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# A CHEMICAL MODEL FOR SEA WATER AT 25°C AND ONE ATMOSPHERE TOTAL PRESSURE*

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ABSTRACT. Dissociation constants involving $Ca^{++}$, $Mg^{++}$, $Na^{+}$, $K^{+}$, $SO_4^{--}$, $HCO_3^{-}$, and $CO_3^{--}$ ions, and individual ion activity coefficients have been used to calculate the distribution of dissolved species in sea water at 25°C and one atmosphere total pressure. The distribution obtained for sea water of chlorinity 19‰ and pH 8.1 are:

| Ion | Molality (Total) | % Free Ion | % Me-$SO_4$ pair | % Me-$HCO_3$ pair | % Me-$CO_3$ pair |
|---|---|---|---|---|---|
| $Ca^{++}$ | 0.0104 | 91 | 8 | 1 | 0.2 |
| $Mg^{++}$ | 0.0540 | 87 | 11 | 1 | 0.3 |
| $Na^{+}$ | 0.4752 | 99 | 1.2 | 0.01 | — |
| $K^{+}$ | 0.0100 | 99 | 1 | — | — |

| Ion | Molality (Total) | % Free Ion | % Ca-anion pair | % Mg-anion pair | % Na-anion pair | % K-anion pair |
|---|---|---|---|---|---|---|
| $SO_4^{--}$ | 0.0284 | 54 | 3 | 21.5 | 21 | 0.5 |
| $HCO_3^{-}$ | 0.00238 | 69 | 4 | 19 | 8 | — |
| $CO_3^{--}$ | 0.000269 | 9 | 7 | 67 | 17 | — |

The activities calculated for free ions are $a_{Ca^{++}} = 0.00264$, $a_{Mg^{++}} = 0.0169$, $a_{Na^{+}} = 0.356$, $a_{K^{+}} = 0.0063$, $a_{CO_3^{--}} = 4.7(10^{-6})$, $a_{HCO_3^{-}} = 9.75\ (10^{-4})$, $a_{SO_4^{--}} = 1.79(10^{-3})$.

## INTRODUCTION

The forms of presentation of the results of chemical analyses of sea water have reflected implicitly theories concerning the nature of salt solutions. Older analyses were presented in terms of individual salts, such as NaCl, $MgCl_2$, and $Na_2SO_4$. These have been superseded by analyses listing most constituents as simple ions, such as $Na^+$, $K^+$, $Cl^-$, or $Br^-$. This change in reporting, of course, is in response to the development of the concept of the complete dissociation of strong electrolytes. On the other hand, the analytical results also take cognizance of the presence of well known undissociated or partly dissociated species, as evidenced by the reporting of $HCO_3^-$ and $H_3BO_3$. Therefore, an analytical report lists, in a qualitative way, the dissolved species currently accepted as being present in sea water. Consequently, there is a tendency to use analytical results as an approximate chemical model of sea water, even though it is recognized that many more dissolved species must be present than those listed.

In the following discussion, an attempt is made to assess the percentages of the major dissolved species present in sea water. Calculations are made for representative sea water of chlorinity 19‰ (Sverdrup, Johnson, and Fleming, 1942, p. 173) at 25°C and one atmosphere total pressure. We regard the chemical model that results as a first approximation to the true picture.

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Eight items in the usual chemical analysis of sea water ($Na^+$, $K^+$, $Mg^{++}$, $Ca^{++}$, $Cl^-$, $HCO_3^-$, $CO_3^{--}$, and $SO_4^{--}$) make up more than 99 percent of the dissolved solids. Enough chemical data are available for these species to make possible the assessment of most important interactions, and thus to calculate the proportion of each that exists as the free ion, as well as the proportion present as complexes.

Our procedure is to accumulate thermodynamic dissociation constants involving these eight species, and then to use them in conjunction with estimated values for individual ion activity coefficients, to obtain the concentrations of all species exceeding a percent or two of the total.

We use the term *complex* to describe any association between cations and anions or anionic radicals. Also, we use the term *ion pair* loosely to refer to any complexes in which the ratio of cation to anion or anionic radical is unity.

We wish to express our appreciation to P. K. Weyl of the Shell Development Company who read the manuscript critically and made many helpful suggestions, and to Paul Mangelsdorf of the Woods Hole Oceanographic Institution, with whom we had several informative discussions of the physical-chemical problems involved in developing the model.

