COMPONENTS:	EVALUATOR:
(1) Methane; CH_4; [74-82-8] (2) Water-d₂; D_2O; [7789-20-0]	Rubin Battino Department of Chemistry Wright State University Dayton, OH 45435 USA June 1984

CRITICAL EVALUATION:

The Solubility of Methane in Water-d₂. $[CH_4 + D_2O]$.

Three laboratories report the solubility of methane in water-d₂. Two of the studies are at a methane partial pressure of about atmospheric over the 278 - 318 K temperature range (1, 2), and the third paper (3) covers the 278 - 518 K temperature interval at partial pressures up to 3.5 MPa. All three laboratories present data of similar precision.

The data have been treated to obtain three smoothing equations. The first equation is from a linear regression of the mole fraction solubility at a partial pressure of 0.101325 MPa over the 278 - 318 K temperature range from papers 1 and 2.

$$\ln x_1 = -55.6499 + 73.9115/\tau + 18.6065 \ln \tau \qquad (1)$$

where $\tau = T/100$ K. The equation has a standard deviation of 0.013 in $\ln x_1$ or about 1.0 per cent in x_1 at the middle of the temperature interval.

The second equation is the equation used to construct the table of tentative solubility values. For this equation the pressure dependent data of Crovetto et al.(3) were extraplolated to a methane partial pressure of 0.101325 MPa and combined with the atmospheric solubility data from papers 1 and 2 to obtain the equation

$$\ln x_1 = -120.894 + 164.161/\tau + 67.1928 \ln \tau - 6.6750 \tau \qquad (2)$$

for the 278 - 518 K temperature interval for a methane partial pressure of 0.101325 MPa. The standard deviation in $\ln x_1$ is 0.017 which is about 1.7 per cent in x_1 at the middle of the temperature range.

The third equation is from a linear regression of the mole fraction methane solubility as a function of temperature and pressure from paper 3.

$$\ln x_1 = -55.6332 + 75.0373/\tau + 20.3725 \ln \tau + 0.848085 \ln (p/\text{MPa}) \quad (3)$$

where p is the methane fugacity and $\tau = T/100$ K. The standard deviation in $\ln x_1$ is 0.029 which is about 0.9 per cent in x_1 at the middle of the temperature range. The equation is for a temperature range of 278 - 518 K and a pressure (methane fugacity) up to 3.5 MPa.

Equation 2 is the evaluator's choice to represent the mole fraction solubility of methane in water-d₂ (heavy water) for the 278 - 518 K temperature range at a methane partial pressure of 0.101325 MPa. Values of

COMPONENTS:	EVALUATOR:
(1) Methane; CH_4; [74-82-8]	Rubin Battino
	Department of Chemistr
(2) Water-d$_2$; D_2O; [7789-20-0]	Wright State University
	Dayton, OH 45435 USA
	June 1984

CRITICAL EVALUATION:

the solubility and thermodynamic changes based on Equation 2 are given

below in Table 1.

Table 1.   The solubility of methane in water-d$_2$ at 25 K intervals over the
the 273.15 to 573.15 K temperature interval at a methane partial
pressure of 0.101325 MPa.

          Thermodynamic changes for the transfer of one mole of methane
from the gas pahse at a partial pressure of 0.101325 MPa to the
infinitely dilute solution.

T/K	Mol Fraction $10^5 x_1$	Ostwald Coefficient $10^2 L/cm^3 cm^{-3}$	$\Delta \overline{G}_1^0/$ kJ mol^{-1}	$\Delta \overline{H}_1^0/$ kJ mol^{-1}	$\Delta \overline{S}_1^0/$ J K^{-1} mol^{-1}	$\Delta \overline{C}_{p_1}^0/$ J K^{-1}mol^{-1}
273.15	5.170	5.789	22.415	-21.576	-161.1	282.7
298.15	2.636	3.213	26.137	-14.823	-137.4	257.5
323.15	1.824	2.388	29.317	- 8.702	-117.7	232.2
348.15	1.555	2.164	32.047	- 3.212	-101.3	206.0
373.15	1.527	2.239	34.405	+ 1.646	- 87.8	181.7
398.15	1.648	2.526	36.458	5.873	- 76.8	156.5
423.15	1.890	3.007	38.264	9.468	- 68.1	131.2
448.15	2.250	3.686	39.877	12.433	- 61.2	105.9
473.15	2.729	4.570	41.341	14.766	- 56.2	80.7
498.15	3.333	5.654	42.698	16.467	- 52.7	55.4
523.15	4.057	6.904	43.985	17.537	- 50.6	30.2
548.15	4.890	8.246	45.236	17.976	- 49.7	4.9
573.15	5.806	9.552	46.482	17.783	- 50.1	-20.3

The Ostwald coefficient is defined as volume of gas per volume of
pure solvent.

