# 14. INTERSTITIAL WATER STUDIES, LEG 15 – CHEMICAL MODEL OF SEAWATER AND SALINE WATERS<sup>1</sup>

# H. James Simpson, Lamont-Doherty Geological Observatory, Columbia University, Palisades, New York

and

Taro Takahashi,<sup>2</sup> Queens College, City University of New York, Flushing, New York

## ABSTRACT

The chemical model proposed originally by Garrels and Thompson (1962) is revised in order to make the model consistent with the  $pCO_2$ , total dissolved  $CO_2$  concentration, and total carbonate ion concentration values obtained for seawater and highly alkaline Mono Lake water. An increase in the dissociation constant for NaCO<sub>3</sub><sup>-</sup> complex by a factor of 5 and an increase in the dissociation constant for MgCO<sub>3</sub>° by 50 per cent have been found to be necessary. This revision was necessitated to interpret chemical data obtained for widely varying composition of natural waters such as the Leg 15 sediment interstitial waters, and highly saline lake waters.

# MAJOR ION COMPLEXING MODEL FOR SALINE WATERS

### Introduction

The chemistry of saline natural solutions such as seawater differs substantially from the properties predicted from measurements in dilute single-component solutions. For example, the solubility of calcium carbonate in seawater is several hundred times that predicted from experiments in dilute solutions. Most treatments of carbonate chemistry in seawater are based on the use of "apparent" dissociation constants for carbonic and boric acids, to allow for the changed effectiveness or "activity" of ionic species in the seawater matrix. Two systems of apparent constants (Buch, 1951, Lyman, 1956) are most frequently used.

A more complicated, but potentially more powerful, approach to the modeling of seawater major ion chemistry was proposed by Garrels and Thompson (1962). In this model the increased solubility of calcium carbonate in seawater is partially explained by individual ion activity coefficients which are substantially lower than those in dilute solutions ( $7Ca^{++} = 0.28$ ,  $7CO_3^{=} = 0.20$ ) and partially by the presence of major ion complexes, such as NaCO<sub>3</sub><sup>-</sup>, which reduce the amount of "free" carbonate ion in solution. Furthermore, in interstitial waters, ratios of the major ions can deviate substantially from seawater, and therefore the treatment of carbonate system equilibria becomes more complicated. One approach is to alter the apparent constants for seawater on the basis of the chemical changes measured in pore waters, using the constants proposed by Garrels and Thompson (1962). (See Hammond and Broecker, this volume). Another approach is to use directly the same system of model constants, with measured pore water chemical data to calculate the distribution of carbonate species. These two procedures would yield identical results if all the systems of constants were mutually compatible.

A new method of determining the total carbonate ion concentration in saline solutions was recently developed (Simpson and Broecker, in press; Simpson, 1970). This method is independent of any system of apparent constants or chemical model parameters. The data obtained in the development of this method support the system of apparent constants determined by Lyman (1956) and suggest a substantial disagreement with the distribution of carbonate species calculated from the chemical model of Garrels and Thompson (1962).

The purpose of this paper is to propose revisions in the system of constants used in chemical model calculations. Data obtained in several saline natural waters, including seawater, are used to determine the new constants. The revisions are suggested to provide better parameters for model calculations of the carbonate system in pore waters. The results of an application of this work to the carbonate equilibria in the Leg 15 interstitial water samples are described in detail by Takahashi et al. in this volume.

# **Discrepancies in Current Models**

The model developed for total carbonate ion determination requires the measurement of the partial pressure of carbon dioxide gas ( $pCO_2$ ) in equilibrium with the initial solution, plus two more  $pCO_2$  measurements which are made after the addition of a known amount of strong base (e.g., KOH) and after the further addition of boric acid. These three  $pCO_2$  measurements, plus  $\Sigma CO_2$  are used to compute the total carbonate ion concentration of the

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<sup>&</sup>lt;sup>2</sup>Also associated with Lamont-Doherty Geological Observatory, Palisades, N. Y. and University Institute of Oceanography, City University of New York, New York, N. Y.

original solution, without the use of any system of apparent dissociation constants, or any major ion complexing constants.

Part of the  $pCO_2$  and  $\Sigma CO_2$  data for a Bermuda surface water sample reported elsewhere (Simpson and Broecker, in press; Simpson, 1970) is given in Table 1. Using the measured values of  $pCO_2$  and  $\Sigma CO_2$ , total carbonate ion and pH are calculated from three independent sets of constants and compared with the value obtained for  $(CO_3^{=})_T$  by the "base-borate addition" method. The value obtained with Lyman's constants agrees within 2 per cent, while those obtained with Buch's and Garrels-Thompson's chemical model are 13 and 34 per cent higher, respectively. The pH values obtained using the three sets of constants also disagree substantially.

## Justification for Revision in Chemical Model Parameters

The agreement between the base-borate addition values for total carbonate ion with those calculated from Lyman's constants supports the reliability of those values. Furthermore, Takahashi et al. (1970, Table 3, p. 7654) have shown that the *p*H values measured for Pacific surface- and deep-water samples, using the NBS scale, agree within experimental uncertainty ( $\pm 0.02 \ pH$  unit) with the *p*H values calculated from *p*CO<sub>2</sub> and  $\Sigma$ CO<sub>2</sub> values using Lyman's constants.

Because of the independent evidence supporting the validity of Lyman's constants, it is reasonable to suggest changes in the parameters of the chemical model proposed by Garrels and Thompson (1962) to effect agreement in the computed values of both total carbonate ion and pH. A number of changes in the major ion complex constants involving sulfate have been suggested (Kester and Pytkowicz, 1969). These changes have very little effect on the distribution of carbonate species and thus do not resolve the discrepancies between Lyman's apparent constants and chemical model calculations.

