

COMPONENTS:	EVALUATOR:																				
(1) Methane; CH ₄ ; [74-82-8]																					
(2) Sulfur compounds	H. Lawrence Clever																				
Carbon disulfide; CS ₂ ; [75-15-0]	Chemistry Department																				
Sulfinylbismethane or dimethyl-	Emory University																				
sulfoxide; C ₂ H ₆ SO; [67-68-5]	Atlanta, GA 30322 USA																				
	1985, April																				
CRITICAL EVALUATION:																					
<p>Both Kobatake and Hildebrand (ref 1) and Powell (ref 2) report the solubility of methane in carbon disulfide as a function of temperature. The studies were carried out in the same laboratory. There is a brief comment in the Powell paper saying his apparatus is capable of better accuracy than the earlier work. Powells mole fraction solubility values range from 4.7 to 1.3 per cent smaller than the Kobatake and Hildebrand values as the temperature increases from 288 to 308 K. We class both data sets as tentative, but prefer the Powell data on the basis of his statement.</p>																					
<p>Powell gives only the 298.15 K solubility value in his paper along with the value of 'R(slope)' from the log x_1 vs. log T straight line. The solubility values calculated from his information are consistent with the thermodynamic changes for the transfer of one mole of methane from the gas at 0.101325 MPa to the infinitely dilute solution of</p>																					
$\Delta H_1^0/kJ \text{ mol}^{-1} = -1.04 \quad \text{and} \quad \Delta S_1^0/J \text{ K}^{-1} \text{ mol}^{-1} = -58.9$																					
<p>The smoothed solubility values were calculated from the information in Powell's paper.</p>																					
<p>Table 1. The solubility of methane in carbon disulfide. Tentative values of the mole fraction solubility as a function of temperature at a methane partial pressure of 0.101325 MPa.</p>																					
<table border="1"> <thead> <tr> <th data-bbox="141 949 317 979">T/K</th> <th data-bbox="317 949 538 979">10³x₁</th> <th data-bbox="538 949 686 979">T/K</th> <th data-bbox="686 949 1252 979">10³x₁</th> </tr> </thead> <tbody> <tr> <td data-bbox="141 979 317 1010">273.15</td> <td data-bbox="317 979 538 1010">1.322</td> <td data-bbox="538 979 686 1010">293.15</td> <td data-bbox="686 979 1252 1010">1.281</td> </tr> <tr> <td data-bbox="141 1010 317 1040">278.15</td> <td data-bbox="317 1010 538 1040">1.311</td> <td data-bbox="538 1010 686 1040">298.15</td> <td data-bbox="686 1010 1252 1040">1.272</td> </tr> <tr> <td data-bbox="141 1040 317 1070">283.15</td> <td data-bbox="317 1040 538 1070">1.301</td> <td data-bbox="538 1040 686 1070">303.15</td> <td data-bbox="686 1040 1252 1070">1.263</td> </tr> <tr> <td data-bbox="141 1070 317 1120">288.15</td> <td data-bbox="317 1070 538 1120">1.291</td> <td data-bbox="538 1070 686 1120">308.15</td> <td data-bbox="686 1070 1252 1120">1.254</td> </tr> </tbody> </table>		T/K	10 ³ x ₁	T/K	10 ³ x ₁	273.15	1.322	293.15	1.281	278.15	1.311	298.15	1.272	283.15	1.301	303.15	1.263	288.15	1.291	308.15	1.254
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<p>Dymond (ref 3) and Lenoir <i>et al.</i> (ref 4) report the solubility of methane in sulfinylbismethane (dimethylsulfoxide) at 298.15 K by different methods. Dymond used a volumetric method. Lenoir <i>et al.</i> used a GLC-retention time method with the methane at a relatively low partial pressure.</p>																					
<p>The mole fraction solubility values calculated at 298.15 K for a methane partial pressure of 0.101325 MPa are:</p>																					
<p>Dymond 3.86 x 10⁻⁴</p>																					
<p>Lenoir <i>et al.</i> 4.10 x 10⁻⁴</p>																					
<p>The values differ by about 6 percent which is satisfactory for such different methods. Both values are classed as tentative, but the Dymond value is preferred when actually working at atmospheric pressure (0.101325 MPa).</p>																					
REFERENCES:																					
