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APPENDIX

The geometric model (Figure 7) and theory for two-dimensional diffusion through a cluster of aligned elliptic cylinders are completely analogous to those for a bed of aligned spheroidal particles (Neale and Nader, 1976). Consequently, the present theory is summarized only very briefly here. Elliptic coordinates $[\xi, \eta]$ which are related to Cartesian coordinates by

$$x = a \sinh \xi \sin \eta \tag{A1}$$

$$y = a \cosh \xi \cos \eta \tag{A2}$$

are employed (where $0 \leqq \xi < \infty$, $0 \leqq \eta < 2\pi$).

For diffusion in the x direction, a solution of Laplace's equation

$$\nabla^2 c = 0 \tag{A3}$$

is sought which satisfies the following boundary conditions:

$$\text{at} \quad \xi = \xi_0, \quad q_\xi = 0 \tag{A4}$$

$$\text{at} \quad \xi = \xi_1, \quad q_\xi = -Q \cos\theta \tag{A5}$$

where q_ξ is given by the appropriate form of Fick's law; namely

$$q_\xi = -D \frac{1}{a\sqrt{\sinh^2 \xi + \sin^2 \eta}} \frac{\partial c}{\partial \xi} \tag{A6}$$

and, from basic geometry

$$\cos\theta = -\frac{\cosh \xi \sin \eta}{\sqrt{\sinh^2 \xi + \sin^2 \eta}} \tag{A7}$$

General solutions of Equation (A3) in elliptic coordinates are available in the literature (Moon and Spencer, 1961). The particular solution which satisfies Equations (A3) to (A7) may be verified to be

$$c = c_0 - (Qa/D) \left[\frac{\cosh \xi - \tanh \xi_0 \sinh \xi}{\tanh \xi_1 - \tanh \xi_0} \right] \sin \eta \tag{A8}$$

The effective diffusivity D_x is determined (Neale and Nader, 1976) by applying the macroscopic form of Fick's law to the unit cell depicted in Figure 7; namely

$$Q = D_x (c_A - c_B)/L \tag{A9}$$

where $L = 2a \sinh \xi_1 \sin \eta$. Combining Equations (A9) and (A8), we get the sought prediction for D_x, which is presented in Equation (9) of the main text (note that $E = \tanh \xi_0$ and $T = \tanh \xi_1$). The porosity of the unit cell must be equal to the porosity ϵ of the original system (Neale and Nader, 1976) in order to ensure macroscopic homogeneity of the modelled system; thus

$$1 - \epsilon = \frac{\sinh \xi_0 \cosh \xi_0}{\sinh \xi_1 \cosh \xi_1} \tag{A11}$$

The hyperbolic terms in this equation may be expressed solely in terms of E and T. Solving the resulting equation analytically for T then, we get Equation (12) of the main text.

A similar set of calculations can be performed for the case of diffusion in the y direction, yielding the prediction for D_y/D presented in Equation (10). In reality, however, it is far more convenient to make avail of a standard mathematical transformation. Thus, it may be verified that Equations (A8) and (9) become valid for flow in the y direction upon replacing each $\sinh\xi$ term by $\cosh\xi$ and each $\cosh\xi$ term by $\sinh\xi$ (this may be interpreted physically as an interchange of any minor axis, of length $2a \sinh\xi$, with the corresponding major axis, of length $2a \cosh\xi$, and vice versa).

The prediction for D_z [Equation (11)] follows without proof, since the cross-sectional area available for diffusion does not change in the z direction. (The results for diffusion developed here are actually independent of the size distribution for clusters of aligned cylinders having equal eccentricity.)

Manuscript received August 12, 1976; revision received November 9, and accepted November 15, 1976.

Thermodynamics of the Sulfur Dioxide-Seawater System

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The solubility of sulfur dioxide in seawater in the range 10° to 25°C and 10^{-5} to 1 molal is predicted based on a simplified chemical model. Estimates are also given of the resulting *p*H and the attendant distribution of sulfur and carbon dioxide species. Sulfur dioxide is considerably more soluble in seawater or other naturally alkaline waters than in pure water.

SCOPE

A novel pretreatment process for desalination that softens seawater and reduces corrosion has been proposed independently by Roy and Yahalom (1968) and Bromley (1969). In this process, sulfur dioxide from power plant flue gases or other inexpensive sources is injected directly into the seawater in a sparger, packed or a spray tower. This process is economical, permits better *p*H control

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than the sulfuric acid pretreatment process (Bromley et al., 1961), and reduces corrosion by furnishing adequate amounts of sulfite ion to scavenge oxygen. Knowledge of the thermodynamics of the sulfur dioxide seawater system is basic to the understanding of this process.

Another area of major interest in recent years is the control of sulfur dioxide emissions from power plants and industry. Many of the processes involve the adsorption of sulfur dioxide into an alkaline medium. Seawater is probably the cheapest alkaline medium, and the control of sulfur dioxide emissions and pretreatment for desalination could be profitably combined for plants sited near coastal waters.

