) \]
Figure 24. Plot of $\log (m_{Sr_{s}^{2+}} - m_{Sr_{t}^{2+}})$ versus time in minutes for strontianite dissolution at 40° C and $P_{CO_2} = 0.8$ atmosphere. The slope of the line, $2.28 \times 10^{-3}$, is the rate constant, $k$, in min$^{-1}$. 
Figure 25. Plot of \( \log (m_{\text{Ba}^2+} - m_{\text{Ba}^2+}^t) \) versus time in minutes for witherite dissolution at 40° C and \( P_{\text{CO}_2} = 0.81 \) atmosphere. The slope of the line, 2.65 \( \times 10^{-3} \), is the rate constant, \( k \), in \( \text{min}^{-1} \).
The first order relationship between \( R \) and \( (m_{Me^{2+}} - m_{Me^{2+}}) \) should also be valid using \( HCO_3^- \) as a variable; since, for the experiments which approach equilibrium, the dissolution reaction is

\[
MeCO_3(s) + H_2CO_3 = Me^{2+} + 2HCO_3^-
\]  

(56)

and electrical neutrality is largely maintained by increasing \( HCO_3^- \) concentrations. Figures 26 and 27 are plots of \( \log R \) versus \( \log (m_{HCO_3^-} - m_{HCO_3^-}) \) and \( (m_{HCO_3^-} - m_{HCO_3^-}) \) versus time for strontianite dissolution at 40\(^\circ\) C. These figures show that there is essentially no difference in the quality of fit for a first order reaction controlled by \( (m_{HCO_3^-} - m_{HCO_3^-}) \) or \( (m_{Sr^{2+}} - m_{Sr^{2+}}) \). The same situation is true for witherite dissolution at 40\(^\circ\) C. The dependence upon \( m_{HCO_3^-} \) might be interpreted as either an adsorption reaction of an associated acid at the mineral surface or combined with \( m_{Me^{2+}} \) dependence, as a precipitation (i.e. back) reaction at the mineral surface.

To test these mechanisms for precipitation control of the overall rate, certain preliminary assumptions were made. They are that the concentration of carbonic acid, \( H_2CO_3 \), is constant throughout the experimental runs and does not cause changes in the reaction rate during these runs. Aqueous diffusion is not considered to be the rate limiting step for the dissolution of strontianite and witherite because of the constant reaction rates under stirred and unstirred
Figure 26. Plot of log $R$ versus log ($m_{\text{HCO}_3}^-_s$ - $m_{\text{HCO}_3}^-_t$) for strontianite dissolution at 40° C and $P_{\text{CO}_2} = 0.81$ atmosphere. The slope, 1.05, is the same as in figure 22, using the variable log ($m_{\text{Sr}^{2+}}_s$ - $m_{\text{Sr}^{2+}}_t$).
Figure 27. Plot of $\log \left( \frac{m_{\text{HCO}_3^-}}{m_{\text{HCO}_3^-}} \right)$ versus time in minutes for strontianite dissolution at 400°C and $P_{\text{CO}_2} = 0.8$ atmosphere. The slope of the line, $2.29 \times 10^{-3}$, is essentially the same as that determined using $\log \left( \frac{m_{\text{Sr}^{2+}}}{m_{\text{Sr}^{2+}}} \right)$. 
conditions and because the activation energies are considerably higher than 4.5 kilocalories per mole expected for aqueous diffusion.

The fact that \( n \) is approximately equal to 1 suggests that a back reaction is effecting the overall reaction rate. The hypothesis employed is that the mechanism for this surface reaction is the same for dissolution and precipitation (principle of microscopic reversibility). There is no experimental proof to support this hypothesis; but, it is the simplest possible assumption and in the absence of negative evidence is preferred to a more complicated one.

The overall reaction rate which is experimentally determined may be expressed as

\[
R = R_f - R_b \quad (57)
\]

where \( R \) is the overall reaction rate, \( R_f \) is the forward reaction rate, and \( R_b \) is the back reaction rate. Two approaches using the rate information determined far from equilibrium were employed to determine the forward reaction rate in order to calculate the back reaction rate. Because data far from equilibrium are available only for strontianite dissolution, the discussion of back reaction rates is restricted to strontianite.

