(*3*) and Wu, Birky, and Hepler (*4*). Disproportionation of hypobromite to bromate occurs slowly at the temperature of the experiments. In this work, however, because of the limited accuracy of the calorimetric results, no correction to the $-\Delta H$ values for hypobromite loss was made.

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Solubility of Carbon Dioxide in Pure Water, Synthetic Sea Water, and Synthetic Sea Water Concentrates at −5° to 25° C. and 10- to 45-Atm. Pressure

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Experimental equipment and procedure are described for measuring high pressure, low temperature solubility of gases in liquids. Experimental results are given for the solubility of CO_2 in distilled water, synthetic sea water, and synthetic sea water concentrates in the —5° to 25° C., 10- to 45-atm. range.

IN 1960 the Jacobs Engineering Co., Pasadena, Calif., under contract to the State of California, Department of Water Resources, issued a report (*7*) of a preliminary engineering study of its proposed process for saline water demineralization. This process, a freezing, or alternatively a hydrate process, proposed the use of carbon dioxide as a direct contact refrigerant or hydrating agent. The report pointed out the dearth of reliable experimental data on the solubility of carbon dioxide in liquids of interest, sea water and sea water concentrates produced by the freezing of pure ice from sea water.

The university agreed to undertake an experimental program to supply the necessary data. It was originally believed that this work would be relatively routine; that this did not prove to be the case has been chronicled in the annual report (*17, 18*) and most recently the final project report (*19*) of the university's Sea Water Conversion Laboratory, which is based upon Munjal's thesis (*12*).

Prior work in this field can be conveniently divided into the solubility of carbon dioxide in water and in salt solutions.

The solubility of carbon dioxide in water has been investigated by numerous workers from the time of Wrobleski (*23, 24, 25*) in 1882. The data in the literature have been compiled by several writers (*13, 14, 16*), the most recent of whom are Dodds, Stutzman, and Sollami (*4*), who covered the information available through 1955. Since then the works of Bartholome and Friz (*1*) and Loparest (*9*) have appeared. The agreement among the results of the various investigators is by no means as good as is desirable, particularly in the higher pressure region. Hydrate formation in this higher pressure area, delineated by Larson (*8*) who worked out the phase diagram for the CO_2—H_2O system, may well account for at least some of the disagreement.

The solubility of CO_2 in solutions of various inorganic salts [NaCl, $NaNO_3$, Na_2SO_4, KNO_3, $Mg(NO_3)_2$, and $MgSO_4$] at 1-atm. pressure is summarized by Markham and Kobe (*11*) in their literature survey. Findlay and Creighton (*5*) investigated KCl solutions.

Surprisingly enough, especially considering the importance of carbon dioxide in the biological field, apparently no experimental measurements have been made on the solubility of CO_2 in sea water. Quoted values for this property are usually taken from Buch (*3*); these tables were based on Bohr's (*2*) estimate that the gas solubility was the same in sea water as in a NaCl solution containing the same quantity of dissolved solids. Lyman (*10*) has examined this assumption, and concludes that Buch's values are slightly high.

A much more complete review of prior work, including many tables, is given by Munjal (*12*) and in the project report (*19*).

EXPERIMENTAL EQUIPMENT

From a functional point of view the equipment used in the experimental work served two purposes: to prepare a sample at equilibrium at a known pressure and temperature, and to ascertain the composition of that sample. The components or subsystems of the equi-

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librium assembly are: the pressure vessel, or autoclave, or bomb, the agitation mechanism, the constant temperature system, the pressure-control system, and the sample-withdrawal system. These various units are briefly described below, and in much more complete detail by Munjal (*12*) and in the project report (*19*).

Pressure Vessel. The pressure vessel is made of cast Monel and is 3 1/2 inches in inside diameter by 7 inches in inside height, 1/2-inch wall thickness with a hemispherical bottom. The closure flange is cast integrally with the vessel. The cover plate is a forged Monel blank welding flange. Design pressure is 1500 p.s.i. This unit with the assembled piping (Monel tubing) connections is shown schematically in Figure 1.

