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COMPLEXES AFFECTING THE SOLUBILITY OF CALCIUM CARBONATE IN WATER — PHASE II

By Thurston E. Larson, F. W. Sollo, Jr.
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ABSTRACT

COMPLEXES AFFECTING THE SOLUBILITY OF CALCIUM CARBONATE IN WATER - PHASE II

The water utilities in this country have a tremendous investment in the miles of pipe, valves, and other appurtenances in the water distribution systems. Failure to protect these systems against corrosion and excessive scale formation could necessitate replacement of the distribution systems at an estimated cost of $25 billion. Calculation of the true equilibrium or saturation pH, pH_s , for calcium carbonate and adjustment of the water to that pH is essential to supply water of high quality and to avoid corrosion and scale formation in these water distribution systems. Experience has shown that in some cases the actual pH must be from 0.6 to 1.0 unit above pH_s , as determined from the calcium and alkalinity analyses. Certain complexes may be responsible in part for this fact. The specific objective of this study was to evaluate the dissociation constants of the complexes so that the optimum pH can be more accurately calculated. A titration method was used to measure the effects of complex formation on the pH of reaction mixtures and appropriate computer programs were developed to calculate the dissociation constants. Experimental procedures and results from the determination of dissociation constants for complexes of magnesium, calcium and sodium with carbonate, bicarbonate, hydroxide, and sulfate and a method to utilize these constants in calculating pH_s in public water supplies are discussed.

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INTRODUCTION

The equilibrium or saturation pH for calcium carbonate is an important criterion in the treatment of our water supplies. Calculation of the true pH_S, and adjustment of the water to that pH, are essential to avoid corrosion and incrustation in our water distribution systems and in the household plumbing of the individual customers served. Prevention of deterioration of these systems is important because of both cost of replacement or repair and the fact that corrosion of the system will result in deterioration of water quality after the water leaves the treatment plant.

Distribution system piping is often coal tar lined cast iron, although in recent years there has been a growing interest and use of cement lined pipe, asbestos cement pipe, and reinforced plastics. Because of imperfections in the coal tar linings, cast iron is subject to deposits or incrustation (scale formation).

Either corrosion or incrustation may necessitate cleaning and relining, or, in many cases, replacement of piping. The first effect of corrosion or incrustation that is noted is an increase in head loss through the lines and a major increase in pumping costs. Another effect of corrosion is the appearance of "red water" at the household tap. This "red" water is due to hydrated iron oxide particles which cause the water to be turbid and unsightly and cause staining of household appliances and porcelain ware. Clothing laundered in such water is also stained.

Since the water is used for human consumption, corrosion inhibitors, such as chromates and nitrites, cannot be used. Other treatment chemicals such as polyphosphates and silicates, with or without zinc as an additive, have been used for certain water qualities with an effectiveness ranging from zero to near 100%. The most widely used and economical protection which can be applied is adjustment of the water quality so that a thin deposit of calcium carbonate develops in the pipes. Formation of a thin deposit of $CaCO_3$ requires adjustment of the pH of water to the point at which it is slightly supersaturated with calcium carbonate. Under these conditions, corrosion is retarded by the film of calcium carbonate, but the deposit is not heavy enough to interfere with flow.

Calcium carbonate is only slightly soluble in water. The solubility product, K_s, at 25°C is 4.62×10^{-9}, indicating that if equivalent concentrations of calcium and carbonate ion were formed, only 6.8 mg/l of calcium carbonate would be soluble. The solubility decreases with increasing temperature but increases with increasing mineral concentration.

By analysis, the total calcium concentration, alkalinity, and pH or negative log of the hydrogen ion activity can be determined. The alkalinity, in equivalents, is equal, in most potable water, to the sum of twice the carbonate, plus the bicarbonate and hydroxyl ion concentrations. From these determinations we can calculate the carbonate concentration in the water, and the pH at which the water would be saturated with calcium carbonate, using the following relationships:

$$K_w = (H^+)\ (OH^-)$$

$$K_1 = (H^+)\ (HCO_3^-)/(H_2CO_3)$$

$$K_2 = (H^+)\ (CO_3^=)/(HCO_3^-)$$

$$K_s = (Ca^{++})\ (CO_3^=)$$

The discussion above assumes that calcium and the various forms of alkalinity appear only as the free ion, or as a solid, $CaCO_3$. However, there is evidence in the literature, and in this report, that there are also complexes of these ions which are soluble, appearing in the gross analyses, but undissociated, so that they are not effective in the solubility equilibrium. The complexes which are potentially important are those formed by the common cations, Ca^{++}, Mg^{++}, and Na , with the $CO_3^{=}$, HCO_3^{-}, OH , and $SO_4^{=}$ anions.

Experience in the water works industry has shown that it is often necessary to adjust to a pH value 0.6 to 1.0 pH units higher than the calculated pH of saturation for waters with low hardness and alkalinity in order to minimize corrosion and yet not cause excessive scale formation (1). The required difference between the adjusted pH and the saturation value depends upon the water analysis. This difference is particularly high in cases of high magnesium or sulfate concentrations. It appears probable that this effect is largely due to formation of the complexes $CaSO_4^{0}$, $CaCO_3^{0}$, and $MgCO_3^{0}$, with minor effects from the other complexes mentioned above.

Although complexes are completely soluble, they are not ionized, so that ions combined in the complexes are not effective in the various chemical equilibria associated with calcium carbonate solubility. However, the usual chemical analysis will include the portion complexed due to decomposition of the complex during analysis. Laws of mass action govern the formation of these complexes, so that the degree of complex formation is usually denoted by the dissociation constant, such as

$$K_{dMgCO_3^{0}} = (Mg^{++})\ (CO_3^{=})/(MgCO_3^{0}).$$

This equation indicates that the dissociation constant for the magnesium carbonate complex is equal to the product of the activities of the free magnesium and carbonate ions divided by the activity of the complex. With the use of the activity coefficients of the individual ions, this K_d may be converted to a K_d' based on concentrations of the ions in equilibrium. This "constant" is valid only for a specific temperature and ionic strength.

This project was designed to evaluate the true thermodynamic dissociation constants for a number of complexes at temperatures ranging from 5° to 25°C and at ionic strengths in the range normally found in potable public water supplies, i.e., .002 to .02. Although a number of other investigators have developed dissociation constants for each of the complexes studied, most of their work was conducted at room temperature (~25°C), and ionic strengths too high to be directly applicable to public water supplies. A few also based their calculations on concentrations rather than the ion activities as used in this study. Table 1 contains a list of pK_d ($-\log K_d$) values determined in this study at 25°C and the values reported by other investigators (2-26). An exhaustive compilation of dissociation constants was prepared by Sillen and Martell (27). Other sources for the constants evaluated in this study include compilations by Davies (28), Garrels and Christ (29), and Thrailkill (30). Thrailkill lists a number of the constants and applies these values in calculating the degree of saturation of several waters with respect to both calcite and dolomite.

The constants developed in this work were used in the calculation of pH_s and driving force index (DFI) of several waters. The method and sample results are given in a later section.

EXPERIMENTAL DETAILS

Reagents

Reagent-grade chemicals, meeting American Chemical Society specifications, were used whenever commercially available. Additional chemicals used were the highest grade available.

The water used in making up all reagent solutions and buffers was prepared by passing the laboratory's main supply of deionized water through a mixed-bed ion exchange column consisting of 20-50 mesh Amberlite IR 120-H and Amberlite A284-0H. This "polishing" technique gave water which had a specific conductance of 1×10^{-7} ohm^{-7} cm^{-7} and was free from carbonate and carbon dioxide.

The reagent solutions were stored in containers with stoppers which were fitted with an absorption tube filled with Ascarite to absorb CO_2 from the entering air. As an additional precautionary measure, Ascarite was used as a "scrubber" to remove any impurities from the N_2 gas before it was bubbled into the titration beaker.

Stock Solutions

1. Standard buffer solutions were prepared in accordance with specifications recommended by the U.S. National Bureau of Standards.. The buffers were checked against Beckman standard and precision buffer solutions. The salts were dried for two hours at 110°C before weighing.
    a. Phthalate buffer, .05M solution, pH 4.01 at 25°C:

        10.211g $KHC_8H_4O_4$ per liter

b. Phosphate buffer, .025M solution, pH 6.865 at 25°C:

$3.40g\ KH_2P0_4 + 3.55g\ Na_2HPO_4$ per liter

2. Potassium perchlorate, $KClO_4$, approximately 0.1M, using an atomic absorption method to determine the K concentration:

    $13.86g\ KClO_4$ per liter with 6.93×10^{-6} M KOH added to adjust the pH to 6.8 ± 0.2

3. Magnesium perchlorate, $Mg(ClO_4)_2$, approximately 0.24M, standardized . by the EDTA titrimetric method (31):

    $53.6g\ Mg(ClO_4)_2$, anhydrone, per liter with 4×10^{-4} M $HClO_4$ added to adjust the' pH to 6.6 ± 0.2

4. Calcium perchlorate, $Ca(ClO_4)_2.6H_2O$, standardized by the EDTA titrimetric method (31):

    a. approximately 0.3M:

        $100g\ Ca(ClO_4)_2.6H_20$ per liter with 4×10^{-6} M KOH added to adjust the pH to 6.6 ± 0.2

    b. approximately 0.075M:

        $25g\ Ca(ClO_4)_2.6H_20$ per liter with 7×10^{-7} M KOH added to adjust the pH to 6.6 ± 0.2

5. Sodium perchlorate, $NaClO_4$, approximately 0.1 M, using an atomic absorption method to determine the concentration of Na^+:

    $12.25g\ NaClO_4$ per liter with 5×10^{-6} M $HClO_4$ added to adjust the pH to 6.6 ± 0.2

6. Potassium carbonate, K_2CO_3, primary standard 0.1M:

    $13.821g\ K_2C0_3$ per liter

7. Perchloric acid, $HClO_4$, approximately 0.23N:

    20 ml of 11.75 N $HClO_4$ was diluted to 1 liter, then standardized against 0.2N primary standard K_2CO_3

8. Potassium hydroxide, KOH, approximately 0.04M:

    2.5g KOH per liter, diluted 1 + 1, then standardized against .02N H_2SO_4 to a phenolphthalein endpoint

9. Potassium sulfate, K_2SO_4, approximately 0.2M, using the gravimetric method (31) to determine the $SO_4^=$ concentration:

    34.86g K_2SO_4 per liter with 9×10^{-6} M KOH added to adjust pH to 7.0 ± 0.2

Equipment

A Beckman research model pH meter, equipped with a Beckman #39000 research GP Glass electrode and a Beckman #39071 frit-junction calomel (with sidearm) reference electrode, was used to measure the pH of the solutions. The relative accuracy of the pH meter is specified by the manufacturer to be ±.001 pH.

The titration cell used in these experiments consisted of a 500-ml Berzelius beaker fitted with a size #14 rubber stopper. Mounted in the stopper are pH measuring electrodes, a 10-ml micro burette, a gas bubbler, and a reagent addition access tube. A constant temperature bath and cooler suitable for work in the 2°C to 50°C range was used to control the temperature in a second, smaller Plexiglas water bath surrounding the titration cell. In the titration experiments, temperature was controlled to ±0.1°C. Samples were stirred gently throughout each experiment by means of a magnetic stirrer. A hypodermic syringe was used to transfer a known amount of CO_2-free demineralized water into the titration beaker prior to the addition of the desired salts.