The possible adjustments in the chemical model parameters suggested by the data in Table 1 should involve the major ion complexes containing bicarbonate and carbonate ions (Na  $CO_3^-$ , NaHCO<sub>3</sub>°, MgCO<sub>3</sub>°, MgHCO<sub>3</sub>+, CaCO<sub>3</sub>°, CaHCO<sub>3</sub>+). Assuming the individual ion activity coefficients are reasonably well known, there are six complex constants which might be adjusted to bring chemical model values of  $(CO_3^=)_T$  and pH into agreement with values calculated from Lyman's apparent constants. As will be shown, it is not possible to select a unique set of values for these six constants using only the data for Bermuda surface water.

The carbonate equilibria in several high salinity lakes have been examined with base-borate addition experiments (Simpson, 1970). One of these lakes, Mono Lake, having a total dissolved solids content approximately twice that of seawater, has more than 100 times the  $\Sigma CO_2$  and approximately 1000 times the  $(CO_3^{=})_T$  content of surface ocean water. Magnesium and calcium concentrations are only 2 and 1 per cent, respectively, of seawater values and are therefore essentially trace elements in Mono Lake. Thus the relative proportion of the carbonate species and alkaline earths are drastically different in Mono Lake and seawater. Yet the total carbonate ion in Mono Lake calculated from Garrels and Thompson's model parameters is also substantially higher (21%) than the values obtained from addition experiments, the same trend as was seen for seawater (see Table 2).

The only chemical model parameters which can resolve the differences for Mono Lake are the constants affecting  $NaCO_3^-$  and  $NaHCO_3^\circ$ . Combining the data from seawater and Mono Lake allows a unique set of model parameters to be selected.

#### Model Parameters and Calculation Procedures

Two separate approaches have been taken here to arrive at a set of constants which satisfies both the seawater and Mono Lake data. One approach was to make the smallest possible number of changes in complex constants to make Lyman's constants and chemical model calculations compatible within certain error limits. A graphical procedure was used to indicate which constants should be changed and by how much. A second, and largely independent, approach was taken by solving sets of simultaneous equations using both the Mono Lake and seawater data. The equations were solved to give precise agreement for this set of experimental data for both the chemical model calculation and one made with Lyman's apparent constants. The final solutions differ somewhat in details, but both give essentially the same picture.

A large number of empirical constants are necessary for chemical model calculations. The choice of activity coefficients and dissociation constants used here are outlined below. They differ slightly in detail from those used by Garrels and Thompson (1962), largely because it was felt necessary to use a set of activity coefficients which were

TABLE 1 Total Carbonate Ion in Bermuda Surface Water

	Calculated with Lyman's Constants	Calculated with Buch's Constants	Calculated with Garrels- Thompson Model	Measured by Base-Borate Addition Method
pCO <sub>2</sub> (10 <sup>-6</sup> atm) <sup>a</sup>	384	384	384	384
$\Sigma CO_2$ (mM/kg)	2.088	2.088	2.088	2.088
$(CO_3^{=})_T (mM/kg)$	0.226	0.252	0.298	0.223
pH(NBS)	8.194	8.168	8.161	1

<sup>a</sup>Temperature =  $22.4^{\circ}$ C.

TABLE 2						
<b>Total Carbonate</b>	Ion	in	Mono	Lake		

	Calculated with Garrels- Thompson Model	Measured by Base-Borate Addition Method
pCO2 (10-6 atm) <sup>a</sup>	412	412
$\Sigma CO_2$ (mM/kg)	333	333
$(CO_3^{=})_T (mM/kg)$	255	210
pH (NBS)	9.82	-

<sup>a</sup>Temperature = 10.3°C.

consistent over a large enough range in ionic strength to include both seawater ( $I \approx 0.7$ ) and Mono Lake ( $I \approx 1.3$ ).

The original experimental values for the complex constants, in terms of "primed" constants, were used for the solution by simultaneous equations (see below). The graphical solution plots were constructed using pK values. The conversion from K' to pK formulation was made using the set of activity coefficients listed in Table 3. Activity coefficients were first selected from plots of mean activity coefficients listed in Harned and Owen (1958) at the ionic strength calculated from the chemical data. After a new set of complex constants was determined, the ionic strength was recalculated including major ion complexing, and the set of activity coefficient values shown in Table 3 was selected. The final set of complex constants was determined using these activity coefficients.

The complex constants used for the initial model calculations (Table 4) were taken from Garrels and Thompson (1962). The carbonic acid dissociation constants were interpolated from Harned and Davis (1943) ( $K_1$ ) and Harned and Scholes (1942) ( $K_2$ ). The solubility of CO<sub>2</sub> in distilled water was taken from Li and Tsui (1971) ( $\alpha_0$ ), as was the solubility of CO<sub>2</sub> in seawater at a chlorinity of 20.25% ( $\alpha_s$ ). The value of  $\alpha_s$  in Mono Lake was calculated from  $\alpha_o$  and activity coefficient plots of CO<sub>2</sub> against ionic strength ( $\gamma CO_2 = \alpha_o/\alpha_s$ ).