Agitation Mechanism. The agitation system used rocks the pressure vessel through an angle of 29.6 degrees 58.3 cycles per minute. As shown in Figure 2, the system comprises a 1/2-hp. motor, geared speed reducer, driving wheel, driving arm with cam follower connection to driving wheel, and the autoclave holder on the oscillating shaft. This design was adapted from one successfully used in the Berkeley Petroleum Engineering Department for hydrocarbon *P-V-T* work.

Constant Temperature System. The constant temperature system or thermostat is made up of three tanks fabricated from sheet copper and thermally insulated with 2 inches of Foamglas. The first tank, the chiller, has copper coils on the inside through which evaporating Freon-12 circulates as needed to cool the heat transfer medium, a methanol-water solution, to a fraction of a degree below the desired equilibrium temperature. The chiller tank is stirred with a propeller agitator. The methanol solution, used in preference to brine to minimize corrosion problems, is pumped at a manually controlled rate to the autoclave tank.

The autoclave tank, and the sampling assembly tank connected to it by a vertical slot, are both agitated or stirred by the rocking of the pressure vessel or autoclave. An electric immersion heater, thermostatically controlled, heats the subcooled methanol to the desired temperature. The methanol solution is returned to the chiller tank by gravity flow. Temperature control with this system was ±0.06° C. The temperature was recorded continuously on a Foxboro industrial-type instrument.