One method of calculating the forward reaction rate is to use the data obtained far from equilibrium. Combining the first and third terms of equation (54) into one constant, the predicted forward rate is
\[ R_f = 3.08 \times 10^{-5} + 8.65 \times 10^{-6} (a_{H^+})^{0.13} \]  

(58)

if one assumes that the back reaction is not yet significant. A second option is to assume that the forward reaction rate is constant, which means that the forward reaction is zero order reaction. This would be the case if the adsorption of \( \text{H}_2\text{CO}_3 \) at the mineral surface were the rate limiting step for the forward reaction. Table 3 contains the calculated values of \( R_B \) resulting from the former approach. The back reaction rate was calculated by subtracting the observed reaction rate from the calculated forward reaction rate. Plots of \( R_B \) versus \( (m_{\text{HCO}_3^-}^s - m_{\text{HCO}_3^-}^t) \), \( m_{\text{HCO}_3^-}^s \), \( (m_{\text{Sr}^{2+}}^s - m_{\text{Sr}^{2+}}^t) \), and \( (a_{\text{Sr}^{2+}} a_{\text{CO}_3^{2-}})/K \) were constructed; the plot of \( (a_{\text{Sr}^{2+}} a_{\text{CO}_3^{2-}})/K \) was included to determine if the principle of mass action, equation (14), might be applicable to the back reaction rate. Furthermore, a plot of \( \log R_B \) versus \( \log (a_{H^+}^t - a_{H^+}^s) \) was made to determine if hydrogen ion activity might be related to the back reaction in a less complicated manner than \( \log R \) versus \( \log (a_{H^+}^t - a_{H^+}^s) \). Both methods of calculating the forward reaction rate yield a non-linear plot for the first 25 minutes of the reaction; however, the calculated back reaction rate using equation (58) provides a better data fit of the variables tested for the period from 30 to 400 minutes.

Figure 28, a plot of \( R_B \) versus \( (a_{\text{Sr}^{2+}} a_{\text{CC}_3^{2-}})/K \), demonstrates that for \( (a_{\text{Sr}^{2+}} a_{\text{CO}_3^{2-}})/K > 0.3 \) a linear relation-
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Figure 28. Plot of $R_b$ versus $(a_{Sr}^{2+} a_{CO_3}^{2-})/K$ for strontianite dissolution at 40°C and $P_{CO_2} = 0.81$ atmosphere. A linear relationship exists between the plotted variables once the reaction has proceeded beyond $(a_{Sr}^{2+} a_{CO_3}^{2-})/K = 0.3$. 
ship exists between three variables. Consequently, the principle of mass action may be applied to the back reaction as equilibrium is approached and be expressed as

$$R_b = k(a_{Sr}^{2+} a_{CO_3}^{2-})$$

(59)

where $k = 4.0 \times 10^5$. Figure 29, a plot of $R_b$ versus $(m_{HCO_3}^3 - m_{HCO_3}^3 t)$, represents the best data fit of the investigated variables. The intercept value, or rate at equilibrium, is slightly lower (7%) than predicted from the experimental values determined far from equilibrium, pH = 4.5.

The maximum value that $(m_{HCO_3}^3 - m_{HCO_3}^3 t)$ can attain is the value at $t = 0$ and is shown by an X at $R_b = 0.0$. A better fit of the data obtained by approaching equilibrium might be possible if the constant and exponent in equation (58) were adjusted; however, this would negate the value of the rate experiments performed far from equilibrium. Figure 30, a plot of $R_b$ versus $m_{HCO_3}^{2-}$, demonstrates that substituting $m_{HCO_3}^{2-}$ for $(m_{HCO_3}^{2-} - m_{HCO_3}^{2-} t)$ does not improve the quality of the data fit.