TABLE 3	
Activity Coefficients	

	New York	
	Seawater $(I = 0.7)^a$	Mono Lake (I = 1.3) <sup>a</sup>
Ca <sup>++b</sup>	0.27	0.27
Mg <sup>++b</sup>	0.34	0.38
Na <sup>+b</sup>	0.71	0.73
K <sup>+b</sup>	0.63	0.59
SO4 <sup>b</sup>	0.10	0.06
HCO3-	0.67	0.64
CO3=c	0.21	0.18
Complex + or -	0.67	0.64
Complex O <sup>d</sup>	1.16	1.30
H <sub>2</sub> O	0.982	0.963

<sup>a</sup>Ionic strength and activity coefficients adjusted after final complex constants chosen.

bHarned and Owen, 1958.

cGarrels, et al., 1961.

dGarrels and Christ, 1965.

# **Graphical Solution**

The concentration of free and complexed major ionic species was computed using the constants in Tables 3 and 4. The sum of all species containing  $CO_3^{=}$  (i.e., free  $[CO_3^{=}] +$  $NaCO_3^- + MgCO_3^\circ + CaCO_3^\circ)$  equals total carbonate ion. The computed values of  $(CO_3^-)_T$  were then plotted against pH. Then a set of identical calculations, using the same empirical  $pCO_2$  and  $\Sigma CO_2$  data, were performed, with each of the six major ion complex constants allowed to vary, holding the others fixed. The results of these calculations are shown in Figures 1 to 4. The first three figures contain points from seawater calculations, while the fourth concerns Mono Lake. On each of the first three figures is a rectangular area centered on the point representing the  $(CO_3^{=})_T$  and pH values calculated using Lyman's apparent constants. For Mono Lake there is much less control on the estimate of the correct pH, because there is no system of apparent constants. Thus a band covering a range of pH values is used instead of the rectangle used for seawater.

From calculations varying six complex constants for Mono Lake, the only constants which could be changed to satisfy the total carbonate ion data are NaCO<sub>3</sub><sup>-</sup> and NaHCO<sub>3</sub>° (Figure 4). From Figure 1, a change in NaCO<sub>3</sub><sup>-</sup> rather than NaHCO<sub>3</sub>° satisfies both  $(CO_3^{=})_T$  and pH restrictions. Thus a change in the complex constant for NaCO<sub>3</sub><sup>-</sup> is indicated. The magnitude of change was based on fitting the Mono Lake data (Figure 4). The original Garrels et al. (1961) value of  $pK_3 = +1.27$  was changed to  $pK_3 = +0.52$ .

From Figure 1, a change in NaCO<sub>3</sub><sup>-</sup> complexing does not completely remove the discrepancy in the seawater data. From Figures 2 and 3, a change in either MgCO<sub>3</sub> or CaCO<sub>3</sub> complexing is indicated. For simplicity, only MgCO<sub>3</sub>° is allowed to vary because of the smaller change necessary to fit the seawater data. Changing the original Garrels et al. (1961) value of  $pK_5 = +3.42$  to  $pK_5 = +3.30$ , in addition to the NaCO<sub>3</sub><sup>-</sup> change suggested above, satisfies both the Mono Lake and seawater data for (CO<sub>3</sub><sup>=</sup>)<sub>T</sub> and pH.

Figure 5 shows the combined effect of these changes for the Bermuda surface seawater data.

# **Simultaneous Equation Solution**

There is sufficient information in the combination of Mono Lake and seawater experimental data to determine a unique set of major ion complex constants for the carbonate-bicarbonate system of six constants, as suggested by the trends in Figures 1 to 5. Such a determination is detailed below, assuming the values of  $(CO_3^{=})_T$  and pH for seawater are known precisely from Lyman's constants and the  $(CO_3^{=})_T$  in Mono Lake is known precisely from the base-borate addition experiments.

The carbonate equilibria in saline water can be described as follows:

$$K_1 = \frac{a_{\rm H}^+ \cdot \gamma_{\rm HCO_3}^- ({\rm HCO_3})_T/u}{a_{\rm H_2O} \cdot p_{\rm CO_2} \cdot \gamma_{\rm CO_2} \cdot a_s}$$
(1)

$$K_{2} = \frac{a_{\rm H}^{+} \cdot \gamma_{\rm CO_{3}} = ({\rm CO_{3}}^{=})_{T}/\nu}{\gamma_{\rm H \, CO_{3}} - ({\rm H \, CO_{3}})_{T}/u}$$
(2)

	10.3°C	22.4°C		10.3°C	22.4°C
$K_1 = \frac{a_{\rm H}^+ \times a_{\rm HCO_3}^-}{a_{\rm H_2O} \times \boldsymbol{\alpha}_o \times p_{\rm CO_2}}$	3.47 × 10 <sup>-7</sup>	4.29 × 10 <sup>-7</sup>	$K_1' = K_1 \times \left(\frac{\boldsymbol{\gamma}_{\mathrm{H}_2\mathrm{O}} \times \boldsymbol{\alpha}_o}{\mathrm{HCO}_3 \times \boldsymbol{\alpha}_s}\right)$	6.83 × 10 <sup>-7</sup>	7.29 × 10 <sup>-7</sup>
$K_2 = \frac{a_{\rm H}^+ \times a_{\rm CO_3}^-}{a_{\rm HCO_3}^-}$	3.24 × 10 <sup>-11</sup>	4.40 × 10 <sup>-11</sup>	$K_{2}' = K_{2} \times \left(\frac{\gamma_{\rm HCO_{3}}}{\gamma_{\rm CO_{3}}}\right)$	1.16 × 10-10	1.41 × 10 <sup>-10</sup>
$\alpha_o$ (M/kg/atm)	$5.04 \times 10^{-2}$	$3.57 \times 10^{-2}$			
$\alpha_s$ (M/kg/atm)	$3.88 \times 10^{-2}$	$3.08 \times 10^{-2}$			
		р <i>К</i> (1	1)	K' (2)	
K3 (NaCO3 <sup></sup> )		+1.2	7	2.40 × 10 <sup>-1</sup>	
$K_4$ (CaCO <sub>3</sub> °)		+3.2	1	$1.27 \times 10^{-2}$	
K <sub>5</sub> (MgCO <sub>3</sub> °)		+3.4	2	$6.25 \times 10^{-3}$	
$K_6$ (NaHCO <sub>3</sub> °)		-0.2	0	3.89 X	
K7 (CaHCO3+)		+1.2	8	$1.96 \times 10^{-1}$	
$K_8$ (MgHCO <sub>3</sub> <sup>+</sup> )		+1.1	8	$1.92 \times 10^{-1}$	
$K_9 (NASO_4^-)$		+0.8	2	1.42	
$K_{10}$ (CaSO <sub>4</sub> °)		+2.4	2	$1.64 \times 10^{-1}$	
$K_{11}$ (MgSO4°)		+2.4	8	$1.14 \times 10^{-1}$	
$K_{12}(\text{KSO}_4)$		+1.0	4	$4.09 \times 10^{-1}$	

