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COMPLEXES AFFECTING THE SOLUBILITY OF CALCIUM CARBONATE IN WATER

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ABSTRACT

COMPLEXES AFFECTING THE SOLUBILITY OF CALCIUM CARBONATE IN WATER

The equilibrium or saturation pH for calcium carbonate is an important criteria in the treatment of our water supplies. In lime softened waters, particularly, which contain somewhat more magnesium than calcium on an equivalent basis, the true value of the pH_s is frequently found to be higher than the theoretical value by 0.3 to 0.4 units. The existence of complexes of magnesium and calcium with carbonate, bicarbonate, hydroxide and sulfate would explain this phenomenon. Calculation of the true pH of saturation, and adjustment of the water to that pH, is essential to avoid corrosion and incrustation in our water distribution systems. The objectives of this project were to evaluate the dissociation constants of the calcium and magnesium complexes with the hydroxide, carbonate, and bicarbonate anions at temperatures of 5, 15, and 25°C. This work was conducted at ionic strengths in the range from .002 to .02, corresponding roughly to waters with total dissolved solids contents of 100 to 1,000 mg/l. The dissociation constants have been determined in terms of activities, so that they are valid at least over the range of ionic strengths at which the tests were made. 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. Dissociation constants have been developed for the complexes of calcium and magnesium with the hydroxide and carbonate anions at 5, 15, and 25°C. The bicarbonate complex of magnesium was studied at 25°C, but no reliable and valid dissociation constant for this complex was obtained from the study. It appears probable that the constant for the calcium bicarbonate complex may be equally difficult to evaluate. The development of reliable dissociation constants of the complexes studied in this project, and a method to utilize them in calculating pH_s would be an aid in producing water of high quality and preventing deterioration of water distribution systems, which accounts for about 60% of the total investment in water utilities.

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INTRODUCTION

Corrosion and scale formation in water distribution systems are generally controlled by pH adjustment. The proper pH depends on the calcium and alkalinity concentrations, but is also affected by formation of certain complexes. If a portion of the calcium and a portion of the alkalinity or carbonate are complexed, this would reduce the concentrations of free ions effective at equilibrium, and make the true pH_s higher than that calculated from the gross concentrations found by analysis. The specific objective of this project was to evaluate the dissociation constants for these complexes so that the optimum pH can be more accurately calculated.

The dissociation constants of interest were those of the complexes formed by the calcium and magnesium ions with the carbonate, bicarbonate, and hydroxide anions. In this project supported by OWRR under grants No. A-051-ILL and S-029-ILL, the dissociation constants for $MgCO^{\circ}_3$, $MgOH^+$, $CaCO^{\circ}_3$, and $CaOH^+$ have been determined at 5, 15, and 25°C. Attempts to determine a constant for the $MgHCO^+_3$ complex were unsuccessful. Both the magnesium and the calcium bicarbonate complexes will be evaluated as this study continues.

BACKGROUND

The water utilities in the United States have a tremendous investment in the miles of pipe, valves, and other appurtenances in the water distribution systems. The replacement cost of these distribution systems is estimated at $25 billion. In addition, each home served by these distribution systems has additional piping and generally a hot water heater.

The distribution system piping is largely coal tar lined cast iron, although in recent years there has been a growing interest in cement lined pipe, and plastics have been used for some small service lines. Due to imperfections in the coal tar linings, the cast iron pipe is subject to corrosion, and, depending upon water quality, the entire system may be subject to deposits, or incrustation.

Either corrosion or incrustation may necessitate cleaning and relining, or, in many cases, replacement of the piping. The first effect 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 rusty water contains hydrated iron oxide suspended as particles and causes the water to be turbid and unsightly. It causes staining of household appliances and porcelain ware, and clothes laundered in such water are also stained.

Since the water is used for human consumption, corrosion inhibitors, such as chromates and nitrites, cannot be used. 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 developes in the pipes. This requires adjustment of the pH of the water to a point where 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. Other treatment chemicals such as polyphosphates and silicates, with or without zinc as an additive, have been used with an effectiveness ranging from zero to 100%.

Calcium carbonate is only slightly soluble in water. The solubility product, K_s, at 25°C is 4.55×10^{-9}, indicating that if equivalent concentrations of calcium and carbonate ion were formed, only 6.8 mg/1 of calcium carbonate would be soluble. The solubility decreases with increasing temperature and increases with increasing mineral concentration.

By analysis, the total calcium concentration, the alkalinity, and the pH, or negative log of the hydrogen ion activity can be determined. The alkalinity, in equivalents, is equal, in most potable waters, 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:

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

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

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

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

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 unionized, 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 waterworks industry has shown that it is often necessary to adjust a water to a pH value 0.5 to 1.0 pH units higher than the calculated pH of saturation 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, being particularly high in cases of high magnesium or sulfate concentrations. It appears probable that this is largely due to formation of the complexes, $CaSO_4^{\circ}$, $CaCO_3^{\circ}$ and $MgCO_3^{\circ}$, with minor effects from the other complexes mentioned above.

pH is a logarithmic function, and a change of 1.0 unit corresponds to a ten-fold change in hydrogen ion concentration. At the lower pH levels, carbonate ion concentration also changes by a factor very nearly equal to ten, although this factor rapidly decreases above pH 9.5. Thus it appears that these complexes are a major factor in the solubility of calcium carbonate. Similarly, it can be seen that, due to the logarithmic nature of the pH scale, a slight error in pH adjustment may lead to a condition of gross under- or over-saturation.

Either of these conditions causes deterioration of the distribution system and household plumbing. Over-saturation leads to excessive scale formation and under-saturation induces corrosion.

Complexes are completely soluble but not ionized, so that the ions combined in the complexes are not effective in the various chemical equilibria, although the usual chemical analysis would 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 a dissociation constant, such as

$$K_{dMgCO_3} = \frac{(Mg^{++})\ (CO_3^{--})}{(MgCO_3^{\circ})} .$$

This 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. These may be reduced to concentrations by applying the proper activity coefficients for the particular ions at the temperature and ionic strength of the solution in question.

Greenwald (2), in 1941, indicated that complexes are formed by calcium and magnesium with both the bicarbonate and carbonate ion. Two different approaches were used to obtain the dissociation constants for $CaCO_3^{\circ}$, $CaHCO_3^{+}$, and the corresponding magnesium complexes.

Garrels, Thompson, and Siever (3) and Garrels and Thompson (4) reported measurement of several of the constants involved and used both their own and previously reported data to calculate the portions of the sodium, calcium, and magnesium which are complexed as the sulfate, carbonate, and bicarbonate in sea water at 25°C.

Unfortunately, the data from these sources is not directly applicable to potable waters. Greenwald worked at an ionic strength of 0.152 and made no attempt to include activity coefficients in his calculations. This ionic strength is far higher than that found in public water supplies. Potable waters generally have ionic strengths in the range of 0.002 to 0.02. Garrels worked at ionic strengths of 0.1 to 5.0 since his primary interest appeared to be sea water. He included activity coefficients in his calculations, but his data for the dissociation constant of $MgCO_3^\circ$ showed a marked variation at the lower ionic strengths indicating that the values he reported may not be applicable in the range of potable waters.