Because the forward reaction rate appears to be controlled by proton adsorption at the mineral surface, it is logical to assume that the correspondence between the back reaction rate and $m_{HCO_3}^{-}$ represents a deprotonation reaction. In the following discussion, supporting evidence for this conclusion is provided by experiments conducted to determine
Figure 29. Plot of $R_b$ versus $(m_{HCO_3}^s - m_{HCO_3}^t)$ for strontianite dissolution at 40° C and $P_{CO_2} = 0.81$ atmosphere. Projection of the data to saturation $(m_{HCO_3}^s = m_{HCO_3}^t)$ yields a rate of $2.34 \times 10^{-5}$ min$^{-1}$. $R_b$ was calculated using equation (58) as discussed in the text; the calculated value at the equilibrium pH, 5.81, is $2.325 \times 10^{-5}$ min$^{-1}$. This close agreement supports the internal consistency of the values used for $m_s^i$ and $m_t^i$. The symbol X denotes the value of $(m_{HCO_3}^s - m_{HCO_3}^t)$ at time $t = 0$. 
Figure 30. Plot of $R_b$ versus $m_{\text{HCO}_3^-}$ for strontianite dissolution at 40°C and $P_{\text{CO}_2} = 0.81$ atmosphere. Comparison with figure 29 shows that both $m_{\text{HCO}_3^-}$ and $(m_{\text{HCO}_3^-}_{s} - m_{\text{HCO}_3^-}_{t})$ are non-linear with respect to $R_b$ during the first 25 minutes of the dissolution reaction.
the surface charge of calcite.

The zero point of charge, ZPC, of a mineral is the pH at which the mineral surface has an equal amount of positive and negative charges. At lower pH values the surface contains an excess of positive charges which are balanced by an excess of anions in the counter ion layer adjacent to the mineral surface. Theoretically, the ZPC should have as a value of the pH of minimum solubility for a mineral which dissolves congruently (Somasundaran and Agar, 1967). Using various techniques, Somasundaran and Agar (1967) determined that the ZPC for calcite was positive for pH's less than eight and interpreted the surface charge to be controlled by Ca species. The experimental changes in pH which they observed closely agree with those predicted from thermodynamic data. All alkaline earth carbonates would be expected to behave in a similar fashion, and as long as the pH increases during dissolution the surface charge should still be positive (cf. Parks, 1967; Stumm and Morgan, 1970, p. 479). Consequently, the strontianite and witherite mineral surfaces are believed to have been positively charged during the dissolution experiments which approached equilibrium.

Adsorbed ions in the fixed layer on the mineral surface effect the surface charge; however, the charge of the lattice ions which are most abundant on the mineral surface control the overall surface charge (cf. Parks, 1967). Therefore, it is reasonable to assume that Sr and Ba ions
predominate on the mineral surface (cf. Somasundaran and Agar, 1967). If the back reaction at the mineral surface is represented schematically as

\[
\text{\text{+ +}} \quad \text{M M} \quad + \text{HX}^- \quad \rightarrow \quad \text{M M} \quad \text{X X} \quad + \text{H}^+ \\
\text{\text{X X} + + +} \quad \text{M M M M} \quad \text{X X} \quad \text{X X} \quad \text{M M M M M M} \\
\text{\text{X X X X}} \\
\text{\text{X X X X}}
\]

either the adsorption of the bicarbonate ion, \( \text{HX}^- \), or the breaking of an \( \text{O-H} \) bond constitute the rate limiting process.

The positive surface charge suggested for strontianite and witherite under the experimental conditions is in agreement with the rate limiting steps proposed both for dissolution and precipitation. For dissolution, protonation of the \( \text{CO}_3^{2-} \) lattice ion and desorption as \( \text{HCO}_3^- \) would result in a stepwise removal of the surface layer and in a positive surface charge. Similarly, the precipitation mechanism would be dependent upon \( \text{HCO}_3^- \) ion adsorption and deprotonation. The positive surface charge implies that lattice cations are present in abundance and that precipitation is controlled by \( \text{HCO}_3^- \).
SUMMARY AND SUGGESTIONS
FOR FUTURE WORK

This study was undertaken to investigate the dissolution kinetics of barium and strontium carbonates. The major conclusions are:

1) Strontianite and witherite dissolution approaching equilibrium appears to be controlled by a surface reaction for the conditions investigated. Their dissolution rates were not affected by different stirring conditions and their calculated activation energies, 8.4 and 10.0 kilocalories respectively, are considerably greater than would be expected for an aqueous diffusion rate controlling mechanism.

