

<p>COMPONENTS:</p> <ol style="list-style-type: none"> 1. Methane; CH₄; [74-82-8] 2. Sea Water 	<p>EVALUATOR:</p> <p>Denis A. Wiesenburg Biological & Chemical Oceanography Branch - Oceanography Division Naval Ocean Research & Development Activity NSTL Station, Mississippi 39529 U.S.A. April 1983</p>
<p>CRITICAL EVALUATION:</p> <p>There are three reports of the solubility of methane in sea water (1-3), but only one of these has an extensive amount of data. Yamamoto <u>et al.</u> (1) report 201 solubility measurements for distilled water and five salinities (27.738, 33.461, 33.515, 33.629, 39.379 ‰) for many different temperatures between 273.91 and 303.16 K. Their solubility measurements are estimated to have an accuracy of 0.5%. Atkinson and Richards (2) reported seven calculated solubilities for sea water of 36‰ salinity based on 12 unreported measurements of methane solubility in sea water having a salinity of 40‰. Their measurement technique was not reported. They determined a linear relationship for their data with temperature and used Winkler's (4) values for the solubility of methane in distilled water to calculate the Bunsen coefficients for 36‰ salinity, assuming solubility to be a linear function of salinity between 0 and 40‰. Their calculated data in the temperature range 273.15 - 303.15 K was from 6% greater to 5% less than the results of Yamamoto <u>et al.</u> (1). Yamamoto <u>et al.</u> (1) reported that R. F. Weiss made one measurement of methane solubility at 288.24 K and salinity 36.425‰ using the Scholander microgasometric technique (5). The value he obtained ($\alpha = 0.03023$) agreed within 0.7% with the measurements of Yamamoto <u>et al.</u> (1) at that temperature and salinity.</p> <p>Stoessell and Byrne (3) reported three averaged methane solubility measurements at 298.15 K for sea water with a salinity of 34.84‰ at high methane pressures (2410, 3790, 5170 kPa). Their values, when converted to Bunsen coefficients at 1 atm, showed up to +10% variation with those of Yamamoto <u>et al.</u> (1) and were not included in the smoothing equation.</p> <p>The experimental results of Yamamoto <u>et al.</u> (1) are considered to be of sufficient reliability to use in a smoothing equation. This decision was based not only on the quality control during their experiments and self-consistency of the measurements, but also upon the fact that these investigators had measured hydrogen solubility (6) using the same methods and equipment and obtained good agreement with other published results (7). Their methane data (1) have been fitted (8) by the method of least squares to an equation developed by Weiss (9) which expresses solubility as the natural logarithm of the Bunsen coefficient, α, and is consistent with both the integrated form of the van't Hoff equation and the Setchenow salt effect relation. The equation for methane is valid from 273.15 to 303.15 K and a salinity range, S, of 0 to 40‰. The smooth equation reproduced the combined hydrogen data with a root-mean-square deviation of 1.8×10^{-4} units ($\sim 0.39\%$). The equation is</p> $\ln \alpha = -68.8862 + 101.4956 (100K/T) + 28.7314 \ln (T/100 K) \\ + S [-0.076146 + 0.043970 (T/100 K) - 0.0068672 (T/100K)^2]$ <p>where S is the salinity in parts per thousand. Wiesenburg and Guinasso (8) give an extensive table of methane Bunsen coefficients calculated from the above equation.</p> <p>Although the Bunsen solubility coefficients are well defined by the above equation, for practical purposes, oceanographers require the atmospheric equilibrium solubility values in their work. Weiss (9) has proposed an equation similar to the above which expresses the atmospheric equilibrium solubility from moist air at 1 atm total pressure, in units of volume (STP) dm⁻³, as a function of salinity and temperature. In working with samples from the depths of the ocean, it is also advantageous to express atmospheric solubilities in terms of mol kg⁻¹, which are pressure and temperature independent (9,10). Weiss' atmospheric solubility equation is based on the assumption of a constant atmospheric concentration of methane. Since methane is variable in the atmosphere, Weiss' (9) equation has been modified (8) to include the atmospheric concentration</p>	

