line fit of the above experimental points. The correlation coefficient is 0.9994. This confirms that the He–CH_4 system behaves ideally, that is that D_{12} is linear with gas density within at most 0.2% up to at least 112 atm (116 kg/cm^2) and that the Taylor equation for the overall dispersion $D_{12}*$ is precisely followed. The intercept gave a value of the diffusion coefficient at atmospheric pressure of 0.6857 cm^2/s. This value agrees moderately with our previous measured value, 0.6929, and the values 0.6895 cm^2/s calculated from Marrero and Mason's (*3*) best fit equation. The slight discrepancy of this pressure-extrapolated value from the other values is attributed to uncertainty in the ancient pressure gage used for these high pressures.

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Equilibrium Solubilities of Methane, Carbon Monoxide, and Hydrogen in Water and Sea Water

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Measured Bunsen solubility coefficients reported in the literature are used to derive functions that permit accurate calculation of the concentration of methane, carbon monoxide, and hydrogen in water and sea water at equilibrium with the normal atmosphere. Bunsen coefficients are fitted to equations established by Weiss which give Bunsen coefficients as functions of temperature and salinity. Tables of Bunsen coefficients covering the temperature range −2 to +30 °C and the salinity range 0–40 parts per thousand are calculated for each gas from the fitted equations. The data are also fitted to an atmospheric equilibrium solubility function, which has a form similar to the Bunsen coefficient equation, but which includes the atmospheric gas concentration as a variable. Coefficients for this equation are given to allow calculation of the concentration of dissolved methane, carbon monoxide, and hydrogen in equilibrium with moist air at 1 atm total pressure in units of nL/L, nmol/L, nL/kg, and nmol/kg sea water.

Since Craig and Gordon (*7*) reported finding nitrous oxide in sea water, the list of chemically unstable gases found in the ocean has grown to include methane (*25*), carbon monoxide (*28*), hydrogen (*36*), and others (*26*). These unstable gases are produced biogenically and there has been considerable study of factors governing their release, consumption, and distribution in sea water. Seiler and Schmidt (*24*) have reviewed the early studies of these gases in the ocean and the work continues today at an intensified pace (*5, 6, 14, 23*). Oceanic surface waters appear to act as a source to the atmosphere for most reduced gases (*14, 23, 27, 41*) with bottom water, oxygen minimum zones, and anoxic waters perhaps acting as sinks (*4, 5, 6, 17*). In the search for sources and sinks of gases which are biologically produced or consumed, we must know the normal atmospheric equilibrium solubility values for these gases in sea water as a function of temperature and salinity.

Bunsen coefficients for methane, carbon monoxide, and hydrogen are found in the literature (*8, 10, 13, 37, 40*), but equations expressing atmospheric solubilities as functions of temperature and salinity have not been determined for these reduced gases, as they have for oxygen, nitrogen, argon and various inert gases (*31, 32, 34*). Since previous studies of reduced gases have not derived equations for atmospheric equilibrium solubilities, we calculate here the numerical ex-

pressions that permit rapid, accurate determination of atmospheric solubilities of methane, carbon monoxide, and hydrogen. Our derivations are based on the equations of Weiss (*31*), which express atmospheric equilibrium solubility as a function of temperature and salinity. Nitrous oxide is not considered here, since there have been no measurements of nitrous oxide solubilities over temperature and salinity ranges large enough to allow application of our method.

Data Analysis

Raw Data. Precise measurements of Bunsen solubility coefficients, β, are available in the literature for methane (*40*), carbon monoxide (*10, 37*), and hydrogen (*8, 13*) in distilled water and sea water over various temperature and salinity ranges. The Bunsen coefficient, β, is defined as the volume of gas, reduced to 0 °C and 1 atm of pressure (standard temperature and pressure) contained in a unit volume of water at the temperature of the measurement when the partial pressure of the gas is 1 atm. Only raw, unsmoothed solubility data for methane, carbon monoxide, and hydrogen, given by the various authors, were used in our analysis. Selection of data was based upon the temperature and salinity ranges of measurements, level of agreement with other workers for distilled water solubilities, and the precision and susceptibility of the experimental method to systematic errors. Most of the data used (*8, 10, 40*) were determined by using microgasometric techniques (*9*). Douglas (*9*) estimated the accuracy of microgasometric methods to be about ±0.26%. Discussions of accuracies of other methods are given by the individual authors and will receive only limited mention here.