2) Strontianite dissolution, far from equilibrium for pH values ranging from 1.5 to 6.5 and with a continuously renewed N₂ gas phase, may be expressed by the equation

\[
dm_{Sr^{2+}}/dt = k_1(a_{H^+})^{0.92} + k_2(a_{H^+})^{0.13}
\]

where \( k_1 \approx 2.4 \times 10^3 \) \( k_2 \). The rate limiting step is believed to be protonation of the \( CO_3^{2-} \) lattice anion.

3) Strontianite dissolution, far from equilibrium at a pH of 4.5 and with a continuously renewed N₂-CO₂ gas phase, may be expressed by
the following equation employing the Langmuir adsorption isotherm

$$\frac{dm_{Sr^{2+}}}{dt} = k_3 + \frac{aP_{CO_2}}{1 + bP_{CO_2}}$$

where $k_3 = 2.35 \times 10^{-6}$, $a = 1.3 \times 10^{-4}$, and $b = 4.2$. The investigation showed that increasing the concentration of the reaction product, $H_2CO_3$, increased the dissolution rate. This indicates that carbonic acid or one of its ionization products, $HCO_3^-$ and $CO_3^{2-}$, facilitates the dissolution process. If deprotonation of carbonic acid at the mineral surface is the mechanism which facilitates dissolution, then the effectiveness of carbonic acid is approximately $1/100$ that of the hydrogen ion.

4) The back reaction rate for strontianite and witherite dissolution is believed to be controlled by adsorption and deprotonation of $HCO_3^-$ at the mineral surface. The back reaction rate for strontianite dissolution approaching equilibrium was calculated using the dissolution rates obtained far from equilibrium. Both first order variables, $(m_{HCO_3^+} - m_{HCO_3^-})$ and $(m_{Sr^{2+}} - m_{Sr^{2+}}^t)$, provided
satisfactory agreement with the calculated back reaction rate; however, the principle of microscopic reversibility and the postulated surface charge suggest that Sr$^{2+}$ is not the rate limiting species for the back reaction.

Suggestions for future research resulting from this investigation are:

1) Future work should utilize material which has been aged in a saturated solution. This should result in the healing of surface defects and the dissolution and reprecipitation of the very fine material. Control of grain size in this study was not adequate to assign specific rate constants based upon calculated surface areas. Microscopic examination of the samples showed that there was significant retention of -200 mesh material which persisted despite the acid wash and distilled water rinses.

2) The role of H$_2$CO$_3$ as a general acid catalyst for carbonate mineral dissolution should be reinvestigated and compared with other acids having dissociation constants of about the same value.

3) The role of mineral crystallographic structure could be investigated using calcite and aragonite. The late stage shift to a high order mechanism observed by Plummer (1972) for calcite was not
noted for strontianite or witherite which have the aragonite lattice structure.

4) The kinetic expression

\[ \frac{dm_{Me^{2+}}}{dt} = k(a_{H^+}^{t} - a_{H^+}^{s})^{n} \]

should be investigated further for strontianite and witherite dissolution. Use of equipment similar to that described by Morse (1974) should permit experimental determination of the reaction rate at fixed pH values to within 0.05 units of the equilibrium pH. Such experiments could determine if a family of lines, as used with strontianite and witherite dissolution data, truly represent different dissolution stages with different molecularities or if these lines only represent approximations of the reaction rate.
REFERENCES CITED


Carpenter, A. B., and Miller, J. C., 1969, Geochemistry of saline subsurface water, Saline County (Missouri): Chem. Geol., v. 4, p. 135-167.