1. Kobatake, Y.; Hildebrand, J. H. <i>J. Phys. Chem.</i> <u>1961</u> , <i>65</i> , 331-5.																					
2. Powell, R. J. <i>J. Chem. Eng. Data</i> <u>1972</u> , <i>17</i> , 302-4.																					
3. Dymond, J. H. <i>J. Phys. Chem.</i> <u>1967</u> , <i>71</i> , 1829-31.																					
4. Lenoir, J.-Y.; Renault, P.; Renon, H. <i>J. Chem. Eng. Data</i> <u>1971</u> , <i>16</i> , 340-2.																					

COMPONENTS: (1) Methane; CH ₄ ; [74-82-8] (2) Carbon disulfide; CS ₂ ; [75-15-0]		ORIGINAL MEASUREMENTS: Powell, R. J. <i>J. Chem. Eng. Data</i> <u>1972</u> , <i>17</i> , 302 - 304.		
VARIABLES: T/K: 273.15 - 303.15 p ₁ /kPa: 101.325 (1 atm)		PREPARED BY: P. L. Long H. L. Clever		
EXPERIMENTAL VALUES:				
T/K	Mol Fraction 10 ⁴ x ₁	Bunsen Coefficient α/cm ³ (STP) cm ⁻³ atm ⁻¹	Ostwald Coefficient L/cm ³ cm ⁻³	N = R $\frac{\Delta \log x_1}{\Delta \log T}$
298.15	12.72	0.471	0.514	-0.87
<p>The Bunsen and Ostwald coefficients were calculated by the compiler.</p> <p>The author states that the solubility measurements were made over the temperature interval of about 273.15 to 303.15 K, but only the solubility value at 298.15 K was given in the paper. The slope, N=R(Δlog x₁/Δlog T), was given.</p> <p>Smoothed Data: For use between 273.15 and 303.15 K</p> <p>The smoothed data were calculated by the compiler from the slope, N, in the form</p> $\log x_1 = \log (12.72 \times 10^{-4}) - (0.87/R) \log (T/298.15)$ <p>with R = 1.9872 cal K⁻¹ mol⁻¹.</p>				
T/K	Mol Fraction 10 ³ x ₁			
273.15	1.322			
278.15	1.311			
283.15	1.301			
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298.15	1.272			
303.15	1.263			
AUXILIARY INFORMATION				
METHOD/APPARATUS/PROCEDURE: The apparatus is the Dymond and Hildebrand (1) apparatus which uses an all glass pumping system to spray slugs of degassed solvent into the gas. The amount of gas dissolved is calculated from the initial and final pressures. The solvent is degassed by freezing, pumping, and followed by boiling under reduced pressure.		SOURCE AND PURITY OF MATERIALS: (1) Methane. Source not given. Stated to be manufacturer's research grade, dried over CaCl ₂ before use. (2) Carbon disulfide. Source not given. Stated to be manufacturer's spectrochemical grade.		
		ESTIMATED ERROR: $\delta x_1/x_1 = \pm 0.002$ $\delta N/\text{cal K}^{-1} \text{ mol}^{-1} = \pm 0.1$		
		REFERENCES: 1. Dymond, J. H.; Hildebrand, J. H. <i>Ind. Eng. Chem. Fundam.</i> <u>1967</u> , <i>6</i> , 130.		

COMPONENTS: (1) Methane; CH ₄ ; [74-82-8] (2) Carbon disulfide; CS ₂ ; [75-15-0]		ORIGINAL MEASUREMENTS: Kobatake, Y.; Hildebrand, J. H. <i>J. Phys. Chem.</i> <u>1961</u> , <i>65</i> , 331 - 335.																										
VARIABLES: T/K: 288.16 - 307.95 P/kPa: 101.325 (1 atm)		PREPARED BY: M. E. Derrick H. L. Clever																										
EXPERIMENTAL VALUES:																												
<table border="1"> <thead> <tr> <th colspan="2">Temperature</th> <th>Mol Fraction</th> <th>Bunsen Coefficient</th> <th>Ostwald Coefficient</th> </tr> <tr> <th><i>t</i>/°C</th> <th><i>T</i>/K</th> <th>10²<i>x</i>₁</th> <th>α/cm³ (STP) cm⁻³ atm⁻¹</th> <th>L/cm³ cm⁻³</th> </tr> </thead> <tbody> <tr> <td>15.01</td> <td>288.16</td> <td>1.351</td> <td>0.506</td> <td>0.534</td> </tr> <tr> <td>25.00</td> <td>298.15</td> <td>1.312</td> <td>0.486</td> <td>0.530</td> </tr> <tr> <td>34.80</td> <td>307.95</td> <td>1.269</td> <td>0.464</td> <td>0.523</td> </tr> </tbody> </table>				Temperature		Mol Fraction	Bunsen Coefficient	Ostwald Coefficient	<i>t</i> /°C	<i>T</i> /K	10 ² <i>x</i> ₁	α/cm ³ (STP) cm ⁻³ atm ⁻¹	L/cm ³ cm ⁻³	15.01	288.16	1.351	0.506	0.534	25.00	298.15	1.312	0.486	0.530	34.80	307.95	1.269	0.464	0.523
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The Bunsen and Ostwald coefficients were calculated by the compiler. Smoothed Data: For use between 288.16 and 307.95 K. $\ln x_1 = -7.5787 + 2.8034/(T/100K)$ The standard error about the regression line is 3.59 x 10 ⁻⁶ .																												
