The Solubility of CO_2 in Water and Sea Water

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The newly measured solubility constant of CO_2 in water, α_0, and in sea water and NaCl solution, α, can be easily shown by the Setchénow equation $\log \alpha/\alpha_0 = (0.00404 - 0.000037\ t) \times Cl\%_0 = (0.126 - 0.00115\ t) \times m$ where $\alpha_0 = 770.5 - 29.78\ t + 0.6823\ t^2 - 0.00709 \times t^3$ (10^{-4} moles/liter/atm). The previous α data in water and NaCl solution by Bohr (1899) and in sea water by Krogh (1904) essentially agree with this report. Buch's (1951) estimation of α in sea water from Bohr's data is proved to be valid.

The solubility of CO_2 in water and NaCl solution has been well studied by many investigators [*Bohr*, 1899; *Markham and Kobe*, 1941; *Harned and Davis*, 1943; *Morrison and Billett*, 1952]. However, there are only two reports on the measurements of solubility of CO_2 in sea water [*Krogh*, 1904; *Stewart and Munjal*, 1970].

Buch et al. [1932] estimated the solubility of CO_2 in sea water from Bohr's NaCl solution data by assuming that the effect of a given weight of sea salts on solubility of gas is the same as that of an identical weight of NaCl. Buch's calculated values fall quite close to *Krogh*'s [1904] results. So far Buch's estimated values have been widely used, though there is some skepticism [*Lyman*, 1956; *Skirrow*, 1965] on the validity of Buch's assumption and on the accuracy of Krogh's experimental results. The most recent data by *Stewart and Munjal* [1970] are systematically about 10 to 20% lower than Buch's. To clarify these discrepancies the solubility of CO_2 in acidified sea water, NaCl solution, and distilled water have been redetermined in the laboratory using an infrared gas analyzer technique.

Method

A pure CO_2 gas (99.99 $\pm$ 0.01% on dry basis, when 200 ml of this gas was frozen out in a liquid nitrogen trap, no residual gas was detected on a manometer) saturated with water vapor was bubbled through a 25-ml aqueous sample in an equilibration chamber (Figure 1). The equilibration chamber was immersed in a constant temperature water-bath and was open to the air at the top through a small glass tube (2-mm diameter). After bubbling CO_2 gas through the equilibration chamber overnight, one to two grams of sample was drawn from the equilibration chamber through its side arm using an airtight glass syringe (Figure 1). Then, the sample was needled into a CO_2-extraction system through a serum rubber stopper. The dissolved CO_2 in the sample
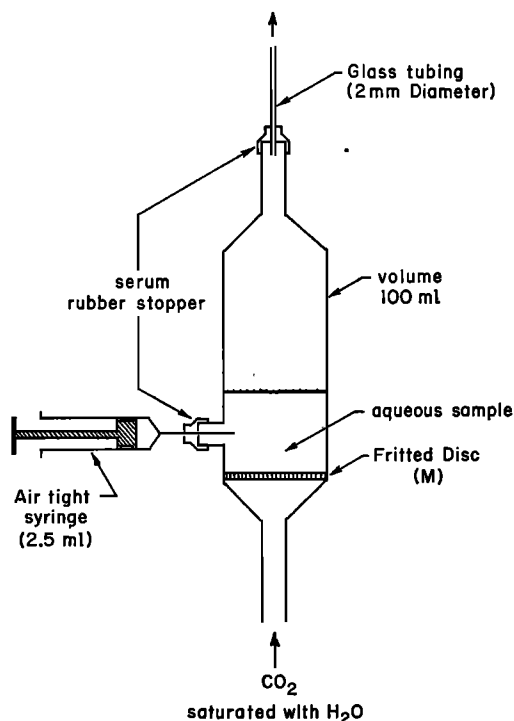

Fig. 1. The detail of the equilibration chamber

TABLE 1.   The Measured Solubility Constant of CO_2 in Water, NaCl Solution, and Sea Water
(10^{-4} moles/liter/atm)