Procedures

A titration procedure was used to measure the dissociation constants of the complexes studied. For most of this work, either calcium, magnesium, or sodium perchlorate was the titrant added to a solution containing the anion of the complex being evaluated. A variation of this general titration procedure was used to measure the $CaSO_4^0$ constant. Determination of dissociation constants for the carbonate and sulfate complexes is based on the change in pH and is complicated by the formation of the corresponding hydroxide complex ($MgOH^+$, $CaOH^+$, or $NaOH^\circ$). Titrations of solutions with no carbonate or bicarbonate were used to determine dissociation constants for the hydroxide complexes. The bicarbonate complex also had to be considered in the carbonate complex determinations.

In the titrations with carbonate present, the change in pH noted upon addition of $Mg(ClO_4)_2$, for example, includes: (1) that due to change in ionic strength, and (2) that due to complex formation. In effect, each mol of MgOH or $MgCO_3^0$ formed removes a mol of 0H~ from the equilibrium. The formation of $MgHCO_3^+$ has an indirect effect on the pH since it reduces the total carbon dioxide in the equilibrium.

In all of the experiments in this study, potassium perchlorate was added as required for ionic strength adjustment. Carbon dioxide free water was used and precautions were taken to avoid gain or loss of carbon dioxide. Samples were stirred gently throughout the experiment and temperature was accurately controlled. Under these conditions, equilibrium pH was the only measurement required.

Prior to each titration, the pH electrodes were calibrated in the appropriate standard buffer, at the temperature of the test. The rubber stopper electrode assembly was then tightly fitted into a 500-ml Berzelius beaker. The beaker was purged with N_2. A known volume of water was transferred into the beaker and after the temperature of the water reached the desired level, the desired salts were added. The initial volume of sample was such that a minimum of head space remained. Once all the salts had been added and a constant desired temperature was reached, the reagent access hole in the rubber stopper assembly was closed and N_2 bubbling discontinued. An initial pH was recorded and the titration was begun within this closed system.

A slight variation of this general procedure was used in the $MgHCO_3^+$, $CaHCO_3^+$, and $NaHCO_3^0$ experiments. For these bicarbonate complex experiments, pure CO_2 was bubbled through water, then through a dry test tube before bubbling into the sample solution. When the $HCO_3^- - CO_3^=$ equilibrium was reached, as denoted by a stable pH over a period of several minutes, the titration was begun.

CALCULATIONS

The calculations required are rather complex, hut can he handled by computer methods. The required relationships have been derived and appropriately programmed. Seven of the equilibria involved in the calculation of calcium hydroxide, bicarbonate, carbonate, and sulfate are:

1.	H_2O	$\rightleftarrows$	H^+	+	OH^-	K_w
2.	H_2CO_3	$\rightleftarrows$	H^+	+	HCO_3^-	K_1
3.	HCO_3^-	$\rightleftarrows$	H^+	+	$CO_3^=$	K_2
4.	$CaOH^+$	$\rightleftarrows$	Ca^{++}	+	OH^-	K_{dCaOH^+}
5.	$CaHCO_3^+$	$\rightleftarrows$	Ca^{++}	+	HCO_3^-	$K_{dCaHCO_3^+}$
6.	$CaCO_3^0$	$\rightleftarrows$	Ca^{++}	+	$CO_3^=$	$K_{dCaCO_3^0}$
7.	$CaSO_4^0$	$\rightleftarrows$	Ca^{++}	+	$SO_4^=$	$K_{dCaSO_4^0}$

Similar equilibria with magnesium and sodium exist.

If we examine reactions 4 and 6 above, in titrations with $Ca(ClO_4)_2$, added Ca^{++} causes formation of $CaOH^+$ and $CaCO_3^0$ complexes, reducing the concentrations of OH and $CO_3^=$ anions. This causes a further ionization of H_2O, HCO_3^-, and H_2CO_3, increasing the H concentration to the point where equilibrium is again established. A portion of the added Ca is removed from the equilibrium by the complexing process.

The value of the dissociation constant for the CaOH complex (reaction 4), in the absence of CO_2, is easily calculated with a known value for K_w, the concentration of calcium added, and the initial and final pH measurements. Since few ions are involved in the equilibrium, a fairly simple computer program was sufficient to calculate K_{dCaOH^+} (Table 2). Once the value for the K_{dCaOH^+} complex has been determined,

dCaOH

then it is used along with the other constants K_w, K_1 and K_2 to determine a value for the $K_{dCaCO_3^0}$ complex.

In the remainder of this report, dissociation constants of the complexes are shown as K_{dXY}, where X represents the cation and Y the anion involved, with no indication of the valence of the complex. This avoids confusion in some of the equations. For example, K_{dMgHCO_3} represents the dissociation constant of the $MgHCO_3^+$ complex.

The thermodynamic constants K_w, K_1, K_2, K_s and the constants for the complexes studied in this project are based on ion activities, and vary with temperature, but not with ionic strength. Since the calculations were based at least partially on mass balances, most of the quantities had to be calculated as concentrations. The dissociation constants thus developed were corrected for ionic strength with the appropriate activity coefficients, as in the following example:

$$K_{dCaOH} = (K'_{dCaOH})\ (\gamma_{Ca^{++}})\ (\gamma_{OH^-})/(\gamma_{CaOH^+})$$

K denotes the true thermodynamic constant, K is the constant for a particular ionic strength based on concentrations, and γ is the activity coefficient of the particular ion.

Ion activity coefficients, γ_i, were calculated with the extended Debye-Hückel equation (32):

$$-\log(\gamma_i) = A\ z_i^2 \sqrt{\mu}\ /\ (1 + B\ a_i \sqrt{\mu})$$

where z is the valence or change on the ion, μ is the ionic strength of the solution, and a is the size of the ion. A and B are constants dependent upon the dielectric constant, ε, and the absolute temperature, T. Approximate values for a., the ion size parameter of a number of selected ions, have been estimated by Kielland (33) and used by Butler (32) to calculate values of single ion activity coefficients at various ionic strengths. The values of "a" for the individual ions used in this project are listed below:

ion	a_i
H^+	9
OH^-	3
Na^+, HCO_3^-, $SO_4^=$	4
$CO_3^=$	5
Ca^{++}	6
Mg^{++}	8

An ion size parameter of six was used for the univalent charged complexes (MgOH , CaOH , $MgHC0_3^+$, $CaHCO_3^+$, $NaCO_3^-$), while the activity coefficient for uncharged ion-pairs was assumed to be unity. The ionic strength of a solution is defined as one-half the summation of the products of the molal concentrations of the ions in solution and the square of their respective valences, $\Sigma(C z_i^2)/2$.

Ion activity represented by parenthesis, e.g. (Ca), is related to ion concentration by the relation (Ca) = γ_{Ca}++ $[Ca^{++}]$ where the brackets [ ] denote concentration in moles per liter and γ is the activity coefficient as calculated by the extended Debye-Hiickel equation.

Table 3 is a listing of the constants for A and B, K_w, K_1, K_2, and K_S and the reference sources (32, 34-38) and equations used for calculating these constants at 5, 15, and 25°C. The K values in Table 3 are related to the corresponding K values by the following relationships:

$$K_w = (K'_w)\ (\gamma_{H^+})\ (\gamma_{OH^-})$$

$$K_1 = (K'_1)\ (\gamma_{H^+})\ (\gamma_{HCO_3^-})/(H_2CO_3)$$

$$K_2 = (K'_2)\ (\gamma_{H^+})\ (\gamma_{CO_3^=})/(\gamma_{HCO_3^-})$$

$$K_s = (K'_s)\ (\gamma_{Ca^{++}})\ (\gamma_{CO_3^=})$$

Corresponding pK values can be calculated by taking the negative logarithm of the K value, i.e., pK = -log K.

The general format of the computer programs written to calculate the dissociation constants for the various complexes studied was the same. This format is followed in the program for the calculation of K_{dCaOH}, and dCaOH' is listed in Table 2. Briefly, the input data from the titration experiments include the temperature (°C), the necessary constants from Table 3, the initial reagent concentrations added, the initial volume of solution (VI), and the measured pH (PHR), prior to the addition of standard titrant of known molarity (M). From this input data, an initial estimate of the ionic strength of the solution is calculated, i.e., MUR = [KCL] + [KOH]. Subsequently, in section one of the program, activity coefficients for the various ions are calculated and are used in turn to calculate K and ion concentration values. The ionic strength is then refined with use of these calculations which define the initial or reference condition.

In section two of the K_{dCaOH} program, for each addition of titrant and the resulting change in pH, volume corrections are applied to the calculation of the ionic strength, ion activity coefficients, and concentrations of the free and the associated ions in the solution. In titrations with neutral salts, such as $Ca(ClO_4)_2$, the calculations are based on the fact that, except for the volume change and excluding the effect of complex formation, the alkalinity remains constant. Thus in CO_2-free solutions titrated with Ca^{++}, any decrease in the alkalinity represents complex formation. If the reference concentrations, without any complex, are represented by $[OH_R^-]$ and $[H_R^+]$, and the ratio of initial to final volume by VC, then our definition of alkalinity becomes,

$$ALK = VC\ ([OH_R^-] - [H_R^+]).$$

In the final condition then, the concentration of the complex, CaOH , is defined as:

$$[CaOH^+] = ALK - [OH^-] + [H^+]$$

As in the calculation of the ion concentrations in the reference condition, this calculation requires an initial estimate of the ionic strength, MU = MUE + 3(ML) (M) / (VI), which is refined by repetitive calculation of the individual ion concentrations as well as of the complex.

After the concentrations of the CaOH complex and the individual ions forming this complex were determined, K_d', the constant for a particular ionic strength based on these concentrations, was calculated as in the following example:

$$K'_{dCaOH} = [Ca^{++}]\ [OH^-]/[CaOH^+]$$

The dissociation constant, K_d, for the CaOH complex is then calculated in terms of activities by using the relationship between ion, ion-pair activity coefficient values, and the calculated K_d', i.e.,

$$K_{dCaOH} = (K_{dCaOH}') \, (\gamma_{Ca^{++}}) \, (\gamma_{OH^-})/(\gamma_{CaOH^+}).$$

In solutions containing carbonates and bicarbonates, a somewhat more complicated expression is required to determine the quantity of complex formation. In such solutions, the quantity of complex formation was determined from changes either in alkalinity by the usual definition, or by changes in the quantity (alkalinity - total carbon dioxide). The latter is equivalent to [0H~ - H + $CO_3^=$ - $H_2CO_3^\circ$] in the original solution, and [0H~ - H + $CO_3^=$ - $H_2CO_3^\circ$ + CaOH + $CaCO_3^\circ$] in the final solution, after addition of calcium. Thus the formation of one mol of the hydroxide or carbonate complex results in a depletion of (alkalinity - total carbon dioxide) by one mol.

The concentrations of these ions were calculated as functions of the original carbonate addition, K_1', K_2', K_w', and the pH, both in the initial condition, and after addition of the titrant.

The calculations were considered to be reliable when the dissociation constants obtained for a majority of the points along the titration curve fell within a fairly narrow and acceptable range of values. For each complex studied, the final dissociation constant, K_d, was calculated as an average, $\bar{x}$, of a number of observations, n. Within each experiment any one calculated K_d value which was markedly different from the others was not included in the calculation of the average K . The standard deviation, a, was determined by the formula:

$$\sigma = \pm \sqrt{\Sigma(\bar{x} - x)^2 / (n - 1)}$$

where x = each individual observed K_d value,

$\bar{x}$ = the average K_d value of a known number of observations,

n = the number of observed values.