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<p>CRITICAL EVALUATION:</p> <p>as a variable. The data set for methane (1) has been fitted (8) to the equations</p> $\ln c_1/nl \text{ dm}^{-3} = f_g - 412.1710 + 596.8104 (100/T) + 379.2599 \ln (T/100) - 62.0757 (T/100) + S[-0.059160 + 0.032174 (T/100) - 0.0048198(T/100)^2]$ $\ln m_1/nmol \text{ kg}^{-1} = f_g - 417.5053 + 599.8626 (100/T) + 380.3636 \ln (T/100) - 62.0764 (T/100) + S[-0.064236 + 0.034980 (T/100) - 0.0052732 (T/100)^2]$ <p>where f_g is the mole fraction of methane in dry air. In these calculations methane was assumed to be an ideal gas. Vapor pressure for pure water was calculated using the equation of Bridgeman and Aldrich (11) and corrected for salinity effects using the expression of Robinson (12). Knudsen's (13) formula was used to calculate densities. These two equations can be used to calculate the atmospheric equilibrium solubility of methane under any given conditions of temperature, salinity, and atmospheric concentration. Using an atmospheric methane mole fraction of 1.41×10^{-6} (14) the equations reproduce the individual calculated atmospheric solubilities with a root-mean-square deviation of 0.48%.</p> <p><u>References</u></p> <ol style="list-style-type: none"> 1. Yamamoto, S.; Alcauskas, J. B.; Crozier, T. E. <i>J. Chem. Eng. Data</i> <u>1976</u>, <i>21</i>, 78. 2. Atkinson, L. P.; Richards, F. A. <i>Deep-Sea Res.</i> <u>1967</u>, <i>14</i>, 673. 3. Stoessell, R. K.; Byrne, P. A. <i>Clays Clay Miner.</i> <u>1982</u>, <i>30</i>, 67. 4. Winkler, L. W. <i>Ber. dt. chem. Ges.</i> <u>1891</u>, <i>24</i>, 3602. 5. Scholander, P. F. <i>J. Biol. Chem.</i> <u>1947</u>, <i>167</i>, 235. 6. Crozier, T. E.; Yamamoto, S. J. <i>J. Chem. Eng. Data</i> <u>1974</u>, <i>19</i>, 242. 7. Gordon, L. I.; Cohen, Y.; Standley, D. R. <i>Deep Sea Res.</i> <u>1977</u>, <i>24</i>, 937. 8. Wiesenburg, D. A.; Guinasso, H. L., Jr. <i>J. Chem. Eng. Data</i> <u>1979</u>, <i>24</i>, 356. 9. Weiss, R. F. <i>Deep-Sea Res.</i> <u>1970</u>, <i>17</i>, 721. 10. Kester, D. in "Chemical Oceanography" v. 1 2nd Edition, J. P. Riley and G. Skirrow, eds. Academic Press, New York, <u>1975</u>, pp. 497-556. 11. Bridgeman, O. C.; Aldrich, E. W. <i>J. Heat Transfer</i> <u>1964</u>, <i>86</i>, 279. 12. Robinson, R. A. <i>J. Mar. Biol. Assoc. U.K.</i> <u>1954</u>, <i>33</i>, 449. 13. Knudsen, M. Hydrographical Tables, G. E. Gad, Copenhagen, <u>1901</u>. 14. Prabhakara, C.; Dalu, G.; Kunde, V. G. <i>J. Geophys. Res.</i> <u>1974</u>, <i>79</i>, 1744. 	