We have chosen the Bunsen solubility data of Yamamoto et al. (*40*) as the best data for methane since it covers a wide range of temperatures and salinities and compares well with some earlier data for distilled water (*2, 3*). The raw solubility data of Douglas (*10*) was used for carbon monoxide. Douglas' values of chlorinity were converted to salinity, by using the equation S‰ = 1.80655(Cl‰) (*39*). The lowest salinity at which Douglas measured solubility was 27.8 ‰; we therefore have combined his data with the distilled water measurements made by Winkler (*37*) for our calculations. The oxygen solubility measurements made by Winkler (*37*) as part of the same work during which he measured carbon monoxide solubility, differ by less than 0.4% from the oxygen data reported by Weiss (*31*). This leads us to believe that Winkler's 1906 measurements were

Table I. Constants for Calculation of Bunsen Solubility Coefficients, β, According to Equation 1

gas	A_1	A_2	A_3	B_1	B_2	B_3
CH_4	−68.8862	101.4956	28.7314	−0.076 146	0.043 970	−0.006 867 2
CO	−47.6148	69.5068	18.7397	0.045 657	−0.040 721	0.007 970 0
H_2	−47.8948	65.0368	20.1709	−0.082 225	0.049 564	−0.007 868 9

Table II. Bunsen Solubility Coefficients for Methane Where β Is Expressed as mL of CH_4 (STP) Dissolved in 1 mL of H_2O

temp, °C	salinity, parts per thousand								
	0	10	20	30	32	34	36	38	40
−2			0.052 69	0.048 93	0.048 21	0.047 50	0.046 80	0.046 11	0.045 44
−1			0.051 11	0.047 49	0.046 80	0.046 12	0.045 45	0.044 78	0.044 13
0	0.057 38	0.053 36	0.049 61	0.046 13	0.045 46	0.044 80	0.044 16	0.043 52	0.042 89
1	0.055 66	0.051 78	0.048 18	0.044 83	0.044 18	0.043 55	0.042 93	0.042 31	0.041 71
2	0.054 02	0.050 29	0.046 82	0.043 58	0.042 97	0.042 36	0.041 75	0.041 16	0.040 58
3	0.052 45	0.048 86	0.045 52	0.042 40	0.041 81	0.041 22	0.040 64	0.040 06	0.039 50
4	0.050 97	0.047 51	0.044 28	0.041 27	0.040 70	0.040 13	0.039 57	0.039 02	0.038 47
5	0.049 55	0.046 21	0.043 10	0.040 20	0.039 64	0.039 09	0.038 55	0.038 02	0.037 49
6	0.048 20	0.044 98	0.041 97	0.039 17	0.038 63	0.038 10	0.037 58	0.037 06	0.036 55
8	0.045 69	0.042 68	0.039 87	0.037 25	0.036 75	0.036 25	0.035 76	0.035 28	0.034 80
10	0.043 40	0.040 59	0.037 96	0.035 50	0.035 03	0.034 56	0.034 10	0.033 64	0.033 20
12	0.041 32	0.038 68	0.036 21	0.033 89	0.033 45	0.033 01	0.032 58	0.032 15	0.031 73
14	0.039 42	0.036 94	0.034 61	0.032 43	0.032 01	0.031 59	0.031 18	0.030 78	0.030 38
16	0.037 68	0.035 34	0.033 14	0.031 08	0.030 68	0.030 29	0.029 90	0.029 52	0.029 15
18	0.036 09	0.033 88	0.031 80	0.029 84	0.029 47	0.029 09	0.028 73	0.028 37	0.028 01
20	0.034 64	0.032 54	0.030 56	0.028 71	0.028 35	0.028 00	0.027 65	0.027 30	0.026 96
22	0.033 30	0.031 31	0.029 43	0.027 66	0.027 32	0.026 98	0.026 65	0.026 32	0.026 00
24	0.032 08	0.030 18	0.028 38	0.026 70	0.026 37	0.026 05	0.025 73	0.025 42	0.025 11
26	0.030 96	0.029 14	0.027 42	0.025 81	0.025 50	0.025 19	0.024 89	0.024 59	0.024 29
28	0.029 93	0.028 18	0.026 54	0.024 99	0.024 69	0.024 40	0.024 11	0.023 82	0.023 53
30	0.028 98	0.027 30	0.025 72	0.024 24	0.023 95	0.023 66	0.023 38	0.023 11	0.022 83