Cl ‰	t,°C				
	0.7	4.0	10.2	20.0	30.0
0	750.1	660.3	530.2	391.1	299.7
10.0			486.3		
20.0		552.6	448.2	335.9	261.4
29.0		508.6	416.2	313.8	246.3
0.6413 m NaCl		554.7		335.8	261.8

was then flushed out with N_2 gas for analysis using the infrared gas analyzer technique [*Broecker and Takahashi*, 1966; *Li*, 1967]. To save time we usually connected four equilibration chambers, which contained different samples, parallel to a common CO_2 gas source for one run. The samples consist of distilled water, acidified sea water with 10, 20, and 29 Cl ‰ and 0.6413 m NaCl-solution, which is equivalent to 20 Cl ‰ sea water if Buch's assumption is correct. The acidified samples were prepared by adding 0.04 grams of 8N HCl to every 50 grams of sea water or NaCl solution to reduce the pH to below 3. The added acid corresponds to an increase of the chlorine ion concentrations of the sample by about 0.23 grams Cl⁻/liter. To make sure that the sample is saturated with CO_2 gas, the equilibration was reached from both undersaturation and supersaturation for the run at 10°C. Identical results were obtained by approaching from both ends, therefore the equilibrations were all reached by undersaturation for the remaining experiments. The temperature control of water bath is good to ± 0.02°C, and the measurement of the atmospheric pressure ± 0.005 mm Hg.

RESULT AND DISCUSSION

The observed solubility constants of CO_2, α, in samples at different temperatures are given in Table 1 in units of CO_2 (10^{-4} moles)/solvent (liter)/P_{CO_2} (atm) and also plotted in Figure 2. Each data point represents the average of two determinations. The reproducibility of data is within 0.5% or better. The uncertainty in CO_2 standard gas calibration (±0.5 ppm) affects the absolute accuracy of α by about ±0.5 × 10^{-4} moles/liter/atm.

The most striking result is that α in 0.6413 m NaCl solution and in 20 Cl ‰ sea water are identical within experimental uncertainty (0.5%). It means that Buch's assumption is correct. Also, as shown in Table 1, the effect of salts on α averaged about 5 × 10^{-4} mole/liter/atm (about 1%) per unit change of chlorinity at 4°C, and about 2 × 10^{-4}/liter/atm at 30°C; therefore, the effect of the added acid on α is within the experimental uncertainty and is negligible as mentioned by *Krogh* [1904].

The solubility constant of CO_2 in water, α_0, can be represented by a polynomial equation
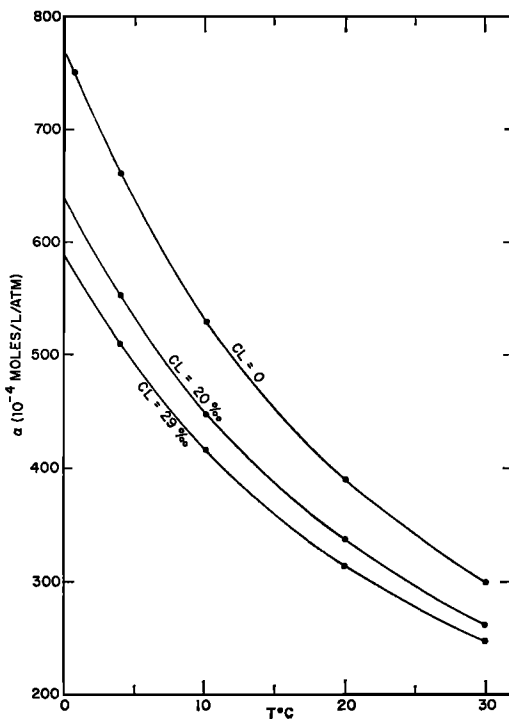

Fig. 2.   The plot of measured α as the function of temperature. The smooth curves are the plots of equations 1 and 2a.