Greenwald's data show considerable scatter, probably due to inadequacies of equipment available at that time for accurate measurement of pH. This paper leaves much to be desired on details of procedures and calculations.

The constants reported by Greenwald and Garrels are given in Table I. Some disagreement between these values, particularly for K_{dCaCO_3}, is apparent, even after correcting Greenwald's values for activity.

Garrels accepted Greenwald's values for $K_{dMgHCO_3^+}$ and $K_{dCaHCO_3^+}$, correcting them to zero ionic strength. He indicated that his data with magnesium could be equally well explained by a $Mg(HCO_3)_3^-$ complex.

Greenwald's value for the magnesium carbonate complex, corrected to zero ionic strength, is

$$K_{dMgCO_3} = K'_d \frac{\gamma_{Mg^{++}}\,\gamma_{CO_3^{--}}}{\gamma_{MgCO_3^\circ}} = 4.26 \times 10^{-3} \times \frac{0.41 \times 0.33}{1.03}$$

$$= 5.6 \times 10^{-4}.$$

This may be compared with Garrels' value of 4.0×10^{-4}, determined by measurement of the change in pH of a Na_2CO_3-$NaHCO_3$ solution with added $MgCl_2$. In their calculations of this constant, Greenwald and Garrels appear to have neglected the effect of the $MgOH^+$ complex on their results. The magnitude of this effect would depend upon the exact experimental conditions.

Doner and Pratt (5) found that the presence of magnesium and sulfate ions increased the solubility of calcium carbonate, concluding that the effect was due to a combination of complex formation and changes in the crystalline form of the solid phase.

Nakayama (6) determined constants for $MgCO_3^\circ$ and $MgHCO_3^+$ at 25°C and ionic strengths of 0.04 to 0.120. His value for K_{dMgCO_3} was 5.75 x 10^{-4}, extrapolated to zero ionic strength, which is in good agreement with Greenwald's value of 5.6 x 10^{-4}, corrected to zero ionic strength, but is in rather poor agreement with Garrels' value of 4.0 x 10^{-4}. Nakayama's value for $K_{dMgHCO_3^+}$ was 5.89 x 10^{-2} which is in reasonable agreement with Greenwald's value of 6.9 x 10~^{2}, corrected to zero ionic strength.

Greenwald's value for the calcium carbonate complex, corrected to zero ionic strength, is

$$K_{dCaCO_3} = K'_d \frac{\gamma_{Ca^{++}} \gamma_{CO_3^{--}}}{\gamma_{CaCO_3^\circ}} = 1.0 \times 10^{-3} \times \frac{0.34 \times 0.33}{1.03}$$

$$= 1.09 \times 10^{-4}.$$

Garrel's value of 6.3 x 10^{-4} for the calcium carbonate complex is in rather poor agreement with Greenwald's value of 1.09 x 10^{-4}.

Nakayama (7) determined constants associated with the $CaCO_3^\circ$ and $CaHCO_3^+$ complexes, and found no evidence of a $Ca(HCO_3)_2^\circ$ complex. His value for $K_{dCaHCO_3^+}$ was 5.64 x 10^{-2} which is in reasonable agreement with that of Greenwald, corrected for ionic strength, but his value for K_{dCaCO_3} was 0.329 x 10^{-4} which is not in agreement either with Greenwald's value of 1.09 x 10^{-4}, corrected for ionic strength, or that of Garrels', 6.3 x 10^{-4}

Morel and Morgan (8) recently presented a method for computing chemical equilibria in systems containing a number of complexes and insoluble phases. It appears that once the dissociation constants of the complexes which affect the solubility of calcium carbonate in water are available, Morel and Morgan's method may be useful in calculating these complexes for practical applications.

Thrailkill (9) quoted a number of the dissociation constants from various sources and applied these values in calculating the degree of saturation of several waters with respect to both calcite and dolomite.

The previous work has been carried out almost exclusively at 25°C, except Greenwald's work which was at 22°C. The purpose of this study was to extend this work over the temperature range of normal public water supplies, 5 to 25°C, as well as to confirm or correct a number of the reported constants.

EXPERIMENTAL

Materials and Methods

Equipment:

A Beckman research model pH meter, equipped with a Beckman #39000 research GP Glass electrode and a Beckman #39170 fibre-junction calomel 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. An Orion divalent cation liquid membrane electrode was used to measure activities of Mg at 25°C and the resulting potential measured to ±0.1 mV accuracy.

The titration cell used in these experiments consisted of a 500-ml Berzelius beaker fitted with a size #14 rubber stopper. The pH-measuring electrodes, a 10-ml micro burette, and N_2 bubbler and reagent addition access tube are mounted in the stopper. 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 plexiglass 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 placed under the smaller water bath. 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.

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-OH. This "polishing" technique gave water with a specific conductance of 1×10^{-7} ohm^{-1} cm^{-1} and was free from carbonate and carbon dioxide.

All possible precautions were taken to reduce the effect of CO_2 from the air. Reagent solutions were stored in containers with stoppers which were fitted with an absorption tube filled with Ascarite to absorb the 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 made up in accordance with specifications recommended by the U.S. National Bureau of Standards. The buffers were checked against Beckman standard and precision buffer solutions and agreed within the limits of accuracy set by the U.S. National Bureau of Standards.
    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:
        3.40 g KH_2PO_4 + 3.55 g $Na_2 HPO_4$ per liter
        (the salts were dried for two hours at 110°C
        before weighing)
    c. Borate buffer, .01M solution, pH 9.18 at 25°C:
        3.814 g $Na_2B_4O_7 \cdot 10H_2O$ per liter
2. Potassium perchlorate, $KC10_4$, approximately 0.1M:
    13.86 g $KC10_4$ per liter with 6.93 x 10"^{6} M KOH added for pH adjustment. Atomic Absorption was the method used to determine the concentration of K^+.
3. Magnesium perchlorate, $Mg(C10_4)_2$, approximately 0.24M:
    53.6 g $Mg(C10_4)_2$, anhydrone, per liter with 4 x 10^{-4}M $HC10_4$ added to adjust pH to 6.6 ± 0.2. These solutions were standardized by the EDTA titrimetric method (10).
4. Calcium perchlorate, $Ca(C10_4)_2 \cdot 6H_2O$,
    a. approximately 0.3M:
        100 g $Ca(C10_4)_2 \cdot 6H_2O$ per liter with 4 x 10"^{6} M KOH added to adjust the pH to 6.6 ± 0.2.

b. approximately 0.075M:

25 g $Ca(C10_4)_2 \cdot 6H_2O$ per liter with 7×10^{-7} M KOH added to adjust pH to 6.6 + 0.2.

Calcium solutions were standardized by the EDTA titrimetric method (10).

5. Potassium Carbonate, K_2CO_3, primary standard 0.1 M:

   13.821 g K_2CO_3 per liter

6. Perchloric acid, $HC10_4$, approximately 0.23M:

   Diluted 20 ml of 11.75 N $HC10_4$ to 1 liter.