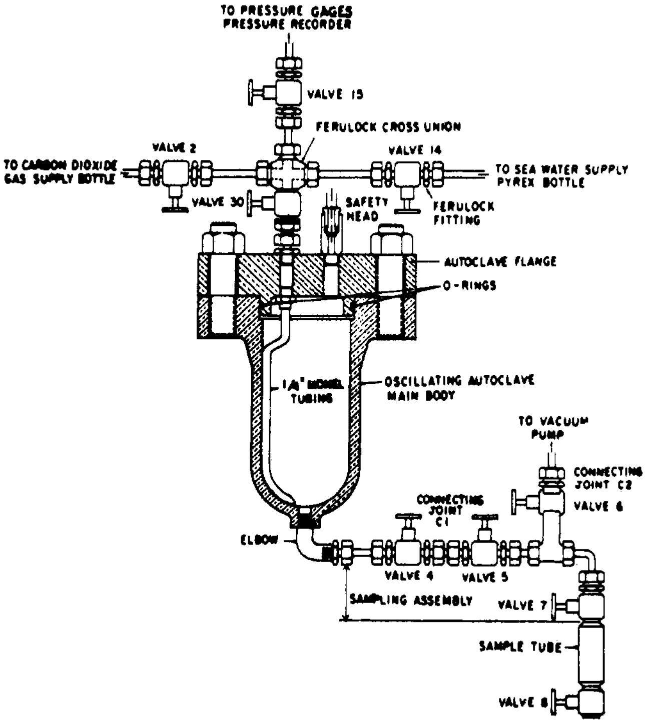

Figure 1. Assembly of oscillating autoclave with sample tube and controls

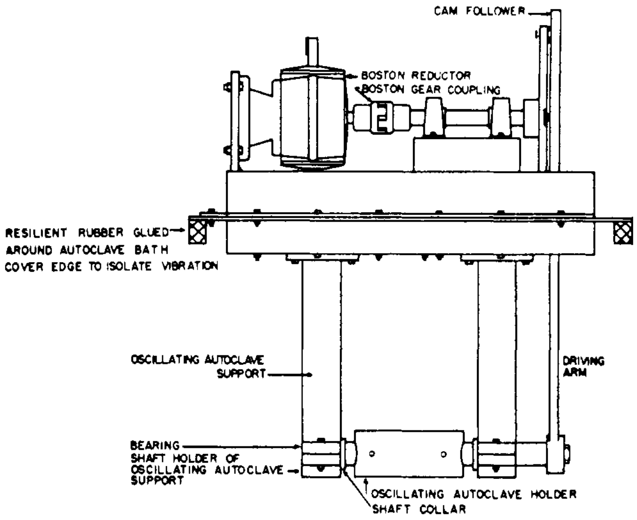

Figure 2. Front view of mechanical shaking assembly

Pressure Measurement and Control. The autoclave was pressurized by admitting gas from a standard liquefied CO_2 cylinder (Matheson Co., research grade, 99.99% purity), and the pressure was reduced, if required, by venting gas. All pressure control was manual. Pressure was measured with calibrated precision Bourdon-tube gages of 0 to 100, 0 to 500, and 0 to 1500 p.s.i. range. With these gages pressures could be read to ±0.25 p.s.i. below 500 p.s.i. and to ±0.50 p.s.i. in the higher range. Pressure was monitored with a standard Foxboro industrial instrument.

Sampling Assembly. The containers for the pressurized equilibrium samples were double-ended Monel tubes closed on each end with Monel needle valves, all manufactured by Hoke, Inc., Englewood, N. J. The valves required lapping in for pressure-tight operation. The sample tube and the connections to the autoclave are shown in Figure 1.

The sampling assembly is immersed in the auxiliary sampling tank maintained at the same temperature as the equilibrium vessel. The original tank for the equilibrium bomb did not provide sufficient room for convenient manipulation during the sampling process, which necessitated its enlargement by the addition of the third tank.

The entire assembly of all components of the equilibrium equipment is shown schematically in Figure 3.

Chemical Analysis Equipment. The method for chemical analysis of the liquid sample was to distill the CO_2 out of the sample, absorb it in an excess of standard $Ba(OH)_2$, and back-titrate the excess base. The apparatus and procedure have been described (*12, 19, 20*).

SYNTHETIC SEA WATER PREPARATION

Since natural sea water is variable in composition, all sea water used in these experiments was prepared synthetically. The recipe used for this synthetic sea water was that developed by Brujewicz as reported in

Table I. Synthetic Sea Water Composition (*21*)

Component	Concentration	
	G./kg.	G./l.
NaCl	26.518	27.133
$MgCl_2$	2.447	2.504
$MgSO_4$	3.305	3.382
$CaCl_2$	1.141	1.167
KCl	0.725	0.742
$NaHCO_3$	0.202	0.207
NaBr	0.083	0.085
Total Salts	34.420	35.220
H_2O	965.579	964.78

Table II. Solubility of CO_2 in Distilled H_2O

Pressure, Atm.	G. CO_2 per 100 G. H_2O				
	0° C.	5° C.	10° C.	12.4° C.	25° C.
10	3.133	2.603	2.102	...	...
20	...	4.492	3.801	...	2.403
25	5.988	...	...	...	...
30	6.614	...	...	...	...
38	...	6.342	5.455	...	...
45	...	...	...	5.503	4.110

Subow's "Oceanographical Tables" (*21*). Relatively concentrated solutions of the various salts used (all reagent grade chemicals) were first made up in deaerated distilled water, and then standardized by chemical analysis to determine the exact salt content. The synthetic sea water was then made up from these stock solutions by volumetric measurement. For synthetic sea water of normal salt concentration the composition is given in Table I; the more concentrated solutions, threefold and fivefold concentrates, are what the name indicates.

The CO_2 in the 0.202 gram of $NaHCO_3$ per kg. of synthetic sea water is included in the values for grams of CO_2 per 100 grams of solvent reported in this work; the effect of doing this is to add not more than 1 part in the second decimal place.

EXPERIMENTAL PROCEDURE

Temperature setting in the autoclave bath is the first operation, accomplished by adjusting the refrigeration thermostat so that the heat transfer liquid is maintained approximately 0.06° C. below the desired set point, with the transfer pump operating. Finally the heater control is adjusted to the desired temperature. Because of the large thermal capacity of the system, and consequent slow response, this procedure required a day or more.