The determination of the dissociation constants of the complexes studied is dependent upon accuracy in pH measurements. The results of a number of sensitivity studies indicated that an error made in the standardization of the pH meter, reflected by a constant error in both the initial and final pH readings, produces a minimal error in the calculated K_d. However, if we assume that the initial pH reading is correct and assume an error in the final pH reading, the resulting error in K_d can be quite substantial. The following example taken from a $MgSO_4^\circ$ test in which the final pH alone was varied by ±.001 units illustrates this degree of sensitivity:

initial pH = 10.609

ml $Mg(ClO_4)_2$ added	final pH	Calculated K_{dMgSO_4}	% error in K_d
5.07	10.536	9.78×10^{-3}	
5.07	10.537	8.80×10^{-3}	-10%
5.07	10.535	1.10×10^{-2}	+12%

RESULTS

The complexes evaluated in this study are discussed individually in the following pages. Values for the dissociation constants for these complexes at three temperatures and information regarding standard deviation values, composition of the initial sample solution, and titrant have been compiled and listed in Table 4.. It should be mentioned again that in this study we (1) used a titration procedure and measured the change in pH to determine the dissociation constants, (2) calculated the values of the constants in terms of activity, and (3) determined the final K_d value for each complex by taking an average of the most consistent results.

In general it was not difficult to determine a reasonable range of K, values within each experiment and to eliminate outliers before calculating an average K_d value for each complex. It was not unexpected that the outliers most frequently resulted from the first and second aliquot additions of titrant. This simply indicated that the quantity of complex formed early in the titration is low and the calculated result is, therefore, more sensitive to the small experimental errors which are inherent in the determination of the constants. Slight impurities or contaminants in the reagent solutions, errors in the measurement of titrant, and errors in pH are only a few examples of such experimental uncertainties.

Hydroxide Complexes

The hydroxide complexes, $MgOH^+$, $CaOH^+$, $NaOH^\circ$, were evaluated by titration of KOH-$KClO_4$ solutions with either standard magnesium, calcium, or sodium perchlorate solution.

<u>$MgOH^+$</u>. During the first few months of this project, various methods and procedures for evaluating the complexes were examined. Two titration procedures were tested to determine K_{dMgOH} at 25°C. In one set of tests, $Mg(ClO_4)_2$ - $KClO_4$ solutions were titrated with a standard KOH solution. The K_d calculated from these data was 8.36×10^{-3} ($pK = 2.08$). In a second experiment, KOH - $KClO_4$ solutions were titrated with a neutralized solution of $Mg(ClO_4)_2$. The K_{dMgOH} value resulting from this test was 8.17×10^{-3} ($pK_d = 2.09$). The second procedure of titrating with a neutral solution of magnesium perchlorate was chosen because the results were more reproducible. Taking such precautionary measures as frequent preparation and standardization of the stock reagent solutions (particularly KOH), constant protection of these solutions with CO_2 absorbents, and purging the beaker and the test solutions with nitrogen reduced the primary problem of CO_2 contamination to a minimum.

The value determined in this study at 25°C is in good agreement with Gjaldbaek's (3) K_{dMgOH} of 7.95×10^{-3} ($pK_d = 2.10$) at 18°C, but in poor agreement with either Stock and Davies (2) or with Hostetler's (4) values of 2.63×10^{-3} and 2.51×10^{-3}, respectively.

Gjaldbaek titrated solutions of $MgCl_2$ saturated with magnesium hydroxide. Stock and Davies and Hostetler titrated $MgCl_2$ solutions with $Ba(OH)_2$. Stock and Davies, working with solutions ranging in pH from 7.99 to 9.49, did not take particular care to exclude CO_2 from their experiments. They calculated ion activity coefficients by use of the Davies equation,

$$-\log(\gamma) = 0.5z^2 \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2\mu\right).$$

Hostetler tried to exclude all CO_2 from his experiments by purging the airtight reaction vessel with nitrogen throughout the titration. His work was done at pH levels ranging from 8.4 to 10.7 and ionic strengths from .023 to 0.14. Hostetler used the same extended Debye-Hückel equation that was used in this study for the evaluation of ion activity coefficients. He also calculated a constant for MgOH from one set of brucite solubility experiments explaining that the results from the first two sets of experiments were "erratic and inconclusive". His average pK, value from his solubility test was 2.81 ($K_d = 1.55 \times 10^{-3}$) but the internal disagreement in the five points that he averaged ranged from a $K_{dMgOH} = 1.2 \times 10^{-3}$ to 2.45×10^{-3} — a two-fold difference. Hostetler states a preference for the titration method for determining K_{dMgOH}. However, within his four titration experiments (26 data points which averaged to a K_d value of 2.95×10^{-3}, $pK_d = 2.53$), the disagreement in values ranged from $K_d = 1.90 \times 10^{-3}$ ($pK_d = 2.72$) to 4.36×10^{-3} ($pK_d = 2.36$). This is again a variation by a factor of two. Hostetler concludes that the value of the dissociation constants for MgOH can be estimated no closer than 1.4×10^{-3} to 4.5×10^{-3}, or a $pK_d = 2.60 \pm .25$.

The value of K_{dMgOH} obtained in this study at 25°C is approximately three times greater than Hostetler's value. Since Hostetler's data should be considered the result of a reasonable and thoughtful study, perhaps the soundest conclusion that can be drawn from these differences is that the constant for MgOH cannot be determined with a high degree of accuracy with the methods and equipment available at this time. As a check on possible causes for the difference between Hostetler's constant and the constant determined in this work, Hostetler's value for A and B (.5085, .3281) and for a_{OH^-} and $a_{Mg^{++}}$ (3.5 and 6.5) were used to recalculate data from this study. These calculations showed a negligible increase of about 1.5% in the average K_{dMgOH} at 25°C.

The determination of K_{dMgOH} in this project was conducted at a range of ionic strength from .005 to .02 and a range of pH from 9.9 to 11.3. Pertinent data from two titrations are listed in Table 5.

$\underline{CaOH^+}$. A comparison of the constant from this study ($K_d = 4.17 \times 10^{-2}$) with values from other sources (Table 1) shows good agreement with the value of Gimblett and Monk (5) ($K_d = 4.30 \times 10^{-2}$) at 25°C. Gimblett and Monk also gave a pK_d value of 1.34 ($K_d = 4.60 \times 10^{-3}$) at 15°C and Thrailkill (30), using their work as his source for pK_{dCaOH}, gives an extrapolated value of 1.31 ($K_d = 4.90 \times 10^{-2}$) at 5°C. Bates et al. (6) summarize the work done by a number of investigators, giving their own values for the CaOH constant as $K_d = 5.4 \times 10^{-2}$ or 7.1×10^{-2} ($pK_d = 1.27$ or 1.15), thereby supporting their observation that a number of uncertainties are involved in the determination of this constant.

In this study, the constant for CaOH was evaluated in a range of ionic strength from .008 to .032 and pH from 10.6 to 11.8. Table 6 contains two sets of titration data for K_{dCaOH} at 25°C.

$\underline{NaOH^\circ}$. In this work, the range of pH of the solutions was 10.1 to 11.1 and the range of ionic strength was .007 to .020. Data from two titrations at 25°C are shown in Table 7. The $NaOH^\circ$ constant determined in this study is 1.77×10^{-1} ($pK_d = 0.75$) at 25°C and is considerably smaller than that reported by other sources.

Darken and Meier (7) estimated a K ~ 5 for $NaOH^\circ$ (pK ~ -0.7) by conductivity measurements but do not regard these data as very conclusive evidence of the formation of this complex. From kinetic studies, Bell and Prue (8) calculated a similar constant for $NaOH^0$ also noting that activity coefficients suggest that NaOH is incompletely dissociated. Gimblett and Monk (5) used data from the EMF measurements of two eariler sources, Harned and Mannweiler (39) and Harned and Hamer (34), to calculate the following average K_{dNaOH} values at 5, 15, and 25°C:

6.5 ± 0.9 and 2.8 ± 0.4 at 5°C
6.5 ± 0.9 and 2.9 ± 0.2 at 15°C
5.9 ± 1.4 and 3.7 ± 0.3 at 25°C

The first value from each set refers to Gimblett and Monk's calculations using the data of Harned and Mannweiler (39), and the second to that from Harned and Hamer (34). Gimblett and Monk attribute the variations in their results to large random errors induced by small experimental uncertainties. This is a reasonable explanation since a large dissociation constant indicates that the quantity of complex formed is small and therefore more sensitive to errors inherent in the determination of the constant.

Carbonate Complexes

The dissociation constants of the carbonate complexes, $MgCO_3^0$, $CaCO_3^0$, $NaCO_3^-$, were determined by titration of carbonate-bicarbonate solutions with magnesium, calcium, or sodium perchlorate solutions. The assumption made was that a solution of $KClO_4$ and K_2CO_3 (or total CO_2) treated with $HClO_4$ will produce added $KClO_4$ and a mixture HCO_3^- and $CO_3^=$. The concentrations of HCO_3^- and $CO_3^=$ will vary with both pH and total CO_2. The change in pH noted upon titrating with $Mg(ClO_4)_2$, as an example, results from change in ionic strength and complex formation. The hydroxide complex is also important to the carbonate complex equilibrium. For example, neglecting the effect of the $MgOH^+$ complex, the constant for $MgCO_3^0$ at 25°C was found to be 1.15×10^{-3} ($\sigma = \pm .000047$) as compared to the value listed in Table 4 (1.26×10^{-3}, $\sigma = \pm .00003$) which does include the effect of the corresponding MgOH -complex. If accurate values are to be obtained for the carbonate constants, the formation of the corresponding hydroxide complex should be accounted for in the calculations.

$MgCO_3^0$ The range of pH in this work was 9.4 to 10.8 and the range of ionic strength was .004 to .025. At 25°C the constant for $MgCO_3^0$ determined in this study is 1.26×10^{-3} ($pK_d = 2.9$) and is ~ 2 to 3 times larger than values reported by the sources listed in Table 1, i.e., Greenwald (9)» Garrels et al. (10), and Nakayama (11). The results from two titration tests at 25°C are listed in Table 8.

From titration experiments in the pH range of 6.7 to 9.8 and μ of .152, Greenwald calculated an apparent constant, K_d', of 4.26×10^{-3} for $MgCO_3^0$ at 22°C based on concentrations. By application of the proper activity coefficients for correction to zero ionic strength, Greenwald's value for the $MgCO_3^0$ complex is calculated as:

$$K_{dMgCO_3} = (K'_{dMgCO_3})\,(\gamma_{Mg^{++}})\,(\gamma_{CO_3^=})/(\gamma_{MgCO_3^0})$$

$$= 4.26 \times 10^{-3} \times .41 \times .33/1.03 = 5.6 \times 10^{-4}$$

This may be compared with the value of 4.0×10^{-4}, determined by Garrels et al. by measurement of the change in pH of a Na_2CO_3 - $NaHCO_3$ solution with added $MgCl_2$. The range of pH. of these tests was 8.6 to 9.8 and the range of ionic strength was 0.09 to 4.6. In their calculations of the $MgCO_3^\circ$ constant, Greenwald and Garrels appear to have neglected the effect of $MgOH^+$ on their results. The magnitude of this effect would depend upon the exact experimental conditions.