COMPONENTS:		ORIGINAL MEASUREMENTS:			
1. Methane; CH ₄ ; [74-82-8] 2. Sea Water		Yamamoto, S.; Alcauskas, J. B.; Crozier, T. E. <i>J. Chem. Eng. Data</i> <u>1976, 21, 78-80.</u>			
EXPERIMENTAL VALUES:					
Salinity ‰.					
0.0		27.738		33.461	
Temp/K	Bunsen Coefficient α	Temp/K	Bunsen Coefficient α	Temp/K	Bunsen Coefficient α
273.91	0.05592	275.22	0.04431	274.75	0.04305
273.93	0.05612	275.23	0.04433	274.75	0.04299
273.94	0.05613	275.23	0.04418	274.75	0.04294
273.95	0.05600	275.24	0.04412	274.75	0.04304
273.95	0.05591	275.24	0.04410	274.80	0.04282
273.96	0.05604	275.24	0.04410	274.85	0.04301
278.07	0.04957	275.30	0.04420	274.85	0.04302
278.09	0.04963	275.55	0.04385	274.85	0.04298
278.10	0.04973	275.63	0.04394	274.88	0.04291
278.11	0.04963	282.60	0.03650	274.94	0.04312
278.12	0.04968	282.60	0.03657	274.94	0.04278
284.05	0.04235	282.60	0.03637	274.95	0.04287
284.08	0.04216	282.60	0.03626		
284.08	0.04242	282.60	0.03659		
284.09	0.04224	282.60	0.03660		
284.09	0.04220	282.60	0.03648		
284.09	0.04238	282.60	0.03669		
284.10	0.04224	282.61	0.03670		
284.10	0.04226	282.68	0.03631		
284.11	0.04252	282.69	0.03611		
291.14	0.03606	282.70	0.03640		
291.15	0.03603	282.70	0.03667		
291.16	0.03619	282.70	0.03649		
291.17	0.03607	282.71	0.03653		
291.17	0.03606	282.90	0.03620		
297.25	0.03196	288.15	0.03238		
297.26	0.03192	288.15	0.03213		
297.30	0.03189	288.15	0.03212		
297.31	0.03211	288.15	0.03204		
297.32	0.03200	288.25	0.03218		
302.67	0.02915	288.25	0.03213		
302.69	0.02913	288.25	0.03236		
302.69	0.02915	288.25	0.03200		
302.69	0.02911	288.25	0.03205		
302.70	0.02901	293.15	0.02918		
		293.15	0.02916		
		293.15	0.02918		
		293.20	0.02901		
		293.35	0.02905		
		293.36	0.02919		
		294.55	0.02902		
		294.55	0.02895		
		294.85	0.02902		
		298.30	0.02664		
		298.32	0.02645		
		298.35	0.02641		
		298.35	0.02632		
		298.40	0.02644		
		298.40	0.02621		
		298.45	0.02640		
		298.45	0.02646		
		298.50	0.02659		
		298.55	0.02658		
		298.65	0.02609		
		298.75	0.02636		

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COMPONENTS:

1. Methane; CH₄; [74-82-8]
2. Sea Water

ORIGINAL MEASUREMENTS:

Yamamoto, S.; Alcauskas, J. B.;
Crozier, T. E. *J. Chem. Eng. Data*
1976, 21, 78-80.

EXPERIMENTAL VALUES:

Salinity ‰.

33.515		33.629		39.379	
Temp/K	Bunsen Coefficient α	Temp/K	Bunsen Coefficient α	Temp/K	Bunsen Coefficient α
280.00	0.03706	273.88	0.04409	283.45	0.03287
280.40	0.03705	273.93	0.04388	283.50	0.03306
280.48	0.03687	273.94	0.04396	283.50	0.03261
280.50	0.03712	273.96	0.04396	283.50	0.03307
280.50	0.03680	273.96	0.04389	283.50	0.03310
280.50	0.03682	279.80	0.03742	283.50	0.03271
280.55	0.03692	279.80	0.03771	283.50	0.03291
280.57	0.03682	279.81	0.03767	283.50	0.03315
280.57	0.03690	279.89	0.03700	287.96	0.02987
280.57	0.03681	279.90	0.03739	288.00	0.02992
280.57	0.03707	291.75	0.02902	288.14	0.02953
280.60	0.03680	291.75	0.02893	288.24	0.02996
280.60	0.03693	291.77	0.02899	288.24	0.02974
280.62	0.03677	291.80	0.02889	288.24	0.02981
280.65	0.03698	291.80	0.02898	288.24	0.02934
280.75	0.03687	291.81	0.02886	288.24	0.02973
280.79	0.03704	291.85	0.02897	293.15	0.02684
286.63	0.03218	291.85	0.02895	293.15	0.02698
286.63	0.03214	291.85	0.02880	293.20	0.02696
286.63	0.03208	291.85	0.02893	293.24	0.02673
286.68	0.03214	297.95	0.02584	293.25	0.02699
286.68	0.03207	297.95	0.02582	293.95	0.02685
286.68	0.03210	297.98	0.02580	297.85	0.02489
286.68	0.03216	298.00	0.02578	298.05	0.02478
286.69	0.03210	298.00	0.02563	298.05	0.02475
		298.00	0.02578	298.05	0.02479
		298.00	0.02585	298.10	0.02477
		298.00	0.02573	298.10	0.02459
		298.00	0.02579	298.10	0.02472
		298.03	0.02583	303.11	0.02248
		302.61	0.02420	303.11	0.02292
		302.61	0.02412	303.11	0.02288
		302.62	0.02402	303.11	0.02285
		302.64	0.02406	303.11	0.02266
		302.66	0.02409	303.14	0.02292
		302.69	0.02405	303.16	0.02260
		302.71	0.02418	303.16	0.02286