   Standardized the dilute $HC10_4$ against 0.2N primary standard K_2C0_3.

7. Potassium hydroxide, KOH, approximately 0.04M:

   2.5g KOH per liter

   Standardized the diluted KOH solution against .02N H_2SO_4 to a phenolphthalein endpoint.

Procedures:

A titration procedure has been used to determine the dissociation constants of $MgOH^+$, $MgCO_3^0$, $CaOH^+$, and $CaCO_3^0$. Adding an alkali to a solution of potassium bicarbonate produces a pH shift predictable from the bicarbonate-carbonate equilibrium constant, K_2'. With calcium or magnesium present, the quantities of carbonate and bicarbonate effective in the equilibrium are modified by the complex formation. Two equilibria are involved so that the solution requires the method of successive approximations.

For most of this work, a variation of this procedure was used. Either calcium perchlorate or magnesium perchlorate was the titrant added to a solution containing carbonate and bicarbonate ions. In this case, the pH change is primarily due to the carbonate ions complexed.

Any determination of these dissociation constants which is based on the change in pH will be complicated by the formation of another complex, $MgOH^+$ (or $CaOH^+$). Titration methods similar to those described above, but in solutions with no carbonate or bicarbonate, were used to determine this dissociation constant.

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 OH^- 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 these experiments, 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. The only measurement required under these conditions was the equilibrium pH.

Prior to each titration, the pH electrodes were calibrated in standard phosphate buffer, at the temperature of the test. The rubber stopper-electrode assembly was then tightly fitted into a 500-ml Berzelius beaker containing a magnetic stirring bar. The beaker was purged with N_2. A known volume of CO_2-free, deionized water was added by means of a hypodermic syringe and after the temperature of the water reached the desired level, the desired salts were added. The initial volume of sample was 430 ml + 1.0 ml, leaving a minimum of head space. 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.

In the $MgHCO_3^+$ experiments, the Orion specific ion liquid membrane electrode was first calibrated in $Mg(ClO_4)_2$ solutions of known, calculated Mg activity. In these experiments, $KC10_4$ was added for ionic strength adjustment, and the resulting potential was measured using the Beckman research pH - millivoltmeter accurate to ± 0.1 mv.

Calculations:

The calculations required are rather complex, but can be handled by computer methods. Most of the required relationships have been derived and appropriately programmed.

Six equilibria are involved. With calcium hydroxide, bicarbonate, and carbonate these are:

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

Similar equilibria with magnesium may be written, and sulfate may be added as a third complexing ion with either calcium or magnesium.

Results of the limited work thus far involving the bicarbonate complex (reaction 5) of magnesium indicated that this complex, if present, is a very weak complex. Therefore, the bicarbonate complex has not been considered in our calculations to date. It is possible that another method, similar to that reported by Hostetler (11) may produce reliable results for this complex. If so, it will be possible to either determine a value for this dissociation constant and use it in our calculations, or prove that the effect of this complex is negligible.

Reactions 4 and 6 involving the hydroxide and carbonate complexes are the reactions of primary interest in this report. In the titrations with $Ca(ClO_4)_2$, for instance, added Ca causes formation of CaOH and

$CaCO_3^\circ$, reducing the concentrations of the OH^- and CO_3^{--} anions. This causes 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 constants for K_w are tabulated in Table II. Since few ions are involved in the equilibrium, a fairly simple computer program was sufficient to calculate K_{dCaOH^+} (Table III). Once the value for the K_{dCaOH^+} complex was determined, then it was used along with the other constants K_W, K_1 and K_2 (Table II) to determine a value for the $K_{dCaCO_3^\circ}$ complex. The method for this step, as outlined in the Procedures section, was the titration of a carbonate-bicarbonate solution with calcium perchlorate.

The thermodynamic constants, K_W, K_1, K_2, and the constants for the complexes $MgOH^+$, $MgCO_3^\circ$, $CaOH^+$, $CaCO_3^\circ$, 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. Using the same example as above:

$$K_{dCaOH^+} = K'_{dCaOH^+} \cdot \frac{\gamma_{Ca^{++}} \cdot \gamma_{OH^-}}{\gamma_{CaOH^+}} .$$

K denotes the true thermodynamic constant, K', the constant for a particular ionic strength, based on concentrations, and $\gamma_{Ca^{++}}$, the activity coefficient of the particular ion.

Ion activity coefficients, γ_i, were calculated vising the extended Debye-Hückel equation (12):

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

where z is the valence or charge on the ion, μ is the ionic strength of the solution, a is the size of the ion, A and B are constants dependent upon e, the dielectric constant which is equal to 78.54, and T, the absolute temperature of the solvent. A = 1.825 x 10^6 X(ET)$^{\mathbf{a}}$, B = 50.3 x $(\varepsilon T)^{-1/2}$. Approximate values for a, the ion size parameter, of a number of selected ions have been estimated by Kielland (13) and used by Butler (12) to calculate values of single ion activity coefficients at various ionic strengths. 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, $1/2\sum C_i z_i^2$.

Ion activity represented by parenthesis, e.g. (Ca), is related to ion concentration by the relation $(Ca^{++}) = \gamma_{Ca^{++}} [Ca^{++}]$ where the brackets [ ] denote concentration in moles per liter and Y is the activity coefficient as calculated by the above equation.

Table II is a listing of the constants for A and B, K_W, K_1, and K_2, and the reference sources used for calculating these constants at 5, 15, and 25°C. The K values in Table II are related to the corresponding K' values by the following relationships:

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

$$K_1 = K'_1 \times \frac{\gamma_{H^+} \times \gamma_{HCO_3^-}}{\gamma_{H_2CO_3}}$$

$$K_2 = K'_2 \times \frac{\gamma_{H^+} \times \gamma_{CO_3^{--}}}{\gamma_{HCO_3^-}}$$

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

The values of A and B in Table II were calculated using 78.54 as the dielectric constant of water. An expression for the variation of this parameter with temperature (14) is being used to recalculate the values of A, B, the activity coefficients, and the various dissociation constants at 5 and 15°C. The change in dissociation constants is expected to be modest. The corrected values will be listed in a later report on this project.

The general format of the computer programs written to calculate the dissociation constants for the various complexes studied was the same. Briefly, the input data from the titration experiments included the temperature and related K, A, and B taken from Table II; the initial conditions of reagent concentrations added, sample volume and the measured pH prior to the addition of the titrant of known molarity.

An initial estimate of the ionic strength of the solution is calculated from this data. Subsequently, 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, using these calculated concentrations, and the activity coefficients, K' values, and ion concentrations are recalculated. These ion concentrations define the initial or reference condition.

With 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 $Ca(C1O_4)_2$, we have based our calculations on the fact that, except for the volume change, the alkalinity remains constant. Thus in CO_2-free solutions, titrated with Ca any decrease in the alkalinity represents complex formation. If we represent the reference concentrations by $[OH_T^-]$ and $[H_T^+]$, and the ratio of initial to final volume by V_c, then

$$[CaOH^+] = V_c \; ([OH_T^-] - [H_T^+]) - [OH^-] + [H^+].$$

As in the calculation of the ion concentrations in the reference condition, this calculation requires an initial estimate of the ionic strength which is refined by repetitive calculation of the individual ion concentrations as well as the complex.

