2 less volatile component

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Solubility of Sulfur Dioxide in Distilled Water and Decarbonated Sea Water

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The solubility of sulfur dioxide in distilled water and decarbonated sea water (salinity 0–40‰) has been measured at a pressure of 1 atm of SO_2 at pH 0.8 over the temperature range 5.8–30 °C. The measurements were made by saturating water with the gas and then analyzing an aliquot of the solution by treating it with hydrogen peroxide and titrating the resultant sulfuric acid with standard sodium hydroxide solution. Values found for the solubility in distilled water agree well with recent published data. The solubility of the gas in sea water decreases slightly with increasing salinity.

Introduction

Suggestions have been made that sulfur dioxide from power plant flue gases could be used for scale prevention and deoxygenation in sea water desaturation plants (*1–3*). In the design of sulfur dioxide absorbers for this purpose it is necessary to have data for the solubility of the gas in sea water. Although many rather discordant values are available for the solubility in pure water (*4–9*) and a few data have been published for aqueous salt solution (*8*, *10*) only one study has been made of the solubility in sea water (*11*). The few data which this study provides are, according to its author, of questionable accuracy—±15%, at best. For this reason it was thought worthwhile to make fresh measurements of the solubility of the gas, covering a wider range of salinities and temperatures. For this purpose a modification of a technique which had been previously used with hydrogen sulfide (*12*) was employed. In this, the acidified sample was sparged with nitrogen to remove oxygen and carbon dioxide. It was then saturated by stirring in a current of sulfur dioxide. Aliquots of the saturated sample were analyzed by allowing them to react with hydrogen peroxide and titrating the resultant sulfuric acid with carbonate-free standard sodium hydroxide. Because there was a tendency to supersaturation at low temperatures, the final equilibration was carried out by stirring the sample very gently for 5 h in a static atmosphere of the gas. The pH values of the saturated solutions were ~0.8.

Experimental Section

Measurement of Physical Parameters and Salinity. Equilibration temperatures were measured by means of mercury in glass thermometers reading to 0.01 °C which had been calibrated by means of a Dymec quartz thermometer that itself had been standardized against a triple point cell. Barometric pressures were measured by using an NPL certified Kew pattern barometer; brass scale corrections were applied.

A Hytech inductive salinometer was used for the measurement of the salinities of samples prior to acidification. Conductivity ratios relative to standard sea water were converted to salinities (g kg^{-1}) by means of the UNESCO conductivity–salinity tables (*13*).

Sulfur Dioxide. The sulfur dioxide used in the present work was of "refrigeration grade" and was supplied by BDH Chemicals Ltd. in 500-g cannisters. Mass spectrometric analysis of the gas showed its purity to exceed the 99.9% specified by the manufacturer.

Sea Water. Surface water (S = ~33‰) from the Irish Sea was filtered through a 0.45-μm filter. Samples of water (10 L) having salinities in the range 10–40‰ were prepared from it by evaporation or dilution with distilled water as appropriate. Acidification to pH 2.8 was carried out by treating 5-L aliquots of the water with 4 mL of 5 M sulfuric acid. After acidification the samples were stored in closely stopped borosilicate glass bottles.

Apparatus. Because supersaturation of sulfur dioxide occurred with ease and because we wished to measure the specific gravity of the saturated solution, it was necessary to modify the saturation vessel which we had used for measurement of the solubility of hydrogen sulfide (*12*). The modified vessel A is shown in Figure 1. It consisted of a water-jacketed glass tube, 40 cm in length and an internal diameter of 5.2 cm. There was a gap of ~2 mm between the inner and outer walls at the bottom to facilitate the use of a magnetic stirrer. At the upper end of the tube were sealed a B24 and a B29 socket and two screwed cap connectors. One of the latter served as a thermometer port, and through the other passed a 9-mm o.d. tube connected to an open ended mercury manometer (R) and a mercury pressure regulator (P). The B29 socket was used to admit a hydrometer which was held upright by a narrow glass tube sealed through the standard cone. The B24 socket was fitted with a cone having sealed through it a gas inlet tube (T) reaching to within 3 cm of the bottom of the saturation vessel. An S13 ball socket at the top of this tube served to connect it to the water sampler and its associated trap N which were the same as those described in our previous paper on the solubility of hydrogen sulfide (see Figure 1 of ref 12).