While the temperature of the system was being set, sample tubes were prepared. This involved lapping in the valves, filling with CO_2 to approximately 100 p.s.i., weighing, and then checking the weight the following day. If tight, the tubes were then evacuated to an absolute pressure of 10 microns or less.

Before charging with liquid, the pressure vessel (autoclave) was pumped down to 10 microns, pressurized with CO_2 to 100 p.s.i., pumped down again, and pressurized and pumped down to 10 microns again. The synthetic sea water storage bottle was then slightly pressurized with CO_2, to 2 to 3 p.s.i., and approximately 800 ml. of the liquid admitted to the autoclave. The pressure in the vessel was then built up to the desired value by admitting CO_2.

Agitation (oscillation) of the autoclave was then started. As the gas goes into solution it is necessary to add more of it, from time to time, to maintain the desired pressure. Equilibrium attainment required from

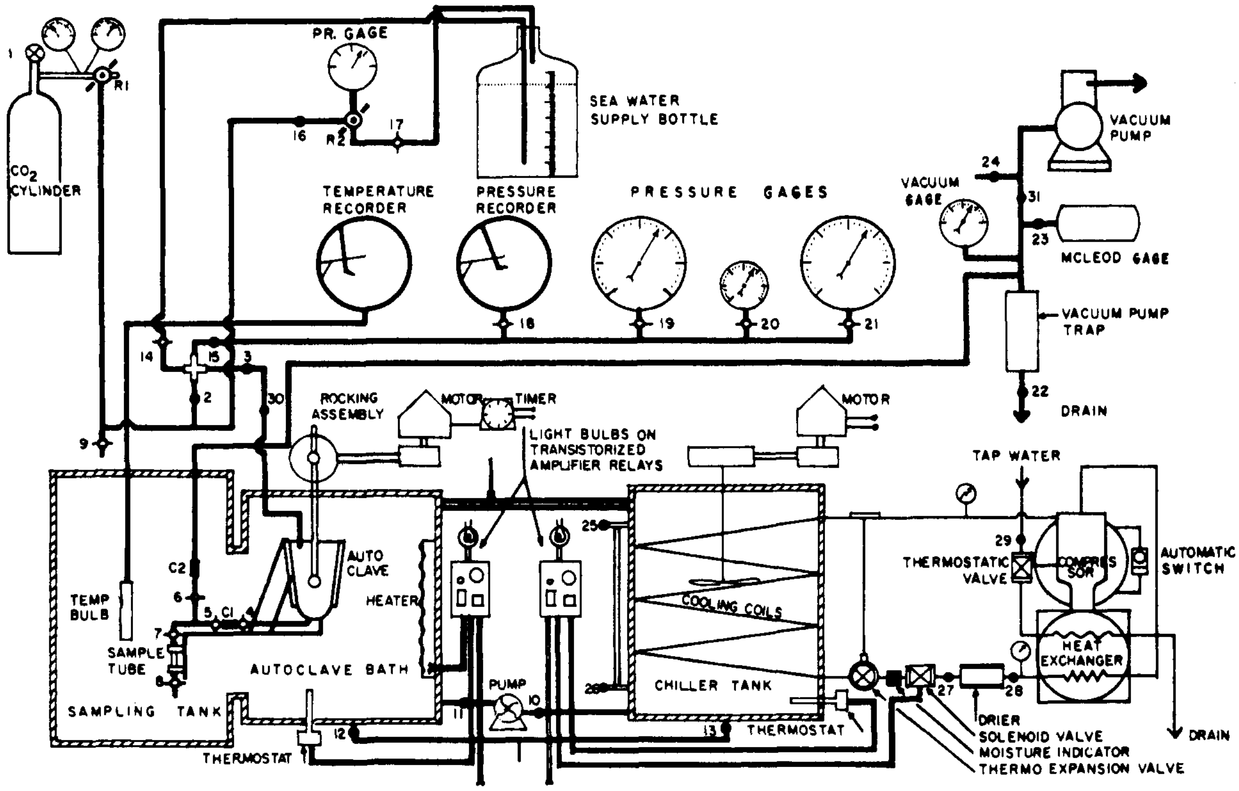

Figure 3. Flow diagram of equilibrium assembly

Table III. Solubility of Carbon Dioxide in Synthetic Sea Water

Pressure, Atm.	G. CO_2/100 G. Solvent						
	−5° C.	0° C.	5° C.	10° C.	12.4° C.	15° C.	25° C.
1	0.310	0.265	0.220	0.191	0.173	0.155	0.110
5	1.446	1.248	1.043	0.889	0.790	0.740	0.551
10	2.752	2.358	2.004	1.701	1.558	1.411	1.023
15	...	3.312	...	...	...	...	...
20	4.781	4.152	3.548	3.042	2.805	2.531	1.822
30	6.412	5.604	4.843	4.140	3.805	3.453	2.397
34	...	6.007	...	...	...	...	...
38	...	...	5.601	4.801	...	...	...
45	...	...	...	...	4.852	4.379	3.090

Table IV. Solubility of Carbon Dioxide in Synthetic Sea Water Concentrate

Pressure, Atm.	G. CO_2/100 G. Solvent		
	0° C.	12.4° C.	25° C.
	3X Salts Content		
10	2.149	1.351	0.907
20	3.892	2.411	1.612
34	5.451	...	...
45	...	4.052	2.751
	5X Salts Content		
10	2.043	1.214	
20	3.552	2.192	
34	5.253	...	