Solubility data for sulfur dioxide in seawater are needed to design a sulfur dioxide absorber. An extensive survey of the literature on solubilities revealed that, even though the solubility of sulfur dioxide in water and other solvents has been widely investigated, equilibrium data reported for the sulfur dioxide-seawater system are limited. Calculated values are presented and compared with the available experimental data in this paper.

CONCLUSIONS AND SIGNIFICANCE

A chemical model based on thermodynamic principles has been successfully applied to calculate the equilibrium solubility of sulfur dioxide in seawater over a temperature range of 10° to 25°C and liquid phase sulfur dioxide concentrations from 10^{-5} to 1 molal. The model predicts that at 25°C, the equilibrium vapor pressure of sulfur dioxide over seawater remains negligible (less than 10^{-5} atm) as long as the seawater *p*H is maintained above 3.7.

Comparison of the predicted sulfur dioxide solubility in seawater with the solubility of sulfur dioxide in water indicates that sulfur dioxide is about two to three times more soluble in seawater than in freshwater. The enhanced solubility in seawater is readily explained when it is recognized that the alkaline components of seawater (mainly HCO_3^- and $SO_4^=$) trap the hydrogen ion released by the reacting sulfur dioxide and thereby promote further hydrolysis and greater solubility. Furthermore, the high (0.7) ionic strength of seawater tends to stabilize the ionized species of aqueous sulfur dioxide (HSO_3^- and $SO_3^=$) and thus encourage greater ionization.

Absorption of sulfur dioxide into seawater acidified with sulfuric acid to neutralize the bicarbonate ion also shows a solubility increase of 50 to 100% over freshwater.

Dissolved sulfur dioxide exists primarily as $SO_3^=$ at *p*H values greater than 7.5. As *p*H is lowered by addition of more sulfur dioxide, $SO_3^=$ concentration increases till it reaches a maximum value at *p*H 5.5. Below this *p*H, HSO_3^- becomes the predominant specie. Concentration of molecular sulfur dioxide in seawater solution becomes significant only at *p*H values below 2, when the equilibrium partial pressure of sulfur dioxide over the solution is greater than 3×10^{-3} atm.

The results of this study could serve as design data for sizing sulfur dioxide absorbers for seawater pretreatment in desalination plants or for flue gas absorbers used in air pollution control.

Accurate experimental data on solubility of sulfur dioxide in seawater, needed for the design of absorption equipment, are not generally available, although Abdulsatar (1971) and Bromley and Read (1970) report a few experimental and estimated values. However, experimental data on the sulfur dioxide-water systems are available and presented by Sherwood (1925), Johnstone and Leppla (1934), Seidell (1940), Plummer (1950), Pearson et al. (1951), Parkison (1956), Rabe and Harris (1963), Hetherington (1968) and for sulfur dioxide in other solvents by Smith and Parkhurst (1922), Hudson (1925), Battino and Clever (1966), and Schroeter (1966).

The study of the interaction of sulfur dioxide with seawater is considerably simplified if it is assumed that the salts of the cations, sodium, potassium, calcium, magnesium, and strontium, are completely ionized, and that their interactions with the weak electrolytes occur through direct physical ion-ion interactions and through their effect on the ionic strength of the solution. It is recognized that the above assumption is not strictly true for the calcium and magnesium salts (Thompson, 1966). However, the error introduced by the assumption in the case of seawater would be negligible because the chemical (alkalinity) effect far outweighs the physical (ionic strength) effect. By virtue of this simplifying assumption, the treatment of this complex system is reduced to that of a much simpler sulfur dioxide-carbon dioxide-water system with the exceptions that the water used in this system contains the bicarbonate and sulfate species in amounts equivalent to those in seawater and that the initial ionic strength and molarities of major ionic species in the water are the same as those of seawater.

A thermodynamic model involving the ion-ion interactions has been set up using an extended version of Debye-Huckel theory of electrolyte solutions developed by Bromley (1972). A similar treatment has been applied successfully by Bromley et al. (1974) to correlate the thermodynamic properties of seawater, like heat capacities and osmotic and activity coefficients.

