

## CARBON DIOXIDE IN WATER AND SEAWATER: THE SOLUBILITY OF A NON-IDEAL GAS

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(Received May 29, 1974; revised and accepted August 22, 1974)

### ABSTRACT

Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.*, 2: 203–215.

New measurements of the solubility of carbon dioxide in water and seawater confirm the accuracy of the measurements of Murray and Riley, as opposed to those of Li and Tsui. Corrections for non-ideal behavior in the gas phase and for dissociation in distilled water are required to calculate solubility coefficients from these sets of data. Equations for the solubilities of real gases are presented and discussed. Solubility coefficients for carbon dioxide in water and seawater are calculated for the data of Murray and Riley, and are fitted to equations in temperature and salinity of the form used previously to fit the solubilities of other gases.

### INTRODUCTION

Until very recently, direct determinations of the solubility of CO<sub>2</sub> in seawater have been limited to a few measurements of Krogh (1904). Most authors have preferred to use approximations based on the solubility of CO<sub>2</sub> in aqueous sodium chloride solutions. Buch et al. (1932) prepared tables of seawater CO<sub>2</sub> solubilities from the Bohr (1899) data for sodium chloride solutions, using the assumption that the effect of sea salt on the solubility is equal to the effect of an equal weight of sodium chloride. Lyman (1957) refined this assumption by considering the salting-out of the various constituents of sea salt, suggesting that the Buch et al. values may be about 0.5% too high.

The lack of direct measurements of CO<sub>2</sub> solubility in seawater has recently been alleviated by two independent sets of data: those of Li and Tsui (1971), determined by infrared analysis, and those of Murray and Riley (1971), determined gravimetrically. Unfortunately, the agreement between these sets of measurements is poor. Whereas the data of Li and Tsui support the values assumed by Buch et al., the solubility data of Murray and Riley are as much as 3.8% lower than those of Li and Tsui at higher temperatures and salinities. The agreement is better at lower temperatures and in distilled water, so that

the differences cannot be expressed either as a constant offset or as a constant factor.

In hopes of resolving these discrepancies, it was decided to make several independent measurements of CO<sub>2</sub> solubility. If it could be shown that a few accurate measurements covering a wide range of temperature and salinity were consistently in close agreement with one of the two sets of data, this would provide strong support for the accuracy of that set at all measured temperatures and salinities.

The second objective of this work was the fitting of the best CO<sub>2</sub> solubility data to an equation in temperature and salinity of the form used previously to fit the solubilities of N<sub>2</sub>, O<sub>2</sub>, and Ar (Weiss, 1970), He and Ne (Weiss, 1971a), H<sub>2</sub> (Crozier and Yamamoto, 1974), and Kr (Weiss and Kyser, in preparation). CO<sub>2</sub> is many times more soluble than any of the gases treated previously, and in the gas phase its departures from the ideal gas approximation are large compared to the accuracy with which its solubility can be measured. Therefore, before the use of such equations is justified, it is necessary to use Henry's law for real gases and to test its validity over a range of partial pressures of CO<sub>2</sub>. Also, it is necessary to test the validity of the logarithmic Setchénow salting-out relation (Weiss, 1970, 1971b) for CO<sub>2</sub> in seawater.

Both Li and Tsui (1971), and Murray and Riley (1971), noted that their measurements would be affected by the dissociation of dissolved hydrated CO<sub>2</sub> to form bicarbonate, and accordingly they acidified their seawater samples to a sufficiently low pH so that this effect could be neglected. However, both studies failed to take this effect into account for their distilled-water measurements, which were made without acidification. Although this effect cancels in direct comparisons between the two sets of measurements, the proper use of Henry's law and of the Setchénow relation requires that the data be corrected for dissociation.

All distilled water CO<sub>2</sub> solubility data discussed in the following sections have been corrected for dissociation using the following approximation:

$$[\text{CO}_2] = [\Sigma \text{CO}_2] - \sqrt{K_1' [\Sigma \text{CO}_2]} \quad (1)$$

where [CO<sub>2</sub>] is the sum of the concentrations of dissolved CO<sub>2</sub> and undissociated hydrated CO<sub>2</sub>, [ΣCO<sub>2</sub>] is the sum of the concentrations of all dissolved CO<sub>2</sub> species as measured in the solubility experiment, and K<sub>1</sub>' is the first apparent dissociation constant at the temperature of the measurement.\*<sup>1</sup> Solubilities measured in distilled water for p<sub>CO<sub>2</sub></sub> ≈ 1 atm are thus reduced by ~ 0.18% at 0°C, to ~ 0.46% at 40°C.