Nakayama determined a constant for $MgCO_3^\circ$ at ionic strengths of 0.04 to 0.12 and pH values of 8.6 to 9.8 by measuring H and Mg ion activities simultaneously and calculating these activities by the extended Debye-Hückel equation. Nakayama's value for K_{dMgCO_3} was 5.75×10^{-4}, extrapolated to zero ionic strength.

$CaCO_3^\circ$ The titration experiments were run at pH values of 9.8 to 10.6 and ionic strengths ranging from .004 to .016. Two sets of experimental data are listed in Table 9. The $CaCO_3^\circ$ constant determined in this study is in excellent agreement with the reported value of Garrels and Thompson (12) using a titration procedure similar to the procedure used in this project. At 25°C, the $CaCO_3^\circ$ constant calculated in this study is 5.98×10^{-4}. Garrels and Thompson gave a K_{dCaCO_3} of 6.3×10^{-4} at 25°C based on pH measurements in a solution of known carbonate concentration during titration with standard $CaCl_2$ solution.

Greenwald (9) determined a constant in terms of concentrations from solubility data at 22°C, $\mu = .152$, and pH = 7.5 to 9.5. Greenwald's value for the $CaCO_3^\circ$ complex, corrected to zero ionic strength, is

$$K_{dCaCO_3} = (K'_{dCaCO_3})\ (\gamma_{Ca^{++}})\ (\gamma_{CO_3^=})/(\gamma_{CaCO_3^\circ})$$

$$= 1.10 \times 10^{-3} \times .34 \times .33/1.03 = 1.09 \times 10^{-4}$$

Nakayama (13) determined a constant of 3.29 × 10^{-5} by measurement of H and Ca activities, using the extended Debye-Hückel theory for dilute solutions to estimate activity coefficients.

Lafon (14) computed a value of K_{dCaCO_3} based on the solubility of calcite in pure CO_2-free water. Assuming a pK_s of 8.40, Lafon estimated the dissociation constant for $CaCO_3^\circ$ to be 7.95 × 10^{-4} (pK_{CaCO_3} = 3.10). Lafon's work emphasized the dependency of the calculated value of K_{dCaCO_3} on the choice of the value of pK_s.

$NaCO_3^-$ The titration experiments were run at pH values from 9.9 to 10.8 and ionic strengths ranging from .008 to .024. Table 10 contains a list of two sets of experimental data at 25°C. The constant determined at 25°C is 6.97 × 10^{-2} (pK_d = 1.16) and agrees quite well with the value of 5.4 × 10^{-2} determined by Garrels et al. (10). Both values, however, are smaller (by ~ 2 times) than Butler and Huston's (15) 1.09 × 10^{-1} (pK_d = 0.96).

Sulfate Complexes

The dissociation constants for the sulfate complexes, $MgSO_4^\circ$, $CaSO_4^\circ$, and $NaSO_4^\circ$, are discussed individually in this section. The dissociation constant for the $MgSO_4^\circ$ complex was determined by titration of K_2SO_4 - KOH - $KClO_4$ solutions with standard $Mg(ClO_4)_2$ titrant. The corresponding MgOH constant was included in the calculation of the constant for $MgSO_4^\circ$. The change in pH noted upon addition of titrant included change in ionic strength and formation of the two complexes, $MgOH^+$ and $MgSO_4^\circ$. The titration procedure for the determination of the $CaSO_4^\circ$ constant uses a slight variation of the procedure for $MgSO_4^\circ$ and will be explained below. The $NaSO_4^-$ constant was not evaluated in this study.

$MgSO_4^0$. Table 11 contains two sets of titration data for $MgSO_4^0$ at 25°C. With a pH range from 9.9 to 10.3 and ionic strengths from .008 to .028, K_{dMgSO_4} at 25°C was calculated as 3.73×10^{-3} ($pK_d = 2.43$). This value agrees with other reported values listed in Table 1. Thrailkill (30), using the 0° and 20° values reported by Nair and Nancollas (l6), interpolated values of $pK_d = 2.16$ at 15°C and 2.04 at 5°C Thrailkill's interpolated values are in good agreement with the 15°C and 5°C values determined in this work.

$CaSO_4^0$. The determination of K_{dCaSO_4} has been extremely difficult and time consuming. Titration of K_2S0_4 - K0H - $KClO_4$ solutions with $Ca(Cl0_4)_2$ repeatedly resulted in negative calculated values for the constant. Preliminary experiments indicated that measuring the effect of the presence of sulfate on the solubility of calcium carbonate might be a useful method for the determination of K_{dCaSO_4} However, the results of the solubility tests were too erratic. A third possible procedure was attempted and was found useful but also extremely sensitive to error in pH measurement. In this procedure, K_{dCaSO_4} was determined by titrating a solution containing calcium and hydroxide ions (as well as the CaOH complex) with K_2SO_4. Formation of the $CaSO_4^0$ complex would reduce the available calcium ion and cause dissociation of the CaOH complex with a resulting increase in pH. With this procedure, a dissociation constant of 4.07×10^{-3} ($pK_d = 2.39$) was found, and this is in good agreement with the results obtained from other sources (l9» 20, 21). Because of the difficulty experienced in developing this constant, no attempt was made to determine values at 5° and 15°C. The constants at 5 and 15°C will be taken from Thrailkill's (30) calculated values of $K_d(5°C) = 6.02 \times 10^{-3}$ and $K_d(15°C) = 5.37 \times 10^{-3}$.

$NaSO_4^-$. Reported values (22, 23) for the NaS_4^- complex ($K_d = 1.9 \times 10^{-1}$) indicate that this complex would not materially affect the calculation of pH_s except in waters with abnormally high sulfate concentrations.

Bicarbonate Complexes

The values of the three bicarbonate complexes, $MgHCO_3^+$, $CaHCO_3^+$, $NaHCO_3^0$, were determined by titration of CO_2 saturated solutions of K_2CO_3 with the corresponding perchlorate solution of the cation, e.g., $Mg(ClO_4)_2$. In these tests pure CO_2, saturated with water vapor, was bubbled through a solution of K_2CO_3 of known concentration. The partial pressure of CO_2 was estimated from the barometric pressure corrected for the vapor pressure of water.

The solubility of CO_2 in water, S, or Henry's law constant, was computed from the data of Harned and Davis (35) by the formula:

$$-\log(S) = -2385.73/T + 14.0184 - .0152642\ T$$

where T is the absolute temperature and S is expressed as moles/liter/atmosphere. The concentration of H_2CO_3 can be calculated as

$$[H_2CO_3] = S \times PCO_2$$

where PCO_2 is the partial pressure of CO_2 in atmospheres.

The original alkalinity of the solution was twice the concentration of K_2CO_3 added, and stayed constant except for dilution by the titrant.

The final alkalinity, neglecting $[CO_3^=]$ at this pH, was

$$ALK = [HCO_3^-] + [OH] - [H^+] + [MgHCO_3^+] \quad \text{and}$$
$$[MgHCO_3^+] = ALK - [HCO_3^-] - [OH^-] + [H^+]$$

Thus, the complex could be calculated from the original alkalinity corrected for change in volume, the final pH, and the concentration of H_2CO_3, using K_W' and K_1'

Attempts to develop a dissociation constant for $MgHCO_3^+$ by other procedures are briefly mentioned in the following section. These methods were unsuccessful.

$MgHCO_3^+$. The $MgHCO_3^+$ complex was first considered in experiments with the $MgCO_3^o$ complex at 25°C. However, if $MgHCO_3^+$ was formed, our methods were not sufficiently sensitive to determine a dissociation constant. In a second experiment, a specific ion electrode which is sensitive to magnesium activities was used. This Orion specific ion liquid membrane electrode was first calibrated in $Mg(ClO_4)_2$ solutions of known, calculated Mg^{++} activity. In these experiments, $KClO_4$. was added for ionic strength adjustment, and the resulting potential was measured with the Beckman research pH-millivoltmeter accurate to ± 0.1 mv.

Unfortunately, the specific ion electrode showed high potassium ion interference and, with varied K activities, it was impossible to correct for this interference with a modified Nernst equation:

$$E = E_o + \frac{RT}{nF} \times \log [(Mg^{++}) + SC \times (K)^n],$$

where SC is the selectivity constant for potassium ion.

However, with constant K^+ activity, it was possible to obtain a reasonable approximation of Mg activity by the simple Nernst equation. To use this approach, it was first necessary to calculate the Mg and K concentrations required for different desired Mg activities and constant K^+ activity. For any set of samples in which K^+ activity is constant, the concentration of Mg to be added to maintain a particular Mg activity was calculated with the extended Debye-Hückel equation. The specific ion electrode was then used to measure the potential. By applying the simple Nernst equation, the actual Mg activity was calculated, and the extended Debye-Hückel equation was used to determine the actual Mg concentration found. The difference between the Mg concentration added and that found was taken as the total concentration of complex formed.

From previously estimated dissociation constants for MgOH and $MgCO_3^o$ and activities for the ions (Mg), (OH), and ($CO_3^=$), the concentration of these complexes was calculated and subtracted from the calculated total complex to yield the concentration of the $MgHCO_3^+$ complex. Then the concentration product constant, K_d', for the $MgHCO_3^+$ complex was calculated and by application of the appropriate activity coefficients, the dissociation constant, K , was determined.

This method of calculating $K_{dMgHCO3}$ was applied to data from two samples in which K_2CO_3 was added to provide the desired concentration of K and the pH of the samples was adjusted to pH 5.995. In the first sample the [K^+] added was .002 moles/1 and the resulting value for $K_{dMgHCO3}$ was 1.037×10^{-2} ($pK_d = 1.984$). For the second sample in which [K] added was .01 moles/1, the resulting K_d was 2.892×10^{-2} ($pK_d = 1.593$).

Neither of these values agrees with the value of pK_d = 1,23 determined by Nakayama using the specific ion electrode. The degree of reliability obtainable from this method did not appear promising.

The titration method based on the solubility of CO_2 in solutions of K_2CO_3 was tested and gave more consistent results as shown in Table 12. The $MgHCO_3^+$ constant developed by this method is 4.11×10^{-2} (pK_d = 1.38) at 25°C over a pH range of 5.2 to 6.4 and ionic strengths of .006 to .08.

Hostetler (24), used a similar titration procedure based on the shift of pH upon addition of $Ba(0H)_2$ to solutions of Mg saturated with CO_2. He reported values of pH, y, and $[HCO_3^-]$ and used 6.38 for pK_1 ($K_1 = 4.17 \times 10^{-7}$). Hostetler assumed the CO_2 solubility was 1.60 g/l and determined five pK_d values for $MgHCO_3^+$ ranging from 0.83 to 1.05 with ionic strengths from .070 to .064 and pH 3.88 to 5.63. His average $p_{KdMgHCO3}$ is 0.95 ($K_d = 1.12 \times 10^{-1}$).

Hostetler's data were recalculated using Harned and Davis' value for solubility (S = .03422 - .008213μ) and $K_1 = 4.456 \times 10^{-7}$. The five values after recalculation gave an average pK_d of 0.966 ($K_d = 1.08 \times 10^{-1}$) with a range from 0.86 to 1.05. Hostetler's constant is ~ 3 times larger than the constant developed in this study and ~ 2 times the value given by Nakayama (11) or by Greenwald (9)•

Nakayama, working at ionic strengths of *.0k* to .12, used a specific ion electrode to determine a constant for $MgHCO_3^+$ at 25°C of 5.89×10^{-2} (pK_d = 1.23), extrapolated to zero ionic strength. Nakayama's value is similar to Greenwald's constant of 6.95×10^{-2} (pK_d = 1.16), corrected to zero ionic strength.