as reliable as those made by Douglas (*10*) and that little precision is lost by combining the two data sets. Neither Winkler (*37*) nor Douglas (*10*) corrected their carbon monoxide solubility data for changes in volume of the aqueous phase caused by dissolution of the gas. In the present treatment, we have corrected their data for this effect, using a value of 36 cm³/mol for the partial molal volume of carbon monoxide (*15*). This correction increased the solubility coefficients by about 0.16%. Two recent studies, Crozier and Yamamoto (*8*) and Gordon et al. (*13*), have established the Bunsen solubility coefficients for molecular hydrogen in sea water over the oceanic range of temperature and salinity. These two studies agree to within 0.5%. Rather than evaluate which is the better data set, we have simply combined the raw data from both studies and used the combined set in our analysis. The sources for the raw data are summarized in Table V.

In our calculations we have assumed that methane, carbon monoxide, and hydrogen behave like ideal gases. Weiss (*33*) has noted that deviations from ideality must be considered for gases whose deviation is greater than the precision of the solubility measurements. He has shown the importance of this effect for krypton and carbon dioxide solubilities (*33, 34*). We calculated deviations from ideality for methane, carbon monoxide, and hydrogen by using van der Waals' equation of state and constants given by Weast (*30*). Deviations of −0.26%, −0.12%, and +0.07% were determined for methane, carbon monoxide, and hydrogen, respectively. Since these deviations are less than the precision of the original measurements, no corrections for nonideal effects are required in our treatment of the data.

Bunsen Calculations. Weiss (*31, 32*) has shown that Bunsen solubilities can be described as a function of temperature and salinity by using a single equation. He expressed the temperature dependence of solubility at constant salinity by an integrated form of the van't Hoff equation and used the Setchénow relation to describe the salinity effect. Combining these two relationships he developed a Bunsen solubility equation of the form

$$\ln \beta = A_1 + A_2(100/T) + A_3 \ln (T/100) +$$
$$S\%o[B_1 + B_2(T/100) + B_3(T/100)^2] \quad (1)$$

where A_i and B_i are constants, T is the temperature in degrees Kelvin, and $S\%o$ is the salinity in parts per thousand.

We have fitted the raw solubility data for methane (*40*), carbon monoxide (*10, 37*), and hydrogen (*8, 13*) to eq 1 to determine the constants by the method of least squares. A computer program was used which simultaneously calculated all six constants from a single fit of all the data using a linear least-squares (LLSQAR) subroutine of the International Mathematical and Statistical Library which is based on the algorithm of Golub and Reinsch (*11*). Constants obtained by fitting the raw Bunsen coefficients for each gas to eq 1 are given in Table I. Calculations were carried out in double precision (approximately 16 decimal digits); use of the truncated values presented in Table I does not affect the accuracy of calculated solubility coefficients. Figure 1 shows the percent deviation of the measured data for each gas from the fit to eq 1. The root-mean-square deviation of experimental data from calculated, in terms of β, was 1.8 × 10^{-4} for methane, 1.3 × 10^{-4} for carbon monoxide, and 7.8 × 10^{-5} for hydrogen or 0.49%, 0.42%, and 0.46%, respectively. The Bunsen solubilities for methane, carbon monoxide, and hydrogen for the temperature range −2 to +30 °C and the salinity range 0–40 parts per thousand, as calculated from eq 1, are given in Tables II, III, and IV.