Procedure

A 650-mL sample of acidified sea water was placed in the saturation vessel, and after being brought to thermal equilibrium it was degassed by bubbling with oxygen-free nitrogen via tube

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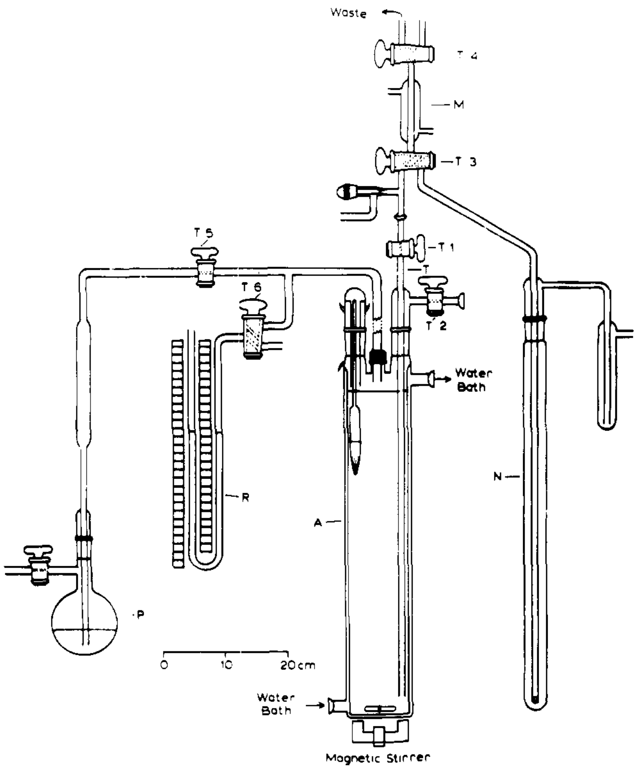

Figure 1. Apparatus used for the measurement of the solubility of sulfur dioxide.

T while stirring gently. After 2 h the flow of nitrogen was stopped and saturation with sulfur dioxide was commenced at a flow rate of ~40 mL min^{-1}. During this saturation period stopcock T_5 was opened and the excess gas was vented via the mercury pressure regulator. The passage of gas was continued for ~16 h with gentle stirring. At the end of this period a suitably graduated hydrometer was rapidly introduced into the saturator. The gas was passed for a further few minutes before its supply was turned off and the inlet stopcock T_5 was closed. Gentle stirring was continued for a further 5 h, after which stopcock T_6 was closed and the stirrer was switched off. The readings of the barometer, manometer, thermometer, and hydrometer were then noted. During the final stages of the equilibration, the sampler (M) was brought to the equilibration temperature and connected to the top of the deoxygenation/saturation vessel. Sampling of the saturated water was carried out by applying a pressure of sulfur dioxide via the outlet tube while stopcock T_5 was closed. After ~60 mL had passed through the sampler, stopcocks T_3 and T_4 were closed and the sample was checked for freedom from bubbles. Following this, stopcocks T_3 and T_4 were opened and the sample was allowed to run into trap N which contained 150 mL of hydrogen peroxide solution. Transfer of the sample was aided by passing a slow current of nitrogen through the sampler for ~1 h. The contents of the trap were then transferred quantitatively to a conical flask fitted with a gas delivery tube, and while sparging with nitrogen, the solution was titrated with carbonate-free standard sodium hydroxide solution, by using phenolphthalein as indicator.

A blank was run in order to make allowance for the sulfuric acid used to acidify the sample and the phosphoric acid present as a preservative in the hydrogen peroxide. This was carried out by performing a duplicate run using nitrogen in place of sulfur dioxide.

The reproducibility of the method, including the saturation stage, was checked by making six replicate measurements of the solubility of sulfur dioxide in distilled water at 30.10 and 9.97 °C. These gave coefficients of variation of 0.08 and 0.10%, respectively.