In solutions containing carbonates and bicarbonates, this mass balance must also include the carbonate alkalinity. This requires terms representing $(2[CO_3^{--}] + [HCO_3^-])$. Knowing the original input of carbonate, these can be expressed as functions of total carbon dioxide, $[H^+]$, K_1', and K_2'. This results in a somewhat more complicated expression.

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

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

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

Table III gives the computer program used for the calculation of the dissociation constant for the $CaOH^+$ complex. A similar program was written for the MgOH complex using the proper ion activity coefficients. Most of the terms appearing in Table III need no explanation. The terms which may be confusing are defined below:

R, e.g. PHR, denotes initial conditions before the addition of Ca^{++} titrant. The absence of the R notation refers to final conditions after addition of titrant.

MU = μ = ionic strength

M = the concentration of standard titrant expressed in moles per liter

CAT = total concentration of calcium

C = [CaOH], concentration of complex

KPD1 = K'_{dCaOH^+}

KD1 = K_{dCaOH^+}

The calculations were considered to be reliable when the same dissociation constant was obtained for a majority of the points along the titration. 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 individual calculated K_d value which was markedly different from the others was not included in the calculation of the average K_d. The standard deviation, o, was determined by the formula:

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

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.

Sensitivity Tests:

In order to have some indication of the sensitivity of our tests to experimental errors, components of our original data from the first sample in Table VI b were varied and the dissociation constant for the CaOH complex was recalculated based on these variations. The reference pH of the sample is 10.575. After the addition of 5 ml of $Ca(C10_4)_2$ titrant, the measured pH is 10.525 and the calculated $K_{dCaOH}+$ for this data point is 0.356514×10^{-1}. The changes we made and the corresponding variation in the recalculated $K_{dCaOH}+$, expressed in terms of percent error, are listed below.

1) If both the pHR and final pH values are varied by + .01 pH, only a ± .05% error results.
2) If only the final pH reading is increased by .002 pH, a + 9.27% error results. A decrease of .002 pH in the final pH, produces a -7.86% error in the calculated K_d value.
3) If a + 1.% error had been made in the standardization of the $Ca(C10_4)_2$ titrant, a ± 1.57% difference will be found in the K_d value.
4) An error of +0.5 units in the pH of the titrant would produce a -.04% error in K_d, a -0.5 unit-error in the titrant pH would produce an error of +.02% in the calculated $K_{dCaOH}+$.

We have concluded from this sensitivity study that an error made in the standardization of the pH meter, reflected by a constant error in both initial and final pH readings would produce a very small error in the calculated K_d. However, if we assume that the initial pH reading is correct and an error of .002 occurs in making the final pH reading, (or the reverse of this), the resulting error in K_d is approximately 9%. Errors in the concentration of titrant would produce some error in the calculated K_d. However, inadequate neutralization of this titrant - within reasonable limits, of course - does not appear to cause appreciable errors in the value of K_{dCaOH^+}.

RESULTS

The dissociation constant for $MgCO_3^\circ$ complex was first determined, assuming that this was the only complex formed. It was later realized that MgOH complex was also formed, affecting the $MgCO_3^\circ$ results, so a constant was determined for the dissociation of the MgOH complex. The $MgHCO_3^+$ complex was also considered, but if this complex was formed, neither the titration method nor Mg activity measurements with a specific-ion liquid membrane electrode gave a reliable dissociation constant for this complex.

Dissociation constants were also determined for the CaOH and $CaCO_3^\circ$ complexes by titration with standard $Ca(C10_4)_2$. Difficulties due to $CaCO_3$ precipitation were anticipated in using this titration procedure for $CaCO_3^\circ$. The results of some preliminary work, however, indicated that such experiments would be possible since precipitation was not as rapid as expected. These results appeared to support a statement by Garrels and Thompson (4) that, "The measurement of the dissociation constant for $CaCO_3^\circ$ is facilitated by the fact that calcium carbonate - bicarbonate solutions that are much supersaturated with respect to calcite will persist for several minutes with out precipitating. Thus, it is possible to measure the pH of solutions where the activity product $(a_{Ca^{++}})$ $(a_{CO_3^{--}})$ is as large as $10^{-6.8}$."

The complexes evaluated in this study are discussed individually in the following pages. The dissociation constant for the MgOH , $MgCO_3^\circ$, CaOH , and $CaCO_3^\circ$ complexes each are tabulated at the temperatures studied along with the results of studies by other investigators.

In comparing our results with those of other investigators, the interested reader should keep in mind that (1) we used a titration procedure to determine the dissociation constants, (2) we calculated the values of the constants in terms of activities using the extended Debye-Hückel equation to determine ion activity coefficients, (3) the K_d values were calculated by taking an average of n observations and (4) the pK_d values were calculated by taking the negative logarithm of the calculated K_d, i.e., $pK_d = - \log K_d$.

The MgOH* Complex

The dissociation constant for the MgOH complex was determined by two procedures at 25°C. In the first procedure, $KC10_4$- KOH solutions were titrated with $Mg(C10_4)_2$ solution. Table IV contains a summary of the pertinent data from these titrations. The 18 resulting values give an average $K_{dMgOH}+ = .819 \times 10^{-2}$ by this procedure.

In the second procedure, $KC10_4$-$Mg(C10_4)_2$ solutions were titrated with KOH. The 39 resulting values obtained by this procedure give an average $K_{dMgOH}+ = .836 \times 10^{-2}$. Therefore, our final value of the dissociation constant for the MgOH complex at 25°C is taken as an average of data points from both titration procedures. And as illustrated in the following table, our value does not agree with the value determined by Stock and Davies (15) later tabulated by Davies, in Hamer (16) using the Davies equation to calculate their ion activity coefficients.

K_{dMgOH^+}

<u>STOCK and Davies (15)</u>: titration of $MgCl_2$ solutions with $Ba(OH)_2$, range of pH = 7.99 - 9.49, calculated Y using the Davies equation:

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

temp.	5°C	15°C	25°C
K_d	--	--	0.260×10^{-2}
pK_d			2.58

<u>THIS WORK</u>: range of pH = 9.9 - 11.3, range of μ = .005 - .02

K_d	1.054×10^{-2}	0.983×10^{-2}	0.830×10^{-2}
pK_d	1.98	2.01	2.08
σ*	±.00011	±.00073	±.00074
n	20	18	57

* refers to standard deviations from the K_d values

The $MgCO_3^\circ$ Complex:

The dissociation constant of the $MgCO_3^\circ$ complex was determined by titration of carbonate-bicarbonate solutions with $Mg(C10_4)_2$ solution. We have assumed that a solution of $KC10_4$ and K_2CO_3 (or total $C0_2$) treated with $HC10_4$ will produce added $KC10_4$ and a mixture of HCO_3^- and CO_3^{--}. The concentrations of these ions will vary with both pH and CO_{2T}. The change in pH noted upon titrating with $Mg(C10_4)_2$ therefore includes that due to change in ionic strength and that due to complex formation. Table V contains a summary of data from two separate titrations. The averages of n calculated values for $K_{dMgCO_3^\circ}$ at 5, 15, and 25°C determined in this study and those determined by other investigators are tabulated below. Corresponding K_{dMgOH^+} values are included in our calculations of $K_{dMgCO_3^\circ}$.