In measuring Bunsen coefficients for carbon monoxide, Douglas (*10*) drew smooth curves through his raw data and used these graphs to prepare a table of solubilities for temperatures ranging from −2 to +30 °C and salinities between 27.1 and 37.9 parts per thousand (chlorinities of 15–21‰). Douglas' table is adequate for sea water but is not applicable to the fresh or brackish waters often found in estuaries. Since carbon monoxide production has been associated with biological production in several studies (*17, 26*) and biological activity is often several orders of magnitude greater in estuaries than in the open ocean, a knowledge of carbon monoxide solubilities in these salinity ranges is important to our understanding of biological sources and sinks of this gas. Our equation for carbon monoxide solubility is applicable to waters of salinities from 0 to 40‰.

In processing their Bunsen solubility data for methane and hydrogen, Yamamoto et al. (*40*), Crozier and Yamamoto (*8*),

Table III. Bunsen Solubility Coefficients for Carbon Monoxide Where β Is Expressed as mL of CO (STP) Dissolved in 1 mL of H_2O

temp, °C	salinity, parts per thousand								
	0	10	20	30	32	34	36	38	40
−2			0.033 01	0.031 03	0.030 65	0.030 28	0.029 91	0.029 54	0.029 18
−1			0.032 20	0.030 28	0.029 92	0.029 55	0.029 19	0.028 83	0.028 48
0	0.035 51	0.033 41	0.031 43	0.029 57	0.029 21	0.028 85	0.028 50	0.028 16	0.027 82
1	0.034 66	0.032 62	0.030 69	0.028 88	0.028 53	0.028 19	0.027 85	0.027 51	0.027 18
2	0.033 84	0.031 85	0.029 99	0.028 23	0.027 89	0.027 55	0.027 22	0.026 89	0.026 57
3	0.033 05	0.031 12	0.029 31	0.027 60	0.027 27	0.026 94	0.026 62	0.026 30	0.025 99
4	0.032 30	0.030 43	0.028 66	0.026 99	0.026 67	0.026 36	0.026 04	0.025 73	0.025 43
5	0.031 58	0.029 75	0.028 04	0.026 42	0.026 11	0.025 80	0.025 49	0.025 19	0.024 89
6	0.030 88	0.029 11	0.027 44	0.025 86	0.025 56	0.025 26	0.024 96	0.024 67	0.024 38
8	0.029 57	0.027 90	0.026 32	0.024 83	0.024 54	0.024 25	0.023 97	0.023 69	0.023 42
10	0.028 36	0.026 78	0.025 28	0.023 87	0.023 60	0.023 33	0.023 06	0.022 80	0.022 54
12	0.027 24	0.025 74	0.024 33	0.022 99	0.022 73	0.022 48	0.022 22	0.021 97	0.021 73
14	0.026 21	0.024 79	0.023 45	0.022 18	0.021 94	0.021 69	0.021 45	0.021 22	0.020 98
16	0.025 24	0.023 90	0.022 64	0.021 44	0.021 20	0.020 97	0.020 75	0.020 52	0.020 30
18	0.024 35	0.023 09	0.021 88	0.020 75	0.020 53	0.020 31	0.020 09	0.019 88	0.019 67
20	0.023 53	0.022 33	0.021 19	0.020 11	0.019 90	0.019 70	0.019 49	0.019 29	0.019 09
22	0.022 76	0.021 62	0.020 55	0.019 53	0.019 33	0.019 13	0.018 94	0.018 75	0.018 56
24	0.022 04	0.020 97	0.019 95	0.018 99	0.018 80	0.018 61	0.018 43	0.018 25	0.018 07
26	0.021 37	0.020 37	0.019 40	0.018 49	0.018 31	0.018 13	0.017 96	0.017 79	0.017 62
28	0.020 75	0.019 80	0.018 89	0.018 03	0.017 86	0.017 69	0.017 53	0.017 36	0.017 20
30	0.020 18	0.019 28	0.018 42	0.017 60	0.017 45	0.017 29	0.017 13	0.016 98	0.016 82