TABLE 4 Initial Constants for Model Calculations

(1) 
$$pK_3 = -\log_{10}\left(\frac{a_{\text{Na}} + \times a_{\text{CO}3}}{a_{\text{Na}} + \cos^2 a_{\text{CO}3}}\right)$$

(2)  $K_3' = \frac{[Na^+] \times [CO_3^-]}{[NaCO_3^-]}$ 

where  $K_1$  and  $K_2$  are the first and second (thermodynamic) dissociation constants for carbonic acid;  $a_{\rm H}$ +,  $a_{\rm HCO3}^-$ , and  $a_{\rm CO3}^-$  indicate the activity of respective ions;  $\gamma_{\rm CO2}^ \gamma_{\rm HCO3}^-$ ,  $\gamma_{\rm CO3}^-$ , etc., indicate activity coefficients;  $p_{\rm CO2}^-$ , the partial pressure of CO<sub>2</sub> exerted by the solution;  $\alpha_o$  and  $\alpha_s$ , the solubility of CO<sub>2</sub> in pure water and saline solutions respectively;  $({\rm HCO}_3^-)_T$  and  $({\rm CO}_3^-)_T$ , the total bicarbonate and carbonate ion concentrations; u, the ratio of the total to free bicarbonate ion concentration; and  $\nu$ , the ratio of the total to free carbonate ion concentrations. Parameters u and  $\nu$  are further defined by:

$$u = (\text{HCO}_3^{-})_T / \text{CO}_3^{=}) = 1 + \frac{\Sigma \text{Na}}{wK_6'} + \frac{\Sigma \text{Ca}}{xK_7'} + \frac{\Sigma \text{Mg}}{yK_8'} (3)$$

$$v = (CO_3^{=})_T / (HCO_3^{=}) = 1 + \frac{\Sigma Na}{wK'_3} + \frac{\Sigma Ca}{xK'_4} + \frac{\Sigma Mg}{yK'_5}$$
 (4)

$$w = \frac{\Sigma Na}{(Na^+)} = 1 + \frac{(CO_3^-)_T}{\nu K'_3} + \frac{(HCO_3^-)_T}{uK'_6} + \frac{\Sigma SO_4}{zK'_9}$$
(5)

$$x = \frac{\Sigma Ca}{(Ca^{++})} = 1 + \frac{(CO_3^{=})_T}{\nu K'_4} + \frac{(HCO_3^{-})_T}{uK'_7} + \frac{\Sigma SO_4}{zK'_{10}}$$
(6)

$$y = \frac{\Sigma Mg}{(Mg^{++})} = 1 + \frac{(CO_3^{-})_T}{\nu K'_5} + \frac{(HCO_3^{-})_T}{uK'_8} + \frac{\Sigma SO_4}{zK'_{11}}$$
(7)

$$z = \frac{2\text{SO}_4}{(\text{SO}_4^{=})} = 1 + \frac{2\text{Na}}{wK'_9} + \frac{2\text{Ca}}{xK'_{10}} + \frac{2\text{Mg}}{yK'_{11}}$$
(8)

where  $\Sigma Na$ ,  $\Sigma Mg$ ,  $\Sigma Ca$ , and  $\Sigma SO_4$  are the total concentration of respective atomic and molecular species; (Na<sup>+</sup>), (Ca<sup>++</sup>), (Mg<sup>++</sup>), (HCO<sub>3</sub><sup>-</sup>), (CO<sub>3</sub><sup>=</sup>), and (SO<sub>4</sub><sup>=</sup>), the concentrations of free (or uncomplexed) ionic species; and K'<sub>i</sub>, the apparent thermodynamic dissociation constants for respective complex species. Since the concentration of the  $KSO_4^-$  complex species is small, it is not included in the present discussion.

### Mono Lake Water

The total sodium concentration,  $\Sigma Na$ , in Mono Lake water exceeds the concentration of Mg by nearly 1000 times and that of Ca by nearly 10,000 times (Table 5). Therefore, the third and fourth terms in the right hand side of Eqs. (3) and (4) (i.e., the concentrations of the Ca and Mg complexes) are negligible compared to the second term in the respective equations (i.e., the concentrations of NaHCO<sub>3</sub>° and NaCO<sub>3</sub><sup>-</sup> complexes), since the values for w, x, and y range between 1 and 1.2. Accordingly, Eqs. (3) and (4) may be simplified in the case of the Mono Lake water:

$$u = 1 + \frac{\Sigma Na}{wK_6'}, \quad v = 1 + \frac{\Sigma Na}{wK_3'}$$
 (9)



Figure 1. Calculated values of total carbonate ion  $(CO_3^{\approx})_T$ and pH, using different values of complex constants involving sodium and carbonate or bicarbonate. Circle indicates values computed with the complex constants used by Garrels and Thompson (1962). Shaded square centers on values computed with Lyman's constants. Area of square indicates approximate uncertainty limits. Experimental data for Bermuda surface seawater.