$\alpha_0 = 770.5 - 29.78\ t + 0.6823$

$$\times\ t^2 - 0.00709 \times t^3 \qquad (1)$$

and α in sea water and NaCl solution by Setchénow equation (see Figure 3a and 3b)

$\log \alpha_0/\alpha$

$\quad = (0.00404 - 0.000037\ t) \times \text{Cl} \permil \qquad (2a)$

$\quad = (0.126 - 0.00115\ t) \times m \qquad (2b)$

or

$\log \alpha_0/\alpha$

$\quad = (0.00485 - 0.000037\ t) \times \text{Cl} \permil \qquad (3a)$

$\quad = (0.151 - 0.00115\ t) \times m \qquad (3b)$

if α is expressed in the unit of CO_2 (10^{-4} moles)/ solution (kg)/P_{CO_2} (atm), where t is temperature in °C, and m represents molality. The difference between α_0 reported here and previous investigations [Bohr, 1899; Markham and Kobe, 1941; Harned and Davis, 1943; Morrison and Billett, 1952] is given in Figure 4. The present data
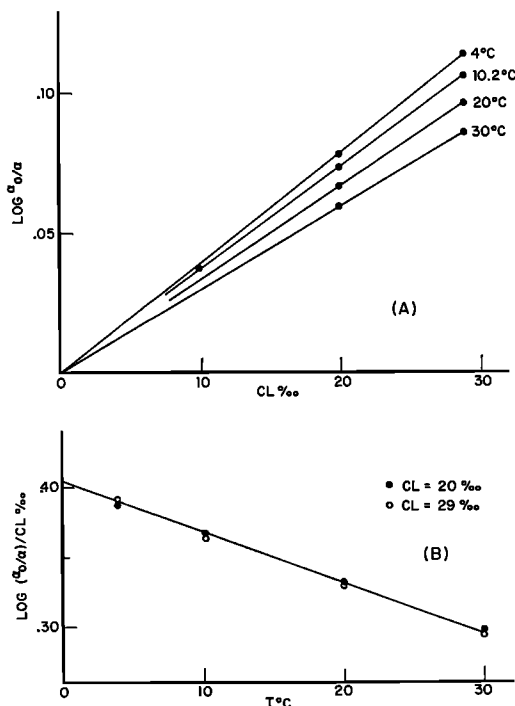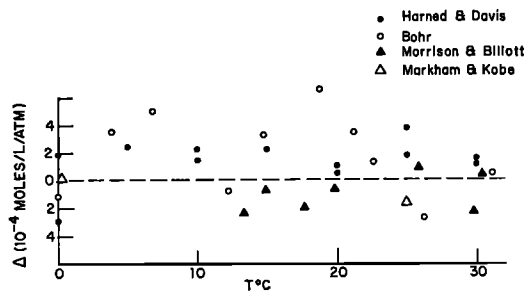

Fig. 4. The comparison between α_0 obtained from equation 1 and from previous investigators where $\Delta = \alpha_0$ (previous work) $-\alpha_0$ (present work).

agree well with previous investigations within $\pm 2.5 \times 10^{-4}$ mole/liter/atm except some scattering points by Bohr [1899]. The smoothed α data in water and in one molal NaCl solution by Bohr [1899] and Markham and Kobe [1941] can be well represented by the same Setchénow equation 2b within the experimental uncertainty as shown in Figure 5. The same kind of data by Harned and Davis [1943] can also be expressed by a Setchénow equation but with a different slope (see Figure 5). There is no apparent explanation for the difference.

The recalculated α data (10^{-4} mole/liter/atm) in acidified sea water (35.19 S [salinity] $\permil$) by Krogh [1904] are as follows:

t°C	α	Δ
0.0	639.3	4.8
6.4	506.9	4.4
15.0	386.7	1.1
24.1	298.8	5.9

Fig. 3. (A) The plot of log (α_0/α) against Cl $\permil$ and (B) log (α_0/α) Cl $\permil$ against t°C.
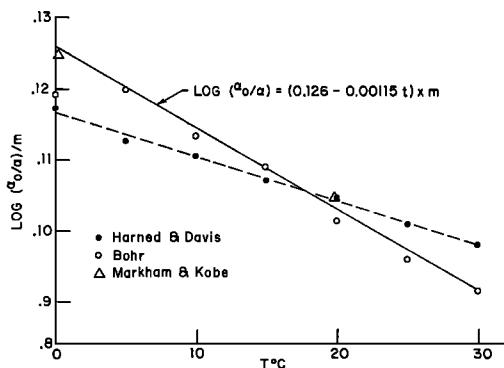

Fig. 5. The plot of log (α_0/α)/m against t°C.

