line fit of the above experimental points. The correlation coefficient is 0.9994. This confirms that the \( \text{He}-\text{CH}_4 \) 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 expressions 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, \( \beta \), 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, \( \beta \), 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 \( S_{\text{‰}} = 1.80655(C_{\text{‰}}) \) (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 (37). This leads us to believe that Winkler's 1906 measurements were

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**Literature Cited**


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and hydrogen by using van der Waals' equation of state and the precision of the original measurements, no corrections for describe the salinity effect. Combining these two relationships of the van't Hoff equation and used the Setchelow relation to he developed a Bunsen solubility equation of the form

\[ \ln \beta = A_1 + A_2 \left( \frac{100}{T} \right) + A_3 \ln \left( \frac{T}{100} \right) + S \% \left[ B_1 + B_2 \left( \frac{T}{100} \right) + B_3 \left( \frac{T}{100} \right)^2 \right] \]  

where \( A_1 \) and \( B \) are constants, \( T \) is the temperature in degrees Kelvin, and \( S \% \) is the salinity in parts per thousand.

We have fitted the raw solubility data for methane \((40)\), carbon monoxide \((10, 37)\), and hydrogen \((\theta, 13)\) 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 \((17)\). 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 the experimental data from calculated, in terms of \( \beta \), was \( 1.8 \times 10^{-4} \) for methane, \( 1.3 \times 10^{-4} \) for carbon monoxide, and 7.8 \( \times 10^{-5} \) for hydrogen or 0.49\%, 0.42\%, and 0.46\%, respectively. The Bunsen solubilities for methane, carbon monoxide, and hydrogen for the temperature range from -2 to +30 \( ^\circ \)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 \( ^\circ \)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 \((\theta)\), 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 dissolusion of the gas. In the present treatment, we have corrected their data for this effect, using a value of 36 cm\(^3\)/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 \((\theta)\) 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 IV.

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 Setchelow equation to describe the salinity effect. Combining these two relationships he developed a Bunsen solubility equation of the form

\[ \ln \beta = A_1 + A_2 \left( \frac{100}{T} \right) + A_3 \ln \left( \frac{T}{100} \right) + S \% \left[ B_1 + B_2 \left( \frac{T}{100} \right) + B_3 \left( \frac{T}{100} \right)^2 \right] \]  

\[(1)\]
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 (0.84–0.05%) 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*) to the partial pressure of the gas (P*).

![Figure 1](image-url)  
**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 (2, 10, 13, 37, 40).
to a constant times the partial pressure of the gas above the solution.

\[ C^* = \beta P_o \]  \hspace{1cm} (2)

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

\[ P_o = \left[ P_t - \frac{h}{100} P_{vp} \right] f_G \]  \hspace{1cm} (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.

\[ C^* = \beta \left[ P_t - \frac{h}{100} P_{vp} \right] f_G \]  \hspace{1cm} (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 the 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 \((7,12)\), 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

\[ C^* = \beta (1 - P_{vp}) f_G \]  \hspace{1cm} (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 \([A_d(T/100)]\) to account for the vapor pressure of water. His atmospheric equilibrium solubility equation is given by

\[ \ln C^* = A_1 + A_2 (100/T) + A_3 \ln (T/100) + A_4 (T/100) + S \% \left[B_1 + B_2 (T/100) + B_3 (T/100)^2\right] \]  \hspace{1cm} (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 Goiff and Granch \((12)\) 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

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**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

<table>
<thead>
<tr>
<th>gas</th>
<th>no. of measmnts</th>
<th>source of exptl Bunsen coeff</th>
<th>(10^4 f_G)</th>
<th>ref for (f_G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>201</td>
<td>Yamamoto et al. ((39))</td>
<td>1.41</td>
<td>Prabhakara et al. ((19))</td>
</tr>
<tr>
<td>CO</td>
<td>63</td>
<td>Douglas ((10))</td>
<td>0.11</td>
<td>Robinson and Robbins ((20))</td>
</tr>
<tr>
<td>H(_2)</td>
<td>4</td>
<td>Winkler ((26))</td>
<td>0.58</td>
<td>Schmidt ((22))</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>222</td>
<td>Crozier and Yamamoto ((8))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_2)O</td>
<td>39</td>
<td>Gordon et al. ((13))</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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**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