THE MODEL

With this approach in mind, let us consider the equations needed to describe a closed, oxygen free sulfur dioxide-carbon dioxide-water system. In this system, twelve molecular species (in addition to water) are present: $SO_2(g)$, $CO_2(g)$, $SO_2(aq)$, HSO_3^-, $SO_3^=$, $HSO_4^=$, $SO_4^=$, $CO_2(aq)$, HCO_3^-, $CO_3^=$, H^+, and OH^-. There is ample evidence (Hetherington, 1968; Schroeter, 1966) that sulfur dioxide is dissolved in water in the molecular form. No stable, H_2SO_3 molecules are found in aqueous solution; that is, the undissociated form of sulfur dioxide in solution is the molecular form. On the other hand, stable H_2CO_3 exists in solution, and both H_2CO_3 and molecular carbon dioxide are considered, even though only carbon dioxide (aq) is shown in the equations and discussion. Thus, we have twenty-four unknowns [m_i (or p_i) and γ_i (or ϕ_i) for each of these species], and to solve for them one must write twenty-four independent equations. These equations are:

Dissociation equilibria:

$$K_1 = \frac{a_{H^+} a_{HSO_3^-}}{a_{SO_2(aq)}} \tag{1}$$

$$K_2 = \frac{a_{H^+} a_{SO_3^=}}{a_{HSO_3^-}} \tag{2}$$

$$K_3 = \frac{a_{H^+} a_{HCO_3^-}}{a_{CO_2(aq)}} \tag{3}$$

$$K_4 = \frac{a_{H^+} a_{CO_3^=}}{a_{HCO_3^-}} \tag{4}$$

$$K_5 = \frac{a_{H^+} a_{SO_4^=}}{a_{HSO_4^-}} \tag{5}$$

$$K_w = a_{H^+} a_{OH^-} \tag{6}$$

Vapor-liquid equilibria:

Since this study is concerned only with low pressures, the fugacity coefficients for both the gases can be set equal to 1.0. Thus

$$\phi_{SO_2} = \phi_{CO_2} = 1 \tag{7, 8}$$

Also, since the gas fugacity is proportional to the activity a, in solution

$$y_{SO_2}\phi_{SO_2}P = y_{SO_2}P = H_{SO_2}a_{SO_2}(aq) \tag{9}$$

$$y_{CO_2}\phi_{CO_2}P = y_{CO_2}P = H_{CO_2}a_{CO_2}(aq) \tag{10}$$

Mass balances:

Using the values for alkalinity, concentration of $SO_4^=$, and pH of sea water from Table 1, the following mass balances can be written for carbon dioxide neglecting the amount present in the gas phase:

$$\text{Total } CO_2 = 2.3 \times 10^{-3} = m_{CO_2(aq)} + m_{HCO_3^-} + m_{CO_3^=} \tag{11}$$

The carbonate ion concentration (10% of the total carbonate in raw seawater) becomes negligible as the pH is lowered and was thus ignored in the chemical model where low pH values are dominant. The carbon dioxide produced by reaction of sulfur dioxide with water is assumed to remain in the liquid phase:

$$\text{Total } SO_4 = 2.71 \times 10^{-2} = m_{HSO_4^-} + m_{SO_4^=} \tag{12}$$

Total concentration of $SO_2(g)$ or $SO_3(aq)$ (all forms considered), whichever is used as the independent variable, is

$$SO_2(g) \quad \text{or} \quad SO_2(aq) = \text{constant} \tag{13}$$

TABLE 1. SEA-WATER COMPOSITION*

Salinity = 33.9 g/kg

Ion	ppt	Molality	B_i(25°C)**
Cl^-	18.6597	0.52627	0.156
$SO_4^=$	2.6039	0.02710	−0.009
HCO_3^-	0.1373	0.00225	−0.039
Br^-	0.0635	0.00080	0.191
F^-	0.0013	0.00007	0.096
H_3BO_3	0.0256	0.00041	—
Na^+	10.3781	0.45140	−0.035
Mg^{++}	1.2505	0.05142	0.043
Ca^{++}	0.3934	0.00981	−0.035
K^+	0.3736	0.00956	−0.087
Sr^{++}	0.0131	0.00015	−0.070
H^+	—	—	0.087
HSO_3^-	—	—	−0.013
HSO_4^-	—	—	−0.013
$SO_3^=$	—	—	−0.087

Density = 1 033.3 − 0.16259t kg/m³ (t°F, liquid temperature)
Ionic strength 0.672
pH of seawater 8.05
Residual alkalinity = 2.3 × 10^{-3} equivalents/kg

* Sverdrup et al. (1959).
** Bromley (1972) or Abdulsattar (1971).

Total H = Initial concentration of H^+ in seawater
+ moles H^+ released owing to dissociation of sulfur dioxide (aq)
+ moles H^+ released owing to dissociation of HSO_3^-
− moles consumed in the formation of carbon dioxide (aq)
− moles consumed in the formation of HSO_4^-

or

$$m_{(H^+)} = \frac{10^{-8.05}}{\gamma_{H^+}} + m_{(HSO_3^-)} + 2m_{(SO_3^=)} - m_{(H_2CO_3)} - m_{(HSO_4^-)} \tag{14}$$

Equation (14) is also a special form of the electroneutrality condition.