APPENDIX B. CONSTANTS USED IN PROGRAM CATCALC

<table>
<thead>
<tr>
<th>Reaction</th>
<th>pH at 30°C</th>
<th>pH at 40°C</th>
<th>pH at 50°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O ↔ H⁺ + OH⁻</td>
<td>13.883</td>
<td>13.535</td>
<td>13.262</td>
<td>a</td>
</tr>
<tr>
<td>H₂O + CO₂ (g) ↔ H₂CO₃</td>
<td>1.53</td>
<td>1.64</td>
<td>1.70</td>
<td>a</td>
</tr>
<tr>
<td>H₂CO₃ ↔ H⁺ + HCO₃⁻</td>
<td>6.33</td>
<td>6.30</td>
<td>6.29</td>
<td>a</td>
</tr>
<tr>
<td>HCO₃⁻ ↔ H⁺ + CO₃²⁻</td>
<td>10.29</td>
<td>10.22</td>
<td>10.17</td>
<td>a</td>
</tr>
<tr>
<td>SrHCO₃⁺ ↔ Sr²⁺ + HCO₃⁻</td>
<td>1.20</td>
<td>1.20</td>
<td>1.20</td>
<td>b</td>
</tr>
<tr>
<td>SrCO₃⁰ ↔ Sr²⁺ + CO₃²⁻</td>
<td>3.10</td>
<td>3.10</td>
<td>3.10</td>
<td>b</td>
</tr>
<tr>
<td>SrCO₃(s) ↔ Sr²⁺ + CO₃²⁻</td>
<td>9.37</td>
<td>9.32</td>
<td>9.28</td>
<td>c</td>
</tr>
<tr>
<td>BaHCO₃(s) ↔ Ba²⁺ + HCO₃⁻</td>
<td>1.10</td>
<td>1.10</td>
<td>1.10</td>
<td>b</td>
</tr>
<tr>
<td>BaCO₃⁰ ↔ Ba²⁺ + CO₃²⁻</td>
<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
<td>b</td>
</tr>
<tr>
<td>BaCO₃(s) ↔ Ba²⁺ + CO₃²⁻</td>
<td>8.48</td>
<td>8.55</td>
<td>8.62</td>
<td>c</td>
</tr>
</tbody>
</table>

Constant from equation (4) in text

<table>
<thead>
<tr>
<th>Constant</th>
<th>T = 30°C</th>
<th>T = 40°C</th>
<th>T = 50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.5144</td>
<td>0.5244</td>
<td>0.5354</td>
</tr>
<tr>
<td>B</td>
<td>0.3292 x 10⁻³</td>
<td>0.3310 x 10⁻³</td>
<td>0.3329 x 10⁻³</td>
</tr>
<tr>
<td>${}^8$MeHCO₃⁺</td>
<td>4.25</td>
<td>4.25</td>
<td>4.25</td>
</tr>
</tbody>
</table>
APPENDIX B. (continued)

a - Garrels and Christ, 1965.
b - Estimated from data in Sillen and Martell, 1964.
c - Estimated from affinity plots.
d - Helgesen, 1967.
e - Estimated from mean value for HCO₃⁻ in Klotz, 1964. All other Ψ₁ values from Klotz, 1964.
This dissertation is accepted on behalf of the faculty of the Institute by the following committee:

[V. Lefebvre]
Adviser

Richard A. Beane

Ray R. Brown

5/2/74
Date
PROGRAM CTCALC

PROGRAM CTCALC WRITTEN BY JOHN SONDEREGGER/NEW MEXICO TECH/1972-3
PROGRAM CTCALCIS DESIGNED TO CALCULATE ALL IMPORTANT SPECIES IN
SOLUTION FOR THE DISSOLUTION OF ALKALAIN EARTH CARBONATES.
THE MASTER VARIABLE FOR THESE CALCULATIONS IS PH
THIS PROGRAM ALSO CALCULATES CHEMICAL AFFINITY AND
THE RATE OF CHANGE OF CONCENTRATION, MOALITY & ACTIVITY OF
THE ALKALAIN EARTH OF INTEREST
THE DOMINANT REACTION IS: MECO3 + 2H+ = ME+2 + H2CO3

REAL TITLE, INAME, KNAME, MNAME, PH
REAL LGAI(3),LUCI(3),LGAK(4),L6GK(4),LGAM(2),LGCM(2),MECO3,LIAP
DIMENSION TITLE(8),ACTVT(3),ACTVM(2),CONC1(5),CONC2(14),CONCM(2),INAME(3),KNAME(2),MNAME(2),AZEROI(3),AZEROK(4)
2*AZEROM(2),CHRI(3),CHRG(4),TIME(200),PH(200),ZSO(3),ZSO(4),
3*ARCHI(3),ARCH(4),DENOM1(3),DENOMK(4),DECONI(3),CHRM(2)
*ACTOF(3),ACIFK(4),ACTCFM(2),CHCNI(3),CHCONK(4),FLOGI(3),
*SFLOGK(4),AFFN(2),ALAMI(3),ALAMK(4),BLAMI(3),BLAMK(4),BLAMM(2)
6*AML(200)