#### HENRY'S LAW AND REAL GASES

King (1969, ch.4) presents an excellent and thorough discussion of Henry's law and its application to real gases over a wide range of pressures. By ex-

\*<sup>1</sup> Values of K<sub>1</sub>' were calculated according to Harned and Davis (1943, eq.15):  
 $\log_{10} K_1' = -3404.71/T + 14.8435 - 0.032786 T$

pressing the activity of the solute in the gas phase by its fugacity, and by making the appropriate thermodynamic correction for the expansion of the solution by the dissolved gas, the "modified Henry's law equation" is obtained:

$$f_i = Q_i x_i \exp(P\bar{v}_i/RT) \quad (2)$$

where  $f_i$  is the fugacity of gas  $i$ ,  $x_i$  is the mole fraction of  $i$  in solution,  $\bar{v}_i$  is the partial molal volume of  $i$  in solution,  $R$  is the gas constant,  $T$  is the absolute temperature,  $P$  is the total pressure at the liquid-gas interface, and  $Q_i$ , the modified Henry's law constant for  $i$ , is a function only of the temperature and the nature of the solvent.

Conveniently, King uses the  $\text{CO}_2$ -water system as an example to illustrate the application of eq.2. Using literature data, with special emphasis on the work of Wiebe and Gaddy (1939; 1940), King (1969, pp.219-220) demonstrates that eq.2 holds over the entire  $\text{CO}_2$ -pressure range from zero to several hundred atmospheres, at a number of different temperatures.\*<sup>2</sup> The use of the modified form of Henry's law to calculate  $\text{CO}_2$  solubilities over wide ranges of total pressures and  $\text{CO}_2$  partial pressures, based on accurate solubility measurements made at pressures near 1 atm, is therefore well justified.\*<sup>3</sup> This is particularly germane to studies dealing with the solubility of natural levels of atmospheric  $\text{CO}_2$ .

In treating the solution of atmospheric gases in natural waters, it is convenient to express the solubility in terms of the Bunsen coefficient  $\beta$ , thereby avoiding the problem of evaluating the mole fraction of the gas in mixed solvents such as seawater. The Bunsen coefficient is defined here as the volume of gas (STP) absorbed per unit volume of the *solution*, at the temperature of the measurement, when the total pressure and the fugacity are both 1 atm.\*<sup>4</sup> This is preferable to the usual definition of  $\beta$  for ideal gases, in which the *partial* pressure is set at 1 atm and the *total* pressure is not specified, because the total pressure is required to define the system (see eq.2). Thus,  $C_i$ , the volume (STP) of gas  $i$  dissolved in a unit volume of *solution* at the temperature of the measurement, is given by the relation:

$$C_i = \beta_i f_i \exp[(1 - P)\bar{v}_i/RT] \quad (3)$$

where:

$$\beta_i = Q_i^{-1} V_i^\dagger \rho N \exp(-\bar{v}_i/RT) \quad (4)$$

and  $V_i^\dagger$  is the volume of one mole of the real gas  $i$  at STP,  $\rho$  is the density of the *solution*,  $N$  is the number of moles in a unit weight of *solvent*, and  $P$  is in atmospheres. Since the solubility of most gases ( $\bar{v} \cong 30 \text{ cm}^3/\text{mole}$ ) is decreased

\*<sup>2</sup> Note that helium solubility measurements by these workers are in excellent agreement with recent microgasometric data (Weiss, 1971a).

\*<sup>3</sup> A more detailed discussion of  $\text{CO}_2$  solubility as a function of pressure is given in the Appendix.

\*<sup>4</sup> Pressures are given here in atmospheres because of the widespread use of this unit to define standard states. Atmospheres may be converted to bars ( $10^5 \text{ newtons/m}^2$ ), the more fundamental unit commonly used in high-pressure work, by multiplying by 0.986923.

by only  $\sim 0.15\%$  per atmosphere increase in total pressure, the small deviations from 1 atm total pressure which are encountered in many natural conditions may be neglected, thereby reducing the exponential term in eq.3 to unity.

In the special case of  $\text{CO}_2$ , solubilities are generally used in calculations of chemical equilibria and are therefore best given in molar (moles/l of solution) or gravimetric (moles/kg of solution) units:

$$[\text{CO}_2] = K_0 f_{\text{CO}_2} \exp[(1 - P)\bar{v}_{\text{CO}_2}/RT] \quad (5)$$

where the constant  $K_0$  equals  $\beta/V^\dagger$  in molar units (moles/l  $\cdot$  atm) or  $\beta/\rho V^\dagger$  in gravimetric units (moles/kg  $\cdot$  atm). Again, the exponential term may be taken as unity at total pressures near 1 atm.