In our work, the value of the dissociation constant for $MgCO_3^\circ$ at 25°C, neglecting the effect of the MgOH complex, was found to be 1.15xl0"^{3} (a = + .000047). It is apparent that the complex, MgOH , is important to this equilibrium. If accurate values are to be obtained for the $MgCO_3^\circ$ constant, the formation of MgOH complex should be accounted for in the calculations.

Using the raw data from Garrels work and our method of calculation, we found that the value of $K_{dMgCO_3^\circ}$ ranged from 1.12×10^{-3} to 2.05×10^{-3}. The median value was about 1.36×10^{-3}. Garrels' tests were performed at very high ionic strength and our calculation of activity coefficients may not be applicable to these high ionic strengths.

$K_{dMgCO_3^\circ}$

GREENWALD (2): titration experiments, range of pH = 6.7 - 9.8, μ = 0.152, determined apparent constants based on concentrations

temp.	5°C	15°C	25°C
K'_d	--	--	4.26×10^{-3}*
pK'_d			2.37
	applying activity corrections:		
K_d			5.6×10^{-4}*
pK_d			3.25

*actual temp. = 22°C

GARRELS (3): titration experiments, range of pH = 8.6 - 9.8, range of μ = .09 - .46

K_d	--	--	4.0×10^{-4}
pK_d			3.4

NAKAYAMA (6): potentiometric estimation of H and Mg ion activities, range of pH = 8.6 - 9.8, range of μ = .04 - .12, calculated Y using the extended Debye-Hückel equation

K_d	--	--	5.75×10^{-4}
pK_d			3.24

THIS WORK: range of pH = 9.4 - 10.8, range of μ = .004 - .025

K_d	1.53×10^{-3}	1.51×10^{-3}	1.26×10^{-3}
pK_d	2.81	2.82	2.90
σ**	±.000065	±.000054	±.000028
n	35	24	40

**refers to standard deviations from the K_d values.

The $CaOH^+$ Complex;

The dissociation constant for the CaOH complex was determined by titration of $KC10_4$-KOH solutions with standard $Ca(C10_4)_2$ solution. Table VI a and b contains a summary of the data from these titrations at 25°C only.

As illustrated in the table below, our values at 15° and 25°C agree very well with those calculated by Gimblet and Monk (17). No direct reference to 5°C was found in the work by Gimblet and Monk. However, Thrailkill (9) quotes Gimblet and Monk as the source for pK_{dCaOH^+} and gives an extrapolated value of pK_d at 5°C.

K_{dCaOH^+}

GIMBLET and MONK (17): EMF measurements, calculated Y using Davies equation:

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

Temp.	5°C	15°C	25°C
K_d	4.90xl0"^{2}*	4.60xl0"^{2}	4.30xl0"^{2}
pK_d	1.31	1.34	1.36

*determined by extrapolation by Thrailkill (9)

THIS WORK: range of pH = 10.5 - 11.9, range of μ = .008 - .026

K_d	3.379xl0"^{2}	4.317xl0^{-2}	4.166xl0^{-2}
pK_d	1.47	1.36	1.38
a**	±.00624	±.0103	±.00602
n	23	26	29

** refers to standard deviations from K_d values.

The $CaCO_3^\circ$ Complex:

The dissociation constant for $CaCO_3^\circ$ complex was determined by titration of carbonate - bicarbonate solutions with $Ca(ClO_4)_2$ solution. As in the determination of the $MgCO_3^\circ$ complex, $KClO_4$-K_2CO_3 solutions were treated with $HClO_4$ to produce added $KClO_4$ and a mixture of HCO_3^--CO_3^{--} the exact concentrations of these ions being dependent upon both pH and total CO_2. Table VII contains a summary of data from two of the titrations that were made at 25°C. The averages of n calculated values for $K_{dCaCO_3^\circ}$ found in this study and values determined by other investigators are tabulated below. Corresponding K_{dCaOH^+} values are included in our calculation of $K_{dCaCO_3^\circ}$. Our value at 25°C is in excellent agreement with that of Garrels and Thompson (4) who used a titration procedure similar to our method to obtain the dissociation constant for the $CaCO_3^\circ$ complex.

$K_{dCaCO_3^\circ}$

GREENWALD (2): solubility experiments, range of pH = 7.5 - 9.5, μ =.152, values calculated in terms of concentration

Temp.	5°C	15°C	25°C
K'_d			1.00×10^{-3}*
pK'_d			3.00

applying activity corrections:

K_d	—	—	1.09×10^{-4}*
pK_d			3.96

*actual temp. = 22°C

NAKAYAMA (7): solubility experiments, measurement of H and Ca ion activities, activity coefficients were derived from the extended Debye-Hückel theory

K_d	—	—	3.29×10^{-5}
pK_d			4.48

LAFON (18): solubility experiments, calculated values in terms of activities

K_d	—	—	7.95×10^{-4}
pK_d			3.1

GARRELS and THOMPSON (4): titration experiments similar to ours, calculated value in terms of activities, very high ionic strengths

K_d	—	—	6.3×10^{-4}
pK_d			3.2

THIS WORK: range of pH = 9.80 - 10.60, range of μ = .005 - .02

K_d	6.812×10^{-4}	6.744×10^{-4}	5.996×10^{-4}
pK_d	3.16	3.17	3.22
σ**	±.0000072	±.0000196	+.0000354
n	41	21	25

** refers to standard deviations from K_d values.

The $MgHCO_3^+$ Complex:

The $MgHCO_3^+$ complex was considered in experiments at 25°C with $MgCO_3^0$. However, if the $MgHCO_3^+$ complex was formed, our methods are not sufficiently sensitive to determine a dissociation constant. In a second attempt, tests were conducted in which pH and total carbon dioxide were varied, so as to maintain constant carbonate ion concentration while the bicarbonate ion concentration was varied over a considerable range. It was expected that these tests would be helpful in determining whether or not a bicarbonate complex is formed. However, this approach also yielded inconclusive results. In a third approach, a specific ion electrode which is sensitive to magnesium activities was used.

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:

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

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 using the extended Debye-Hückel equation. The specific ion electrode was then used to measure the potential and by applying the simple Nernst equation, the actual Mg activity was calculated, and the extended Debye-Hückel equation 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 $MgCO_3^\circ$ 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_d, was determined.

This method of calculating $K_{dMgHCO_3^+}$ 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 and the resulting value for $K_{dMgHCO_3^+}$ was 1.037×10^{-2} ($pK_d = 1.984$). For the second sample in which $[K^+]$ added was .01 the resulting K_d was 2.892×10^{-2} ($pK_d = 1.593$).