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AUXILIARY INFORMATION																												
METHOD/APPARATUS/PROCEDURE: The apparatus consists of a gas measuring buret, an absorption pipet, and a reservoir for the solvent. The buret is thermostated at 25°C, the pipet at any temperature from 5 to 30 °C. The pipet contains an iron bar in glass for magnetic stirring. The pure solvent is degassed by freezing with liquid nitrogen, evacuating, then boiling with a heat lamp. The degassing process is repeated three times. The solvent is flowed into the pipet where it is again boiled for final degassing. Manipulation of the apparatus is such that the solvent never comes in contact with stopcock grease. The liquid in the pipet is sealed off by mercury. Its volume is the difference between the capacity of the pipet and the volume of mercury that confines it. Gas is admitted into the pipet. Its exact amount is determined by P-V measurements in the buret before and after introduction of the gas into the pipet. The stirrer is set in motion. Equilibrium is attained within 24 hours.		SOURCE AND PURITY OF MATERIALS: (1) Methane. Matheson Co., Inc. Research grade. Dried by passage over P ₂ O ₅ followed by multiple trap vaporization and evacuation at liquid N ₂ temperature. (2) Carbon disulfide. Mallinckrodt Chemical Works. Analytical Reagent grade. Shaken successively with Hg and HgCl ₂ , filtered, distilled, and stored over Hg more than 5 days before use.																										
		ESTIMATED ERROR: $\delta T/K = 0.02$ $\delta x_1/x_1 = 0.003$																										
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COMPONENTS: (1) Methane; CH ₄ ; [74-82-8] (2) Sulfinylbismethane or dimethyl sulfoxide; C ₂ H ₆ OS (CH ₃ SOCH ₃); [67-68-5]	ORIGINAL MEASUREMENTS: Dymond, J. H. <i>J. Phys. Chem.</i> <u>1967</u> , <i>71</i> , 1829-1831.								
VARIABLES: <i>T</i> /K: 298.15 <i>p</i> /kPa: 101.325 (1 atm)	PREPARED BY: M. E. Derrick H. L. Clever								
EXPERIMENTAL VALUES: <table border="1" data-bbox="216 533 1060 656"> <thead> <tr> <th><i>T</i>/K</th> <th>Mol Fraction $10^4 x_1$</th> <th>Bunsen Coefficient $\alpha/\text{cm}^3(\text{STP})\text{cm}^{-3}\text{atm}^{-1}$</th> <th>Ostwald Coefficient $L/\text{cm}^3\text{cm}^{-3}$</th> </tr> </thead> <tbody> <tr> <td>298.15</td> <td>3.86</td> <td>0.121</td> <td>0.132</td> </tr> </tbody> </table> <p>The Bunsen and Ostwald coefficients were calculated by the compiler.</p>		<i>T</i> /K	Mol Fraction $10^4 x_1$	Bunsen Coefficient $\alpha/\text{cm}^3(\text{STP})\text{cm}^{-3}\text{atm}^{-1}$	Ostwald Coefficient $L/\text{cm}^3\text{cm}^{-3}$	298.15	3.86	0.121	0.132
<i>T</i> /K	Mol Fraction $10^4 x_1$	Bunsen Coefficient $\alpha/\text{cm}^3(\text{STP})\text{cm}^{-3}\text{atm}^{-1}$	Ostwald Coefficient $L/\text{cm}^3\text{cm}^{-3}$						
298.15	3.86	0.121	0.132						
AUXILIARY INFORMATION									
METHOD/APPARATUS/PROCEDURE: The liquid is saturated with the gas at a gas partial pressure of 1 atm. The apparatus is that described by Dymond and Hildebrand (1). The apparatus uses an all-glass pumping system to spray slugs of degassed solvent into the gas. The amount of gas dissolved is calculated from the initial and final gas pressure.	SOURCE AND PURITY OF MATERIALS: (1) Methane. Phillips Petroleum Co. Dried. (2) Dimethylsulfoxide. Matheson, Coleman and Bell Co. Spectro-quality. Dried and fractionally frozen. m.p. 18.37°C.								