**************************************************************************************

I__ OR ___I ARE CATIONIC SPECIES VARIABLES
K__ OR ___K ARE ANATONIC SPECIES VARIABLES
M__ OR ___M ARE NEUTRAL COMPLEX SPECIES VARIABLES
NUMA = NUMBER OF ITERATIONS EMPLOYED
NUMB = NUMBER OF DATA POINTS AS INPUT
MECO3 = INSTABILITY CONSTANT FOR DISSOCIATION OF THE NEUTRAL
SPECIES (ION PAIR) MECO3
BETAH = INSTABILITY CONSTANT FOR MEMC03 COMPLEX
AMOL = MOLALITY OF HCL ACID
AML = NUMBER OF MILLILITERS OF HYDROCHLORIC ACID ADDED
PCO2 = PARTIAL PRESSURE OF CO2 GAS
DELM = TIME INCREMENT
LIAP = ALOGI(ION ACTIVITY PRODUCT)
ARG = ALOG10(O/PK)
QOK = (IAP/K(EQUILIR,1))
MEQOP = OPTION TO INCLUDE THE MEAN VALUE OF THE REACTION AFFINITY
OVER THE REACTION INTERVAL *** IF DESIRED SET MEQOP = 1

**************************************************************************************

READ(5,100)TITLE
WRITE(6,101)TITLE
READ(5,131)T, PKW,PK0, PK1, PK2
WRITE(6,130)T
TK = T + 273.15
RT = (1,987*TK)/1000,0
E=0,100000E-30
WRITE(6,99)
READ(5,102)INAME(I,1),INAME(I,2),AZEROI(I),CHRG(I),BLAMI(I),I=1
13
WRITE(6,103)INAME(I,1),INAME(I,2),AZEROI(I),CHRG(I),BLAMI(I),I=1
13
READ(5,102)KNAME(K,1),KNAME(K,2),AZEROK(K),CHRGK(K),BLAMK(K),K=1
14
WRITE(6,103)KNAME(K,1),KNAME(K,2),AZEROK(K),CHRGK(K),BLAMK(K),K=1
14
C