Activity Coefficients

Activity coefficients for each of the eight dissociated species are

$$\text{anion } M, \text{ long } \gamma_M = -\frac{AZ_M{}^2I^{1/2}}{1+I^{1/2}} + B_M \sum_x m_x + \sum_x B_x m_x$$

TABLE 2. THERMODYNAMIC CONSTANTS IN AQUEOUS SOLUTIONS AT 25°C, AT INFINITE DILUTION

Reacting species	Symbol	Value*	Reference
$SO_2(aq), H^+, HSO_3^-$	K_1	1.72×10^{-2}	Campbell and Maass (1930)
$HSO_3^-, H^+, SO_3^=$	K_2	6.24×10^{-8}	Tartar and Garretson (1941)
$CO_2(aq), H^+, HCO_3^-$	K_3	4.45×10^{-7}	Robinson and Stokes (1968)
$HCO_3^-, H^+, CO_3^=$	K_4	4.70×10^{-11}	Latimer and Hildebrand (1965)
$HSO_4^-, H^+, SO_4^=$	K_5	1.04×10^{-2}	Robinson and Stokes (1968)
H_2O, H^+, OH^-	K_w	1.01×10^{-14}	Latimer and Hildebrand (1965)
$SO_2(g), SO_2(aq)$	H_{SO_2}	0.794	Rabe and Harris (1963)
$CO_2(g), CO_2(aq)$	H_{CO_2}	28.80	Munjal and Stewart (1971)

* Units for the H values are $\frac{\text{(kg)(atm)}}{\text{gmole}}$

$$\text{cation } x,\ \log \gamma_x = -\frac{A_\gamma Z_x^2 I^{1/2}}{1 + I^{1/2}} + B_x \sum_M m_M + \sum_M B_M m_M \quad (15 \text{ to } 22)$$

Activity coefficients for sulfur dioxide (aq) and carbon dioxide (aq) are given the values suggested by Rabe and Harris (1963) and Garrels and Christ (1965), respectively:

$$\gamma_{SO_2}(aq) = 0.98 \qquad (23)$$

$$\gamma_{CO_2}(aq) = 1.13 \qquad (24)$$

Input to the Model

Data required by the model are the composition of seawater, the dissociation constants, the Henry's law constants, and the activity coefficients as functions of temperature. Most of the required information was obtained from the literature and where not available, estimates were made using standard thermodynamic techniques.

Table 1 lists the composition of seawater used in this study, and Table 2 lists the values of the appropriate thermodynamic constants for the sulfur dioxide-water system at 25°C. Values at other temperatures were obtained by using the reported correlations or by interpolations on a log K vs. $1/T$ plot.

Estimates of the single ion activity coefficients needed to relate the activities of the dissolved species to their respective concentrations were obtained from an extended version of the Debye-Hückel theory as proposed by Bromley (1972). According to this version, which is simpler but less accurate than Bromley (1973), the activity coefficient of a cation in a solution of ionic strength I is represented by Equations (15) to (22). The B values (at 25°C) for use in the activity coefficient expressions are given in Table 1. Values at other temperatures were estimated by assuming that variations in individual B values would follow the variations of overall B for the sea salt as a whole. Bromley et al. (1974) report the temperature dependence of $B_{\text{sea salt}}$ and this information were used to estimate the temperature dependence of the various B_M's and B_x's. The values of A_γ at various temperatures were interpolated from values in Lewis et al. (1961).

COMPUTATIONAL PROCEDURE

Calculations were carried out as follows. An initial estimate of ionic strength, activity coefficients, partial pressure of sulfur dioxide, and estimate were provided to start the calculations. Then the concentrations of sulfur dioxide (aq), HSO_3^-, $SO_3^=$, HCO_3^-, $CO_3^=$, carbon dioxide (aq) and the corresponding activity coefficients were calculated from Equations (1) through (22). A new (H^+) was calculated from Equation (14) and compared with the assumed value. If the two are not within 0.1% of each other, new estimates of ionic strength, etc., are made and the calculations repeated until convergence. A Newton-Raphson procedure was used to estimate new guesses. The calculations were carried out on a Control Data Corporation 6400 computer.

The convergence was poor for initial estimates far removed from the true value.

RESULTS

The calculated equilibrium solubility of sulfur dioxide in seawater over a temperature range of 10° to 25°C and liquid phase sulfur dioxide concentration from 10^{-5} to 1 molal is summarized in Table 3. Also listed in Table 3 is the pH of the equilibrated seawater solution. The low sulfur dioxide partial pressure data from Table 3 are plotted in Figure 1. Also shown for comparison are the freshwater data from Rabe and Harris (1963), Edwards et al. (1975), and the data obtained by Sridhar (1975) during absorption studies on seawater acidification with sulfuric acid to a pH of 4.3.