$CaHCO_3^+$ The dissociation constant for the $CaHCO_3^+$ complex at 25°C is calculated in this study as 5.64×10^{-2} and is in excellent agreement with Nakayama's (13) value and Greenwald's (9) solubility data, corrected to zero ionic strength. Titration experiments were run at pH values of 5.47 to 5.86, and ionic strengths of .016 to .053. Two sets of experimental data are given in Table 13.

The existence of the $CaHCO_3^+$ complex was first reported by Greenwald (9) who measured values for $CaHCO_3^+$ by both titration and solubility experiments. Greenwald's constant based on titration at 22°C, ranged between K_d values of 8.9×10^{-2} and 1.55×10^{-1} while the constant derived from solubility measurements was 5.5×10^{-2}. The latter value is in excellent agreement with Nakayama's (13) constant of 5.64×10^{-2} calculated from activity data. Using a conductometric method, Jacobson and Langmuir (25) more recently reported values of $K_{dCaHCO3}$ at temperatures of 15, 25, 35, and 45°C. Their reported values of pK = .88 ($K_d = 1.3 \times 10^{-1}$) at 15°C and pK = 1.0 ($K_d = 1.0 \times 10^{-1}$) at 25°C are roughly two times greater than the values determined in this study.

$NaHCO_3^\circ$ Table 14 lists the experimental data used in the determination of this constant. The value of the dissociation constant for $NaHCO_3^\circ$ developed in this study is 3.9×10^{-2} at 25°C ($pK_d = 1.41$) and is considerably different from other reported values. A nearly 20-fold difference separates this constant and Nakayama's (26) value of 6.9×10^{-1} ($pK_d = 0.16$), while the constants for $NaHCO_3^\circ$ reported by Garrels and Thompson (12) and by Butler (15) are ~ 50 times greater ($K_d = 1.8$ to 2.0).

CALCULATION OF pH_s AND DFI USING THESE CONSTANTS

A method was developed to calculate the complexes present in a water of known analysis, and the complexes which would be present at the pH of saturation for calcium carbonate. This calculation used a quantity termed TCO_2, defined as the sum of the molar concentrations of carbonate and bicarbonate. H_2CO_3 was neglected since its concentration would be negligible in the pH range of interest.

To determine the pH , $TC0_2$ was calculated from the pH and alkalinity of the sample. The usual pH , not considering complexes, was then calculated from the following equations:

$$[H^+] = [Ca^{++}] \cdot [TCO_2] \cdot K_2' / K_s' - K_2'$$

$$pH_s = -\log [H^+]$$

This hydrogen ion concentration and TCO_2 were used to determine the hydroxide, carbonate, and bicarbonate concentrations which would be present at this calculated pH . These concentrations and the original calcium, magnesium, sodium, and sulfate concentrations were used to calculate estimated concentrations of the complexes, as in the following example:

$$[MgOH^+] = [Mg^{++}] \cdot [OH^-] / K'_{dMgOH}$$

This produced an array of twelve complex concentrations. The original values of the calcium, magnesium, sodium, sulfate, and TCO_2 concentrations were corrected by subtracting the concentrations of the appropriate complexes .

With these corrected concentrations, another estimate of pH_s was made, and this pH and the corrected TCO_2 concentration were used for another estimate of the hydroxide, carbonate, and bicarbonate concentrations. This process was then repeated until a stable pH_s resulted, indicating that all of the equilibria were satisfied by the concentrations calculated. This pH was taken to be the true pH including the effects of complex formation.

DFI, or driving force index, defined as the product of the calcium and carbonate activities divided by K , is another measure of the tendency for a water to deposit calcium carbonate. A DFI of 1.0 indicates equilibrium, while higher values indicate supersaturation and lower values indicate a tendency to dissolve calcium carbonate. In contrast to pH and the saturation index, the DFI is not a logarithmic quantity and large changes in DFI may be associated with small changes in saturation index.

To calculate DFI, a procedure very similar to that for the calculation of pH_s was followed. The difference was that pH_s was not calculated and each iteration of the calculation was based upon the original pH of the sample. Thus this calculation gave the concentration of the complexes in the original sample and the concentrations of the various ions, corrected for these complexes. DFI was finally calculated from these corrected concentrations.

These calculations were performed with a variety of water analyses to determine the extent of the effect of these complexes. In all cases studied, using analyses typical of water supplies in Illinois, the complexes cause apparent shifts in pH and saturation index of from 0.02 to 0.3 units.

A water with 50 mg/l of calcium, 100 mg/l of alkalinity (both as calcium carbonate), 250 mg/l of total dissolved solids, and with varied pH, magnesium, sodium, and sulfate content is used as an illustration of the results of these calculations. The results are given in Tables 15, 16, and 17.

SUMMARY

The equilibrium or saturation pH for calcium carbonate is frequently found to be higher than the theoretical value, particularly in lime softened waters containing appreciable quantities of magnesium. This difference appears to be due to the formation of complexes of calcium and magnesium and (to a lesser extent) of sodium with bicarbonate, carbonate, sulfate, and hydroxide ions. Calculation of the true pH of saturation, and adjustment of the water to that pH, is essential to maintenance of water quality in distribution systems. The deterioration of water quality from improper adjustment of pH_s could result in corrosion and incrustation in water distribution systems and in household plumbing. In order to calculate the true pH of saturation accurate values of the dissociation constants for the complexes must by known.

The true thermodynamic dissociation constants of the calcium, magnesium, and sodium complexes with the hydroxide, carbonate, sulfate, and bicarbonate anions were evaluated in this study at ionic strengths normally found in potable public water supplies. A titration procedure was used at temperatures of 5, 15, and 25°C. The constants were determined at ionic strengths generally in the range of .002 to .02 and were developed in terms of activities, so they are valid at least over the range of ionic strengths at which the tests were made.

A number of other workers have developed constants for each of the complexes evaluated in this study. However, most of these workers conducted their studies only at room temperature (~25°C) and ionic strengths too high to be applicable to public water supplies, while others based their calculations on concentrations rather than the ion activities used in this study. For example, Greenwald (9) evaluated the carbonate and bicarbonate complexes of calcium and magnesium at 22°C only and at nearly constant ionic strength ($\mu = 0.15$). His constants were calculated on the basis of molarities rather than activities. Garrels and his co-workers (10, 12, 29) determined or calculated thermodynamic dissociation constants (based on activities) for the carbonate, bicarbonate, and sulfate complexes of calcium, magnesium, and sodium over a range of ionic strengths, up to and including that of seawater, at 25°C and one atmosphere pressure.

Although the major application of this work would be in the area of treatment of public water supplies, the equilibria involved here are also of importance in their effect on the calcium carbonate equilibria and the buffer system controlling the pH in groundwaters, lakes and reservoirs.

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Table 1.

Comparison of Dissociation Constants From Different Sources

K_d expressed as $-\log K_d$

T = 25°C, unless specified

Complex	Reference	Method	$-\log K_d$
$MgOH^+$			
	*	titration - pH	2.09
	(2)	glass electrode	2.59
	(3)	potentiometric, 18°	2.10
	(4)	solubility	2.60
$CaOH^+$			
	*	titration - pH	1.38
	(5)	EMF, H electrode	1.37
	(6)	EMF, H electrode	1.15 to 1.27
$NaOH^\circ$			
	*	titration - pH	0.75
	(7)	conductivity	-0.70, or no cpx
	(8)	kinetic	-0.70
	(5)	EMF, H electrode	-0.77 to -0.57
$MgCO_3^\circ$			
	*	titration - pH	2.90
	(9)	titration, 22°	3.25
	(10)	titration - pH	3.40
	(11)	potentiometric	3.24
$CaCO_3^\circ$			
	*	titration - pH	3.22
	(9)	solubility, 22°	3.96
	(12)	titration - pH	3.20
	(13)	activity	4.48
	(14)	solubility	3.10
$NaCO_3^-$			
	*	titration - pH	1.16
	(10)	titration - pH	1.27
	(15)	potentiometric	0.96
$MgSO_4^\circ$			
	*	titration - pH	2.43
	(16)	EMF, H electrode	2.25
	(17)	EMF, H electrode	2.36
	(18)	conductivity, 18°	2.21
$CaSO_4^\circ$			
	*	titration - pH	2.39
	(19)	solubility	2.31
	(20)	conductivity, 18°	2.28
	(21)	activity	2.27
$NaSO_4^-$			
	*	-----	--
	(22)	conductivity	0.72
	(23)	conductivity, 18°	0.70
$MgHCO_3^+$			
	*	titration - pH	1.38
	(24)	titration - pH	0.95
	(9)	pH - glass electrode, 22°	1.16
	(11)	potentiometric	1.23
$CaHCO_3^+$			
	*	titration - pH	1.25
	(9)	titration - pH, 22°	1.05, 0.81
	(9)	solubility, 22°	1.26
	(13)	activity	1.25
	(25)	conductivity	1.00
$NaHCO_3^\circ$			
	*	titration - pH	1.41
	(12)	pH - glass electrode	-0.25
	(26)	activity	0.16
	(15)	potentiometric	-0.30

* Results of this research

Table 2.

Fortran IV G Program for Calculation of K_{dCaOH^+}

```
C
C      PRØGRAM NUMBER FS-5A  CAØH+
C
       IMPLICIT REAL*8 (A-H,K,M,Ø-Z)
C
       KW=.1008D-13
       A=.511618DO
       B=.329202DO
C      T=25DO
C
       PRINT 3
3      FØRMAT ('1')
       PAGE=0
9      CØNTINUE
       PAGE=PAGE+1
       READ (5,1) KCL,KØH,M,VI,PHR,ML,PH
1      FØRMAT ( 7F10.0)
       PRINT 2, KCL,KØH,M,VI,PHR,ML,PH
2      FØRMAT ( 7E18.8)
C
C      SECTIØN ØNE
C
       MUR=KCL+KØH
       DØ 4 J=1,4
       AMU=A*DSQRT(MUR)
       BMU=B*DSQRT(MUR)
       GHR=10DO**(-AMU/(1DO+9DO*BMU))
       GØHR=10DO**(-AMU/(1DO+3DO*BMU))
       KPW=KW/(GHR*GØHR)
       HR=(10DO**(-PHR))/GHR
       ØHR=KPW/HR
       MUR=KCL+(KØH+HR+ØHR)/2DO
4      CØNTINUE
C
C      SECTIØN TWØ
C
       MU=MUR+3DO*ML*M/VI
       DØ 5 J=1,6
       AMU=A*DSQRT(MU )
       BMU=B*DSQRT(MU )
       GH = 10DO**(-AMU/(1DO+9DO*BMU))
       GØH = 10DO**(-AMU/(1DO+3DO*BMU))
       VC=VI/(VI+ML)
       ALK=VC*(ØHR-HR)
       KPW=KW/(GH*GØH)
       H=(10DO**(-PH))/GH
       ØH=KPW/H
       C= ALK - ØH + H
       IF (C.LE.O.) GØ TØ 13
       IF (J.EQ.6) GØ TØ 6
       CAT=ML*M/(VI+ML)
       CA=CAT-C
       MU=VC*KCL+CAT+2DO*CA+(VC*KØH+C+ØH+H)/2DO
5      CØNTINUE
6      CØNTINUE
       KPD1=CA*ØH/C
       GCA=10DO**(-4DO*AMU/(1DO+6DO*BMU))
       GC=10DO**(-AMU/(1DO=6DO*BMU))
       KD1=KPD1*GCA*GØH/GC
C
       PRINT 2,MUR,HR,ØHR,KPD1,KD1
       PRINT 7,MU,H,ØH,CAT,CA,C
7      FØRMAT ( 6E18.8//)
13     CØNTINUE
       IF (PAGE.LT.4) GØ TØ 9
       PRINT 3
       PAGE=0
       GØ TØ 9
       END
```

Table 3.