<table>
<thead>
<tr>
<th>gas</th>
<th>units</th>
<th>(A_1)</th>
<th>(A_2)</th>
<th>(A_3)</th>
<th>(A_4)</th>
<th>(B_1)</th>
<th>(B_2)</th>
<th>(B_3)</th>
<th>test value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>nL/L</td>
<td>-412.1710</td>
<td>596.8104</td>
<td>379.2599</td>
<td>-62.0757</td>
<td>0.059 160</td>
<td>0.032 174</td>
<td>-0.004 819</td>
<td>8.48</td>
</tr>
<tr>
<td></td>
<td>nmol/L</td>
<td>-415.2807</td>
<td>596.8104</td>
<td>379.2599</td>
<td>-62.0757</td>
<td>0.059 160</td>
<td>0.032 174</td>
<td>-0.004 819</td>
<td>8.48</td>
</tr>
<tr>
<td></td>
<td>nmol/kg</td>
<td>-414.3956</td>
<td>599.8626</td>
<td>380.3636</td>
<td>-62.0764</td>
<td>0.064 236</td>
<td>0.034 980</td>
<td>-0.005 273</td>
<td>2.46</td>
</tr>
<tr>
<td></td>
<td>nmol/kg</td>
<td>-417.5053</td>
<td>599.8626</td>
<td>380.3636</td>
<td>-62.0764</td>
<td>0.064 236</td>
<td>0.034 980</td>
<td>-0.005 273</td>
<td>2.46</td>
</tr>
<tr>
<td>CO</td>
<td>nL/L</td>
<td>-169.4951</td>
<td>263.5657</td>
<td>159.3252</td>
<td>-29.4967</td>
<td>0.051 198</td>
<td>-0.044 591</td>
<td>0.008 646</td>
<td>2.535</td>
</tr>
<tr>
<td></td>
<td>nmol/L</td>
<td>-172.6048</td>
<td>263.5657</td>
<td>159.3252</td>
<td>-29.4967</td>
<td>0.051 198</td>
<td>-0.044 591</td>
<td>0.008 646</td>
<td>2.535</td>
</tr>
<tr>
<td></td>
<td>nmol/kg</td>
<td>-172.4995</td>
<td>267.6796</td>
<td>161.0862</td>
<td>-29.4967</td>
<td>0.046 103</td>
<td>-0.041 767</td>
<td>0.008 189</td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td>nmol/kg</td>
<td>-175.6092</td>
<td>267.6796</td>
<td>161.0862</td>
<td>-29.4967</td>
<td>0.046 103</td>
<td>-0.041 767</td>
<td>0.008 189</td>
<td>2.47</td>
</tr>
<tr>
<td>H(_2)</td>
<td>nL/L</td>
<td>-314.3572</td>
<td>455.8526</td>
<td>297.5313</td>
<td>-49.2778</td>
<td>-0.070 143</td>
<td>0.041 069</td>
<td>-0.006 376</td>
<td>3.978</td>
</tr>
<tr>
<td></td>
<td>nmol/L</td>
<td>-317.4769</td>
<td>455.8526</td>
<td>297.5313</td>
<td>-49.2778</td>
<td>-0.070 143</td>
<td>0.041 069</td>
<td>-0.006 376</td>
<td>3.978</td>
</tr>
<tr>
<td></td>
<td>nmol/kg</td>
<td>-317.7827</td>
<td>459.3798</td>
<td>299.2600</td>
<td>-49.3946</td>
<td>-0.074 474</td>
<td>0.043 363</td>
<td>-0.006 742</td>
<td>2.925</td>
</tr>
<tr>
<td></td>
<td>nmol/kg</td>
<td>-320.3079</td>
<td>459.3798</td>
<td>299.2600</td>
<td>-49.3946</td>
<td>-0.074 474</td>
<td>0.043 363</td>
<td>-0.006 742</td>
<td>2.925</td>
</tr>
</tbody>
</table>

\(a\) Test values were calculated at \(T = 10^\circ C\) and \(S = 34\%\) and atmospheric concentrations given in Table V.
in $C^* = \ln f_0 + A_1 + A_2(T/100) + A_3 (T/100) + A_4(T/100) + s\%[B_1 + B_2(T/100) + B_3(T/100)^2]$ (7)

This equation is a more general form of the atmospheric equilibrium solubility equation that Weiss (37) 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 mL/L and mol/mL. A total pressure of 1 atm was assumed and a value of $f_0$ equal to 1 was used. Since the natural logarithm of 1 equals 0, using $f_0 = 1$ 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 (18) formula for $c_1$ was used to calculate densities ($c_1 = \text{density} - 1 \times 10^8$) which, together with atmospheric solubilities in mmol/L, were used to calculate solubilities in units of mL/L and mol/L. The mmol/L sea water “Mokai” (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 (LSQAR) 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 mL/L, mol/mL, and mmol/L 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 ($f_0$) for methane, carbon monoxide, and hydrogen of $1.41 \times 10^{-6}$, $0.11 \times 10^{-6}$, and $0.58 \times 10^{-6}$, 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.

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