Comparison of (see Table 4 and Figure 2) the model results at 12.8°C (55°F) with the experimental data reported by Bromley (1970) indicates that the model approximates the real system quite well. No direct com-

TABLE 3. SULFUR DIOXIDE—SEAWATER EQUILIBRIA*

Temp. °C	10°C (50°F)		12.8°C (55°F)		15.6°C (60°F)		21.1°C (70°F)		25°C (77°F)	
P_{SO_2} atm	pH	T_{SO_2}†	pH	T_{SO_2}	pH	T_{SO_2}	pH	T_{SO_2}	pH	T_{SO_2}
4.5×10^{-13}	7.65	2.336×10^{-5}	7.65	2.157×10^{-5}	7.67	1.958×10^{-5}	7.70	1.675×10^{-5}	7.71	1.575×10^{-5}
8.97×10^{-13}	7.56	3.164×10^{-5}	7.57	2.921×10^{-5}	7.58	2.652×10^{-5}	7.61	2.267×10^{-5}	7.62	2.126×10^{-5}
7.17×10^{-12}	7.27	7.360×10^{-5}	7.28	6.788×10^{-5}	7.30	6.167×10^{-5}	7.33	5.524×10^{-5}	7.34	4.902×10^{-5}
3.59×10^{-11}	7.04	1.360×10^{-4}	7.05	1.259×10^{-4}	7.07	1.144×10^{-4}	7.09	9.748×10^{-5}	7.10	9.076×10^{-5}
1.79×10^{-10}	6.78	2.500×10^{-4}	6.80	2.311×10^{-4}	6.82	2.102×10^{-4}	6.58	1.792×10^{-4}	6.86	1.668×10^{-4}
8.97×10^{-10}	6.51	4.568×10^{-4}	6.52	4.238×10^{-4}	6.55	3.866×10^{-4}	6.58	3.307×10^{-4}	6.59	3.082×10^{-4}
8.97×10^{-9}	6.04	1.028×10^{-3}	6.06	9.673×10^{-4}	6.09	8.944×10^{-4}	6.14	7.799×10^{-4}	6.16	7.326×10^{-4}
8.07×10^{-8}	5.42	1.800×10^{-3}	5.46	1.743×10^{-3}	5.51	1.667×10^{-3}	5.59	1.531×10^{-3}	5.62	1.470×10^{-3}
5.99×10^{-7}	4.67	2.204×10^{-3}	4.72	2.185×10^{-3}	4.79	2.158×10^{-3}	4.90	2.101×10^{-3}	4.95	2.072×10^{-3}
1.79×10^{-6}	4.21	2.288×10^{-3}	4.27	2.279×10^{-3}	4.34	2.266×10^{-3}	4.46	2.240×10^{-3}	4.51	2.227×10^{-3}
4.48×10^{-6}	3.82	2.347×10^{-3}	3.91	2.494×10^{-3}	3.95	2.330×10^{-3}	4.08	2.313×10^{-3}	4.13	2.306×10^{-3}
1.79×10^{-5}	3.34	3.085×10^{-3}	3.39	3.012×10^{-3}	3.45	2.921×10^{-3}	3.56	2.795×10^{-3}	3.60	2.755×10^{-3}
7.17×10^{-5}	2.90	4.535×10^{-3}	2.94	4.359×10^{-3}	2.99	4.139×10^{-3}	3.09	3.823×10^{-3}	3.13	3.722×10^{-3}
1.79×10^{-4}	2.64	6.426×10^{-3}	2.68	6.125×10^{-3}	2.73	5.750×10^{-3}	2.81	5.208×10^{-3}	2.85	5.033×10^{-3}
4.48×10^{-4}	2.40	9.680×10^{-3}	2.44	9.167×10^{-3}	2.48	8.537×10^{-3}	2.56	7.611×10^{-3}	2.60	7.310×10^{-3}
2.69×10^{-3}	1.97	2.489×10^{-2}	2.00	2.332×10^{-2}	2.04	2.151×10^{-2}	2.12	1.877×10^{-2}	2.15	1.785×10^{-2}
8.97×10^{-3}	1.69	5.220×10^{-2}	1.72	4.859×10^{-2}	1.76	4.460×10^{-2}	1.84	3.846×10^{-2}	1.87	3.634×10^{-2}
2.69×10^{-2}	1.44	1.114×10^{-1}	1.47	1.031×10^{-1}	1.51	9.427×10^{-2}	1.58	8.048×10^{-2}	1.61	7.560×10^{-2}
7.17×10^{-2}	1.22	2.353×10^{-1}	1.25	2.164×10^{-1}	1.29	1.975×10^{-1}	1.36	1.671×10^{-1}	1.39	1.563×10^{-1}
4.48×10^{-1}	0.80	1.116	0.83	1.019	0.87	9.270×10^{-1}	0.94	7.756×10^{-1}	0.96	7.211×10^{-1}

* Calculations using chemical model for seawater.

† T_{SO_2} = Total sulfur dioxide concentration, gmoles/kg.