## DISSOCIATION CONSTANTS FOR MAJOR DISSOLVED SPECIES

A summary of dissociation constants for the major dissolved species in sea water is given in table 1. The values are presented as the negative log of the thermodynamic dissociation constant, for the reaction between dissolved species, e.g., in the case of $CaHCO_3^+$:

$$CaHCO_3^+ \rightleftarrows Ca^{++} + HCO_3^-,$$

and the equilibrium:

$$\frac{(a_{Ca^{++}})(a_{HCO_3^-})}{(a_{CaHCO_3^+})} = K_{diss} = 10^{-pK_{diss}} .$$

TABLE 1

Dissociation constants for major species at 25°C and one atmosphere total pressure

| Anions | $HCO_3^-$ | $CO_3^{--}$ | $SO_4^{--}$ |
|---|---|---|---|
| Cations | Dissociation Constants (as negative logs) | | |
| $K^+$ | — | — | 0.96 |
| $Na^+$ | -0.25 | 1.27 | 0.72 |
| $Ca^{++}$ | 1.26 | 3.2 | 2.31 |
| $Mg^{++}$ | 1.16 | 3.4 | 2.36 |

The dissociation constants given here are thermodynamic constants, and as such, their values are independent of the ionic strength of the aqueous solution to which they may be applied. They are not, however, independent of temperature and pressure.

These constants have been selected as the only ones required to describe quantitatively important interactions among the ions we are considering in sea water. None of the cations interacts strongly with chloride ion; no evidence has been found for association to $NaCl^\circ$, $KCl^\circ$, $CaCl^+$, or $MgCl^+$ (Davies, in

Hamer, 1959). Dissociation constants for $NaOH^\circ$ and $KOH^\circ$ are large; those for $CaOH^+$ and $MgOH^+$ are smaller ($pK_{diss} = 1.30$ and 2.58, respectively [Davies, in Hamer, 1959]), but need not be considered at pH values up to 8.5. In our previous work (Garrels, Thompson, and Siever, 1960b) we assumed the absence of any association between $K^+$ and $HCO_3^-$ or $CO_3^{--}$, and found that the assumption yielded useful and consistent results within the limits of error we were prepared to accept (± 10 percent of the activity coefficient). Also, we found that interactions of cations with $HCO_3^-$ and $CO_3^{--}$ in solutions of NaCl, $MgCl_2$, $CaCl_2$, and mixtures of these resembling sea water did not require the assumption of complexes of a higher degree of association than ion pairs (i.e., no species such as $Ca(CO_3)_2^{--}$ or $Ca(OH)_2(CO_3)_2^{4-}$).

The constants for $CaHCO_3^+$ and $MgHCO_3^+$ are modified from the data of Greenwald (1941), by multiplying his values for K′ (the apparent dissociation constant) by the appropriate activity coefficients. Greenwald made his measurements at an ionic strength always near 0.15. At this ionic strength our values for the activity coefficients of $Ca^{++}$, $Mg^{++}$, and $HCO_3^-$ are, respectively, 0.34, 0.41, and 0.76. The calculation is as follows:

$$\frac{(m_{Ca^{++}})(m_{HCO_3^-})}{(m_{CaHCO_3^+})} = K'_{diss} = 0.16 = 10^{-0.80}$$

$$\left(K'_{diss}\right)\left(\frac{(\gamma_{Ca^{++}})(\gamma_{HCO_3^-})}{(\gamma_{CaHCO_3^+})}\right) = K = (0.16)\left(\frac{(0.34)(0.76)}{0.76}\right) = 10^{-1.26}$$

The constants for $NaCO_3^-$ and $MgCO_3^\circ$ are from our own measurements (Garrels, Thompson, and Siever, 1960b), and the method of measurement is described in that paper. The constants for $CaCO_3^\circ$ and $NaHCO_3^\circ$ were determined by us, more recently, using the same general procedure. That is, for $CaCO_3^\circ$, a solution of known concentration of $CO_3^{--}$ is titrated with a standard $CaCl_2$ solution. From the changes in pH the changes in $a_{CO_3^{--}}$ are calculated. Then, by a series of successive refinements, the ionic strength of the solutions, the activity coefficients of the ions, the molalities of the free ions, and finally the activities of the ions and associated species are computed. Confirmation of the reliability of the calculations is achieved when the same dissociation constant is obtained for points along the entire titration.