	ESTIMATED ERROR:								
	REFERENCES: 1. Dymond, J.; Hildebrand, J. H. <i>Ind. Eng. Chem. Fundam.</i> <u>1967</u> , <i>6</i> , 130.								

COMPONENTS: 1. Methane; CH ₄ ; [74-82-8] 2. Sulfinylbismethane, (Dimethylsulfoxide); C ₂ H ₆ SO; [67-68-5]	ORIGINAL MEASUREMENTS: Lenoir, J-Y; Renault, P.; Renon, H. <i>J. Chem. Eng. Data</i> , <u>1971</u> , 16, 340-2.						
VARIABLES:	PREPARED BY: C. L. Young						
EXPERIMENTAL VALUES: <table border="1" data-bbox="303 605 1201 737"> <thead> <tr> <th>T/K</th> <th>Henry's constant $H_{\text{CH}_4}/\text{atm}$</th> <th>Mole fraction at 1 atm* x_{CH_4}</th> </tr> </thead> <tbody> <tr> <td>298.2</td> <td>2440</td> <td>0.000410</td> </tr> </tbody> </table> <p>* Calculated by compiler assuming a linear function of P_{CH_4} vs x_{CH_4}, i.e., $x_{\text{CH}_4}(1 \text{ atm}) = 1/H_{\text{CH}_4}$.</p>		T/K	Henry's constant $H_{\text{CH}_4}/\text{atm}$	Mole fraction at 1 atm* x_{CH_4}	298.2	2440	0.000410
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298.2	2440	0.000410					
AUXILIARY INFORMATION							
METHOD/APPARATUS/PROCEDURE: A conventional gas-liquid chromatographic unit fitted with a thermal conductivity detector was used. The carrier gas was helium. The value of Henry's law constant was calculated from the retention time. The value applies to very low partial pressures of gas and there may be a substantial difference from that measured at 1 atm. pressure. There is also considerable uncertainty in the value of Henry's constant since surface adsorption was not allowed for although its possible existence was noted.	SOURCE AND PURITY OF MATERIALS: (1) L'Air Liquide sample, minimum purity 99.9 molar per cent. (2) Touzart and Matignon or Serlabo sample, purity 99 mole per cent.						
ESTIMATED ERROR: $\delta T/K = \pm 0.1$; $\delta H/\text{atm} = \pm 6\%$ (estimated by compiler).							
REFERENCES:							

COMPONENTS: (1) Methane; CH ₄ ; [74-82-8] (2) Cyclic amines; C ₄ H ₉ N, C ₅ H ₅ N, and C ₅ H ₁₀ N	ORIGINAL MEASUREMENTS: Guerry, D. Jr. Ph.D. thesis, 1944 Vanderbilt University Nashville, TN Thesis Director: L. J. Bircher																																								
VARIABLES: T/K: 293.15, 298.15 P/kPa: 101.325 (1 atm)	PREPARED BY: H. L. Clever																																								
EXPERIMENTAL VALUES: <table border="1" data-bbox="274 511 1029 899"> <thead> <tr> <th>T/K</th> <th>Mol Fraction $x_1 \times 10^4$</th> <th>Bunsen Coefficient α</th> <th>Ostwald Coefficient L</th> </tr> </thead> <tbody> <tr> <td colspan="4" style="text-align: center;">Pyrrolidine; C₄H₉N; [123-75-1]</td> </tr> <tr> <td>293.15</td> <td>14.4</td> <td>0.389</td> <td>0.417</td> </tr> <tr> <td>298.15</td> <td>14.1</td> <td>0.379</td> <td>0.414</td> </tr> <tr> <td colspan="4" style="text-align: center;">Pyridine; C₅H₅N; [110-86-1]</td> </tr> <tr> <td>293.15</td> <td>11.2</td> <td>0.313</td> <td>0.336</td> </tr> <tr> <td>298.15</td> <td>11.2</td> <td>0.310</td> <td>0.338</td> </tr> <tr> <td colspan="4" style="text-align: center;">Piperidine; C₅H₁₁N; [110-89-1]</td> </tr> <tr> <td>293.15</td> <td>18.8</td> <td>0.427¹</td> <td>0.459</td> </tr> <tr> <td>298.15</td> <td>19.0</td> <td>0.430</td> <td>0.469</td> </tr> </tbody> </table> <p>The Ostwald coefficients were calculated by the compiler.</p> <p>¹ The value in the published abstract of the thesis is 0.472. However, the value 0.427 is consistent with the mole fraction value.</p>		T/K	Mol Fraction $x_1 \times 10^4$	Bunsen Coefficient α	Ostwald Coefficient L	Pyrrolidine; C ₄ H ₉ N; [123-75-1]				293.15	14.4	0.389	0.417	298.15	14.1	0.379	0.414	Pyridine; C ₅ H ₅ N; [110-86-1]				293.15	11.2	0.313	0.336	298.15	11.2	0.310	0.338	Piperidine; C ₅ H ₁₁ N; [110-89-1]				293.15	18.8	0.427 ¹	0.459	298.15	19.0	0.430	0.469