In the following discussions, gas volumes and fugacity-pressure corrections are based on the virial equation of state. The appropriate expansions are carried only as far as the second virial coefficient  $B(T)$ , since the terms containing the third virial coefficient were always found to be negligible ( $\sim 10^{-5}$ ). Values of  $B(T)$  in  $\text{cm}^3/\text{mole}$ , for  $\text{CO}_2$  (Sengers et al., 1971) in the range 265–320°K, are well represented by a power series:

$$B(T) = -1636.75 + 12.0408 T - 3.27957 \cdot 10^{-2} T^2 + 3.16528 \cdot 10^{-5} T^3 \quad (6)$$

Thus, for the pure gas (neglecting the small contribution of water vapor), the solubility measurements discussed in the following sections have been corrected using the approximations (Guggenheim, 1967, pp.91 and 97):

$$V(P, T) = V^*(P, T) + B(T) \quad (7)$$

and:

$$\ln(f/P) = B(T) P/RT \quad (8)$$

where  $V$  is the volume of one mole of the real gas, and  $V^*$  is the volume of one mole of ideal gas.

In most natural applications which do not require accuracies greater than  $\sim 0.7\%$ , the fugacity in eq.4 may be taken as equal to the partial pressure. However, if greater accuracy is desired, the fugacity must be calculated. For a nearly pure gas phase, eq.8 will suffice, but for multi-component gas phases, such as  $\text{CO}_2$  in air, it is necessary to calculate fugacity in the mixture.

Useful equations for the calculation of fugacities in binary mixtures are given by Guggenheim (1967, pp.175–177):

$$f_1 = x_1 P \exp[(B_{11} + 2x_2^2 \delta_{12}) P/RT] \quad (9)$$

where the subscripts 1 and 2 refer to the two components of the mixture,  $x$  is the mole fraction, and  $B_{11}$  is the second virial coefficient of the pure gas 1.

The quantity  $\delta_{12}$  is defined by:

$$B_{12} = \frac{1}{2} (B_{11} + B_{22}) + \delta_{12} \quad (10)$$

where  $B_{12}$  is the cross virial coefficient for interactions between gas 1 and gas 2 molecules, and  $B_{11}$  and  $B_{22}$  refer to the pure gases 1 and 2, respectively. In addition to the binary mixtures, equations 8 and 9 may also be applied to mixtures of  $\text{CO}_2$  in air when  $x_{\text{CO}_2} \ll 1$ .

Few direct measurements of cross-virial coefficients exist, so that the quantity  $\delta_{12}$  must be evaluated from theoretical considerations. The quantity  $\delta_{\text{CO}_2\text{-air}}$  has been evaluated from the Lennard-Jones (6-12) potential model following the method of Hirschfelder, Curtiss and Bird (1954, pp.166–170). The results in  $\text{cm}^3/\text{mole}$  for the temperature range 273 to 313°K are well represented by the linear relation:

$$\delta_{\text{CO}_2\text{-air}} = 57.7 - 0.118 T \quad (11)$$

The magnitude of this correction, as opposed to assuming  $\delta = 0$  (Lewis and Randall rule), is about 0.2% in the overall solubility calculation, or about one third of the total deviation from ideal gas behavior.

Calculations of  $\text{CO}_2$  fugacity using the virial equation of state are valid to within 0.1% for total pressures up to  $\sim 10$  atm. Higher pressures require the use of more sophisticated equations of state, such as the Benedict, Webb and Rubin (1940; 1942) equation, which may be used to at least 500 atm (see Appendix).

#### DATA FITTING

The corrected data of Murray and Riley (1971) were fitted to the same equation in temperature and salinity which has been used to fit the solubilities of many other gases (see Introduction). This equation is derived from the integrated van't Hoff equation and the logarithmic Setchénow salinity dependence, and has the form (Weiss, 1970):

$$\ln K_0 = A_1 + A_2(100/T) + A_3 \ln(T/100) + S_{\infty}^0 [B_1 + B_2(T/100) + B_3(T/100)^2] \quad (12)$$

where  $K_0$  may be expressed either in moles/l · atm, referring to a liter of solution at the temperature of the measurement and an atmosphere *fugacity* in the gas phase, or in moles/kg · atm, referring to a kilogram of solution. The  $A$ 's and  $B$ 's are constants,  $T$  is the absolute temperature, and  $S_{\infty}^0$  is the salinity in parts per thousand. The method of fitting the data, and the conditions for justification of the Setchénow equation and the number of terms used in the expansion, are discussed elsewhere (Weiss, 1970).