On the other hand, a division of Eq. (1) with Eq. (2) yields a relationship between u and v:

$$\frac{v}{u^2} = \left(\frac{\gamma_{\text{CO}_2} \gamma_{\text{CO}_3} = K_1}{(\gamma_{\text{H} \text{CO}_3} = )^2 K_2}\right) \times \left(\frac{(\text{CO}_3 = )_T \cdot \alpha_s \cdot p_{\text{CO}_2}}{(\text{H} \text{CO}_3 = )_T^2}\right) (10)$$

Under constant pressure conditions,  $K_1$  and  $K_2$  are a function of temperature alone, and their temperature dependency is well known. The activity coefficients,  $\gamma$ 's, are a function of temperature and ionic strength in aqueous solution and are also known. The solubility of CO<sub>2</sub> in aqueous solutions,  $\alpha_s$ , depends also on the temperature and ionic strength and is accurately known. In the Mono Lake sample water, the temperature, ionic strength,  $pCO_2$ ,  $(CO_3^{=})_T$ , and  $\Sigma CO_2$  have been measured. Therefore,  $(HCO_3^{-})_T$  can be calculated by using a mass balance equation:

$$(\text{HCO}_3^{-})_T = \Sigma \text{CO}_2 - [(\text{CO}_3^{=})_T + \alpha_s \, p \text{CO}_2] \quad (11)$$

where the values for  $\Sigma CO_2$ ,  $(CO_3^{=})_T$ , and  $pCO_2$  are listed in Tables 1 and 2. For the ionic strength (I=1.5) of the



Figure 2. Complex constants varied for magnesium species. The symbols used here are the same as Figure 1.

Mono Lake water,  $\alpha_s$  is 3.88 × 10<sup>-2</sup> M/kg/atm. Thus, the value for  $(\text{HCO}_3^{-})_T$  is 0.123 M/kg. Substituting those values into Eq. (10)

$$v/u^2 = 1.102$$

Furthermore, combination of Eqs. (9) and (10) yields a relation,

$$\nu/u^2 = \left(1 + \frac{\Sigma Na}{wK'_3}\right) \left(1 + \frac{\Sigma Na}{wK'_6}\right)^2$$
(12)

which relates  $K'_3$  to  $K'_6$ , respectively the dissociation constants for the NaCO<sub>3</sub><sup>-</sup> and NaHCO<sub>3</sub><sup>-</sup> complexes. For the Mono Lake water,  $\Sigma$ Na is known, and w ranges between 1.1 and 1.2 depending upon the choice of other complexing constants. Hence, Eq. (12) can be used to determine  $K'_3$  if  $K'_6$  is known. Garrels and Thompson (1962) obtained a K to value of 3.89 (or  $K_6 = 1.78$ ), and more recently Butler and Huston (1970) determined  $K'_6$  to be 4.7 ± 1.0 for the ionic strength of 1.0, and 2.6 ± 1.4 for the ionic strength of 0.5 at room temperature and 1 atm pressure. In view of the agreement between these data, we accepted the  $K'_6$  value of 3.89 by Garrels and Thompson (1962) for the present calculation. Thus, using Eq. (12), and also using a computed value of 1.15 for w,  $K'_3$  has been calculated to be 1.35. This value compares with the  $K'_3$  value of 0.24 obtained by Garrels and Thompson (1962) and that of 0.6 ± 0.6 obtained by Butler and Huston (1970).





Figure 3. Complex constants varied for calcium species. The symbols used here are the same as Figure 1.

Since  $pCO_2$ ,  $(HCO_3^{-})_T$ , and  $a_H$  are known for the Bermuda seawater, the value for u,  $(HCO_3^-)_T/(HCO_3^-)$ , can be calculated from Eq. (1). Using the values of  $a_{\rm H}$  =  $6.383 \times 10^{-9}$  (or pH = 8.195), (HCO<sub>3</sub><sup>-</sup>)<sub>T</sub> =  $1.853 \times 10^{-3}$ M/kg,  $\alpha_s = 3.07 \times 10^{-2}$  M/kg/atm, pCO<sub>2</sub> =  $3.84 \times 10^{-4}$  atm,  $a_{\rm H\,2O} = 0.982$ ,  $\gamma CO_2 = 1.16$ , and  $\gamma_{\rm H\,CO_3} = 0.67$ , the value for u is calculated to be 1.371. Once u is known, then the value for  $\nu$  can be computed to be 7.500 from Eq. (2) using  $(CO_3^{=})_T = 2.23 \times 10^4 \text{ M/kg}$  and  $\gamma_{CO_3}^{=} = 0.21$ . In Eqs. (3) and (4), the values for  $u, v, K'_3$ , and  $K'_6$  have now become known, and  $K'_4, K'_5, K'_7$ , and  $K'_8$  are unknowns. When the new values for u and  $K'_6$  are used in Eq. (3), it is seen that the values for  $K'_7$  and  $K'_8$  obtained by Garrels and Theorem (1062) do not exting Eq. (3) and therefore Thompson (1962) do not satisfy Eq. (3), and, therefore, these values should be revised. Considering the fact that Garrels and Thompson (1962) obtained similar values for  $K'_7$  (= 0.196; the dissociation constant for CaHCO<sub>3</sub><sup>+</sup>) and  $K'_8$  (= 0.192; the dissociation constant for MgHCO<sub>3</sub><sup>+</sup>), and that Ca<sup>++</sup> has similar chemical properties as Mg<sup>++</sup>, we assume  $K'_7$  to be equal to  $K'_8$  in the following calculations. Furthermore, when the  $pCO_2$  value is fixed, the pH value obtainable as a solution for the simultaneous equations is affected sensitively only by the activity of HCO3-, and hence by the choice of  $K'_7$  and  $K'_8$  values. The new values for  $K'_7$  and  $K'_8$  thus computed are 0.235 if the dissociation constant values for sulfate complexes ( $K'_9$  for NaSO<sub>4</sub>-;  $K'_{10}$  for CaSO<sub>4</sub>°; and  $K'_{11}$  for MgSO<sub>4</sub>°) obtained by Garrels et al. (1961) are used and are 0.239 if the  $K'_9$  and  $K'_{10}$  and  $K'_{11}$  values of Kester and Pytkowicz (1968, 1969)