***ALL FIXED VARIABLES HAVE BEEN INPUT***

WRITE(6,325)
WRITE(6,107)
DO 500 I=1,NUMB
   WRITE(5,124)PHIL,I,TIME(I),AML(I)
500 CONTINUE

WRITE(6,325)
ALCO2 = ALOG10(PCO2)
   DO 610 I=1,NUMB
   DO 501 I=1,3
501 ACTCF1(I)=1.00000
610 ACTCFK(I)=ALG01(PCO2)
   DO 600 N=1,NUMA
   DO 502 K=1,4
502 ACTCFK(I)=1.00000
   ACTCFMM(I)=1.00000
   ACTCFM(2)=1.00000
   DO 600 N=1,NUMA
   DO 503 N=1,4
503 CONTINUE
   CONCK(I)=ACTCFK(I)/ACTCFK(I)
   LGCK(I)=ALG010(CONCK(I))
   CONCK(4)=(AMOL*AML(I)*0.001)/(1.000*(AML(L)*0.001))
   CONCK(4)=CONCK(4)+E
   LGCK(4)=ALG010(CONCK(4))
   ACTVTK(4)=CONCK(4)*ACTCFK(4)
   LGAK(4)=ALG010(ACTVTK(4))
   SUMA=CONCK(1)*CONCK(2)+2*CONCK(3)*CONCK(4)
   ACTVI(1)=10.00*LGAI(1)
   CONCI(1,2)=ACTVI(1)/ACTCF1(1)
   SUMB=SUMA*CONCI(1,2)
   QRALL=LGAK(2)+BETHA
   PBALL=10.00*QRALL
   CRUD=(ACTCFK(2)/ACTCFK(3))*PBALL
   CONCI(2,2)=SUMA/(2.0*CRUD)
   CONCI(3,2)=CONCI(2,2)*CRUD
   ACTVI(2)=CONCI(2,2)*ACTCFK(2)
   ACTVI(3)=CONCI(3,2)*ACTCFK(3)
   DO 504 I=1,3
   LGAI(I)=ALG010(ACTVI(I))
   LGCI(I)=ALG010(CONCI(I,2))
504 CONTINUE
   ACTVTK(1)=10.00*LGAM(1)
   LGCM(1)=ALG010(CONCI(1,2))
   LGAM(2)=LGAI(2)+LGAK(3)+MECO3
   ACTVTK(2)=10.00*LGAM(2)
   LGAM(3)=LGAM(2)+LGAI(2)+LGAK(3)+MECO3
   ACTVTK(3)=10.00*LGAM(3)
ACTVTM(2)=10.00*LGAM(2)
CONCM(2)=ACTVTM(2)/ACTCFM(2)
LGCM(2)=ALOG10(CONCM(2)+2))
DSUM=0.0
DO 508 I=1,3
ZSQI(I)=CHRG(I)**2
CCH(I)=CONCI(I)+2)*ZSQI(I)
508 DSUM=DSUM+CHCONI(I)
DO 509 K=1,4
ZSKK(K)=CHRGK(K)**2
CCHK(K)=CONCK(K)**2
509 DSUM=DSUM+CHCONK(K)
BARI=DSUM*0.58
IF(N. EQ. NUMA) GO TO 600
511 SG1=SG1+0.58
DO 512 I=1,3
ABCI(I)=(-1.00)*AAHAT*ZSQI(I)*SQI
DENOM(I)=1.00*(ABHAT*AZEROI(I)*SQI)
FLG2(I)=(ABCI(I)/DENOM(I))*(0.1)*ZSQI(I)*BARI
ACTCF(I)=10.00*FLG2(I)
512 CONTINUE
DO 513 K=1,4
ABCHK(K)=(-1.00)*AAHAT*ZSKK(K)*SQI
DENOMK(K)=1.00*(ABHAT*AZEROK(K)*SQI)
FLG(K)=(ABCHK(K)/DENOMK(K))*(0.1)*ZSQK(K)*BARI
ACTCFK(K)=10.00*FLG(K)
513 CONTINUE
STOICI=CONCI(1)+4.0*CONCI(2)+CONC(3)+CONC(4)+CONC(5)+CONC(6)+CONC(7)
DO 514 M=1,2
ACTCFM(M)=1.00*(XA*STOICI)+(X8*STOICI)**2
514 CONTINUE
WRITE(6,324)
600 CONTINUE
DELTIM=TIME(L)-TIME(L-1)
WRITE(6,114)DELTIM
WRITE(6,116)BARI
LIAI=LGAK(2)+LGAK(3)
WRITE(6,121)BARI
C
KSP SET BELOW
ARG=LGAI(2)+LGAK(3)+PKSP
WRITE(6,115)ARG
QOK=10.00*ARG
WRITE(6,119)QOK
AFF=2.30258*QOK
WRITE(6,113)QOK
AFF=AFF
IF (QOK > 0.0) GO TO 613
C
MEAN VALUE OF AFFINITY IS USED
AFFM = (AFFN(2) + AFFN(1))/2.0
WRITE(6,129)AFFM
613 CONTINUE
CONCA=CONCI(1)+CONC(2)+CONC(3)+CONC(4)+CONC(5)+CONC(6)
WRITE(6,118)TIME(L),CONCA
DO 505 I=1,3
WRITE(6,110)INAME(I),INAME(I),ACTCFI(I)
505 CONTINUE
DO 506 K=1,4
WRITE(6,110)KNAME(K),KNAME(K),ACTCFK(K)
506 CONTINUE
DO 507 M=1,2
WRITE(6,110)MNAME(M),MNAME(M),ACTCFM(M)
507 CONTINUE
WRITE(6,126)
DO S50 I=1,3
WRITE(6,109)INAME(I),INAME(I),CONCI(I),LGCI(I),ACTVTT(I),
325 FORMAT(2IX*130(*+)),//
326 FORMAT(* *100(*+)),//
STOP
END

/∗
//GO,SYSSN DD ∗