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 without 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 equilibrium activity product for calcite is $10^{-8.35}$, that for aragonite is $10^{-8.22}$. These equilibrium activity products were measured by us, and may be calculated from the free energies of formation for these species given in an earlier paper (Garrels, Thompson, and Siever, 1960a).

Values for the dissociation constants for sulfates were taken from the tabulation of Davies (in Hamer, 1959). We have found no evidence of sulfate complexes other than ion pairs.

## DISTRIBUTION OF MAJOR DISSOLVED SPECIES

If we accept the dissociation constants listed in table 1 as measures of the only important interactions among $Na^+$, $K^+$, $Mg^{++}$, $Ca^{++}$, $SO_4^{--}$, $HCO_3^-$, and $CO_3^{--}$, a list of dissolved species can be made whose concentrations will add up to the analyzed values for these ions. The list of species, arranged to express the total concentration of each cation (e.g., $Na^+$ TOTAL), is as follows:

$$Na^+ + NaHCO_3^\circ + NaCO_3^+ + NaSO_4^- = Na^+ \text{ TOTAL}$$
$$K^+ + KSO_4^- = K^+ \text{ TOTAL}$$
$$Ca^{++} + CaHCO_3^+ + CaCO_3^\circ + CaSO_4^\circ = Ca^{++} \text{ TOTAL}$$
$$Mg^{++} + MgHCO_3^+ + MgCO_3^\circ + MgSO_4^\circ = Mg^{++} \text{ TOTAL}$$

Because the dissociation constants for the ion pairs are given in terms of the activities of the species involved, it is necessary to know the individual ion activity coefficients in order to convert concentrations to activities by the relation:

$$a_i = m_i \gamma_i$$

where a is the activity, $\gamma$ the activity coefficient, and m the molality of ion i.

### *Individual Activity Coefficients*

*Uncharged species.*—In general, neutral molecules (cf. Harned and Owen, 1958, p. 531-540) have activity coefficients between 1.1 and 1.2 in solutions of the ionic strength of sea water. In the absence of information on the other species considered here, their activity coefficients are assumed to be the same as that of $H_2CO_3$. The errors in the ensuing calculations, resulting from using any value in the probable range, are slight.

*Charged species.*—Individual ion activity coefficients for $K^+$ and $Cl^-$ may be obtained from mean salt data for KCl ($\gamma \pm KCl$) by assuming that $\gamma K^+ = \gamma Cl^- = \gamma \pm KCl$. It is further assumed that this relation is true not only in pure aqueous KCl solutions but also in sea water.

Values for $\gamma \pm KCl$ were taken from Harned and Owen (1958, p. 498).

Values of $\gamma K^+$ calculated from EMF measurements with a potassium-sensitive glass electrode and a saturated calomel electrode in aqueous KCl solutions showed good agreement with the mean salt data (±2%) and support the original assumption.

Activity coefficients for $HCO_3^-$ and $CO_3^{--}$ were derived in a similar manner from the $\gamma\pm$ values for $KHCO_3$ and $K_2CO_3$. The equations used are:

$$\gamma_{HCO_3^-} = \frac{\gamma^2 \pm KHCO_3}{\gamma \pm KCl}$$

$$\gamma_{CO_3^{--}} = \frac{\gamma^3 \pm K_2CO_3}{\gamma^2 \pm KCl}$$

Values for $\gamma \pm KHCO_3$ and $\gamma \pm K_2CO_3$ were taken from Walker, Bray, and Johnston (1927).

The activity coefficients of $NaCO_3^-$, $MgHCO_3^+$, $CaHCO_3^+$, $KSO_4^-$, and $NaSO_4^-$ were considered to be the same as that of $HCO_3^-$. Similar values would be expected for all singly charged ions of about the same size.