Table IV. Bunsen Solubility Coefficients for Hydrogen Where β Is Expressed as mL of H_2 (STP) Dissolved in 1 mL of H_2O

temp, °C	salinity, parts per thousand								
	0	10	20	30	32	34	36	38	40
−2			0.020 19	0.019 08	0.018 86	0.018 65	0.018 44	0.018 23	0.018 02
−1			0.019 94	0.018 85	0.018 64	0.018 43	0.018 23	0.018 02	0.017 82
0	0.022 01	0.020 82	0.019 70	0.018 64	0.018 43	0.018 23	0.018 02	0.017 83	0.017 63
1	0.021 72	0.020 56	0.019 47	0.018 43	0.018 23	0.018 03	0.017 83	0.017 64	0.017 44
2	0.021 45	0.020 32	0.019 24	0.018 23	0.018 03	0.017 84	0.017 64	0.017 45	0.017 27
3	0.021 18	0.020 08	0.019 03	0.018 04	0.017 84	0.017 65	0.017 47	0.017 28	0.017 10
4	0.020 93	0.019 85	0.018 82	0.017 85	0.017 66	0.017 48	0.017 29	0.017 11	0.016 93
5	0.020 69	0.019 63	0.018 63	0.017 68	0.017 49	0.017 31	0.017 13	0.016 95	0.016 77
6	0.020 45	0.019 42	0.018 44	0.017 51	0.017 33	0.017 15	0.016 97	0.016 79	0.016 62
8	0.020 01	0.019 02	0.018 08	0.017 19	0.017 01	0.016 84	0.016 67	0.016 50	0.016 34
10	0.019 61	0.018 66	0.017 75	0.016 89	0.016 72	0.016 56	0.016 39	0.016 23	0.016 07
12	0.019 24	0.018 32	0.017 45	0.016 62	0.016 46	0.016 30	0.016 14	0.015 98	0.015 83
14	0.018 90	0.018 01	0.017 17	0.016 37	0.016 21	0.016 06	0.015 91	0.015 75	0.015 60
16	0.018 58	0.017 73	0.016 92	0.016 14	0.015 99	0.015 84	0.015 69	0.015 54	0.015 40
18	0.018 30	0.017 47	0.016 68	0.015 93	0.015 78	0.015 64	0.015 49	0.015 35	0.015 21
20	0.018 04	0.017 24	0.016 47	0.015 74	0.015 59	0.015 45	0.015 31	0.015 17	0.015 04
22	0.017 80	0.017 02	0.016 27	0.015 56	0.015 42	0.015 28	0.015 15	0.015 01	0.014 88
24	0.017 59	0.016 83	0.016 10	0.015 40	0.015 27	0.015 13	0.015 00	0.014 87	0.014 73
26	0.017 40	0.016 65	0.015 94	0.015 26	0.015 12	0.014 99	0.014 86	0.014 73	0.014 60
28	0.017 22	0.016 49	0.015 79	0.015 13	0.015 00	0.014 87	0.014 74	0.014 61	0.014 49
30	0.017 07	0.016 35	0.015 67	0.015 01	0.014 88	0.014 75	0.014 63	0.014 50	0.014 38

and Gordon et al. (*13*) fit their own data to eq 1 in a manner similar to that which we have used. Our calculated values agree with their results within 0.22% for methane and 0.35% for hydrogen. A comparison of our smoothed values for pure water (zero salinity) with those of Wilhelm et al. (*35*) shows reasonably close agreement. For methane, the differences range from 0.16% at 0 °C to 1.90% at 30 °C. The differences for carbon monoxide (0.14–1.45%) and hydrogen (0.64–0.05%) at the same temperatures were also in agreement, even though most of the data used in our fits were not at zero salinity. The systematic differences between the methane and carbon monoxide values from our equation and those of Wilhelm et al. (*35*) probably result from the fact that different data sets were used in each derivation.