45	...	3.672	

8 to 14 hours. A first check on the achievement of equilibrium is the pressure remaining constant for some hours.

To make sure that equilibrium had been attained in the early experiments samples were taken at varying times after the constant pressure state had been reached. No detectable changes were found after the pressure remained constant for 4 hours, which became the working criterion for the attainment of equilibrium. Consistency of the data, and agreement (where possible) with published values, are further verification of equilibrium.

In the early stages of the work the possibility of hysteresis effects was checked out by deliberate overpressuring followed by venting to the desired value. The results obtained by the two methods were identical.

When equilibrium had been achieved, sampling of the liquid was undertaken. Oscillation of the vessel was stopped, and it was positioned vertically. Valves 4, 5, and 7 (Figure 3), previously closed, were then opened, causing the system pressure to drop slightly. The system was then repressurized and agitated again for ca. 30 minutes. Valve 8 was then opened. Again pressure dropped, followed by repressuring and agitation. Valves 4, 5, and 7 were then closed and the sample tube was disconnected at *C* 1 and *C* 2. The sample tube was then dried and weighed, and was ready for chemical analysis. Check samples were obtained in the same manner.

RESULTS

Solubility of Carbon Dioxide in Pure Water. To verify the consistency of results obtained with the equipment and procedures used with those of prior workers, where agreement does exist, and to resolve differences also reported, the first series of experiment were made with pure water the solvent (Table II).

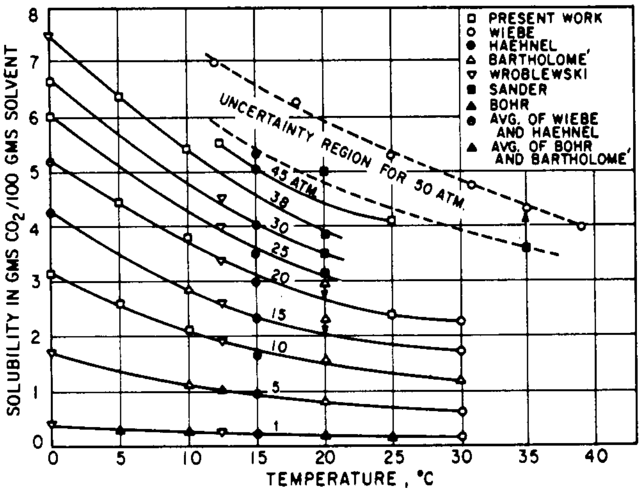

Figure 4. Solubility isobars for CO_2 in distilled water

Data from (*1, 2, 6, 15, 22–25*)