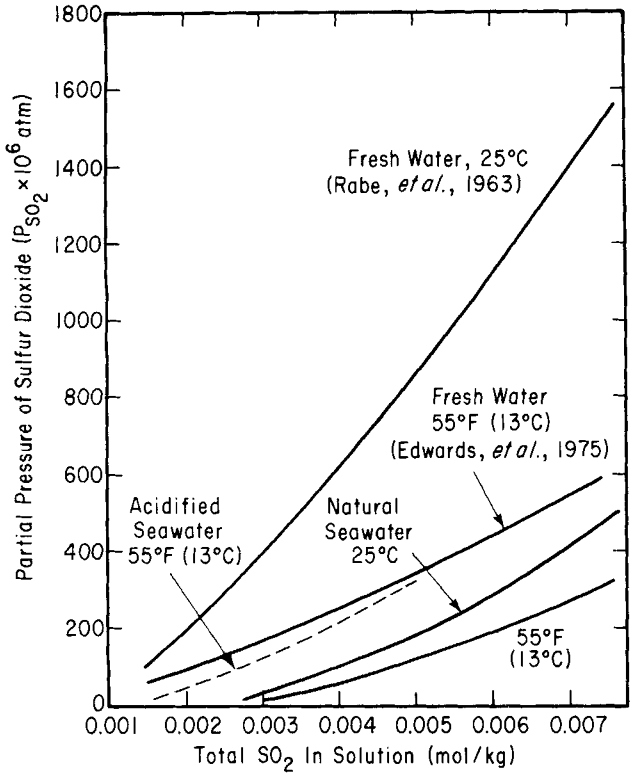

Fig. 1. Partial pressure of sulfur dioxide over water and seawater solutions.

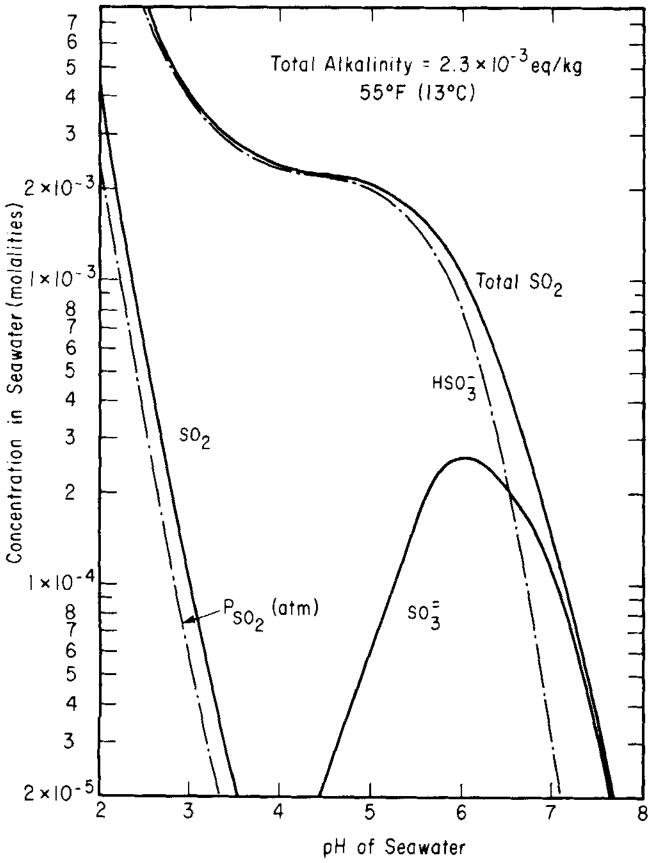

Fig. 3. Concentration of added sulfur dioxide and related species in seawater and their effect on pH.

parison can be made with Abdulsattar's (1971) experimental data because they were obtained at temperatures higher than those used in the model.

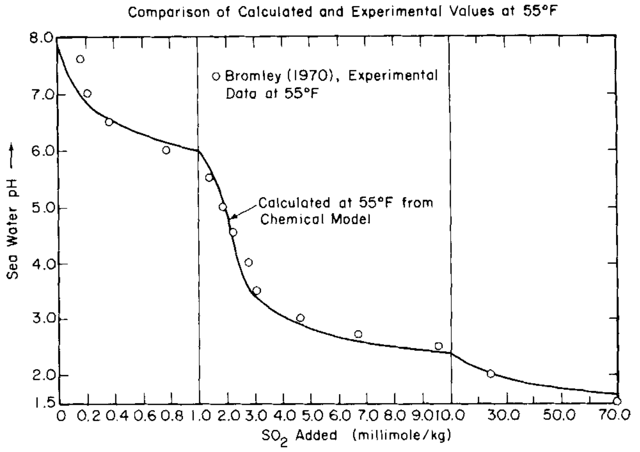

Fig. 2. pH of seawater as a function of sulfur dioxide addition.