The corrected Murray and Riley  $\text{CO}_2$  data showed good agreement with the equations at all stages of the fitting procedure. The data show a root-mean-square deviation from the final fitted equation of  $1.4 \cdot 10^{-4}$  moles/l · atm in  $K_0$ , or about 0.3%. Agreement with the Setchénow relation is shown in Fig.1 by the random nature of the deviations as a function of salinity for each measured isotherm. The fitted values of the constants in eq.12 are listed in Table I for  $K_0$  in molar and in gravimetric units. Values of  $K_0$  at various temperatures

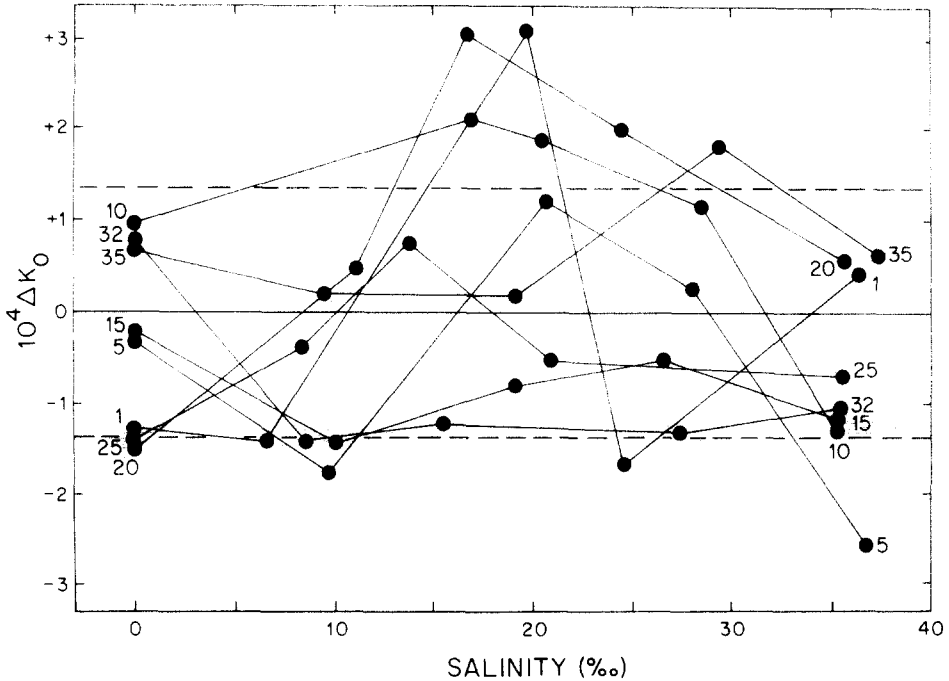


Fig.1. Deviations of the Murray and Riley (1971)  $\text{CO}_2$  solubility data (corrected for dissociation and non-ideality) in moles/l · atm from the fitted curve (eq.12), plotted against salinity. Measurements made at constant temperature are connected by lines, and are labeled to the nearest  $^\circ\text{C}$ . The dashed lines show  $\pm 1$  standard deviation.

and salinities calculated from these constants are listed in Tables II and III.

Salting-out constants (the  $B$ 's in eq.12) were also determined for the solubility of  $\text{CO}_2$  in aqueous NaCl solutions using the data of Bohr (1899), corrected for dissociation. With NaCl concentration expressed as weight percent in solu-

TABLE I

Constants for the calculation of the solubility of  $\text{CO}_2$  in molar and gravimetric units according to eq.12

	Units of $K_0$	
	moles/l · atm	moles/kg · atm
$A_1$	-58.0931	-60.2409
$A_2$	90.5069	93.4517
$A_3$	22.2940	23.3585
$B_1$	0.027766	0.023517
$B_2$	-0.025888	-0.023656
$B_3$	0.0050578	0.0047036

TABLE II

The solubility coefficient  $K_0$  ( $10^{-2}$  moles/l · atm)