Table I. Determined Values of Sulfur Dioxide Solubility in mol L^{-1} at a Total SO_2 Pressure of 760 Torr in Distilled Water and Sea Water, Together with Computed Values and Differences

temp, °C	salinity, g kg^{-1}	exptl value, mol L^{-1}	smooth curve value, mol L^{-1}	% deviation	sp gr of solution
5.82	0.0	2.959	2.959	0.01	1.074
	10.065	2.956	2.956	0.00	1.080
	20.034	2.954	2.954	0.03	1.087
	30.074	2.954	2.953	0.00	1.095
	40.005	2.953	2.953	0.00	1.103
9.97	0.0	2.482	2.491	−0.36	1.067
	10.065	2.479	2.488	−0.36	1.075
	20.034	2.477	2.487	−0.39	1.082
	30.074	2.477	2.486	−0.35	1.088
	40.005	2.476	2.485	−0.36	1.094
14.95	0.0	2.065	2.047	0.87	1.055
	10.065	2.062	2.044	0.87	1.063
	20.034	2.061	2.042	0.92	1.071
	30.074	2.060	2.042	0.87	1.078
	40.005	2.059	2.041	0.87	1.085
19.83	0.0	1.697	1.706	−0.53	1.045
	10.065	1.694	1.704	−0.58	1.052
	20.034	1.693	1.703	−0.58	1.059
	30.074	1.692	1.701	−0.53	1.066
	40.005	1.691	1.700	−0.53	1.074
25.0	0.0	1.419	1.421	−0.14	1.032
	10.065	1.417	1.420	−0.21	1.042
	20.034	1.416	1.418	−0.14	1.050
	30.074	1.414	1.417	−0.21	1.058
	40.005	1.414	1.416	−0.14	1.064
30.1	0.0	1.201	1.199	0.17	1.028
	10.065	1.200	1.198	0.17	1.034
	20.034	1.198	1.196	0.17	1.040
	30.074	1.197	1.195	0.17	1.048
	40.005	1.196	1.194	0.17	1.056

Results

Measurements of sulfur dioxide solubility were made at temperatures over the range ~2–35 °C in both distilled water (acidified and unacidified) and acidified sea water of salinity up to 40‰. The results of these experiments are shown in Table I, together with corresponding values for the specific gravities of the saturated solutions.

Examination of the data showed that, although the temperature dependence of the various sets of data closely fitted the integrated form of the Van't Hoff equation, the salinity dependence at constant temperature could not be expressed satisfactorily by the Setchenow equation (*14*) (see below). It was not, therefore, possible to process the unified data with the type of equation which Weiss (*15*) has used successfully for other gases, since this depends on the Setchenow equation being obeyed. Instead, because the effect of salinity is only small, the data for each salinity were processed by using a four-term version of Weiss' equation from which the salinity terms had been omitted, viz.

$$\ln C = A_1 + A_2(100/T) + A_3 \ln (T/100)$$

where C is the saturation concentration of the gas in appropriate units, T is the absolute temperature, and $A_1 ... A_3$ are constants.

Data from Table I for each salinity were used to derive the constants A_1–A_3 for that salinity and these were then employed to produce tables showing the solubilities at integral values of temperature at 10‰ intervals of salinity (Table II).

Discussion of Results

The integrated form of the Van't Hoff equation (*15*) gave a close representation of the relationship between solubility and temperature for both distilled water and sea water.

Distilled Water. The percentage differences between the data in Table II and selected figures from the literature are shown

Table II. Smoothed Curve Values of Sulfur Dioxide Solubility in Pure Water and Sea Water Expressed as mol L^{-1} at a Total Pressure of 1 Atm

temp, °C	salinity, g kg^{-1}				
	0.0	10.0	20.0	30.0	40.0
5	3.065	3.061	3.059	3.059	3.058
6	2.937	2.933	2.931	2.931	2.930
7	2.815	2.812	2.810	2.810	2.809
8	2.701	2.697	2.696	2.695	2.694
9	2.591	2.588	2.587	2.586	2.585
10	2.488	2.485	2.483	2.482	2.482
11	2.390	2.387	2.385	2.384	2.384
12	2.296	2.293	2.292	2.291	2.290
13	2.208	2.205	2.204	2.202	2.201
14	2.123	2.120	2.119	2.118	2.117
15	2.043	2.040	2.039	2.038	2.037
16	1.966	1.964	1.963	1.961	1.961
17	1.894	1.891	1.890	1.889	1.888
18	1.824	1.822	1.821	1.819	1.819
19	1.758	1.756	1.755	1.754	1.753
20	1.696	1.693	1.692	1.691	1.690
21	1.635	1.633	1.632	1.631	1.630
22	1.578	1.576	1.575	1.573	1.573
23	1.524	1.521	1.520	1.519	1.518
24	1.471	1.469	1.468	1.467	1.466
25	1.422	1.419	1.418	1.417	1.416
26	1.374	1.372	1.370	1.369	1.368
27	1.328	1.326	1.325	1.324	1.323
28	1.285	1.283	1.281	1.280	1.279
29	1.243	1.241	1.240	1.239	1.238
30	1.203	1.201	1.200	1.199	1.198