TABLE 4. COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES AT 12.8°C (55°F)

	This work calculated		Bromley (1970) experimental
*p*H	SO_2 added gmoles/kg	*p*H	SO_2 added gmoles/kg
8.05	0.00	8.1	0.00
7.57	2.92×10^{-5}	7.5	8.3×10^{-5}
7.05	1.26×10^{-4}	7.0	2.1×10^{-4}
6.52	4.24×10^{-4}	6.5	3.6×10^{-4}
6.06	9.67×10^{-4}	6.0	7.3×10^{-4}
5.46	1.74×10^{-3}	5.5	1.4×10^{-3}
—	—	5.0	1.9×10^{-3}
—	—	4.5	2.2×10^{-3}
3.91	2.50×10^{-3}	4.0	2.8×10^{-3}
3.39	3.01×10^{-3}	3.5	3.1×10^{-3}
2.94	4.36×10^{-3}	3.0	4.6×10^{-3}
2.68	6.12×10^{-3}	2.7	6.7×10^{-3}
2.44	9.17×10^{-3}	2.5	9.6×10^{-3}
2.00	2.33×10^{-2}	2.0	2.5×10^{-2}
1.51	9.43×10^{-2}	1.5	7.0×10^{-2}

The seawater used by Bromley was obtained at the Bodega Marine Laboratory of the University of California. The seawater had an alkalinity of 2.38 meg/l (116 p.p.m. as calcium carbonate) and was saturated with air. The seawater used in model had an alkalinity of 2.32 and was assumed to be oxygen free.

The reason for enhanced solubility of sulfur dioxide in seawater over that in freshwater is illustrated by the difference in the slope of the freshwater curves and the slope of the corresponding seawater curves. The larger slope of the freshwater curves contrasted to the gentle slopes of the seawater curves suggests that whereas the solubility of sulfur dioxide in freshwater is limited by extent of dissociation of sulfur dioxide (aq), the same limitation is not as severe in the seawater case where stabilization of the dissociation products allows sulfur dioxide (aq) to ionize to a greater extent.

The variation of the seawater *p*H with the total sulfur dioxide concentration and the corresponding distribution of $HSO_3^=$, SO_3^- and sulfur dioxide (aq) at 12.8°C (55°F) is shown in Figure 3. An interesting feature of this figure is the pronounced peak in the sulfite concentration profile. The existence of this peak is readily explained by recognizing that the sulfite concentration in this system is a result of a balance between the total sulfur dioxide concentration and the hydrogen ion concentration. At high *p*H, where sulfite is the stable species, its concentration is low because the total dissolved sulfur

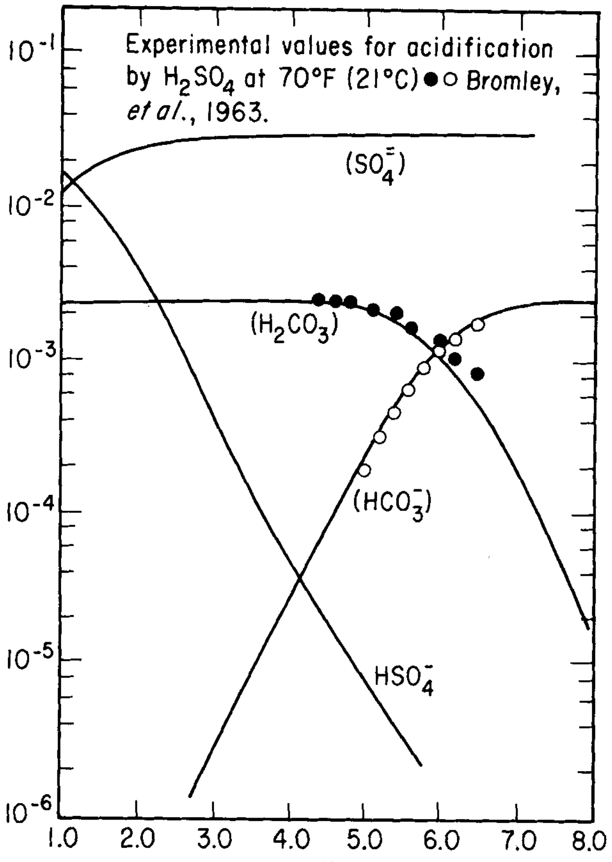

Fig. 4. Effect of sulfuric acid addition to seawater on pH, carbonic acid, and related species.

TABLE 5. ACTIVITY COEFFICIENTS

	Temperature °C				
Species	10°C	12.8°C	15.6°C (60°F)	21.1°C	25°C (77°F)
H^+	0.774	0.778	0.783	0.790	0.795
HSO_3^-	0.571	0.569	0.566	0.563	0.560
$SO_3^=$	0.112	0.110	0.109	0.106	0.104
HCO_3^-	0.556	0.553	0.550	0.549	0.543
HSO_4^-	0.571	0.569	0.566	0.562	0.560
$SO_4^=$	0.121	0.120	0.118	0.116	0.115

dioxide concentration is low. At high concentrations of dissolved sulfur dioxide, the *p*H is low and this favors the formation of bisulfite without further ionization to sulfite. Somewhere between these two extremes a balance is struck between a low hydrogen ion concentration and a relatively high total sulfur dioxide concentration. At this point, we observe a peak in the sulfite concentration.