Miscellaneous Constants and Sources Used in This Study to Determine Dissociation Constants for the Complexes Evaluated

T, °C	5	15	25	Reference
$K_w^{(a)}$	.186502 D-14	.452104 D-14	.100792 D-13	34
$K_1^{(b)}$	.304532 D-6	.380663 D-6	.445611 D-6	35
$K_2^{(c)}$	.279465 D-10	.371986 D-10	.468205 D-10	36
$K_s^{(d)}$	.8145 D-8	.6118 D-8	.4621 D-8	37
$\varepsilon^{(e)}$	85.76	81.94	78.30	38
$A^{(f)}$	.495325	.502976	.511618	32
$B^{(f)}$	.325670	.327338	.329202	32

Equations relating constants to absolute temperature:

(a) Harned and Hamer (34)

$$\log (K_w) = -4787.3/T - 7.1321 \times \log (T) - 0.010365\ T + 22.801$$

$$\text{where } T = 273.07 + t^\circ C$$

(b) Harned and Davis (35)

$$\log (K_1) = -3404.71/T + 14.8435 - .032786\ T$$

$$\text{where } T = 273.07 + t^\circ C$$

(c) Harned and Scholes (36)

$$\log (K_2) = -2902.39/T + 6.498 - .02379\ T$$

$$\text{where } T = 273.07 + t^\circ C$$

(d) Larson and Buswell (37)
By the least squares method, the following equation was found to represent the Larson and Buswell data for K :

$$K_s = 4.55 \times 10^{-9} \times 10^{r}$$

where $r = 1.6154 + 296.48/T - .0087302\ T$ and

$$T = 273.16 + t^\circ C$$

(e) Malmberg and Maryott (38)
The E values from Malmberg and Maryott were used to fit an equation by the least squares procedure. The resulting equation is:

$$\varepsilon = 78.30 - .35579\ X + .83362 \times 10^{-3}(X^2) - .13954 \times 10^{-5}(X^3)$$

$$\text{where } X = t^\circ C - 25$$

(f) Butler (32)

$$A = 1.825 \times 10^6\ (\varepsilon T)^{-3/2}, \quad B = 50.3(\varepsilon T)^{-1/2}$$

$$\text{where } T = 273.13 + t^\circ C$$

Table 4.

Dissociation Constants, Kd, Determined in This Study at Three Temperatures, (a = standard deviation for n data points)

	5°C	15°C	25°C	Sample *, Titrant**
$MgOH^+$ (σ; n)	1.067×10^{-2} (.0012; 21)	9.89×10^{-3} (.00072; 18)	8.17×10^{-3} (.00057; 18)	1,a
$CaOH^+$ (σ; n)	3.23×10^{-2} (.0056; 23)	4.18×10^{-2} (.0096; 26)	4.17×10^{-2} (.0060; 29)	1,b
$NaOH^\circ$ (σ; n)	1.46×10^{-1} (.036; 11)	1.56×10^{-1} (.024; 10)	1.77×10^{-1} (.027; 12)	1,c
$MgCO_3^\circ$ (σ; n)	1.68×10^{-3} (.000095; 35)	1.57×10^{-3} (.00006; 24)	1.26×10^{-3} (.00003; 40)	2,a
$CaCO_3^\circ$ (σ; n)	7.46×10^{-4} (.0000097; 41)	7.13×10^{-4} (.000022; 23)	5.98×10^{-4} (.000035; 25)	2,b
$NaCO_3^-$ (σ; n)	7.54×10^{-2} (.0154; 14)	7.40×10^{-2} (.0133; 21)	6.97×10^{-2} (.0087; 19)	2,c
$MgSO_4^\circ$ (σ; n)	9.23×10^{-3} (.0032; 18)	5.92×10^{-3} (.00168; 18)	3.73×10^{-3} (.00083; 21)	4,a
$CaSO_4^\circ$ (σ; n)			4.07×10^{-3} (.00096; 7)	5,d
$MgHCO_3^+$ (σ; n)	5.00×10^{-2} (.0062; 19)	4.30×10^{-2} (.0085; 10)	4.11×10^{-2} (.0061; 16)	3,a
$CaHCO_3^+$ (σ; n)	4.37×10^{-2} (.0116; 16)	3.41×10^{-2} (.0057; 15)	5.64×10^{-2} (.0068; 13)	3,b
$NaHCO_3^\circ$ (σ; n)			3.90×10^{-2} (.0192; 11)	3,c

* Composition of sample: (1) $KClO_4$ + KOH ; (2) K_2CO_3 + $HClO_4$ + $KClO_4$; (3) K_2CO_3 + CO_2; (4) K_2SO_4 + KOH + $KClO_4$; (5) KOH + $KClO_4$ + Ca $(ClO_4)_2$

** Titrant: (a) $Mg(ClO_4)_2$; (b) $Ca(ClO_4)_2$; (c) $NaClO_4$; (d) K_2SO_4

Table 5.

Determination of K_{dMgOH} by Titration of $KClO_4$-KOH Solutions

With $Mg(ClO_4)_2$, .2257 M at 25°C

Volume, ml	$[Mg_T]$,M	pH	μ	$[MgOH^+]$,M	K_{dMgOH}
Titration 1, initial conditions: $KClO_4$ - .00513 M, KOH - .000143 M					
430.	0.0	10.101	.0053	----	----
431.	5.24×10^{-4}	10.075	.0068	6.4×10^{-6}	7.70×10^{-3}
432.	1.04×10^{-3}	10.052	.0084	1.17×10^{-5}	7.78×10^{-3}
434.	2.08×10^{-3}	10.014	.0114	1.98×10^{-5}	8.10×10^{-3}
435.96	3.08×10^{-3}	9.981	.0144	2.64×10^{-5}	8.16×10^{-3}
438.1	4.17×10^{-3}	9.950	.0176	3.20×10^{-5}	8.26×10^{-3}
440.	5.13×10^{-3}	9.924	.0205	3.65×10^{-5}	8.24×10^{-3}
Titration 2, initial conditions: $KClO_4$ - .00513 M, KOH - .000535 M					
430.	0.0	10.660	.0056	----	----
431.	5.24×10^{-4}	10.638	.0072	1.89×10^{-5}	9.17×10^{-3}
432.04	1.06×10^{-3}	10.614	.0087	3.96×10^{-5}	8.28×10^{-3}
434.02	2.09×10^{-3}	10.567	.0117	7.84×10^{-5}	7.13×10^{-3}
436.02	3.12×10^{-3}	10.534	.0147	1.02×10^{-4}	7.43×10^{-3}
437.95	4.10×10^{-3}	10.504	.0176	1.22×10^{-4}	7.47×10^{-3}
439.96	5.11×10^{-3}	10.477	.0206	1.38×10^{-4}	7.58×10^{-3}

Table 6.

Determination of K_{dCaOH} by Titration of $KClO_4$-KOH Solutions

With $Ca(ClO_4)2$, .2934 M at 25°C

Volume, ml	$[Ca_T]$,M	pH	μ	$[CaOH^+]$,M	K_{dCaOH}
Titration 1, initial conditions: $KClO_4$ - .00565 M, KOH - .002 M					
430.	0.0	11.278	.0077	----	----
431.05	7.15×10^{-4}	11.265	.0098	3.45×10^{-5}	2.73×10^{-2}*
432.08	1.41×10^{-3}	11.258	.0118	4.29×10^{-5}	4.24×10^{-2}
434.02	2.72×10^{-3}	11.244	.0156	6.76×10^{-5}	4.86×10^{-2}
436.04	4.06×10^{-3}	11.227	.0196	1.09×10^{-4}	4.20×10^{-2}
438.04	5.38×10^{-3}	11.218	.0235	1.16×10^{-4}	4.98×10^{-2}
439.90	6.60×10^{-3}	11.204	.0270	1.51×10^{-4}	4.45×10^{-2}
Titration 2, initial conditions: KClO4 - .00565 M, KOH - .008 M					
430.	0.0	11.841	.0136	----	----
431.10	7.49×10^{-4}	11.832	.0156	8.00×10^{-5}	4.02×10^{-2}
432.	1.36×10^{-3}	11.825	.0173	1.42×10^{-4}	4.00×10^{-2}
434.04	2.73×10^{-3}	11.812	.0212	2.37×10^{-4}	4.62×10^{-2}
434.97	3.35×10^{-3}	11.802	.0228	3.57×10^{-4}	3.55×10^{-2}
435.98	4.02×10^{-3}	11.796	.0247	4.01×10^{-4}	3.73×10^{-2}
437.99	5.35×10^{-3}	11.785	.0284	4.77×10^{-4}	4.02×10^{-2}
439.93	6.62×10^{-3}	11.774	.0320	5.62×10^{-4}	4.05×10^{-2}

* Value omitted from final average K_d

Table 7.

Determination of K_{dNaOH} by Titration of $KClO_4$-KOH Solutions With $NaClO_4$, .09946 M at 25°C

Volume, ml	$[Na_T]$,M	pH	μ	$[NaOH^\circ]$,M	K_{dNaOH}
Titration 1, initial conditions: $KClO_4$ - .00594 M, KOH - .00048 M					
400.	0.0	10.634	.0064	----	----
402.	4.95×10^{-4}	10.626	.0071	4.27×10^{-6}	4.47×10^{-2}*
405.	1.23×10^{-3}	10.620	.0082	4.41×10^{-6}	1.06×10^{-1}*
410.	2.42×10^{-3}	10.610	.0099	5.20×10^{-6}	1.72×10^{-1}
415.	3.59×10^{-3}	10.600	.0116	6.51×10^{-6}	1.98×10^{-1}
420.	4.74×10^{-3}	10.589	.0132	9.24×10^{-6}	1.78×10^{-1}
425.	5.85×10^{-3}	10.576	.0148	1.42×10^{-5}	1.38×10^{-1}
430.	6.94×10^{-3}	10.569	.0164	1.34×10^{-5}	1.69×10^{-1}
Titration 2, initial conditions: $KClO_4$ - .00594 M, KOH - .000387 M					
400.	0.0	10.550	.0063	----	----
402.	4.95×10^{-4}	10.545	.0070	8.30×10^{-7}	1.92×10^{-1}
405.	1.23×10^{-3}	10.538	.0081	1.84×10^{-6}	2.11×10^{-1}
410.	2.42×10^{-3}	10.525	.0098	5.10×10^{-6}	1.45×10^{-1}
415.	3.59×10^{-3}	10.511	.0115	9.55×10^{-6}	1.10×10^{-1}*
420.	4.74×10^{-3}	10.503	.0131	9.20×10^{-6}	1.47×10^{-1}
425.	5.85×10^{-3}	10.494	.0147	9.98×10^{-6}	1.63×10^{-1}
430.	6.94×10^{-3}	10.486	.0163	1.02×10^{-5}	1.85×10^{-1}
440.	9.04×10^{-3}	10.471	.0193	1.03×10^{-5}	2.27×10^{-1}

* Values omitted from final average K_d

Table 8.