Values for $\gamma Ca^{++}$ and $\gamma Mg^{++}$ were obtained by using $\gamma\pm$ values from Latimer (1952, p. 354-355) for the respective chlorides, and then calculating the individual ion activity coefficients on the assumptions: (1) that $\gamma K^+ = \gamma Cl^- = \gamma \pm KCl$; (2) that there is no significant complexing in aqueous solution of these salts at the ionic strength of sea water; (3) that activity coefficients in a solution of the pure salt are the same as in sea water at the same ionic strength. The equalities used are:

$$\gamma_{Ca^{++}} = \frac{\gamma^3 \pm CaCl_2}{\gamma^2 \pm KCl}$$

$$\gamma_{Mg^{++}} = \frac{\gamma^3 \pm MgCl_2}{\gamma^2 \pm KCl}$$

$$\gamma_{Na^+} = \frac{\gamma^2 \pm NaCl}{\gamma \pm KCl}$$

The individual ion activity coefficient of $SO_4^{--}$ presented a special problem. All salts for which mean activity coefficient data are available exhibit significant complexing at ionic strengths comparable to that of sea water. However, by using the preceding values for $\gamma K^+$ and $\gamma KSO_4^-$, in conjunction with the dissociation constant for $KSO_4^-$ and $\gamma\pm$ values for $K_2SO_4$, it was possible to calculate values for $\gamma SO_4^{--}$ as a function of ionic strength. Values of $\gamma \pm K_2SO_4$ were obtained from Harned and Owen (1958, p. 553).

The activity coefficient of $Na^+$ was determined by using a sodium-sensitive glass electrode in sodium chloride solutions. The electrode was calibrated at a low value of ionic strength, where reliable values of $\gamma Na^+$ are presumably obtainable for the Debye-Hückel equation, and then measurements were carried to high ionic strengths. The values obtained are in fair agreement with those obtained by the mean salt method,

$$\left(\gamma Na^+ = \frac{\gamma^2 \pm NaCl}{\gamma \pm KCl}\right),$$

but are several percent higher (0.76 as opposed to 0.71) at the ionic strength of sea water.

A summary of the values is given in table 2.

TABLE 2

Activity coefficients of individual species (In sea water of ionic strength 0.70, chlorinity 19‰ at 25°C)

| Dissolved Species | Activity Coefficient |
|---|---|
| $NaHCO_3^\circ$ | 1.13 |
| $MgCO_3^\circ$ | 1.13 |
| $CaCO_3^\circ$ | 1.13 |
| $MgSO_4^\circ$ | 1.13 |
| $CaSO_4^\circ$ | 1.13 |
| $Na^+$ | 0.76 |
| $HCO_3^-$ | 0.68 |
| $NaCO_3^-$ | 0.68 |
| $NaSO_4^-$ | 0.68 |
| $KSO_4^-$ | 0.68 |
| $MgHCO_3^+$ | 0.68 |
| $CaHCO_3^+$ | 0.68 |
| $K^+$ | 0.64 |
| $Mg^{++}$ | 0.36 |
| $Ca^{++}$ | 0.28 |
| $SO_4^{--}$ | 0.12 |
| $CO_3^{--}$ | 0.20 |

### *Calculation of Distribution of Species*

After values of activity coefficients are obtained, the necessary equations are available for calculating the concentration of each species in sea water. The molalities used were recalculated from a tabulation of analyses of representative sea water given by Sverdrup (Sverdrup, Johnson, and Fleming, 1942, p. 173). A mass balance relation can be written for each analyzed constituent, e.g.:

$$m_{Na^+\ \text{TOTAL}} = m_{Na^+\ \text{uncomplexed}} + m_{NaHCO_3^0} + m_{NaCO_3^-} + m_{NaSO_4^-}$$

Also, dissociation constants are available for all ion pairs, e.g.,

$$\frac{a_{Na^+}\, a_{SO_4^{--}}}{a_{NaSO_4^-}} = K\ \text{diss.}$$

Rewriting in terms of molalities and activity coefficients:

$$\frac{\gamma_{Na^+} m_{Na^+} \gamma_{SO_4^{--}} m_{SO_4^{--}}}{\gamma_{NaSO_4^-}\, m_{NaSO_4^-}} = K\ \text{diss.}$$

There are seventeen species, and hence seventeen independent equations are required. The manipulations involved in solving these simultaneously are tedious. Fortunately, a simplification can be made by assuming that the cations occur almost entirely as uncomplexed species. Then the number of unknowns that must be dealt with simultaneously is restricted to four or five. The procedure used here was to assume that the cations are uncomplexed, to obtain a distribution of species, then to correct the original assumption in terms of the results obtained. Thus by a series of approximations it is possible to obtain final distribution values.