Atmospheric Equilibrium Solubilities

Although the Bunsen coefficients for methane, carbon monoxide, and hydrogen have been measured with considerable accuracy, the process of calculating the actual equilibrium concentration of these gases in sea water is not trivial. Henry's law relates the concentration of an ideal gas in solution (C^*)
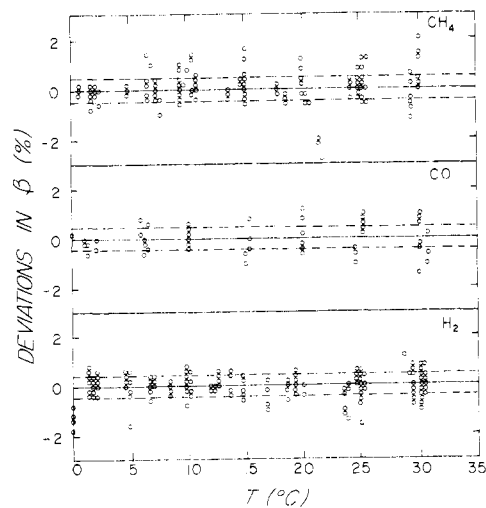

Figure 1. Percent deviations of all raw Bunsen solubility data for methane, carbon monoxide, and hydrogen from the fits to eq 1. The dashed lines show ± the root-mean-squared deviation. Sources of data are indicated in the text (*8*, *10*, *13*, *37*, *40*).

Table V. Source of Data for Calculating Equilibrium Solubilities Which Are Fitted to Equation 7 To Determine the Solubility Coefficients and Molecular Fractions of Atmospheric Gases (f_G) Used for Test Value Calculations

gas	no. of measmnts	source of exptl Bunsen coeff	$10^6 f_G$	ref for f_G
CH_4	201	Yamamoto et al. (39)	1.41	Prabhakara et al. (19)
CO	63	Douglas (10)	0.11	Robinson and Robbins (20)
	4	Winkler (36)		
H_2	222	Crozier and Yamamoto (8)	0.58	Schmidt (22)
	39	Gordon et al. (13)		

Table VI. Constants for Calculation of Solubilities in nL/L, nmol/L, nL/kg, and nmol/kg from Moist Air at 1 Atm Total Pressure, According to Equation 7[a]

gas	units	A_1	A_2	A_3	A_4	B_1	B_2	B_3	test value
CH_4	nL/L	-412.1710	596.8104	379.2599	-62.0757	-0.059 160	0.032 174	-0.004 819 8	48.11
	nmol/L	-415.2807	596.8104	379.2599	-62.0757	-0.059 160	0.032 174	-0.004 819 8	2.146
	nL/kg	-414.3956	599.8626	380.3636	-62.0764	-0.064 236	0.034 980	-0.005 273 2	46.87
	nmol/kg	-417.5053	599.8626	380.3636	-62.0764	-0.064 236	0.034 980	-0.005 273 2	2.091
CO	nL/L	-169.4951	263.5657	159.2552	-25.4967	0.051 198	-0.044 591	0.008 646 2	2.535
	nmol/L	-172.6048	263.5657	159.2552	-25.4967	0.051 198	-0.044 591	0.008 646 2	0.1131
	nL/kg	-172.4995	267.6796	161.0862	-25.6218	0.046 103	-0.041 767	0.008 189 0	2.470
	nmol/kg	-175.6092	267.6796	161.0862	-25.6218	0.046 103	-0.041 767	0.008 189 0	0.1102
H_2	nL/L	-314.3572	455.8526	297.5313	-49.2778	-0.070 143	0.041 069	-0.006 376 3	9.478
	nmol/L	-317.4669	455.8526	297.5313	-49.2778	-0.070 143	0.041 069	-0.006 376 3	0.4228
	nL/kg	-317.1982	459.7398	299.2600	-49.3946	-0.074 474	0.043 363	-0.006 742 0	9.235
	nmol/kg	-320.3079	459.7398	299.2600	-49.3946	-0.074 474	0.043 363	-0.006 742 0	0.4121