Neither of these values agrees with either the value of $pK_d = 1.23$ determined by Nakayama (6) using the specific ion electrode nor the average value of pK, = 0.95 determined by Hostetler (11) using a titration procedure. Hostetler determined five pK, values for $MgHCO_3^+$ complex ranging from 0.83 to 1.05. In the near future, attempts will be made to determine the constant for $MgHCO_3^+$ by procedures similar to Hostetler's method.

DISCUSSION

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 appears to be due to the formation of complexes of calcium and magnesium with bicarbonate, carbonate, and hydroxide ions. Calculation of the true pH of saturation, and adjustment of the water to that pH, is essential to avoid corrosion and incrustation in our water distribution systems. In order to calculate the true pH of saturation accurate values of the dissociation constants for the complexes must be known.

This project was designed to evaluate the true thermodynamic dissociation constants of the calcium and magnesium complexes with the hydroxide, carbonate, and bicarbonate anions 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 μ.

We have developed dissociation constants for the MgOH , $MgCO_3^0$, CaOH , and $CaCO_3^0$ complexes in water using a titration procedure at temperatures of 5, 15, and 25°C. These values are listed in Table VIII. The constants were determined at ionic strengths in the range of .002 - .02 and were developed in terms of activities so that they are valid at least over the range of ionic strengths at which the tests were made.

Attempts to develop a dissociation constant for $MgHCO_3^+$ have not been successful. Other procedures must be tested to determine both this constant and the constant for $CaHCO_3^+$.

A number of other investigators have developed dissociation constants for each of the complexes we have studied. However, it appears that most of these workers conducted their studies only at room temperature (approximately 25°C) and ionic strengths too high to be applicable to public water supplies. A few based their calculations on concentrations rather than the ion activities used in this study.

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 in ground waters, lakes and reservoirs, and the buffer system controlling the pH of these waters.

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REFERENCES

(1) Feitler, H. (1972). Cooling Water Scale Control: The Scale Meter and the Critical pH of Scaling. Materials Protection and Performance 11 (No. 6): 29-33.

(2) Greenwald, I. (1941). The Dissociation of Calcium and Magnesium Carbonates and Bicarbonates. Jour. Biol. Chem. 141: 789-796.

(3) Garrels, R. M., M. E. Thompson, and R. Siever (1961). Control of Carbonate Solubility by Carbonate Complexes. Am. Jour. Sci. 259: 24-45.

(4) Garrels, R. M., and M. E. Thompson (1962). A Chemical Model for Sea Water at 25°C and One Atmosphere Total Pressure. Am. Jour. Sci. 260: 57-66.

(5) Doner, H. E., and P. F. Pratt (1969). Solubility of Calcium Carbonate Precipitated in Aqueous Solutions of Magnesium Sulfate Salts. Soil Sci. Soc. Amer. Proc. 33: 690-693.

(6) Nakayama, F. S. (1971). Magnesium Complex and Ion-Pair in $MgCO_3$-CO_2 Solution System. Jour. Chem. Eng. Data 16: 178-181.

(7) Nakayama, F. S. (1968). Calcium Activity, Complex and Ion-Pair in Saturated CaC03 Solutions. Soil Sci. 106: 429-434.

(8) Morel, F., and James Morgan (1972). A Numerical Method for Computing Equilibria in Aqueous Chemical Systems. Environ. Sci. Technol. 6: 58-67.

(9) Thrailkill, J. (1972). Carbonate Chemistry of Aquifer and Stream Water in Kentucky. Jour. Hydrol. 16: 93-104.

(10) American Public Health Association (1971). Standard Methods for the Examination of Water and Wastewater. 13th edition. American Public Health Assoc, Inc., N.Y. p. 179, p. 84.

(11) Hostetler, P. B. (1963). Complexing of Magnesium with Bicarbonate. J. Phys. Chem. 67: 720-721.

(12) Butler, J. N. (1964). Ionic Equilibrium, a mathematical approach. p. 432-458. Addison-Wesley Publishing Co., Inc., Massachusetts.

(13) Kielland, J. (1937). Individual Activity Coefficients of Ions in Aqueous Solutions. J. Am. Chem. Soc. 59: 1675-1678.

(14) Wyman, J., Jr., and E. N. Ingalls (1938). The Dielectric Constant of Deuterium Oxide. J. Am. Chem. Soc. 60: 1182-1184.

(15) Stock, D. I., and C. W. Davies (1948). The Second Dissociation Constant of Magnesium Hydroxide. Faraday Soc. Trans. 44: 856-859.

(16) Davies, C. W. (1959). Incomplete Dissociation in Aqueous Salt Solutions. p. 19-34. In W. J. Hamer (editor) The Structure of Electrolytic Solutions, John Wiley and Sons, Inc., N.Y.

(17) Gimblet, F. G. R., and C. B. Monk (1954). E. M. F. Studies of Electrolytic Dissociation, Part 7. - Some alkali and alkaline earth metal hydroxides in water. Trans. Faraday Soc. 50: 965-972.

(18) Lafon, G. M. (1970). Calcium Complexing with Carbonate Ion in Aqueous Solutions at 25°C and 1 Atmosphere. Geochim. Cosmochim. Acta. 34: 935-940.

Table I

Dissociation Constants* Reported by Greenwald and Garrels

Greenwald

	K'	pK'		K'	pK'
$K'_{dMgHCO_3^+}$	$1.7 \times 10^{"1}$	0.77	$K'_{dCaHCO_3^+}$	1.6×10^{-1}	0.80
K'_{dMgCO_3}	$4.26 \times 10^{"3}$	2.37	K'_{dCaCO_3}	1.00×10^{-3}	3.00
$K'_{4MgHCO_3^+}$	$3.16 \times 10^{"9}$	8.50	$K'_{4CaHCO_3^+}$	1.26×10^{-8}	7.90

Garrels

	K	pK		K	pK
$K_{dMgHCO_3^+}$	6.9×10^{-2}	1.16	$K_{dCaHCO_3^+}$	5.5×10^{-2}	1.26
K_{dMgCO_3}	4.0×10^{-4}	3.4	K_{dCaCO_3}	6.3×10^{-4}	3.2
K_{dMgSO_4}	$2.3 \times 10^{'3}$	2.36	K_{dCaSO_4}	4.9×10^{-3}	2.31
K_{dNaHCO_3}	1.8	-0.25			
$K_{dNaCO_3^-}$	$5.4 \times 10^{"2}$	1.27			
$K_{dNaSO_4^-}$	$1.9 \times 10^{"1}$	0.72			

* The dissociation constants listed are for ion pairs (e.g., $CaHCO_3^+$, $MgCO_3^\circ$, $NaSO_4^-$). In addition, Greenwald reported and used a related constant, K'_4, defined as follows:

$$K'_4 = \frac{[H^+][MCO_3^\circ]}{[MHCO_3^+]} = \frac{K'_2 \; K'_{dMHCO_3^+}}{K'_{dMCO_3^\circ}}$$

Greenwald's values are based on concentrations and were developed at an ionic strength (μ) of approximately 0.152 and a temperature of 22°C. Garrels[1] values are based on activities and should be independent of ionic strength. They were developed at a temperature of 25°C and would vary with temperature.