concentration and large uncertainty in the absolute value of pH. are used. These  $K'_7$  and  $K'_8$  values are about 25 per cent greater than the respective values obtained by Garrels and

Figure 4. Experimental data for Mono Lake. Shaded area indicates experimental uncertainty in total carbonate ion

Thompson. The values for  $K'_4$  and  $K'_5$  obtained by Garrels and Thompson should also be revised, as they fail to satisfy Eq. (4) when our new value for  $K'_3$  is used. Due to the lack of additional data on  $K'_4$  and  $K'_5$ , we assumed that the  $K'_4$ value of Garrels and Thompson is correct and revised the  $K'_5$  value. This assumption was made due to the fact that a smaller change is needed for  $K'_5$  (for MgCO<sub>3</sub>°) than for  $K'_4$ (for CaCO<sub>3</sub>°) because of a five-fold greater concentration of Mg<sup>++</sup> than Ca<sup>++</sup> in seawater. The value for  $K'_5$  thus calculated is 0.00908 when the dissociation constants for the sulfate ion complexes of Garrels et al. (1961) are used and 0.00918 when those of Kester and Pytkowicz (1968, 1969) are used. These  $K'_5$  values are nearly 50 per cent larger than the  $K'_5$  value of 0.006 obtained by Garrels and Thompson (1962).

The final values of the adjusted complex dissociation constants are summarized in Table 6 and compared with the values obtained from the graphical solution and with the original Garrels and Thompson (1962) values.

The values of the complex constants determined by the solution of simultaneous equations is shown graphically in Figure 6. The differences between the two sets of solutions can be seen by comparing Figures 5 and 6.



TABLE 5



Figure 5. Arrows indicate the change in computed  $(CO_3^{=})_T$  and pH affected by altering the complexing constants for NaCO<sub>3</sub><sup>-</sup> and MgCO<sub>3</sub>° from the values used by Garrels and Thompson (1962). The magnitudes of the changes were determined from Figures 1 and 2 to bring the computed values within the uncertainty limits.

#### DISCUSSION

The apparent dissociation constants of carbonic acid in seawater were calculated as a function of temperature using the chemical model described above. The first and second apparent dissociation constants are related respectively to the thermodynamic constants  $K_1$  and  $K_2$  by:

$$K'_{1} = a_{\mathrm{H}} (\mathrm{HCO}_{3}^{-})_{T} / \alpha_{s} \cdot p \mathrm{CO}_{2}$$
$$= (\gamma_{\mathrm{CO}_{2}} \cdot a_{\mathrm{H}_{2}\mathrm{O}} / \gamma_{\mathrm{HCO}_{3}}^{-}) u \cdot K_{1}$$

and

$$K_{2}' = a_{\rm H} ({\rm CO}_{3}^{=})_{T} / ({\rm HCO}_{3}^{-})_{T}$$
$$= (\gamma_{\rm HCO_{3}}^{-} / \gamma_{\rm CO_{3}}^{-}) \cdot (\nu/u) K_{2},$$

where u and v have been defined by Eqs. (3) and (4). The definitions of  $K'_1$  and  $K'_2$  are identical to those used by Lyman (1956). The values of  $K_1$  and  $K_2$  obtained respectively by Harned and Davis (1943) and by Harned and Scholes (1941) and the values of  $\alpha_0$  and  $\alpha_s$  ( $\gamma_{CO_2} = \alpha_0/\alpha_s$ ) obtained by Li and Tsui (1971) were used for the

	Bermuda Surface Seawater	Mono Lake
Temp (°C)	22.4	10.3
$pCO_2$ (10 <sup>-6</sup> atm)	384	412
$\Sigma CO_2 (10^{-2} \text{ m/kg})$	0.209	34.3
$\Sigma Ca (10^{-2} M/kg)$	1.09	0.014
$\Sigma Mg (10^{-2} M/kg)$	5.57	0.191
ΣNa (10-2 M/kg)	48.9	119
$\Sigma K (10^{-2} M/kg)$	1.04	3.70
$\Sigma SO_4 (10^{-2} M/kg)$	2.94	10.3
ΣC1 (10-2 M/kg)	57.1	51.5
Ionic strength		
(meq <sup>2</sup> /kg)	0.73	1.64
Chlorinity $(^{\circ}/_{\circ\circ})$	20.3	14.5

present calculation in a temperature range of 0° to 25°C. All the activity coefficients (with the exception of  $\gamma CO_2$ ), the activity of water, and the dissociation constants for all the complex ion species were assumed to be independent of temperature. The apparent dissociation constants of carbonic acid in a seawater of 20°/<sub>oo</sub> chlorinity thus calculated are listed in Table 7 and are compared with those of Lyman (1956) and Buch (1951). The first dissociation constants of Buch are corrected to the NBS *p*H scale and also for  $\gamma CO_2$  and  $\gamma_{\rm H_2O}$ , and the second dissociation constants of Buch are corrected for the NBS *p*H scale.