$T(^{\circ}\text{C})$	Salinity (‰)								
	0	10	20	30	34	35	36	38	40
-1	—	—	7.273	6.903	6.760	6.724	6.689	6.620	6.551
0	7.758	7.364	6.990	6.635	6.498	6.465	6.431	6.364	6.298
1	7.458	7.081	6.723	6.382	6.251	6.219	6.187	6.123	6.060
2	7.174	6.813	6.469	6.143	6.017	5.986	5.955	5.894	5.833
3	6.905	6.558	6.229	5.916	5.795	5.766	5.736	5.677	5.619
4	6.650	6.317	6.001	5.701	5.585	5.557	5.528	5.472	5.416
5	6.408	6.088	5.785	5.497	5.386	5.358	5.331	5.277	5.223
6	6.178	5.871	5.580	5.303	5.196	5.170	5.144	5.092	5.040
8	5.751	5.469	5.200	4.945	4.846	4.822	4.797	4.749	4.702
10	5.366	5.105	4.857	4.621	4.529	4.507	4.485	4.440	4.396
12	5.017	4.776	4.546	4.327	4.243	4.222	4.201	4.160	4.119
14	4.700	4.477	4.264	4.062	3.983	3.964	3.945	3.906	3.869
16	4.412	4.205	4.008	3.820	3.747	3.729	3.712	3.676	3.641
18	4.149	3.958	3.775	3.600	3.533	3.516	3.499	3.466	3.434
20	3.910	3.732	3.562	3.400	3.337	3.322	3.306	3.275	3.245
22	3.691	3.526	3.368	3.217	3.158	3.144	3.130	3.101	3.073
24	3.491	3.337	3.190	3.050	2.995	2.982	2.968	2.942	2.915
26	3.307	3.164	3.027	2.897	2.846	2.833	2.821	2.796	2.771
28	3.138	3.005	2.878	2.756	2.709	2.697	2.685	2.662	2.639
30	2.983	2.859	2.741	2.627	2.583	2.572	2.561	2.540	2.518
32	2.840	2.725	2.615	2.509	2.468	2.457	2.447	2.427	2.407
34	2.708	2.601	2.498	2.400	2.361	2.352	2.342	2.323	2.305
36	2.587	2.487	2.391	2.299	2.263	2.254	2.246	2.228	2.211
38	2.474	2.382	2.292	2.207	2.173	2.165	2.157	2.140	2.124
40	2.370	2.284	2.201	2.121	2.090	2.082	2.074	2.059	2.044

tion, and  $K_0$  in moles/l · atm, the constants are:  $B_1 = -0.68330$ ,  $B_2 = 0.40911$ ,  $B_3 = -0.064989$ . Averaged over the temperature range 0–40°C,  $K_0$  is 0.8% higher in a 3.6% NaCl solution than  $K_0$  in seawater of 36‰ salinity, calculated from the salting-out constants in Table I. This difference probably lies within the error of the Lyman (1957) prediction that  $K_0$  in the NaCl solution would be 0.5% higher.

#### EXPERIMENTAL METHOD

Measurements of  $\text{CO}_2$  solubility were carried out by the microgasometric technique used previously to measure He and Ne solubilities (Weiss, 1971a). High-purity  $\text{CO}_2$  (certified  $\geq 99.99\%$ ) was supplied by Matheson Gas Products and gas chromatographic analysis showed  $< 0.01\%$  air contamination. Because of the high solubility of  $\text{CO}_2$  compared to He and Ne, the amount of degassed

water added to the equilibration chamber was reduced to about one third of the total gas volume. Under these conditions, equilibration was extremely rapid (first-order rate constant  $\tau \cong 30$  sec) so that the 6--10 minutes allowed for equilibration were more than adequate. Permeation of  $\text{CO}_2$  through the indicator drop was rapid, and required that the chamber above the drop be filled with pure  $\text{CO}_2$  prior to each equilibration. With this procedure, no drift in the indicator drop could be detected over a period of 1 h.

In order to obtain the most direct comparisons with the work of Murray and Riley and of Li and Tsui, chemical procedures similar to their's were followed. Distilled water measurements were performed without acidification and the corrections for dissociation were made. Surface seawater, collected at La Jolla and evaporated to increase its salinity by  $\sim 2\text{‰}$ , was passed through a  $0.45\mu$  filter, poisoned with 1 mg/liter  $\text{HgCl}_2$ , and its salinity determined to  $\pm 0.004\text{‰}$  by an inductive salinometer. Sulfuric acid ( $\sim 2N$ ) was then added to bring the pH to 2.2 and the salinity was adjusted by gravimetric determination of the amount of  $\text{H}_2\text{O}$  added in the acid solution. Following Murray and

TABLE III

The solubility coefficient  $K_0$  ( $10^{-2}$  moles/kg · atm)