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VARIABLES: T/K: 273.91 - 303.16 CH ₄ P/kPa: 101.325 (1 atm) Salinity/‰: 0 - 39.379	PREPARED BY: Denis A. Wiesenburg
EXPERIMENTAL VALUES: <p style="text-align: center;">See preceding pages</p>	
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE: Solubility determinations were made using the Scholander microgasometric technique (1) as modified by Douglas (2). Pure methane and degassed sea water were introduced into a reaction vessel in a constant temperature room. The vessel was shaken vigorously to allow equilibration between the methane and sea water. The amount of gas absorbed and the volume of sea water were measured volumetrically with a microburet. Bunsen solubility coefficients were calculated from the observed volumes.	SOURCE AND PURITY OF MATERIALS: 1. Methane. Linde Specialty Gas, specified 99.99% purity. 2. Sea Water. Passed through 0.45- μm millipore filter and poisoned with 1 mg/l of HgCl ₂ . Sea water was boiled or diluted with glass distilled water (used for 0 ‰) to obtain desired salinities.
	ESTIMATED ERROR: $\delta T/K = 0.01$ $\delta S/\text{‰} = 0.003$
	REFERENCES: 1. Scholander, P. F. <i>J. Biol. Chem.</i> <u>1947</u> , <i>167</i> , 235-250. 2. Douglas, E. <i>J. Phys. Chem.</i> <u>1964</u> , <i>68</i> , 169-174. <i>ibid.</i> <u>1965</u> , <i>69</i> , 2608-2610.

<p>COMPONENTS:</p> <p>(1) Methane; CH₄; [74-82-8]</p> <p>(2) Sea Water</p>	<p>ORIGINAL MEASUREMENTS:</p> <p>Stoessell, R. K., Byrne, P. A. <i>Clays Clay Miner.</i> <u>1982</u>, 30, 67-72.</p>														
<p>VARIABLES:</p> <p>T/K: 298.15</p> <p>CH₄ P/kPa: 2410 - 5170</p> <p>Salinity/‰: 34.84</p>	<p>PREPARED BY:</p> <p>Denis A. Wiesenburg</p>														
<p>EXPERIMENTAL VALUES:</p> <table border="1" data-bbox="414 537 971 803"> <thead> <tr> <th colspan="2">Pressure</th> <th rowspan="2">molality/mol kg⁻¹</th> </tr> <tr> <th><i>p</i>₁/psia</th> <th><i>p</i>₁/kPa</th> </tr> </thead> <tbody> <tr> <td>350</td> <td>2410</td> <td>0.0263</td> </tr> <tr> <td>550</td> <td>3790</td> <td>0.0400</td> </tr> <tr> <td>750</td> <td>5170</td> <td>0.0514</td> </tr> </tbody> </table> <p>The compiler calculated the pressures in kPa.</p>		Pressure		molality/mol kg ⁻¹	<i>p</i> ₁ /psia	<i>p</i> ₁ /kPa	350	2410	0.0263	550	3790	0.0400	750	5170	0.0514
Pressure		molality/mol kg ⁻¹													
<i>p</i> ₁ /psia	<i>p</i> ₁ /kPa														
350	2410	0.0263													
550	3790	0.0400													
750	5170	0.0514													
<p>AUXILIARY INFORMATION</p>															
<p>METHOD/APPARATUS/PROCEDURE:</p> <p>Solubility determinations were made using a titanium-lined chamber within a stainless steel reaction vessel jacketed by a water bath for temperature control. System pressure was set by controlling the input and output of methane within the chamber's headspace. The vessel was rocked for 3 h to allow equilibration between the methane and sea water. The amount of gas present in the sea water at equilibrium was measured by subsampling the sea water at system pressure and flash evaporating it into a second calibrated, evacuated expansion volume. The pressure of the released gas was measured with a manometer accurate to 0.7 kPa. The gas volume and pressure change were used to compute the moles of gas released and corrections were made for the small amount of dissolved methane not released during flashing. The molalities were not corrected for the volume of dissolved gas.</p>	<p>SOURCE AND PURITY OF MATERIALS:</p> <p>(1) Methane. Matheson ultra high purity, minimum 99.97%.</p> <p>(2) Sea Water.</p> <p>ESTIMATED ERROR:</p> <p>δT/K = 0.1</p> <p>δP/kPa = 7</p> <p>REFERENCES:</p>														