[a] Test values were calculated at $T = 10\ °C$ and $S = 34\%_{00}$ and atmospheric concentrations given in Table V.

to a constant times the partial pressure of the gas above the solution.

$$C^* = \beta P_G \qquad (2)$$

where β is the Bunsen coefficient and P_G is the partial pressure of the specified gas in the atmosphere. P_G is related to the mole fraction of gas (f_G) in the dry atmosphere by the expression

$$P_G = \left[P_t - \frac{h}{100} P_{vp} \right] f_G \qquad (3)$$

where P_t is the total pressure (atm), h is the relative humidity (percent), and P_{vp} is vapor pressure of the solution (atm). Combining eq 2 and 3 gives an expression which can be used to calculate solubilities.

$$C^* = \beta \left[P_t - \frac{h}{100} P_{vp} \right] f_G \qquad (4)$$

Calculations of solubility thus require a knowledge of five factors: the Bunsen coefficient [f(T,S)], the vapor pressure [f(T,S)], the mole fraction of the gas in dry atmosphere, the total (atmospheric) pressure, and the relative humidity. The Bunsen coefficients for a given temperature and salinity have been accurately determined for methane, carbon monoxide, and hydrogen as previously discussed. The vapor pressure of pure water as a function of temperature can be calculated (1, 12), but tabular data most often are used. The lowering of water vapor pressure due to dissolved salts is ignored by many workers; however, the differences involved (2% at 35‰ salinity) are significant and should be included.

Assuming total pressure equals 1 atm and the relative humidity is 100%, eq 4 reduces to

$$C^* = \beta(1 - P_{vp}) f_G \qquad (5)$$

which is the equation most often used for solubility calculations for methane, carbon monoxide, and hydrogen. The mole fractions of these gases in air vary with geographic location and are a function of both the partial pressure and the vapor pressure of water. When considering a sample of sea water, it is often difficult to estimate accurately the mole fraction of a gas in the atmosphere at the site where the water parcel equilibrated with the atmosphere. For surface water studies, it is practical to measure the concentration of various gases in the atmosphere above the water. For studies of deeper water, however, f_G is

normally assumed to be the world-wide average.

Weiss (31) has developed an equation for calculating atmospheric equilibrium from moist air as a function of only temperature and salinity. He used the same temperature and salinity relationships that he used in developing eq 1, but he included one additional temperature-dependent term [$A_4(T/100)$] to account for the vapor pressure of water. His atmospheric equilibrium solubility equation is given by

$$\ln C^* = A_1 + A_2(100/T) + A_3 \ln (T/100) +$$
$$A_4(T/100) + S‰[B_1 + B_2(T/100) + B_3(T/100)^2] \qquad (6)$$

where C^* is the equilibrium solubility in nmol/L (or other appropriate units), A_i and B_i are constants, T is the absolute temperature, and $S‰$ is the salinity in parts per thousand.

Weiss (31, 32, 34) fitted atmospheric solubility data for oxygen, nitrogen, argon, neon, helium, and krypton to eq 6 to describe the atmospheric solubility of these gases relative to water-saturated air at 1 atm total pressure. The standard assumptions of $h = 100\%$ and $P_t = 1$ atm were used, but he calculated the vapor pressure very accurately by using the pure water equation of Goff and Gratch (12) and correcting for salinity by the equation of Witting (38). With the appropriate constants for the gas in question, eq 6 can be used to calculate the equilibrium solubility from the potential temperature and salinity alone. This solubility equation has not been previously applied to reduced trace gases.