Figure 4 is a plot not only of the data obtained in this work but also those of earlier investigators. It shows that, neglecting a few of the published values, consistent experimental data now exist for the solubility of CO_2 in pure water in the 0° to 30° C. temperature range and from 1- to 45-atm. pressure, and that the methods used in this work give results consistent with other work.

Also, Figure 4 points up the uncertainty that exists at 50-atm. pressure. Larson's work (*8*) gives a clue to this: the presence of a hydrate solid phase which would invalidate an all-liquid sample. Since the equipment used was not designed for handling solid phase samples, this pressure was not investigated in this work.

Solubility of Carbon Dioxide in Sea Water and Sea Water Concentrates. The data obtained for the solubility of CO_2 in synthetic sea water, and in synthetic sea water with 3 and 5 times the normal salts concentration, are given in Tables III and IV.

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Physical Properties of a Refrigerant Mixture of Monofluoromonochloromethane and Tetrafluorodichloroethane

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The physical properties presented describe the mixture of 55.1 wt. % monofluoromonochloromethane and tetrafluorodichloroethane, forming a minimum-boiling azeotrope at 291.2° K. The pressure-volume-temperature properties have been measured and correlated with the Martin-Hou equation of state. The vapor pressure and liquid densities were fitted to equations and the critical properties obtained.

THE MATERIALS, monofluoromonochloromethane (Refrigerant 31) and tetrafluorodichloroethane (Refrigerant 114), were obtained from commercial sources and purified by fractional distillation. The purity of each component, as determined by gas chromatography, was 99.9 mole % or better. The precautions in handling the mixture were described in a previous publication (*4*).

As previously (*4*), the term vapor pressure will be used to describe the pressure exerted by a vapor when a state of equilibrium has been reached between a liquid and its vapor. Obviously, this term is used in the general sense here, since the composition of the vapor and liquid are not exactly the same, except at the azeotropic state. However, every effort that was practical was taken to minimize the vapor space above the mixture and to obtain data at the bubble point.

The apparatus and techniques employed were discussed in detail in earlier papers (*1, 3, 4*). However, a few brief remarks are made.

The pressure-volume measurements were obtained on a constant-volume cell constructed of a 300-cc. high-pressure stainless steel cylinder. The sample was confined in the cell with a 5-cm. stainless steel diaphragm. The volume change due to the displacement of the diaphragm from the null point was negligible. Nitrogen was used as the pressure transfer media and the pressure was read on calibrated Heise gages, connected to the system, covering various ranges.

The critical temperature was determined by observation of the meniscus in a sealed glass tube, which was slowly heated and cooled in a stirred liquid bath. The average value of several observations was 415.2° ± 0.1° K.

Extrapolation of the near-critical isochor to the critical temperature determined the critical pressure. This gave a value of 749 ± 1 p.s.i.a.

The critical density was determined by a standard rectilinear diameter plot, using the liquid densities calculated from the liquid density equation and saturated vapor densities calculated from the equation of state. The value determined was 0.539 ± 0.001 gram per cc.

The temperature was measured with a platinum resistance thermometer calibrated by the U. S. National Bureau of Standards (° C. Int., 1948). The volume was determined by calibration with water and corrected for thermal expansion, using the coefficient of thermal expansion for stainless steel.

The liquid densities were determined by a float technique. The calibrated glass floats were corrected for thermal expansion and found accurate to 0.1% over the range covered. The floats were found incompressible in the given pressure range by checking their accuracies in known liquids.