Another useful result obtained from the chemical model is the distribution of the alkaline species in seawater. Figure 4 illustrates this distribution. Also shown in Figure 4 are some experimental values by Bromley et al. (1963) of the carbon dioxide species when sulfuric acid was used as the acidifying agent. Although the calculated values were obtained for acidification by sulfur dioxide while the experimental values are those for acidification by sulfuric acid, the comparison is still valid because at a given *p*H the distribution of the carbonate species would not be affected by the nature of the acidifying agent. The good agreement between the calculated and experimental values indicates that the chemical model represents the real system quite well.

Table 5 lists the calculated activity coefficients for the dissociated portions of the weak electrolytes. The low values (compared to unity) result from stabilization by the ions present in seawater.

It should be noted that it would be expected that the oxygen present in the seawater (usually about 7 p.p.m.) would be converted to sulfate by reaction with sulfite. This probably occurs in a matter of minutes and depends on the amount of trace catalysts present. The effect of oxidation would be to give a lower *p*H for a given amount of sulfur dioxide added.

ACKNOWLEDGMENT

The authors wish to thank the Water Resources Center for financial assistance and Mr. Stanley M. Read for his help in programming the calculations in the early phases of this work.

NOTATION

a = activity
A_γ = constant in Debye-Hückel expression
B = Debye-Hückel parameter
H = Henry's law constant, atm/g mole/kg or atm in Equations (9) and (10)
I = ionic strength $= \frac{1}{2} \sum_i m_i z_i^2$
K = dissociation equilibrium constant
m = concentration, molality, m/kg of solvent
P = pressure, atm
T = temperature, °K
T_{SO_2} = total sulfur dioxide concentration, g mole/kg
y = gas phase mole fraction
z = charge number
γ = molal activity coefficient
ϕ = gas phase fugacity coefficient

Subscripts

M = cation
w = water
x = anion

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APPENDIX: TEMPERATURE DEPENDENCE OF THERMODYNAMIC EQUILIBRIUM CONSTANTS[*]

Values of K_1, the first dissociation constant of sulfur dioxide(aq) at temperatures other than 25°C, were obtained by interpolation on a log K vs. $1/T$ plot. The plot was constructed from the data of Campbell and Maass (1930) who studied K_1 over a temperature range of 5° to 90°C. For K_3, the first dissociation constant of carbon dioxide(aq), and K_5, the second dissociation constant of sulfuric acid, the variation with temperature was estimated from the following correlations reported in Robinson and Stokes (1968):

$$pKH_2CO_3 = \frac{3\,404.71}{T} - 14.8435 + 0.032786T \qquad \text{(A1)}$$

$$pKHSO_4- = \frac{475.14}{T} - 5.0435 + 0.01822T \qquad \text{(A2)}$$

The temperature dependence of HSO_2 and HCO_2 was calculated from the following correlations reported by Rabe and Harris (1963) and Munjal and Stewart (1971), respectively:

$$HSO_2 = \exp\left(- \frac{2\,851.1}{T} + 9.3795 \right) \qquad \text{(A3)}$$

$$HCO_2 = \exp\left(\frac{-2\,734.1}{T} + 16.83 \right) \qquad \text{(A4)}$$

Equation (A4) uses the mole fraction instead of molality as the concentration unit, and hence the calculated value of HCO_2 must be adjusted to conform to the units used in the model.

Manuscript received March 20, 1976; revision received October 16, and accepted November 5, 1976.

Drop Sizes in Annular Gas-Liquid Flows

The droplets that appear in annular gas-liquid flows are formed by the eruption of wavelets from the surface of the wall layer. Ninety per cent of the volume of this dispersed liquid is carried by only about 10% of the drops. We find, as suggested by Wicks and Dukler, that the distribution of drop sizes can be characterized by an upper limit, log normal function with only one of the three parameters, the volume median diameter, a strong function of flow conditions. A method for predicting the average diameter is suggested which is consistent with a theoretical interpretation based on a Kelvin-Helmholtz mechanism, whereby the destabilizing force is the pressure variation over the wavelets.

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SCOPE

When a gas and a liquid are transported in a duct with high gas velocities and with a relatively low ratio of liquid to gas throughput, an annular regime exists whereby a liquid layer flows along the wall and a high velocity gas stream flows concurrently. The liquid layer, which has an agitated wavy surface, can be entrained into the gas.

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[*] K_2 was assumed constant with temperature owing to lack of data at temperatures other than 25°C. The variation of K_4 with temperature was not estimated because this equilibrium was neglected in this study. K_w was assumed constant over the temperature range of interest, 10 to 25°C.