As a sample calculation, consider the distribution of the $SO_4^{--}$ bearing species. The following equations can be written involving mass balance and dissociation constants:

$$m_{SO_4^{--}\ \text{TOTAL}} = m_{NaSO_4^-} + m_{KSO_4^-} + m_{CaSO_4^0} + m_{MgSO_4^0} + m_{SO_4^{--}}\text{uncomplexed} \tag{1}$$

$$\frac{\gamma_{Na^+} m_{Na^+} \gamma_{SO_4^{--}} m_{SO_4^{--}}}{\gamma_{NaSO_4^-} m_{NaSO_4^-}} = K_{NaSO_4^-} \tag{2}$$

$$\frac{\gamma_{K^+} m_{K^+} \gamma_{SO_4^{--}} m_{SO_4^{--}}}{\gamma_{KSO_4^-} m_{KSO_4^-}} = K_{KSO_4^-} \tag{3}$$

$$\frac{\gamma_{Ca^{++}} m_{Ca^{++}} \gamma_{SO_4^{--}} m_{SO_4^{--}}}{\gamma_{CaSO_4^0} m_{CaSO_4^0}} = K_{CaSO_4^0} \tag{4}$$

$$\frac{\gamma_{Mg^{++}} m_{Mg^{++}} \gamma_{SO_4^{--}} m_{SO_4^{--}}}{\gamma_{MgSO_4^0} m_{MgSO_4^0}} = K_{MgSO_4^0} \tag{5}$$

Equations 2, 3, 4, and 5 can be solved in terms of $m_{SO_4^{--}}$, and put in the form indicated by solving #2:

$$m_{SO_4^{--}} = \left(\frac{K_{NaSO_4^-}\, \gamma_{NaSO_4^-}}{\gamma_{Na^+} m_{Na^+} \gamma_{SO_4^{--}}}\right) m_{NaSO_4^-}$$

Numerical values are available for K $NaSO_4^-$, $\gamma NaSO_4^-$, $\gamma Na^+$, $mNa^+$ (assuming all $Na^+$ is uncomplexed), and $\gamma SO_4^{--}$. The resultant value for $mSO_4^{--}$ in terms of $mNaSO_4^-$ can be substituted into equation #1. Successive substitutions of this type permit a solution of equation #1.

Then the original assumption that all cations are uncomplexed can be examined by observing the concentration of $Na^+$ tied up in $NaSO_4^-$; of $K^+$ tied up in $KSO_4^-$, and so on.

This procedure might appear to be almost as cumbersome as an original simultaneous solution involving all seventeen variables, but it quickly emerges that the only significant corrections that have to be made for cation concentration involve only two species: uncomplexed $Mg^{++}$ is modified by the presence of $MgSO_4^\circ$, and uncomplexed $Ca^{++}$ is modified by $CaSO_4^\circ$.

The results of the calculations are given in table 3.

TABLE 3

Distribution of major dissolved species in representative sea water of chlorinity 19‰, pH 8.1, at 25°C and one atmosphere total pressure

| Ion | Molality (Total) | % Free Ion | % Me-$SO_4$ pair | % Me-$HCO_3$ pair | % Me-$CO_3$ pair |
|---|---|---|---|---|---|
| $Ca^{++}$ | 0.0104 | 91 | 8 | 1 | 0.2 |
| $Mg^{++}$ | 0.0540 | 87 | 11 | 1 | 0.3 |
| $Na^+$ | 0.4752 | 99 | 1.2 | 0.01 | — |
| $K^+$ | 0.0100 | 99 | 1 | — | — |

| Ion | Molality (Total) | % Free Ion | % Ca-anion pair | % Mg-anion pair | % Na-anion pair | % K-anion pair |
|---|---|---|---|---|---|---|
| $SO_4^{--}$ | 0.0284 | 54 | 3 | 21.5 | 21 | 0.5 |
| $HCO_3^-$ | 0.00238 | 69 | 4 | 19 | 8 | — |
| $CO_3^{--}$ | 0.000269 | 9 | 7 | 67 | 17 | — |

### *Checks on the Validity of the Model*

There are at present several checks available on the distribution of species presented. Two of these are essentially negative evidences and involve determination of $Na^+$ and $K^+$ activities in sea water, using $Na^+$ and $K^+$ sensitive glass electrodes.