Table 7 shows that the calculated  $K'_2$  values are in good agreement with those determined by Lyman over a temperauture range of 0° to 25°C. This indicates that the dissociation constants for carbonate ion complexes are independent of temperature, or alternatively that the effects of temperature on the dissocation constants for each of the carbonate ion complex species cancel each other and give an appearance that the  $K'_2$  values are independent of temperature. On the other hand, a substantial difference between the calculated values of  $K'_1$  and those of Lyman (1956) is observed at temperatures below 20°C, in spite of the fact that the calculated value was made to agree with Lyman's value of 22.4°C. This discrepancy is due to the fact that the effect of temperature on  $K_1$  determined by Lyman (1956) is about 20 per cent smaller than that on the  $K_1$ values which were calculated on the basis of the temperature dependence of the thermodynamic  $K_1$  values measured by Harned and Davis (1943). Thus, the observed discrepancy leads us to consider that the effect of temperature on the dissociation constants for bicarbonate ion complex species, i.e., NaHCO3°, CaHCO3<sup>+</sup>, and MgHCO3<sup>+</sup>, should not be overlooked in the formulation of the chemical model. Unfortunately, there are little or no data available as yet for the effect of temperature on those complex ion species, and, therefore, the observed discrepancy between temperature dependence of the  $K_1$  values determined by Lyman (1956) and that calculated here cannot be adequately resolved at the present time.

Buch's  $K'_1$  values, on the other hand, are systematically greater than the calculated values by about 5 per cent, but

	Garrels-Thompson		( (T)	Graphical 11s Paper) <sup>a</sup>	Sin H (T	nultaneous Equations his Paper) <sup>a</sup>
	рК	K'	pК	Κ'	pК	Κ'
$K_3(NaCO_3^-)$	1.27	$2.4 \times 10^{-1}$	0.52	1.36	0.52	1.35
$K_4(CaCO_3^\circ)$	3.21	$1.37 \times 10^{-2}$		-	-	-
$K_5(MgCO_3^\circ)$	3.42	$6.25 \times 10^{-3}$	3.30	$8.15 \times 10^{-3}$	3.25	$9.08 \times 10^{-3}$
$K_6(\text{NaHCO}_3^\circ)$	-0.20	3.89	-	-		÷
K7(CaHCO3 <sup>+</sup> )	1.28	$1.96 \times 10^{-1}$	-	-	1.20	$2.35 \times 10^{-1}$
K <sub>8</sub> (MgHCO <sub>3</sub> <sup>+</sup> )	1.18	$1.92 \times 10^{-1}$	-	-	1.10	$2.35 \times 10^{-1}$
Kg(NaSO4-)	0.82	1.42		-		-
$K_{10}(CaSO_4^\circ)$	2.42	$1.65 \times 10^{-1}$		-	-	-
$K_{11}(MgSO_4^\circ)$	2.48	$1.47 \times 10^{-1}$	-		—	-

TABLE 6 Major Ion Complex Constants Used for Model Calculations

<sup>a</sup>Dashes indicate original Garrels and Thompson values were not changed.



Figure 6. Arrows indicate the change in computed  $(CO_3^{=})_T$  and pH effected by altering the complexing constants for  $NaCO_3^{-}$ ,  $MgCO_3^{\circ}$ ,  $CaHCO_3^{+}$ , and  $MgHCO_3^{+}$  from the values used by Garrels and Thompson (1962). The magnitudes of the changes were determined by the simultaneous solution of equations using both Mono Lake and seawater empirical data.

the temperature dependence of his values is similar to that of the calculated values. Edmond and Gieskes (1970) compared the  $K'_1$  values obtained by Lyman (1956) with those by Buch (1951) and observed that Buch's values are consistent with the effect of temperature on the thermodynamic value,  $K_1$ , obtained by Harned and Bonner (1945), whereas Lyman's values are not. On this basis, they concluded that the temperature dependence of  $K'_1$  by Lyman (1956) may be in error. However, such an argument is hardly conclusive for evaluating the reliability of the  $K'_1$ values since the effect of temperature on the apparent dissociation constants in seawater is not necessarily the same as that on the thermodynamic constants, due to varying temperature dependence of the activity coefficients and the complex ion dissociation constants.

Because of those contrasting views arising from insufficient information available, it is premature to conclude whose values for the effect of temperature on the  $K'_1$  values are to be preferred. Therefore, the chemical model presented here should be regarded as tentative until further experimental data are furnished in the future.

## SUMMARY AND CONCLUSIONS

The major conclusion of this paper is the indication of substantial revisions in the chemical model parameters for  $NaCO_3^-$  and  $MgCO_3^\circ$  complexes. The dissociation constants determined here are approximately 5 times and 1.5 times, respectively, the values used in the model calculations of Garrels and Thompson (1962). The changes in  $NaCO_3^-$  and  $NaHCO_3^\circ$  complexing

The changes in NaCO<sub>3</sub><sup>-</sup> and NaHCO<sub>3</sub><sup>°</sup> complexing suggested by Butler and Huston (1970) are in the same direction as those suggested here, but only remove about 30 per cent of the discrepancy suggested by the Mono Lake and seawater data.