Determination of K_{dMgCO_3} by Titration of HCO_3^--$CO_3^=$ Solutions With $Mg(ClO_4)_2$, .2198 M at 25°C

Volume, ml	$[Mg_T]$,M	pH	μ	$[MgOH^+]$,M	$[MgCO_3^0]$,M	K_{dMgCO_3}
Titration 1, initial conditions: K_2CO_3 - .00232 M, $HClO_4$ - .00081 M, $KClO_4$ - .0041 M						
430.	0.0	10.312	.0101	----	----	----
431.	5.10×10^{-4}	10.267	.0110	6.10×10^{-6}	1.49×10^{-4}	1.25×10^{-3}
432.	1.02×10^{-3}	10.227	.0120	1.15×10^{-5}	2.63×10^{-4}	1.31×10^{-3}
434.	2.02×10^{-3}	10.149	.0142	1.97×10^{-5}	4.56×10^{-4}	1.24×10^{-3}
435.	2.53×10^{-3}	10.116	.0154	2.31×10^{-5}	5.24×10^{-4}	1.24×10^{-3}
436.	3.02×10^{-3}	10.086	.0167	2.61×10^{-5}	5.80×10^{-4}	1.24×10^{-3}
438.	4.01×10^{-3}	10.032	.0192	3.10×10^{-5}	6.70×10^{-4}	1.24×10^{-3}
440.	5.00×10^{-3}	9.987	.0219	3.51×10^{-5}	7.32×10^{-4}	1.25×10^{-3}
442.	5.97×10^{-3}	9.948	.0246	3.85×10^{-5}	7.80×10^{-4}	1.26×10^{-3}
Titration 2, initial conditions: K_2CO_3 - .00349 M, $HClO_4$ - .00162 M, $KClO_4$ - .00205 M						
430.	0.0	10.199	.0108	----	----	----
431.	5.10×10^{-4}	10.154	.0116	4.27×10^{-6}	1.81×10^{-4}	1.24×10^{-3}
432.	1.02×10^{-3}	10.112	.0125	8.04×10^{-6}	3.30×10^{-4}	1.26×10^{-3}
434.	2.02×10^{-3}	10.036	.0146	1.42×10^{-5}	5.60×10^{-4}	1.28×10^{-3}
435.	2.53×10^{-3}	10.004	.0157	1.68×10^{-5}	6.41×10^{-4}	1.30×10^{-3}
436.	3.02×10^{-3}	9.969	.0168	1.87×10^{-5}	7.27×10^{-4}	1.26×10^{-3}
438.	4.01×10^{-3}	9.913	.0193	2.24×10^{-5}	8.43×10^{-4}	1.27×10^{-3}
440.	5.00×10^{-3}	9.864	.0218	2.52×10^{-5}	9.31×10^{-4}	1.27×10^{-3}
442.	5.97×10^{-3}	9.821	.0244	2.76×10^{-5}	9.99×10^{-4}	1.27×10^{-3}

Table 9.

Determination of K_{dCaCO_3} by Titration of HCO_3^--$CO_3^=$ Solutions With $Ca(ClO_4)_2$ at 25°C, $K_{dCaOH} = 4.174 \times 10^{-2}$

Volume, ml	$[Ca_T]$,M	pH	μ	$[CaOH^+]$,M	$[CaCO_3^o]$,M	K_{dCaCO_3}
Titration 1, initial conditions: $Ca(ClO_4)_2$ - .08433 M, K_2CO_3 - .00116 M, $HClO_4$ - .00053 M, $KClO_4$ - .00108 M						
430.	0.0	10.135	.0039	----	----	----
430.8	1.58×10^{-4}	10.102	.0042	2.66×10^{-7}	5.16×10^{-5}	5.60×10^{-4}
431.8	3.44×10^{-4}	10.066	.0046	5.49×10^{-7}	1.02×10^{-4}	5.71×10^{-4}
432.9	5.59×10^{-4}	10.026	.0050	8.36×10^{-7}	1.52×10^{-4}	5.69×10^{-4}
433.7	7.25×10^{-4}	9.997	.0054	1.03×10^{-6}	1.85×10^{-4}	5.68×10^{-4}
434.4	8.58×10^{-4}	9.974	.0057	1.17×10^{-6}	2.09×10^{-4}	5.61×10^{-4}
434.8	9.40×10^{-4}	9.961	.0059	1.25×10^{-6}	2.22×10^{-4}	5.62×10^{-4}
435.	9.79×10^{-4}	9.956	.0060	1.29×10^{-6}	2.26×10^{-4}	5.67×10^{-4}
435.5	1.06×10^{-3}	9.943	.0062	1.37×10^{-6}	2.38×10^{-4}	5.65×10^{-4}
435.9	1.14×10^{-3}	9.931	.0064	1.44×10^{-6}	2.49×10^{-4}	5.63×10^{-4}
Titration 2, initial conditions: $Ca(ClO_4)_2$ - .07585 M, K_2CO_3 - .00232 M, $HClO_4$ - .00133 M, $KClO_4$ - .00434 M						
430.	0.0	10.024	.0099	----	----	----
430.7	1.20×10^{-4}	10.006	.0101	1.39×10^{-7}	4.30×10^{-5}	7.12×10^{-4}*
431.5	2.62×10^{-4}	9.981	.0103	2.76×10^{-7}	1.00×10^{-4}	6.01×10^{-4}
431.9	3.39×10^{-4}	9.968	.0104	3.49×10^{-7}	1.28×10^{-4}	5.90×10^{-4}
432.5	4.33×10^{-4}	9.954	.0106	4.42×10^{-7}	1.57×10^{-4}	6.07×10^{-4}
433.	5.17×10^{-4}	9.945	.0108	5.36×10^{-7}	1.74×10^{-4}	6.62×10^{-4}

* Value omitted from final average K_d

Table 10.

Determination of K_{dNaCO_3} by Titration of HCO_3^--$CO_3^=$ Solutions With $NaClO_4$, .09946 M at 25°C

Volume, ml	$[Na_T]$,M	pH	μ	$[NaOH^o]$,M	$[NaCO_3^-]$,M	K_{dNaCO_3}
Titration 1, initial conditions: K_2CO_3 - .00125 M, $HClO_4$ - .00095 M, $KClO_4$ - .00475 M						
400.	0.0	10.094	.0076	----	----	----
402.	4.95×10^{-4}	10.089	.0084	3.12×10^{-7}	3.13×10^{-6}	5.74×10^{-2}
405.	1.23×10^{-3}	10.081	.0091	7.56×10^{-7}	9.00×10^{-6}	4.81×10^{-2}*
410.	2.42×10^{-3}	10.072	.0102	1.46×10^{-6}	1.16×10^{-5}	7.07×10^{-2}
415.	3.59×10^{-3}	10.062	.0112	2.10×10^{-6}	1.68×10^{-5}	6.98×10^{-2}
420.	4.74×10^{-3}	10.050	.0123	2.68×10^{-6}	2.59×10^{-5}	5.70×10^{-2}
425.	5.85×10^{-3}	10.041	.0133	3.24×10^{-6}	3.03×10^{-5}	5.81×10^{-2}
430.	6.94×10^{-3}	10.034	.0143	3.76×10^{-6}	3.18×10^{-5}	6.36×10^{-2}
435.	8.00×10^{-3}	10.027	.0152	4.26×10^{-6}	3.37×10^{-5}	6.71×10^{-2}
440.	9.04×10^{-3}	10.020	.0162	4.72×10^{-6}	3.60×10^{-5}	6.89×10^{-2}
Titration 2, initial conditions: K_2CO_3 - .00375 M, $HClO_4$ - .001425 M, $KClO_4$ - .002375 M						
400.	0.0	10.478	.0122	----	----	----
405.	1.23×10^{-3}	10.470	.0136	1.81×10^{-6}	1.44×10^{-5}	1.28×10^{-1}*
410.	2.42×10^{-3}	10.460	.0146	3.45×10^{-6}	4.78×10^{-5}	7.28×10^{-2}
420.	4.74×10^{-3}	10.443	.0165	6.43×10^{-6}	9.34×10^{-5}	6.78×10^{-2}
425.	5.85×10^{-3}	10.437	.0174	7.84×10^{-6}	9.85×10^{-5}	7.74×10^{-2}
430.	6.94×10^{-3}	10.430	.0184	9.12×10^{-6}	1.13×10^{-4}	7.79×10^{-2}
435.	8.00×10^{-3}	10.423	.0193	1.03×10^{-5}	1.28×10^{-4}	7.69×10^{-2}
440.	9.04×10^{-3}	10.417	.0201	1.15×10^{-5}	1.36×10^{-4}	7.92×10^{-2}

* Values omitted from final average K_d

Table 11.

Determination of K_{dMgSO_4} by Titration of K_2SO_4-KOH Solutions With $Mg(ClO_4)_2$, .2272 M at 25°C, $K_{dMgOH} = 8.17 \times 10^{-3}$

Volume, ml	$[Mg_T]$,M	pH	μ	$[MgOH^+]$,M	$[MgSO_4^0]$,M	K_{dMgSO_4}
			Titration 1, initial conditions: K_2SO_4 - .002636 M, KOH - .0001749 M, $KClO_4$ - .000440 M			
415.	0.0	10.179	.0085	----	----	----
417.	1.09×10^{-3}	10.143	.0108	1.08×10^{-5}	2.41×10^{-4}	3.66×10^{-3}
419.	2.17×10^{-3}	10.111	.0130	1.97×10^{-5}	4.74×10^{-4}	3.13×10^{-3}
421.	3.24×10^{-3}	10.078	.0158	2.82×10^{-5}	5.67×10^{-4}	3.65×10^{-3}
423.	4.30×10^{-3}	10.050	.0183	3.48×10^{-5}	7.14×10^{-4}	3.38×10^{-3}
425.	5.34×10^{-3}	10.023	.0211	4.08×10^{-5}	8.03×10^{-4}	3.41×10^{-3}
427.	6.38×10^{-3}	9.997	.0240	4.62×10^{-5}	8.36×10^{-4}	3.69×10^{-3}
428.	6.90×10^{-3}	9.988	.0249	4.79×10^{-5}	9.96×10^{-4}	2.93×10^{-3}
430.	7.92×10^{-3}	9.963	.0281	5.26×10^{-5}	9.44×10^{-4}	3.55×10^{-3}
			Titration 2, initial conditions: K_2SO_4 - .001758 M, KOH - .0002624 M, $KClO_4$ - .00066 M			
415.	0.0	10.330	.0062	----	----	----
417.	1.09×10^{-3}	10.293	.0084	1.53×10^{-5}	2.60×10^{-4}	2.24×10^{-3}
419.	2.17×10^{-3}	10.257	.0109	2.89×10^{-5}	4.15×10^{-4}	2.43×10^{-3}
421.	3.24×10^{-3}	10.222	.0139	4.12×10^{-5}	4.63×10^{-4}	3.04×10^{-3}
423.	4.30×10^{-3}	10.187	.0174	5.25×10^{-5}	3.64×10^{-4}	5.38×10^{-3}

Table 12.

