COMPONENTS:
(1) Methane; CH₄; [74-82-8]
(2) Sulfur compounds
   Carbon disulfide; CS₂; [75-15-0]
   Sulfinylbismethane or dimethylsulfoxide; C₂H₆SO; [67-68-5]

EVALUATOR:
H. Lawrence Clever
Chemistry Department
Emory University
Atlanta, GA 30322 USA
1985, April

CRITICAL EVALUATION:

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.

Powell gives only the 298.15 K solubility value in his paper along with the value of 'R(slope)' from the log \( x_j \) 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

\[
\Delta H^\circ/KJ/mol^{-1} = -1.04 \quad \text{and} \quad \Delta S^\circ/KJ/Kmol^{-1} = -58.9
\]

The smoothed solubility values were calculated form the information in Powell's paper.

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.

<table>
<thead>
<tr>
<th>T/K</th>
<th>10³x₁</th>
<th>T/K</th>
<th>10³x₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15</td>
<td>1.322</td>
<td>293.15</td>
<td>1.281</td>
</tr>
<tr>
<td>278.15</td>
<td>1.311</td>
<td>298.15</td>
<td>1.272</td>
</tr>
<tr>
<td>283.15</td>
<td>1.301</td>
<td>303.15</td>
<td>1.263</td>
</tr>
<tr>
<td>288.15</td>
<td>1.291</td>
<td>308.15</td>
<td>1.254</td>
</tr>
</tbody>
</table>

Dymond (ref 3) and Lenoir et al. (ref 4) report the solubility of methane in sulfinylbismethane (dimethylsulfoxide) at 298.15 K by different methods. Dymond used a volumetric method. Lenoir et al. used a GLC-retention time method with the methane at a relatively low partial pressure.

The mole fraction solubility values calculated at 298.15 K for a methane partial pressure of 0.101325 MPa are:

- Dymond 3.86 x 10⁻⁴
- Lenoir et al. 4.10 x 10⁻⁴

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).

REFERENCES:
Organic Substances Containing Sulfur

COMPONENTS:
1. Methane; CH₄; [74-82-8]
2. Carbon disulfide; CS₂; [75-15-0]

ORIGINAL MEASUREMENTS:
Powell, R. J.

VARIABLES:
T/K: 273.15 - 303.15
P_J/kPa: 101.325 (1 atm)

PREPARED BY:
P. L. Long
H. L. Clever

EXPERIMENTAL VALUES:

<table>
<thead>
<tr>
<th>T/K</th>
<th>Mol Fraction 10⁴ x₁</th>
<th>Bunsen Coefficient a/cm³(STP) cm⁻³ atm⁻¹</th>
<th>Ostwald Coefficient L/cm³ cm⁻³</th>
<th>N = R(Δlog x₁/Δlog T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>12.72</td>
<td>0.471</td>
<td>0.514</td>
<td>-0.87</td>
</tr>
</tbody>
</table>

The Bunsen and Ostwald coefficients were calculated by the compiler.

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, \( N = R \frac{\Delta \log x_1}{\Delta \log T} \), was given.

Smoothed Data: For use between 273.15 and 303.15 K

The smoothed data were calculated by the compiler from the slope, N, in the form

\[ \log x_1 = \log (12.72 \times 10^{-4}) - (0.87/R) \log (T/298.15) \]

with \( R = 1.9872 \) cal K⁻¹ mol⁻¹.

<table>
<thead>
<tr>
<th>T/K</th>
<th>Mol Fraction 10³ x₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15</td>
<td>1.322</td>
</tr>
<tr>
<td>278.15</td>
<td>1.311</td>
</tr>
<tr>
<td>283.15</td>
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<tr>
<td>293.15</td>
<td>1.281</td>
</tr>
<tr>
<td>298.15</td>
<td>1.272</td>
</tr>
<tr>
<td>303.15</td>
<td>1.263</td>
</tr>
</tbody>
</table>

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 CaCl₂ before use.
2. Carbon disulfide. Source not given. Stated to be manufacturer's spectrochemical grade.

ESTIMATED ERROR:
\[ \delta x_1/x_1 = \pm 0.002 \]
\[ \delta N/cal K^{-1} mol^{-1} = \pm 0.1 \]

REFERENCES:
Organic Substances Containing Sulfur

COMPONENTS:
(1) Methane; CH₄ [74-82-8]
(2) Carbon disulfide; CS₂ [75-15-0]

ORIGINAL MEASUREMENTS:
Kobatake, Y.; Hildebrand, J. H.