$T(^{\circ}\text{C})$	Salinity (‰)								
	0	10	20	30	34	35	36	38	40
-1	—	—	7.158	6.739	6.579	6.539	6.500	6.422	6.345
0	7.758	7.305	6.880	6.479	6.325	6.287	6.249	6.175	6.101
1	7.458	7.024	6.616	6.232	6.085	6.048	6.012	5.941	5.870
2	7.174	6.758	6.367	5.999	5.857	5.822	5.788	5.719	5.651
3	6.904	6.506	6.131	5.777	5.642	5.608	5.575	5.509	5.444
4	6.649	6.267	5.907	5.568	5.438	5.405	5.374	5.310	5.248
5	6.407	6.040	5.695	5.369	5.244	5.213	5.182	5.122	5.062
6	6.177	5.825	5.493	5.180	5.060	5.031	5.001	4.943	4.885
8	5.752	5.427	5.120	4.831	4.720	4.693	4.666	4.612	4.558
10	5.367	5.067	4.784	4.516	4.413	4.388	4.363	4.313	4.263
12	5.019	4.741	4.479	4.231	4.136	4.112	4.089	4.042	3.997
14	4.703	4.446	4.202	3.972	3.884	3.862	3.840	3.797	3.755
16	4.416	4.177	3.951	3.738	3.655	3.635	3.615	3.575	3.536
18	4.155	3.933	3.723	3.524	3.448	3.429	3.410	3.373	3.336
20	3.916	3.710	3.515	3.330	3.258	3.241	3.223	3.189	3.154
22	3.699	3.507	3.325	3.152	3.086	3.069	3.053	3.021	2.989
24	3.499	3.321	3.151	2.990	2.928	2.912	2.897	2.867	2.837
26	3.317	3.150	2.992	2.841	2.783	2.769	2.755	2.727	2.699
28	3.149	2.994	2.846	2.705	2.651	2.638	2.624	2.598	2.572
30	2.995	2.850	2.712	2.580	2.530	2.517	2.505	2.480	2.455
32	2.854	2.718	2.589	2.466	2.418	2.406	2.395	2.372	2.349
34	2.723	2.596	2.476	2.360	2.316	2.305	2.294	2.272	2.250
36	2.603	2.484	2.371	2.263	2.221	2.211	2.201	2.180	2.160
38	2.492	2.381	2.275	2.174	2.134	2.125	2.115	2.096	2.077
40	2.389	2.285	2.186	2.091	2.054	2.045	2.036	2.018	2.000



Riley (1971), the effect of the added  $\text{H}_2\text{SO}_4$  molecules on the salinity was neglected as being insignificant with respect to altering the solubility of  $\text{CO}_2$ . The water was degassed using the same vacuum extraction method as in the previous work (Weiss, 1971a).

The results were calculated in the same manner as previous microgasometric measurements, except that the corrections for non-ideal behavior discussed in the foregoing section were applied. The correction for the expansion of the aqueous phase during equilibration was made using a partial molal volume of  $32.3 \text{ cm}^3$  per mole of  $\text{CO}_2$  (see Appendix). The overall accuracy of these  $\text{CO}_2$  solubility measurements is estimated as  $\pm 0.2\%$ .

## RESULTS AND CONCLUSIONS

The microgasometric experimental values for  $K_0$  in moles/l · atm at several temperatures and salinities, corrected for dissociation and non-ideality, are given in Table IV. Deviations of the microgasometric results from the fitted Murray and Riley data, plotted in Fig.2, show excellent agreement without systematic deviations. At each of the three different temperature and salinity conditions, the range of microgasometric points brackets the fitted curve. The average deviation of all the measured points is  $1.5 \cdot 10^{-5}$  moles/l · atm, and the root-mean-square deviation is  $1.2 \cdot 10^{-4}$  moles/l · atm. Curves for the deviations of the data of Li and Tsui, taken from their equations (1) and (2a) after correction for dissociation and non-ideality, are also plotted in Fig.2. Although their fresh-water measurements are in reasonably good agreement, the seawater data of Li and Tsui show large deviations from the fitted Murray and Riley

TABLE IV

Experimental  $\text{CO}_2$  solubilities: microgasometric determinations of  $K_0$  in moles/l · atm

Salinity (‰)	$t$ (°C)	$K_0 \cdot 10^2$
0.0	20.61	3.848
0.0	20.63	3.843
0.0	20.60	3.867
0.0	20.59	3.834
0.0	20.61	3.840
35.330	6.59	5.071
35.330	6.60	5.063
35.330	6.60	5.068
35.330	6.59	5.041
35.330	20.62	3.245
35.330	20.63	3.272
35.330	20.63	3.245
35.330	20.63	3.255
35.330	20.63	3.254
35.330	20.63	3.252