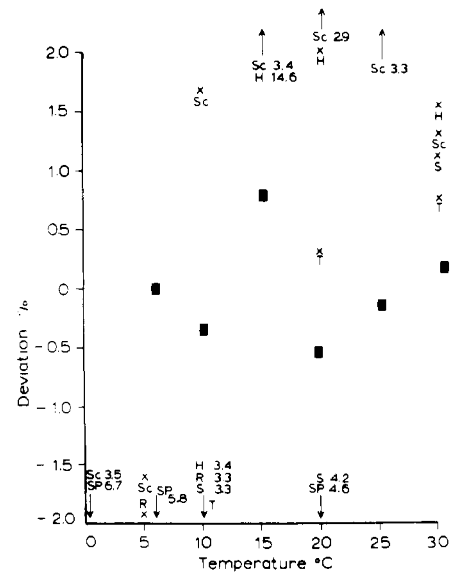

Figure 2. Percentage differences between earlier published values for the solubility of sulfur dioxide in distilled water and those shown in Table II. Values in excess of the latter are designated +. Key to symbols is as follows: Sc = Schönfeld (*4*), S = Sims (*5*), R = Roozeboom (*6*), SP = Smith and Parkhurst (*7*), H = Hudson (*8*), T = Tokunaga (*9*), ■ = experimental data from present work.

diagrammatically in Figure 2. The closest correspondence is found for the values by Tokunaga (*9*) which all are within ~1.7% of those found in the present work. Data from earlier workers lie as much as 4.5% both above and below our values and, in general, show no systematic trend.

Sea Water. The solubility of sulfur dioxide in sea water decreases with increasing salinity. However, in contrast to other gases, the system does not obey Setchenow's equation (*13*), the relationship between salinity and log solubility at constant temperature being nonlinear (Figure 3). The effect of salinity is considerably smaller than that with other gases so far investigated. For sea water of salinity 40‰ it ranges from 0.23% at 5 °C to 0.42% at 30 °C (expressed as the percentage decrease relative to distilled water). This salting-out effect is similar in magnitude to that observed by Fox (*10*) and Terraglio (*16*) for sodium chloride solution and by Hudson (*8*) for a solution of sodium sulfate. Our measurements were made at an SO_2 partial pressure of 1 atm and no valid direct comparison can therefore be made with the data of Abdul Suttar et al. (*17*), who used much lower partial pressures of the gas. Under these conditions a relatively large proportion of the gas is accounted for in neutralizing the natural alkalinity of the sea water. The apparent solubility of the gas is thus increased. It should also be noted that it may not be valid to extrapolate our data to low partial pressures as it is uncertain whether Henry's law is rigidly obeyed by such a soluble gas.

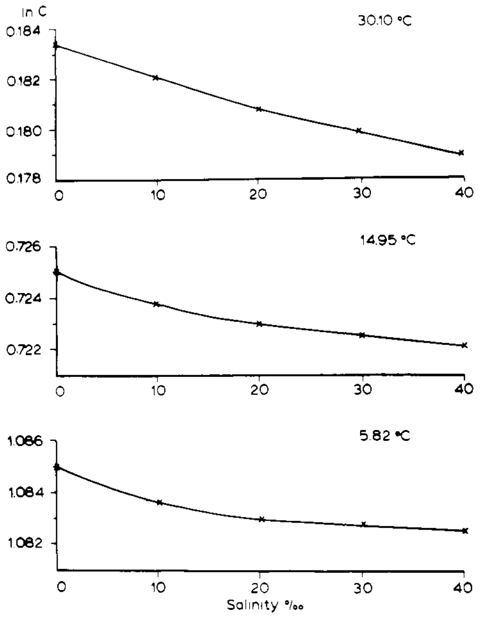

Figure 3. Effect of salinity on the solubility (in mol L^{-1}) of sulfur dioxide at three temperatures.

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