Table II

Debye-Hückel Constants and H_2O - H_2CO_3 Dissociation Constants

$$K_w = (H^+) \cdot (OH^-), \quad K_1 = (H^+) \cdot (HCO_3^-)/(H_2CO_3), \quad K_2 = (H^+) \cdot (CO_3^{--})/(HCO_3^-)$$

Temp. (°C)	A(a)	B(a)	K_w(b)	K_1(c)	K_2(d)
5	.5651	.3403	.186 E-14	3.008 E-07*	2.77 E-11
15	.5359	.3343	.452 E-14	3.722 E-07	3.71 E-ll
25	.5092	.3287	1.008 E-14	4.310 E-07	4.69 E-ll

(a) Butler, J. N.(1964). "Ionic Equilibrium, a mathematical approach." p. 433. Addison Wesley Publishing Co., Inc., Mass.

(b) Harned, H. S. and W. J. Hamer (1933), JACS, V.55, p. 2198.

(c) Shedlovsky, T. and D. A. MacInnes (1935). JACS, V. 57, p. 1710.

* $\log K_1 = 545.56 + 0.12675\ T - 215.21 \log T - 17{,}052/T$

(d) Harned, H. S., and S. R. Scholes, Jr. (1941). JACS, V. 63, p. 1708.

Table III. Computer Program for Calculation of K_{dCaOH^+}

```
C
C       PROGRAM NUMBER FS-5A   CA0H+
C
        IMPLICIT REAL*8 (A-H, K, M, Ø-Z)
C
        KW=.1008E-13
        A=.5092
        B=.3287
C       T=25.
C
        PRINT 3
3       F0RMAT ( '1' )
        PAGE=0
9       CØNTINUE
        PAGE=PAGE+1
        READ (5, 1) KCL, KØH, M, VI, PHR, ML, PH
1       F0RMAT (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=10.**(-AMU/(1.+9.*BMU))
        GØHR=10.**(-AMU/(1.+3.*BMU))
        KPW=KW/(GHR*GØHR)
        HR=(10.**(-PHR))/GHR
        ØHR=KPW/HR
        MUR=KCL+(KØH+HR+ØHR)/2.
4       CØNTINUE
C
C       SECTIØN TWØ
C
        MU=MUR+3.*ML*M/VI
        DØ 5 J=1, 6
        AMU=A*DSQRT(MU  )
        BMU=B*DSQRT(MU  )
        GH  =10.**(-AMU/(1.+9.*BMU))
        GØH =10.**(-AMU/(1.+3.*BMU))
        VC=VI/ (VI+ML)
        ALK=VC*(ØHR-HR)
        KPW=KW/(GH*GØH)
        H=(10.**(-PH))/GH
        ØH=KPW/H
        C=ØH-H-ALK
        IF (C.LE.O.) GØ TØ 13
        IF (J.EQ.6) GØ TØ 6
        CAT=ML*M/(VI+ML)
        CA=CAT-C
```

ERRATUM

The formula for the calculation of C, the 12th line in SECTIØN TWØ of the computer program on page 42, should read as follows:

C = ALK - ØH + H

```
      MU=VC*KCL+CAT+2.*CA+(VC*K0H+C+0H+H)/2.
5     CØNTINUE
6     CØNTINUE
      KPD1 = CA*ØH/C
      GCA=10.**(-4.*AMU/(1.+6.*BMU))
      GC=10.**(-AMU/(1.+6.*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 IV.

Change of pH of $KC10_4$-KOH solutions with added $Mg(C10_4)_2$ solution

T = 25°C, $Mg(C10_4)_2$ = .2257 M

$[KC10_4]$ = .00513 M [KOH] = .000143 M

Vol. (ml)	$[Mg_T]$ x 10^{2},M	pH	$[MgOH^+]$ x 10^{4},M	μ x 10^{1}	K_d x 10^{2}
430.	0.0	10.101R	—	$.053^R$	—
431.	.052	10.075	.064	.068	.770
432.	.104	10.052	.117	.084	.778
434.	.208	10.014	.108	.115	.811
436.	.308	9.981	.263	.145	.817
438.	.417	9.950	.320	.177	.828
440.	.513	9.924	.365	.206	.825

[KC10.J = .00513 M [KOH] = .000285 M

Vol. (ml)	$[Mg_T]$ x 10^{2},M	pH	$[MgOH^+]$ x 10^{4},M	μ x 10^{1}	K_d x 10^{2}
430.	0.0	10.394**	—	$.054^R$	—
431.	.053	10.371	.107	.070	.914
432.	.103	10.350	.202	.085	.874
434.	.208	10.312	.364	.116	.867
436.	.313	10.278	.498	.147	.860
438.	.412	10.248	.609	.176	.848
440.	.511	10.219	.711	.206	.827

[KC10.J = .00513 M [KOH] = .000535 M

Vol. (ml)	$[Mg_T]$ x 10^{2},M	pH	$[MgOH^+]$ x 10^{4},M	μ x 10^{1}	K_d x 10^{2}
430.	0.0	10.660R	—	$.056^R$	--
431.	.052	10.638	.189	.072	.919
432.	.106	10.614	.395	.088	.830
434.	.209	10.567	.783	.118	.714
436.	.312	10.534	1.017	.148	.744
438.	.410	10.504	1.218	.177	.748
440.	.511	10.477	1.384	.207	.759

R = reference conditions before $Mg(C10_4)_2$ is added.

$$K_d = \frac{[Mg^{++}]\ [OH^-]}{[MgOH^+]} \times \frac{\gamma_{Mg^{++}}\ \gamma_{OH^-}}{\gamma_{MgOH^+}}$$

Note: All values have been multiplied by factor shown in heading.

Table V.

Titration of HCO_3^--CO_3^{--} solutions with $Mg(C10_4)_2$ solution.

T = 25°C, K_dMgOH^+ = .83 X 10^{-2}

$[CO_{2T}]$ = .00232 M, $[HC10_4]$ = .00081 M, $[KC10_4]$ = .00410 M

$Mg(C10_4)_2$ = .2198 M

Vol. (ml)	$[Mg_T]$ x 10^{2},M	pH	$[MgOH^+]$ x 10^{4},M	$[MgCO_3^0]$ x 10^{3},M	μ x 10^{1}	K_d x 10^{3}
430.	0.0	10.312^R	--	--	$.101^R$	--
431.	.051	10.267	.060	.149	.110	1.25
432.	.102	10.227	.113	.263	.120	1.31
434.	.202	10.149	.194	.457	.142	1.24
435.	.253	10.116	.227	.525	.154	1.24
436.	.302	10.086	.257	.581	.167	1.25
438.	.401	10.032	.305	.670	.192	1.25
440.	.500	9.987	.346	.733	.219	1.26
442.	.597	9.948	.379	.781	.246	1.26

$[CO_{2T}]$ = .00349 M, $[HC10_4]$ = .00162 M, $[KC10_4]$ = .00205 M

$Mg(C10_4)_2$ = .2198 M

430.	0.0	10.199^R	--	—	$.108^R$	—
431.	.051	10.154	.042	.181	.116	1.24
432.	.102	10.112	.079	.330	.125	1.27
434.	.202	10.036	.140	.560	.146	1.28
435.	.253	10.004	.166	.641	.157	1.31
436.	.302	9.969	.185	.727	.168	1.27
438.	.401	9.913	.221	.843	.193	1.28
440.	.500	9.864	.249	.932	.218	1.27
442.	.597	9.821	.272	.999	.244	1.27

R = reference conditions, before $Mg(C10_4)_2$ is added.

Note: All values have been multiplied by factor shown in heading.

Table VI a

Change of pH of $KC10_4$-KOH solutions with added $Ca(C10_4)_2$ solution.

T = 25°C, $Ca(C10_4)_2$ = .2934 M

$[KC10_4]$ = .00565 M [KOH] = .002 M

Vol. (ml)	$[Ca_T]$ X 10^2, M	pH	$[CaOH^+]$ X 10^3, M	μ X 10^1	K_d X 10^1
430.	0.0	11.278^R	—	$.077^R$	—
431.	.071	11.265	.035	.098	.272*
432.	.141	11.258	.043	.118	.424
434.	.272	11.244	.068	.156	.485
436.	.406	11.227	.109	.196	.419
438.	.538	11.218	.117	.235	.497
440.	.660	11.204	.151	.270	.444
	$[KC10_4]$ =	.00572 M	[KOH] =	.00401 M	
425.	0.0	11.556^R	—	$.097^R$	—
426.	.068	11.548	.028	.117	.615*
429.	.272	11.526	.109	.176	.561
431.	.406	11.511	.175	.214	.485
433.	.537	11.498	.229	.252	.466
435.	.670	11.488	.258	.291	.494
	$[KC10_4]$ =	.00565 M	[KOH] =	.008 M	
430.	0.0	11.841^R	—	.136R	—
431.	.075	11.832	.080	.156	.401
432.	.136	11.825	.142	.173	.399
434.	.273	11.812	.237	.212	.461
435.	.335	11.802	.358	.228	.355
436.	.402	11.796	.402	.247	.372
438.	.535	11.785	.478	.284	.401
440.	.662	11.774	.563	.320	.405

R = reference conditions, before $Ca(C10_4)_2$ is added

*Value omitted from final average K_d

Note: All values have been multiplied by factor shown in heading.

Table VI b

Change of pH of $KC10_4$-KOH solutions with added $Ca(C10_4)_2$ solution.

T = 25°C, $Ca(C10_4)_2$ = .2934 M

$[KC10_4]$ = .00565 M [KOH] = .0004 M

Vol. (ml)	$[Ca_T]$ x 10^2, M	pH	$[CaOH^+]$ x 10^4, M	μ x 10^1	K_d x 10^1
430.	0.0	10.575^R	—	$.060^R$	—
431.	.065	10.565	.038	.080	.489
432.	.138	10.554	.085	.102	.437
434.	.268	10.532	.200	.140	.324
435.	.338	10.525	.222	.161	.356
436.	.403	10.517	.258	.180	.355
438.	.534	10.503	.314	.219	.362
440.	.666	10.490	.365	.258	.368

$[KC10_4]$ = .00565 M [KOH] = .0008 M

Vol. (ml)	$[Ca_T]$ x 10^2, M	pH	$[CaOH^+]$ x 10^4, M	μ x 10^1	K_d x 10^1
430.	0.0	10.868^R	—	$.065^R$	—
431.	.061	10.860	.048	.082	.703*
432.	.132	10.849	.145	.104	.474
434.	.268	10.830	.315	.144	.407
435.	.337	10.821	.396	.164	.392
436.	.403	10.812	.483	.184	.370
438.	.535	10.795	.645	.223	.343
440.	.664	10.780	.781	.261	.332

R = reference conditions before $Ca(C10_4)_2$ is added

* Value omitted from final average K_d

$$K_d = \frac{[Ca^{++}]\,[OH^-]}{[CaOH^+]} \times \frac{\gamma_{Ca^{++}}\,\gamma_{OH^-}}{\gamma_{CaOH^+}}$$

Note: All values <u>have been</u> multiplied by factor shown in heading.

Table VII.

Titration of $HCO_3^- - CO_3^{--}$ solutions with $Ca(C10_4)_2$ solution.

T = 25°C, K_dCaOH^+ = $.4166 \times 10^{-1}$

$[CO_{2T}]$ = .00116 M, $[HC10_4]$ = .00053 M, $[KC10_4]$ = .00108 M

	Vol. (ml)	$[Ca_T]$ x 10^{3}, M	pH	$[CaOH^+]$ x 10^{5}, M	$[CaCO_3^\circ]$ x 10^{3}, M	μ x 10^{1}	K_d x 10^{3}
$Ca(C10_4)_2$ = .08433 M	430.	0.0	10.135^R	——	——	$.039^R$	——
	430.8	.158	10.102	.026	.051	.042	.561
	431.8	.344	10.066	.055	.102	.046	.572
	432.9	.559	10.026	.084	.152	.050	.570
	433.7	.725	9.997	.103	.185	.054	.569
	434.4	.858	9.974	.117	.209	.057	.562
	434.8	.940	9.961	.126	.222	.059	.563
	435.	.979	9.956	.130	.226	.060	.568
	435.5	1.063	9.943	.138	.238	.062	.567
	435.9	1.141	9.931	.144	.249	.064	.565

$[CO_{2T}]$ = .00232 M, $[HC10_4]$ = .00133 M, $[KC10_4]$ = .00434 M

	Vol. (ml)	$[Ca_T]$ x 10^{3}, M	pH	$[CaOH^+]$ x 10^{5}, M	$[CaCO_3^\circ]$ x 10^{3}, M	μ x 10^{1}	K_d x 10^{3}
$Ca(C10_4)_2$ = .07585 M	430.	0.0	10.024^R	——	——	$.099^R$	——
	430.7	.120	10.006	.014	.043	.101	.715*
	431.5	.262	9.981	.028	.100	.103	.603
	431.9	.339	9.968	.035	.128	.104	.592
	432.5	.433	9.954	.044	.157	.106	.610
	433.	.517	9.945	.054	.174	.108	.665

R = reference condition, before $Ca(C10_4)_2$ is added

* Value omitted from final average K_d

Note: All values have been multiplied by factor shown in heading.

Table VIII

Values of the Dissociation Constants Developed in This Study

	Temp., °C		
K_d	5	15	25
$MgOH^+$	1.054×10^{-2}	$.983\times10^{-2}$	$.830\times10^{-2}$
$CaOH^+$	3.379×10^{-2}	4.317×10^{-2}	4.166×10^{-2}
$MgCO_3^\circ$	1.53×10^{-3}	1.51×10^{-3}	1.26×10^{-3}
$CaCO_3^\circ$	6.81×10^{-4}	6.74×10^{-4}	5.99×10^{-4}