If $Na^+$ and $K^+$ are essentially uncomplexed, then their activities in sea water should be equal to the product of their activity coefficients and the total concentration of the element as reported by chemical analysis. Thus:

$$a_{Na^+} = \gamma_{Na^+} m_{Na^+ TOTAL}$$

$$a_{Na^+} = (0.76)(0.4752) = 0.36 = 10^{-0.44}$$

$$a_{K^+} = \gamma_{K^+} m_{K^+ TOTAL}$$

$$a_{K^+} = (0.64)(0.0099) = 0.0063 = 10^{-2.20}$$

The measured values, using cation sensitive glass electrodes are:

$$a_{Na^+} = 10^{-0.46} = 0.35, \quad a_{K^+} = 10^{-2.2} = 0.006$$

The ratios of the activities of $CO_3^{--}$ and $HCO_3^-$ in sea water to the total concentrations of species containing these substances are given in Sverdrup, Johnson, and Fleming (1942). These values of $\gamma$TOTAL are 0.019 for $CO_3^{--}$ and 0.36 for $HCO_3^-$. In the terminology used here, these $\gamma$TOTAL values should be written:

$$\frac{a_{CO_3^{--}}}{m_{CO_3^{--}} + m_{NaCO_3^-} + m_{CaCO_3^\circ} + m_{MgCO_3^\circ}} = \gamma_{CO_3^{--}TOTAL}$$

or:

$$\frac{\gamma_{CO_3^{--}} m_{CO_3^{--}}}{m_{CO_3^{--}} + m_{NaCO_3^-} + m_{CaCO_3^\circ} + m_{MgCO_3^\circ}} = \gamma_{CO_3^{--}TOTAL}$$

similarly:

$$\frac{\gamma_{HCO_3^-} m_{HCO_3^-}}{m_{HCO_3^-} + m_{NaHCO_3^\circ} + m_{CaHCO_3^+} + m_{MgHCO_3^+}} = \gamma_{HCO_3^-TOTAL}$$

If we substitute the percentages of $CO_3^{--}$ and $HCO_3^-$ as calculated for the ratio of the molalities, and $\gamma_{CO_3^{--}}$ uncomplexed and $\gamma_{HCO_3^-}$ uncomplexed in the numerators of the fractions, then the calculated values of $\gamma_{CO_3^{--}}$TOTAL and $\gamma_{HCO_3^-}$ TOTAL are:

$$0.2 \times 0.9 = 0.018 = \gamma_{CO_3^{--}}\text{TOTAL}$$

$$0.68 \times 0.69 = 0.47 = \gamma_{HCO_3^-}\text{TOTAL}$$

Agreement between Sverdrup's values for $\gamma_{CO_3^{--}TOTAL}$ and the one given here is good; presumably all interactions between dissolved species have been adequately described. The calculated value for $\gamma_{HCO_3^-TOTAL}$ is higher than that given by Sverdrup; presumably more $HCO_3^-$ is tied up by complexing than we have found. This is not surprising, because dissociation constants for $HCO_3^-$ species are relatively large, and consequently difficult to determine experimentally.

The calculated distribution of species is not dependent upon pH, but a pH value can be calculated from the activities of carbonate and bicarbonate ions and the second thermodynamic dissociation constant of $H_2CO_3$:

$$a_{H^+} = \frac{10^{-10.33} \times a_{HCO_3^-}}{a_{CO_3^{--}}} = \frac{10^{-10.33} \times 9.75 \times 10^{-4}}{4.7 \times 10^{-6}}$$

$$a_{H^+} = 10^{-8.01};\ pH = 8.01.$$

The value for $K_2\ H_2CO_3$ is taken from Latimer (1952). The pH of the sea water, as calculated from the empirical equation in Sverdrup (Sverdrup, Johnson, and Fleming, 1942, p. 199-201) is 8.11.