Since the Bunsen coefficients for methane, carbon monoxide, and hydrogen have been well established for various temperatures and salinities (8, 10, 13, 37, 40), the only limitation to deriving similar equilibrium solubility equations for these reduced gases is their variability in the atmosphere. Variations in concentrations of the reduced gases are usually small, and again, many workers use the world-wide averages. However, spatial variations of these gases do occur due to their short residence times in the atmosphere. Atmospheric levels of CO and CH_4 (29) as well as H_2 (14, 22, 24) may be slowly increasing due to man-derived sources.

Because the atmospheric concentration of these gases is not constant, we include the atmospheric gas concentration (f_G) as a variable in the atmospheric equilibrium solubility equation. This alteration does not change the form of eq 6; a change in f_G results only in a change in the intercept of the equation. Consequently we can write

$$\ln C^* = \ln f_G + A_1 + A_2(100/T) + A_3 \ln (T/100) +$$
$$A_4(T/100) + S\text{‰}[B_1 + B_2(T/100) + B_3(T/100)^2] \quad (7)$$

This equation is a more general form of the atmospheric equilibrium solubility equation that Weiss (*31*) used for oxygen, nitrogen, and argon. It can be used to calculate the atmospheric equilibrium solubility of any dissolved gas for different values of temperature, salinity, and atmospheric concentration.

We have fitted solubilities to eq 7 to determine the constants needed for calculation of equilibrium solubilities of methane, carbon monoxide, and hydrogen. Equilibrium solubility values were calculated by using eq 5 for each raw Bunsen coefficient datum for each gas in units of nL/L and nmol/L. A total pressure of 1 atm was assumed and a value of f_G equal to 1 was used. Since the natural logarithm of 1 equals 0, using $f_G = 1$ in eq 5 allows the determination of the other constants in eq 7 independent of atmospheric concentration. Vapor pressure was calculated for pure water by using the equation of Bridgeman and Aldrich (*1*). These vapor pressures were corrected for the salinity effect by using the expression of Robinson (*21*). Knudsen's (*16*) formula for σ_t was used to calculate densities ($\sigma_t = [\text{density} -1] \times 10^3$) which, together with atmospheric solubilities in nmol/L, were used to calculate solubilities in units of nL/kg and nmol/kg. The nmol/kg sea water "Mokal" scale (*18*) eliminates most ambiguities caused by temperature and pressure effects in the ocean.

Each resulting data set was fitted to eq 7, again using the linear least-squares (LLSQAR) subroutine of the International Mathematical and Statistical Library. This fit incorporates the salinity and temperature dependence of the vapor pressure term into the salinity and temperature constants in eq 7. The constants determined for solubilities in units of nL/L, nmol/L, nL/kg, and nmol/kg are given in Table VI. Plots of residuals (raw data minus calculated data) for these equations vs. temperature are essentially the same as the plots in Figure 1, since no additional variance results from incorporation of the vapor pressure relationship. All root-mean-squared deviations were small (0.45% for hydrogen to 0.48% for methane) and similar to those for the fitted Bunsen coefficients.

A set of test values is given in Table VI for checking eq 7 at a temperature of 10 °C, a salinity of 34‰, and molecular fractions in dry air (f_G) for methane, carbon monoxide, and hydrogen of 1.41×10^{-6}, 0.11×10^{-6}, and 0.58×10^{-6}, respectively. These concentrations are average atmospheric concentrations given by authors listed in Table V.

Conclusions

The results reported here permit accurate and rapid calculation of atmospheric equilibrium solubilities of methane, carbon monoxide, and hydrogen in distilled water and sea water. The salinity range over which Bunsen solubility coefficients for carbon monoxide can be calculated has been extended to include waters of salinities from 0 to 40 parts per thousand. This new solubility equation for carbon monoxide is applicable to fresh and brackish areas, where carbon monoxide production is probably greater than found in the open ocean. The atmospheric solubility equation has been rewritten with an additional term for atmospheric gas concentration as a variable. This equation, with the constants we have derived, can be used to calculate accurately the atmospheric solubilities of methane, carbon monoxide, and hydrogen under any given conditions of temperature, salinity, and atmospheric concentration. The generalized equation will remain useful even though changes in atmospheric gas concentrations may occur.

Acknowledgment

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