VARIABLES:
T/K: 288.16 - 307.95
P/kPa: 101.325 (1 atm)

PREPARED BY:
M. E. Derrick
H. L. Clever

EXPERIMENTAL VALUES:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Mol Fraction</th>
<th>Bunsen Coefficient (a/cm³(STP) cm³ atm⁻¹)</th>
<th>Ostwald Coefficient (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>
</tr>
<tr>
<td>25.00</td>
<td>298.15</td>
<td>1.312</td>
<td>0.486</td>
</tr>
<tr>
<td>34.80</td>
<td>307.95</td>
<td>1.269</td>
<td>0.464</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>T/K</th>
<th>Mol Fraction</th>
<th>10²x₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>288.15</td>
<td>1.352</td>
<td></td>
</tr>
<tr>
<td>298.15</td>
<td>1.309</td>
<td></td>
</tr>
<tr>
<td>308.15</td>
<td>1.270</td>
<td></td>
</tr>
</tbody>
</table>

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 P₂O₅ followed by multiple trap vaporization and evacuation at liquid N₂ temperature.
(2) Carbon disulfide. Mallinckrodt Chemical Works. Analytical Reagent grade. Shaken successively with Hg and HgCl₂, filtered, distilled, and stored over Hg more than 5 days before use.

ESTIMATED ERROR:
\[
\delta T/K = 0.02 \\
\delta x₁/x₁ = 0.003
\]

REFERENCES:
Organic Substances Containing Sulfur

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.

VARIABLES:

\[
\begin{align*}
T/K & : 298.15 \\
p/kPa & : 101.325 \text{ (1 atm)}
\end{align*}
\]

PREPARED BY:
M. E. Derrick
H. L. Clever

EXPERIMENTAL VALUES:

<table>
<thead>
<tr>
<th>T/K</th>
<th>Mol Fraction $10^x_f$</th>
<th>Bunsen Coefficient $a$/cm$^3$(STP)cm$^{-3}$atm$^{-1}$</th>
<th>Ostwald Coefficient L/cm$^3$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>

The Bunsen and Ostwald coefficients were calculated by the compiler.

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:


(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.
### COMPONENTS:

1. Methane; CH₄; [74-82-8]
2. Sulfanylbismethane, (dimethyl-sulfoxide); C₂H₆SO; [67-68-5]

### ORIGINAL MEASUREMENTS:

Lenoir, J-Y; Renault, P.; Renon, H.  

### VARIABLES:

### EXPERIMENTAL VALUES:

<table>
<thead>
<tr>
<th>T/K</th>
<th>Henry's constant $P_{CH_4}$/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>

* Calculated by compiler assuming a linear function of $P_{CH_4}$ vs $x_{CH_4}$, i.e., $x_{CH_4}(1 \text{ atm}) = 1/P_{CH_4}$.

### 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:**

$\delta T/K = \pm 0.1; \delta P_{CH_4}/atm = \pm 6\%$

(estimated by compiler).

**REFERENCES:**
COMPONENTS:
(1) Methane; CH₄; [74-82-8]
(2) Cyclic amines; C₄H₉N, C₅H₅N, and C₅H₁₀N

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>
<thead>
<tr>
<th>T/K</th>
<th>Mol Fraction x₁ x₁₀⁴</th>
<th>Bunsen Coefficient α</th>
<th>Ostwald Coefficient L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pyrrolidine; C₄H₉N; [123-75-1]</td>
<td></td>
<td></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></td>
<td>Pyridine; C₅H₅N; [110-86-1]</td>
<td></td>
<td></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></td>
<td>Piperidine; C₅H₁₁N; [110-89-1]</td>
<td></td>
<td></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>

The Ostwald coefficients were calculated by the compiler.

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.

AUXILIARY INFORMATION

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 cm³) could be used with almost complete recovery of the sample.
An improved temperature control system was used.

SOURCE AND PURITY OF MATERIALS:
(2) Cyclic amines. The pyridine and pyrrolidine were distilled from BaO under a N₂ atmosphere. The piperidine was distilled from KOH under a N₂ atmosphere.
Experimental data on refractive index, density and vapor pressure are in the thesis.

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. Mallincrodt 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.

ESTIMATED ERROR:
δT/K = 0.05

REFERENCES:
1. Van Slyke, D. D.
   J. Biol. Chem. 1939, 130, 545.
2. Ijams, C. C.
   Ph.D. thesis, 1941
   Vanderbilt University
<table>
<thead>
<tr>
<th>COMPONENTS:</th>
<th>ORIGINAL MEASUREMENTS:</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. Cyclohexylamine; C₆H₁₁N; [108-91-8]</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VARIABLES:</th>
<th>PREPARED BY:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C.L. Young</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>EXPERIMENTAL VALUES:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial pressure of methane = 1 atm = 101.3 kPa.</td>
</tr>
</tbody>
</table>

\[
\begin{array}{|c|c|}
\hline
T/K & \text{Mole fraction of methane, } x_{\text{CH}_4} \\
\hline
303.2 & 0.00192 \\
\hline
\end{array}
\]

**AUXILIARY INFORMATION**

**METHOD/APPARATUS/PROCEDURE:**

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.

**SOURCE AND PURITY OF MATERIALS:**

1. No details given.
2. Degassed and dried over lithium cyclohexylamide.

**ESTIMATED ERROR:**

\[ \delta T/K = \pm 0.1; \ \delta x_{\text{CH}_4} = \pm 1\% \]

**REFERENCES:**