A further test of the validity of the model can be obtained by calculating the activity product of gypsum from the solubility of gypsum in "sea water" as determined by Posnjak (1940). Posnjak dissolved gypsum in an aqueous solution of NaCl, $MgCl_2$, $MgSO_4$, and $K_2SO_4$ according to the ratios found for sea water by the *Challenger* expedition but omitting Ca-bearing salts. We equated the gypsum solubility he observed as follows:

$$m_{Ca^{++}_{TOTAL}} = \text{gypsum solubility} = m_{Ca^{++}} + m_{CaSO_4^{\circ}}.$$

$$m_{SO_4^{--}_{TOTAL}} = \text{gypsum solubility} + \text{original } MgSO_4 \text{ and } K_2SO_4.$$

$$m_{SO_4^{--}_{TOTAL}} = m_{SO_4^{--}} + m_{CaSO_4^{\circ}} + m_{MgSO_4^{\circ}} + m_{KSO_4^{-}} + m_{NaSO_4^{-}}.$$

We solved for $m_{SO_4^{--}}$ and $m_{Ca^{++}}$ using the same procedure illustrated above (p. 62-63). Then, using activity coefficients for $Ca^{++}$ and $SO_4^{--}$, the solubility product of gypsum was calculated.

$$\gamma_{Ca^{++}} m_{Ca^{++}} \gamma_{SO_4^{--}} m_{SO_4^{--}} = K_{CaSO_4 \cdot 2H_2O} = 2.0 \times 10^{-5}.$$

The value given in Latimer (p. 320) is $2.4 \times 10^{-5}$.

The validity of this proposed chemical model for sea water at 25°C and one atmosphere total pressure may be criticized from several different points of view: chemically, because the measurement of individual ion activity coefficients does not rest upon a thermodynamically sound basis, and because the full extent of ion association in solutions as concentrated and containing as many chemical species as sea water does is not known; oceanographically, because the data are applicable to only a limited set of conditions (near surface, and near 25°); and geologically, because the solution and precipitation phenomena for minerals with which sea water is just about saturated cannot be explained in detail by this model.

All of these criticisms are valid, and much further work must be done, but it is our opinion that this model is useful chemically, oceanographically, and geologically, and that the close correspondence obtained between measured and calculated values for $a_{Na^+}$, $a_{K^+}$, pH, $\gamma_{CO_3^{--}}$, $\gamma_{HCO_3^-}$, and the solubility product of gypsum not only demonstrate the fundamental correctness of the model but also are examples of the sorts of problems that may be solved or at least better understood through the use of this model.

## SUMMARY

The distribution of major dissolved species in representative sea water (25°C, 19‰ chlorinity) has been calculated on the assumption that interactions among the major ions result only in the formation of ion pairs. The general picture that emerges is that the major cations in sea water exist chiefly as uncomplexed species; essentially all the $Na^+$ and $K^+$ are uncomplexed, and only about 10 to 15 percent of $Ca^{++}$ and $Mg^{++}$ are tied up. Magnesium ion is the major cation in terms of effectiveness in complexing anions. The anions, on the other hand, except for $Cl^-$, are strongly complexed; most of $CO_3^{--}$, one third of $HCO_3^-$, and nearly half of $SO_4^{--}$ are paired with the various cations.

## REFERENCES

Davies, C. W., 1959, Incomplete dissociation in aqueous salt solutions, *in* Hamer, W. J., ed., Structure of electrolytic solutions: New York, John Wiley and Sons, Inc., p. 26-29.

Garrels, R. M., Thompson, M. E., and Siever, R., 1960a, Stability of some carbonates at 25°C. and one atmosphere total pressure: Am. Jour. Sci., v. 258, p. 402-418.

———— 1960b, Solubility of carbonates in sea water; control by carbonate complexes: Am. Jour. Sci., v. 259, p. 24-45.

Greenwald, Isidor, 1941, The dissociation of calcium and magnesium carbonates: Jour. Biol. Chemistry, v. 141, p. 789.

Harned, H. S., and Owen, B. B., 1958, Physical chemistry of electrolytic solutions: New York, Reinhold Publishing Co., 803 p.

Latimer, W. M., 1952, Oxidation potentials: New York, Prentice-Hall, Inc., 392 p.

Posnjak, E., 1940, Deposition of calcium sulfate from sea water: Am. Jour. Sci., v. 238, p. 559-568.

Sverdrup, H. U., Johnson, M. W., and Fleming, R. H., 1942, The oceans: New York, Prentice-Hall, Inc., 1087 p.

Walker, A. C., Bray, V. B., and Johnston, J., 1927, Equilibrium in solutions of alkali carbonates: Am. Chem. Soc. Jour., v. 49, p. 1235-1256.