The recent changes in sulfate complexes (Kester and Pytkowicz, 1968, 1969) have essentially no effect on the  $(CO_3^{=})_T$  or pH data. The revised sulfate complexes (K<sub>9</sub>,

		$K'_1$ (10-7)		K	$K'_1 (10-10)$	)
(T(°C)	Lyman (1956)	Buch <sup>a</sup> (1951)	This Work <sup>b</sup>	Lyman (1956)	Buch <sup>a</sup> (1951)	This Work <sup>b</sup>
25	10.23	10.8	10.33	8.3	10.4	8.1
22.4	10.00	10.5	10.00	7.7	9.9	7.7
20	9.77	10.2	9.68	7.1	9.3	7.3
15	9.12	9.25	8.96	6.2	8.2	6.4
10	8.51	8.49	8.17	5.5	7.3	5.6
5	7.94	7.74	7.32	4.8	6.3	4.9
0	7.24	6.78	6.41	4.2	5.2	4.2

TABLE 7 Comparison Between the Apparent Dissociation Constants of Carbonic Acid in Seawater (Cl - 20.0°/...) by Lyman, Buch, and This Work

<sup>a</sup>Corrected for NBS pH scale.

<sup>b</sup>Solutions for the simultaneous equations.

 $K_{10}$ ,  $K_{11}$ ,  $K_{12}$ ) from Kester and Pytkowicz are included with the revised  $K_3$  and  $K_5$  values from this study to calculate the distribution of major ions and complexes (Table 8).

The uncertainty of the constants determined here can be estimated in several ways. Comparison of the results of the two solution techniques provides one estimate of uncertainty. Another is provided by the size of the area chosen to obtain the graphical solution (Figures 1 to 4):  $pK(\text{NaCO}_3^-) = +0.52 \pm 0.20$ , and  $pK(\text{MgCO}_3^\circ) = +3.30 \pm 0.04$ .

The effect of temperature on the apparent dissociation constants of carbonic acid in seawater was calculated (Table 7) assuming that the thermodynamic  $K_1$  and  $K_2$  values are a function of temperature as determined respectively by Harned and Davis (1943) and Harned and Scholes (1941) and that the dissociation constants for complex ion species are independent of temperature. The second apparent constant,  $K'_2$ , thus calculated agrees well with those of Lyman (1956) over the temperature range of 0° to 25°C. On the other hand, the temperature dependence of the apparent first dissociation constant,  $K'_1$ , thus calculated is about 20 per cent greater than that obtained by Lyman (1956) but is in agreement with that determined by Buch (1951). The calculated  $K'_1$  values at a chlorinity of  $20^{\circ}/_{\circ\circ}$ , however, are systematically smaller than those obtained by Buch (1951) by about 5 per cent. Due to the lack of experimental data for the effect of temperature on the dissociation constants for various bicarbonate complex ion species, and also due to the lack of a critical criterion for testing the reliability of Lyman's and Buch's data, it is not possible to determine whether or not the effect of temperature on the dissociation constants for bicarbonate complex ion species should be added to the chemical model. Therefore, this model should be considered tentative until critical experimental data are provided in the future.

Despite the lack of any data on the temperature dependence of the dissociation constants of carbonate and bicarbonate complex species, the maximum uncertainty

TABLE 8 Relative Abundance of Various Free and Complex Ion Species Calculated from the Present Model

	Free Ion (%)	Me-SO4 pair (%)	Me-HCO3 pair (%)	Me-CO <sub>3</sub> pair (%)	
Ca <sup>++</sup>	88	10.9	0.6	0.2	
Mg <sup>++</sup>	89	10.3	0.6	0.3	
Na <sup>+</sup>	98	2.2	0.3	0.02	
K+	99	1.2	-	~	
	Free Ion (%)	Ca-anion pair (%)	Mg-anion pair (%)	Na-anion pair (%)	K-anion pair (%)
SO4=	39	4.0	19	37	0.4
HCO <sub>3</sub> <sup>-</sup>	70	3.5	18	8.7	-
CO3=	12	9.3	7.4	4.3	( <del>)</del>
K values	: (-log K <sub>Di</sub>	iss)			
NaCO3 <sup>-</sup>	= +0.52	NaHCO	$3^{\circ} = -0.20$	NaSO4	= +1.28
CaCO3°	= +3.21	CaHCO	$3^{+}=+1.28$	CaSO4	= +2.67
MgCO3°	= +3.30	MgHCC	$_{3}^{+=+1.18}$	MgSO <sub>4</sub>	° = +2.54
- 0				KSO4	= +1.04

introduced in calculating the total carbonate ion concentration in interstitial waters is approximately 5 per cent. As shown in Table 7, the  $K'_2$  values of the chemical model and those of Lyman agree well over the whole temperature range. A maximum discrepancy in  $K'_1$  values of approximately 11 per cent occurs for temperatures near 0°C. Assuming a well defined  $K'_2$  value, the maximum discrepancy in  $(CO_3^{=})_T$  is thus about 5 per cent at 0°C. The discrepancy using the previous complex constant values is 30 per cent at 25°C. Thus the present model, although lacking critical temperature and pressure dependence information, is a substantial improvement and has been applied to the carbonate equilibria study of the Leg 15 interstitial waters by Takahashi et al. (this volume).

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