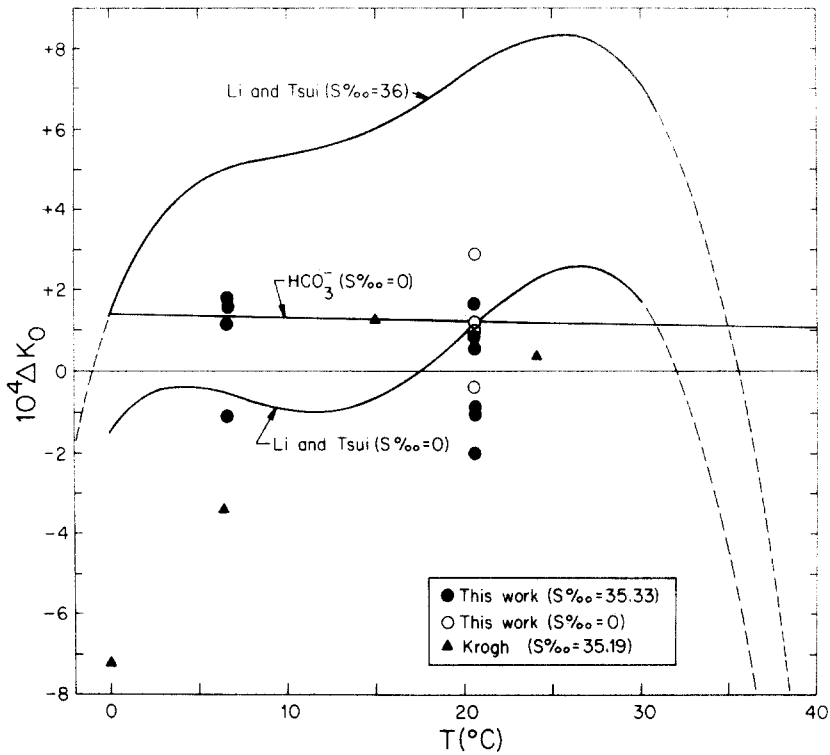


Fig. 2. Deviations of various  $\text{CO}_2$  distilled water and seawater solubility data in moles/l · atm from the fit to the corrected data (see text) of Murray and Riley (1971), plotted against temperature. The curves for Li and Tsui (1971) are taken from their equations (1) and (2a), and, like the data of Krogh (1904), have been corrected for non-ideality and dissociation: the dashed portions of these curves represent the extrapolation of their equations beyond the range of their measurements. The magnitude of the error caused by dissociation for measurements made in distilled water at  $\text{pCO}_2 = 1 \text{ atm}$  is shown by the line labeled " $\text{HCO}_3^-$ ".

data. Fig. 2 also shows the corrected data of Krogh (1904), which agree well with Murray and Riley at the higher temperatures.

The microgasometric results provide independent confirmation of the accuracy of the  $\text{CO}_2$  solubility measurements of Murray and Riley (1971) and show the measurements of Li and Tsui (1971) to be in error by as much as  $\sim 4\%$  at the higher temperatures and salinities. The data of Murray and Riley, corrected for the effects of non-ideal gas behavior and for dissociation in the distilled water measurements, are well represented by the Setchénow and integrated van't Hoff equations used previously to fit the solubilities of several other comparatively ideal gases. Thus,  $\text{CO}_2$  solubilities calculated from eq. 12, using the constants in Table I, are believed to provide the most accurate values in the literature, with an overall accuracy estimated at  $\pm 1 \cdot 10^{-4}$  moles/l · atm or about 0.2%. The solubility of  $\text{CO}_2$  obeys the modified form of Henry's law

(eq.2) and it is therefore necessary to take account of the total pressure, as well as to calculate the fugacity of  $\text{CO}_2$  in the gas phase, if full use is to be made of the accuracy of these solubility data.

#### ACKNOWLEDGEMENTS

I thank T.K. Kyser for his assistance with the laboratory measurements, and H. Craig and S.L. Miller for valuable discussions on the thermodynamics of real gases. This research was supported by a U.S. National Science Foundation grant to the Isotope Laboratory, Scripps Institution of Oceanography.

#### APPENDIX

##### *Carbon dioxide solubility at high pressures*

At pressures greater than  $\sim 10$  atm,  $\text{CO}_2$  fugacities calculated from the virial equation of state, even when carried to the third virial coefficient, show large deviations from the literature values (Deming and Deming, 1939). Far better results are obtained with the Benedict, Webb and Rubin equation of state for pure substances (Benedict et al., 1940) and for mixtures (Benedict et al., 1942), which fit the observed  $p$ - $V$ - $T$  data up to densities of twice the critical density. In the following discussion, Benedict, Webb and Rubin equation constants for pure  $\text{CO}_2$  are taken from the Bishnoi and Robinson (1971)<sup>\*5</sup> volume-dependent fit to the compressibility data of Reamer et al. (1944). Because the Benedict, Webb and Rubin equation is an explicit function of  $V$  and  $T$ , the solution for specific values of  $P$  is obtained by the method of successive approximations.

Fig.3 shows the distilled water  $\text{CO}_2$  solubility data of Wiebe and Gaddy (1940) for the temperature range  $12$ – $40^\circ\text{C}$  and the pressure range  $25$ – $500$  atm, plotted as  $\ln(f/x)$  against the total pressure  $P$ . Fugacities were calculated assuming a pure  $\text{CO}_2$  phase at a pressure of  $P$  minus the vapor pressure of water. Negligible error was introduced by this approximation because of the small fraction of water vapor in the  $\text{CO}_2$ -rich phase. The straight lines plotted at each of the six experimental temperatures were fitted to the Wiebe and Gaddy data by the method of least-squares.