Determination of K_{dMgHCO_3} by Titration of $KHCO_3$ Solutions With $Mg(ClO_4)_2$ at 25°C

Titration 1, initial conditions: $Mg(ClO_4)_2$ - .216 M, K_2CO_3 - .0015 M, BP† - 743.712 mm

Volume, ml	$[Mg_T]$, M	pH	μ	S††	$[MgHCO_3^+]$, M	K_{dMgHCO_3}
400.	0.0	5.294	.0031	3.419×10^{-2}	----	----
402.	1.07×10^{-3}	5.274	.0062	3.417×10^{-2}	4.28×10^{-5}	5.20×10^{-2}
404.	2.14×10^{-3}	5.257	.0092	3.414×10^{-2}	9.62×10^{-5}	4.24×10^{-2}
405.	2.67×10^{-3}	5.250	.0108	3.413×10^{-2}	1.16×10^{-4}	4.24×10^{-2}
408.	4.23×10^{-3}	5.233	.0154	3.409×10^{-2}	1.57×10^{-4}	4.62×10^{-2}
410.	5.27×10^{-3}	5.215	.0183	3.407×10^{-2}	2.32×10^{-4}	3.62×10^{-2}
412.	6.29×10^{-3}	5.207	.0213	3.404×10^{-2}	2.46×10^{-4}	3.96×10^{-2}
415.	7.81×10^{-3}	5.194	.0258	3.401×10^{-2}	2.75×10^{-4}	4.16×10^{-2}
417.	8.80×10^{-3}	5.186	.0287	3.398×10^{-2}	2.93×10^{-4}	4.27×10^{-2}
420.	1.03×10^{-2}	5.176	.0331	3.395×10^{-2}	3.10×10^{-4}	4.54×10^{-2}

Titration 2, initial conditions: $Mg(ClO_4)_2$ - .244 M, K_2CO_3 - .0096 M, BP - 741.68 mm

Volume, ml	$[Mg_T]$, M	pH	μ	S††	$[MgHCO_3^+]$, M	K_{dMgHCO_3}
350.	0.0	6.049	.0185	3.407×10^{-2}	----	----
358.5	5.78×10^{-3}	6.002	.0335	3.395×10^{-2}	1.66×10^{-3}	2.34×10^{-2}*
364.	9.44×10^{-3}	5.977	.0429	3.387×10^{-2}	2.08×10^{-3}	2.98×10^{-2}
370.3	1.33×10^{-2}	5.954	.0540	3.378×10^{-2}	2.38×10^{-3}	3.61×10^{-2}
379.9	1.92×10^{-2}	5.930	.0706	3.364×10^{-2}	2.49×10^{-3}	4.75×10^{-2}
385.	2.44×10^{-2}	5.912	.0788	3.358×10^{-2}	2.76×10^{-3}	4.69×10^{-2}

† BP = barometric pressure in millimeters of mercury

†† S = solubility of CO_2 in moles/liter/atmosphere

* Value omitted from final average K_d

Table 13.

Determination of K_{dCaHCO_3} by Titration of $KHCO_3$ Solutions With $Ca(ClO_4)_2$, .3104 M at 25°C

Volume, ml	$[Ca_T]$,M	pH	μ	$S^{\dagger\dagger}$	$[CaHCO_3^+]$,M	K_{dCaHCO_3}
Titration 1, initial conditions: K_2CO_3 - .003 M, BP† - 745.49 mm						
400.	0.0	5.592	.0065	3.417×10^{-2}	----	----
402.	1.54×10^{-3}	5.572	.0108	3.413×10^{-2}	-3.08×10^{-5}	-0.203*
404.	3.07×10^{-3}	5.556	.0151	3.410×10^{-2}	6.34×10^{-5}	1.74×10^{-1}*
405.	3.83×10^{-3}	5.548	.0173	3.408×10^{-2}	1.17×10^{-4}	1.12×10^{-1}*
408.	6.09×10^{-3}	5.530	.0238	3.402×10^{-2}	2.11×10^{-4}	8.93×10^{-2}*
410.	7.57×10^{-3}	5.516	.0280	3.400×10^{-2}	3.10×10^{-4}	7.08×10^{-2}*
412.	9.04×10^{-3}	5.506	.0323	3.396×10^{-2}	3.61×10^{-4}	6.92×10^{-2}*
414.	1.05×10^{-2}	5.495	.0365	3.392×10^{-2}	4.29×10^{-4}	6.44×10^{-2}
416.	1.19×10^{-2}	5.488	.0407	3.389×10^{-2}	4.50×10^{-4}	6.76×10^{-2}
418.	1.34×10^{-2}	5.479	.0449	3.385×10^{-2}	4.99×10^{-4}	6.57×10^{-2}
420.	1.48×10^{-2}	5.471	.0490	3.382×10^{-2}	5.37×10^{-4}	6.51×10^{-2}
Titration 2, initial conditions: K_2CO_3 - .006 M, BP - 745.49 mm						
400.	0.0	5.868	.0123	3.412×10^{-2}	----	----
401.	7.74×10^{-4}	5.861	.0144	3.410×10^{-2}	1.31×10^{-4}	3.66×10^{-2}*
402.	1.54×10^{-3}	5.855	.0166	3.408×10^{-2}	1.81×10^{-4}	5.40×10^{-2}
404.	3.07×10^{-3}	5.842	.0208	3.405×10^{-2}	3.32×10^{-4}	5.57×10^{-2}
405.	3.83×10^{-3}	5.836	.0229	3.403×10^{-2}	4.00×10^{-4}	5.62×10^{-2}
407.	5.34×10^{-3}	5.822	.0269	3.400×10^{-2}	6.00×10^{-4}	4.86×10^{-2}
408.	6.09×10^{-3}	5.817	.0290	3.398×10^{-2}	6.50×10^{-4}	5.03×10^{-2}
410.	7.57×10^{-3}	5.806	.0331	3.395×10^{-2}	7.83×10^{-4}	4.96×10^{-2}
414.	1.05×10^{-2}	5.787	.0413	3.388×10^{-2}	9.90×10^{-4}	5.05×10^{-2}
416.1	1.20×10^{-2}	5.779	.0456	3.385×10^{-2}	1.06×10^{-3}	5.23×10^{-2}
420.	1.48×10^{-2}	5.764	.0536	3.378×10^{-2}	1.20×10^{-3}	5.37×10^{-2}

† BP = barometric pressure in millimeters of mercury

†† S = solubility of CO_2 in moles/liters/atmosphere

* Values omitted from final average K,

Table 14.

Determination of K_{dNaHCO_3} by Titration of $KHCO_3$ Solutions

With $NaClO_4$, .18594 M at 25°C

Volume, ml	$[Na_T]$,M	pH	μ	S††	$[NaHCO_3^o]$,M	K_{dNaHCO_3}
Titration 1, initial conditions: K_2CO_3 - .0015 M, BP - 737.108 mm						
400.	0.0	5.242	.0028	3.420×10^{-2}	----	----
401.	4.64×10^{-4}	5.232	.0033	3.419×10^{-2}	4.01×10^{-4}	3.57×10^{-4}*
405.	2.30×10^{-3}	5.227	.0051	3.418×10^{-2}	3.66×10^{-4}	1.18×10^{-2}
410.	4.54×10^{-3}	5.219	.0073	3.416×10^{-2}	3.44×10^{-4}	2.64×10^{-2}
415.	6.72×10^{-3}	5.210	.0094	3.414×10^{-2}	3.35×10^{-4}	3.99×10^{-2}
420.	8.85×10^{-3}	5.202	.0116	3.412×10^{-2}	3.25×10^{-4}	5.34×10^{-2}
425.	1.09×10^{-2}	5.196	.0136	3.411×10^{-2}	3.07×10^{-4}	6.89×10^{-2}
Titration 2, initial conditions: K_2CO_3 - .003 M, BP - 746.252 mm						
400.	0.0	5.542	.0057	3.417×10^{-2}	----	----
402.	9.25×10^{-4}	5.538	.0066	3.416×10^{-2}	5.26×10^{-4}	3.48×10^{-3}*
405.	2.30×10^{-3}	5.527	.0079	3.415×10^{-2}	5.81×10^{-4}	1.31×10^{-2}
410.	4.54×10^{-3}	5.511	.0101	3.414×10^{-2}	6.50×10^{-4}	2.52×10^{-2}
415.	6.72×10^{-3}	5.494	.0121	3.412×10^{-2}	7.38×10^{-4}	3.26×10^{-2}
420.	8.85×10^{-3}	5.484	.0142	3.410×10^{-2}	7.47×10^{-4}	4.23×10^{-2}
425.	1.09×10^{-2}	5.476	.0162	3.409×10^{-2}	7.38×10^{-4}	5.25×10^{-2}
430.	1.30×10^{-2}	5.469	.0182	3.407×10^{-2}	7.22×10^{-4}	6.30×10^{-2}

† BP = barometric pressure in millimeters of mercury

†† S = solubility of CO_2 in moles/liter/atmosphere

* Values omitted from final average K_d

Table 15

Effect of Complexes on pH and DFI

Constant Conditions:

pH = 8.18

Ca^{++} = 50.

Alk = 100.

TDS = 250.

Ignoring Complexes:

pH_s = 8.179

DFI = 1.002

Na^{+}	Mg^{++}	$SO_4^{=}$	pH_s	DFI
0.	0.	0.	8.20	1.0
0.	0.	75.	8.24	0.9
0.	0.	200.	8.30	0.8
0.	50.	0.	8.21	0.9
0.	50.	75.	8.24	0.9
0.	50.	200.	8.30	0.7
0.	100.	0.	8.21	0.9
0.	100.	75.	8.24	0.9
0.	100.	200.	8.30	0.7
40.	100.	200.	8.31	0.7

NOTE: Concentrations of Ca^{++}, Mg^{++}, and alkalinity are expressed in mg/l as $CaCO_3$. Na , $SO_4^{=}$, and TDS are expressed as mg/l of the ions involved.

Table 16.

Effect of Complexes on pH_s and DFI

Constant Conditions:

pH = 8.68

Ca^{++} = 50.

Alk = 100.

TDS = 250.

Ignoring Complexes:

pH_s = 8.180

DFI = 3.047

Na^+	Mg^{++}	$SO_4^=$	pH_s	DFI
0.	0.	0.	8.21	2.8
0.	0.	75.	8.25	2.6
0.	0.	200.	8.31	2.3
0.	50.	0.	8.21	2.8
0.	50.	75.	8.25	2.6
0.	50.	200.	8.31	2.3
0.	100.	0.	8.22	2.7
0.	100.	75.	8.25	2.5
0.	100.	200.	8.31	2.3
40.	100.	200.	8.32	2.2

NOTE: Concentrations of Ca^{++}, Mg^{++}, and alkalinity are expressed in mg/l as $CaCO_3$. Na^+, $SO_4^=$, and TDS are expressed as mg/l of the ions involved.

Table 17.

Effect of Complexes on pH and DFI

Constant Conditions:

pH = 9.18

Ca^{++} = 50.

Alk = 100.

TDS = 250.

Ignoring Complexes:

pH_s = 8.182

DFI = 8.574

Na^+	Mg^{++}	$SO_4^=$	pH_s	DFI
0.	0.	0.	8.24	7.2
0.	0.	75.	8.27	6.7
0.	0.	200.	8.33	5.9
0.	50.	0.	8.24	7.1
0.	50.	75.	8.28	6.6
0.	50.	200.	8.33	5.9
0.	100.	0.	8.24	7.0
0.	100.	75.	8.28	6.5
0.	100.	200.	8.33	5.8
40.	100.	200.	8.35	5.7

NOTE: Concentrations of Ca^{++}, Mg^{++}, and alkalinity are expressed in mg/l as $CaCO_3$. Na^+, $SO_4^=$, and TDS are expressed as mg/l of the ions involved.