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METHOD/APPARATUS/PROCEDURE: A Van Slyke-Neill Manometric Apparatus manufactured by the Eimer and Amend Co. was used. The procedure of Van Slyke (1) for pure liquids was modified (2) so that small solvent samples (2 cm ³) could be used with almost complete recovery of the sample. An improved temperature control system was used.	SOURCE AND PURITY OF MATERIALS: Pyrrolidine. Pyrrole was prepared and catalytically reduced to pyrrolidine. B.p. (750 mmHg) t/°C 88.12 - 88.26 (corr.). Pyridine. Mallinckrodt Chemical Co. Purified and distilled. B.p. (743.9 mmHg) t/°C 114.96 - 115.06 (corr.). Piperidine. Part was a commercial sample (Eastman Kodak Co.), part prepared by reduction of pyridine. B.p. (752.4 mmHg) t/°C 106.00 - 106.17.																																								
SOURCE AND PURITY OF MATERIALS: (1) Methane. Prepared by hydrolysis of crystalline methyl Grignard reagent. Passed through conc. H ₂ SO ₄ , solid KOH, and Dririte. (2) Cyclic amines. The pyridine and pyrrolidine were distilled from BaO under a N ₂ atmosphere. The piperidine was distilled from KOH under a N ₂ atmosphere. Experimental data on refractive index, density and vapor pressure are in the thesis.	ESTIMATED ERROR: $\delta T/K = 0.05$ REFERENCES: 1. Van Slyke, D. D. <i>J. Biol. Chem.</i> 1939, 130, 545. 2. Ijams, C. C. Ph.D. thesis, 1941 Vanderbilt University																																								

<p>COMPONENTS:</p> <ol style="list-style-type: none"> 1. Methane; CH₄; [74-82-8] 2. Cyclohexylamine; C₆H₁₁N; [108-91-8] 	<p>ORIGINAL MEASUREMENTS:</p> <p>Keevil, T.A.; Taylor, D.R.; Streitwieser, A.</p> <p><i>J. Chem. Engng. Data.</i> <u>1978</u>, <i>23</i>, 237-239.</p>				
<p>VARIABLES:</p>	<p>PREPARED BY:</p> <p>C.L. Young</p>				
<p>EXPERIMENTAL VALUES:</p> <p style="text-align: center;">Partial pressure of methane = 1 atm = 101.3 kPa.</p> <table style="width: 100%; border: none;"> <thead> <tr> <th style="text-align: center; width: 50%;">T/K</th> <th style="text-align: center; width: 50%;">Mole fraction of methane, x_{CH_4}</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">303.2</td> <td style="text-align: center;">0.00192</td> </tr> </tbody> </table>		T/K	Mole fraction of methane, x_{CH_4}	303.2	0.00192
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303.2	0.00192				
<p>AUXILIARY INFORMATION</p>					
<p>METHOD/APPARATUS/PROCEDURE:</p> <p>Volumetric apparatus of moderate accuracy. Solvent confined to glass bulb and known amount of gas added. Pressure measured using a mercury manometer together with a null point manometer in which the gas pressure was balanced by dry air. Details in source.</p>	<p>SOURCE AND PURITY OF MATERIALS:</p> <ol style="list-style-type: none"> 1. No details given. 2. Degassed and dried over lithium cyclohexylamide. <p>ESTIMATED ERROR:</p> <p style="text-align: center;">$\delta T/K = \pm 0.1$; $\delta x_{\text{CH}_4} = \pm 1\%$</p> <p>REFERENCES:</p>				