According to eq.2, if  $\bar{v}$  is independent of  $P$ , then  $\ln(f/x)$  plotted as a function of  $P$  at constant  $T$  should give a straight line with intercept  $\ln Q$  and slope  $(\bar{v}/RT)$ . This relationship is strongly supported by the experimental data as shown in Fig.3. The root-mean-square deviation of the Wiebe and Gaddy measurements about the six straight lines is  $\sim 0.8\%$ , and there is no systematic indication of departure from linearity. The slopes of these lines correspond to remarkably constant values of  $\bar{v}$ , with a mean of  $32.3$   $\text{cm}^3/\text{mole}$  and a standard deviation of  $0.5$   $\text{cm}^3/\text{mole}$ . Thus, the data show no significant variation in  $\bar{v}$ , either as a function of  $T$  over the range  $12$ – $40^\circ\text{C}$ , or as a function of  $P$  up to  $500$  atm.

Results of the fit to the corrected Murray and Riley distilled water data (eq.12), measured at  $1$  atm, are also plotted in Fig.3. The overall agreement with the Wiebe and Gaddy data is good, although there may be a systematic difference at  $12^\circ\text{C}$  (the Wiebe and Gaddy data also show the greatest scatter at this temperature). On the average, the solubilities at  $1$  atm obtained from the linear fits to the Wiebe and Gaddy data are  $0.4\%$  lower in  $\beta$  (or higher in  $Q$ ), and show a  $2\%$  root-mean-square difference.

<sup>\*5</sup> The constants, converted from English to metric units (atm, l, mole,  $^\circ\text{K}$ ):  $A_0 = 1.9521940$ ,  $B_0 = 0.033065171$ ,  $C_0 = 170449.55$ ,  $a = 0.25264437$ ,  $b = 6.6041298 \cdot 10^{-3}$ ,  $c = 19592.012$ ,  $\alpha = 4.7117009 \cdot 10^{-5}$ ,  $\gamma = 4.3414415 \cdot 10^{-3}$ ,  $R = 0.08205601$ .

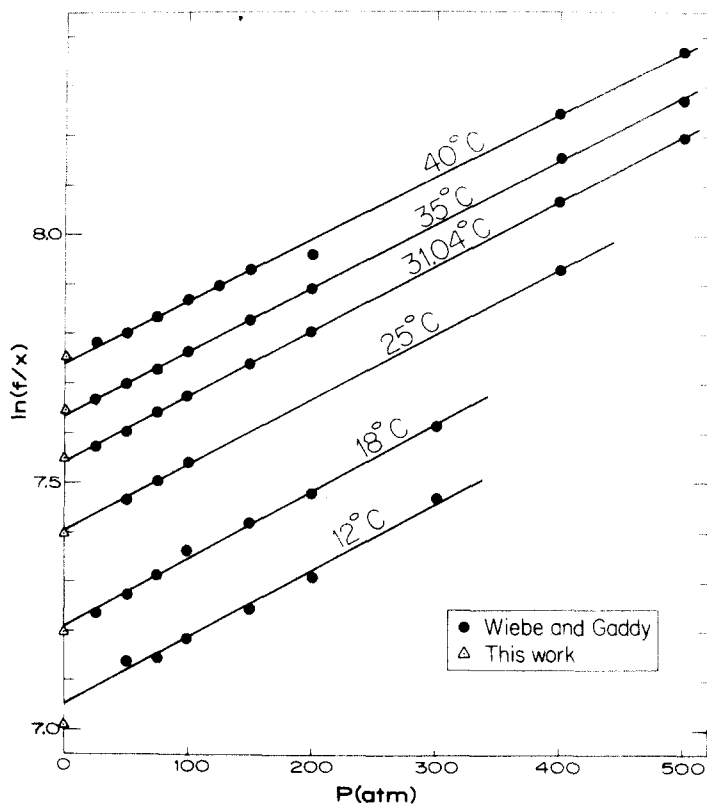


Fig.3. High-pressure distilled water  $\text{CO}_2$  solubility data of Wiebe and Gaddy (1940) plotted as the logarithm of the fugacity to mole fraction ratio, against the total pressure. Solubilities at 1 atm calculated from eq.12 are plotted for the temperatures of the Wiebe and Gaddy measurements.

In summary, the high-pressure solubility data show that the modified form of Henry's law (eqs.2, 3, or 5) is valid for  $\text{CO}_2$  in water over the entire pressure range of 0–500 atm, which corresponds to a dissolved  $\text{CO}_2$  concentration range of 0–1.7 molar. Assuming that  $\bar{v}$  for  $\text{CO}_2$  is the same in seawater as in distilled water, as was shown by Enns et al. (1965) for  $\text{O}_2$ , the solubility of  $\text{CO}_2$  in seawater at high pressures may also be calculated from these equations.

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