TABLE 2. α in Water and in Sea Water (10^{-4} moles/liters/atm)

Cl ‰	$t°C$															
	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
0	771	714	662	615	572	534	499	468	440	414	391	370	351	333	316	300
15	670	622	579	539	503	470	441	414	390	369	349	331	315	299	285	271
16	664	617	573	534	499	466	437	411	387	366	346	329	312	297	283	269
17	658	611	568	530	494	462	434	408	384	363	343	326	310	295	281	267
18	652	605	563	525	490	459	430	404	381	360	341	324	308	293	279	265
19	646	600	558	520	486	455	426	401	378	357	339	321	306	291	277	264
20	640	594	553	516	482	451	423	398	375	355	336	319	303	289	275	262
21	634	589	548	511	478	447	419	395	372	352	333	317	301	287	273	260

where Δ (10^{-4} moles/liter/atm) is the difference between the present α, calculated from equations 1 and 2a, and Krogh's α. Krogh's data are in average about 4×10^{-4} moles/liter/atm lower than the present values.

Stewart and Munjal [1970] equilibrated the synthetic sea water without acidifying (34.42 *S‰* and with alkalinity or [HCO$_3^-$] = 24×10^{-4} moles/kg) with pure CO$_2$ gas. The α can be calculated from their one atmospheric observation by making proper corrections for CO$_2$ contributed from alkalinity. The results are shown below in units of 10^{-4} moles/liter/atm.

$t°$	α	Δ
0	581	65
5	479	60
10	414	41
15	333	57
25	232	68

On the average, α's by *Stewart and Munjal* [1970] are about 60×10^{-4} mole/liter/atm

lower than the present data. Since *Stewart and Munjal* [1970] did not give the solubility of CO$_2$ in pure water at 1 atmospheric pressure, it is hard to depict the source of this discrepancy.

In summary the present work has shown that the solubility constant of CO$_2$ in water and NaCl solution by *Bohr* [1899] and in sea water by *Krogh* [1904] are essentially correct and *Buch et al*'s assumption is proved to be valid. For comparison, Table 2 gives α values as calculated from equations 1 and 2a, and Table 3 gives the difference between Table 2 and *Buch*'s [1951] similar table. In general both agree within $\pm 2 \times 10^{-4}$ moles/liter/atm.

In determination of the apparent dissociation constants K_1' and K_2' of carbonic acid in sea water, both *Buch* [1951] and *Lyman* [1957] adapted essentially the α values by *Buch* [1951]. Therefore, if there is any doubt on the accuracy of their K_1' and K_2' [*Takahashi et al.*, 1970], certainly we can rule out the α values as the main source of error.

Li [1967] has shown that solubility constants of N$_2$, O$_2$, Ar gases in water, NaCl solution, and sea water also can be well related by Setché-

TABLE 3.   Difference in α between Table 2 and *Buch*'s Table [1951] (10^{-4} mole/liter/atm)

Cl ‰	$t°C$															
	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
0	1	2	0	−4	−4	−2	−3	−4	−2	−3	−3	−2	0	1	2	1
15	−4	−1	1	1	−1	−2	−1	−2	−3	−2	−2	0	1	0	1	1
16	−3	0	0	1	0	−2	−1	−2	−3	−2	−2	0	0	0	2	1
17	−2	0	1	2	−1	−2	0	−2	−3	−2	−2	−1	0	1	3	1
18	−1	0	1	1	0	−1	−1	−2	−3	−2	−2	0	1	1	2	1
19	0	1	1	1	0	−1	−2	−2	−3	−2	−1	0	2	2	2	2
20	0	1	2	2	0	−1	−1	−2	−2	−1	−1	0	1	2	2	2
21	1	2	2	2	1	−1	−2	−1	−2	−2	−1	0	1	2	2	2

now equation, and Buch's assumption, more or less, does apply to the above-mentioned gases. Therefore, it is feasible to obtain α of a certain gas in sea water to a first approximation, at least, if α's of the same gas in water and NaCl solution are known.

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