There is a minimum in the mole fraction solubility near a temperature
of 373.15 K.

REFERENCES.

1. Ben-Naim, A.; Wilf, J.; Yaacobi, M. *J. Phys. Chem.* <u>1973</u>, *77*, 95-102.

2. Cosgrove, B. A.; Walkley, J. *J. Chromatogr.* <u>1981</u>, *216*, 161-7.

3. Crovetto, R.; Fernandez-Prini, R.; Japas, M. L.
J. Chem. Phys. <u>1982</u>, *76*, 1077-86.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methane; CH$_4$; [74-82-8] (2) Water-d$_2$; D$_2$O; [7789-20-0]	Ben-Naim, A.; Wilf, J.; Jaacobi, M. *J. Phys. Chem.* <u>1973</u>, *77*, 95 102.
VARIABLES: T/K = 278.15 - 298.15 P_1/kPa = 101.325	PREPARED BY: H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Mol Fraction	Ostwald Coefficient
t/^{0}C	T/K	$10^5 x_1$	L/cm^3 cm^{-3}
5	278.15	4.36	0.0549
10	283.15	3.79	0.0485
15	288.15	3.33	0.0434
20	293.15	2.97	0.0393
25	298.15	2.68	0.0360

The compiler added the Kelvin temperatures.

The compiler calculated the mole fraction solubility values at 1 atm (101.325 kPa) partial pressure using real methane gas molar volumes. The use of real molar volumes inplace of ideal volumes increases the mole fraction solubility by about 0.22 percent.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The method of Ben-Naim and Baer (ref 1) was used. The apparatus was modified by the addition of Teflon stopcocks. The degassed solvent in a volumetric container is forced by a stirrer created vortex up side arms and through tubes containing solvent vapor saturated gas. The gas uptake is measured on a buret at constant pressure.	(1) Methane. Matheson Co., Inc. Purity 99.97 percent. (2) Water-d$_2$. Darmstadt. Purity 99.75 percent. Used as received.
	ESTIMATED ERROR: $\delta L/L = \pm 0.005$ (compiler)
	REFERENCES: 1. Ben-Naim, A.; Baer, S. *Trans. Faraday Soc.* <u>1963</u>, *59*, 2735.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methane; CH_4; [74-82-8]	Cosgrove, B. A.; Walkley, J.
(2) Water-d$_2$; D_2O; [7789-20-0]	*J. Chromatogr.* <u>1981</u>, *216*, 161 - 7.

VARIABLES:	PREPARED BY:
T/K = 278.15 - 318.15 p_1/kPa = 101.325	H. L. Clever

EXPERIMENTAL VALUES:

Temperature T/K	Mol Fraction $10^4 x_1$
278.15	0.4371
283.15	0.3732
288.15	----
293.15	0.3006
298.15	0.2655
303.15	0.2382
308.15	0.2172
313.15	0.2080
318.15	0.1854

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A 20 ml volume of degassed solvent (sublimation technique) is transferred to a previously evacuated (10^{-4} mmHg) saturation cell immersed in an insulated controlled (± 0.01 K) water bath. The gas is dispersed through the constantly stirred solution at 1 atm by a course, fritted glass disc. Saturation is obtained within a few hours. Prior to analysis the solution is allowed to sit under one atm gas pressure for one hour.	(1) Methane. No information. (2) Water-d$_2$. No information.

METHOD/APPARATUS/PROCEDURE (continued):

A saturated sample is withdrawn from the saturation cell using a greaseless, gas tight (2.500 ± 0.001 ml) Gilmont syringe. A 0.250 ml sample is injected to "wet" the frit. It is stripped and then four 0.500 ml samples are injected sequentially into the cell. The stripped gas is dried before entering the column. The gas is analyzed on a dual filament conductivity detector. Calibrations with pure gas are made dry before and wet after each series of runs.

ESTIMATED ERROR:

$\delta x_1/x_1$ = ± 0.015 (compiler)

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:

(1) Methane; CH$_4$; [74-82-8]
 	
(2) Water-d$_2$ or deuterium oxide; D$_2$O;
    [7789-20-0]
	Crovetto, R.; Fernández-Prini, R.;
	    Japas, M. L.
	
	J. Chem. Phys. <u>1982</u>, *76*, 1077-86.

VARIABLES:	PREPARED BY:
T/K = 298.2 - 517.5 p/MPa = 1.773 - 7.220	R. Fernández-Prini

EXPERIMENTAL VALUES:

T/K	Total Pressure p/MPa	Methane Volume Fraction, y_1	Methane Fugacity f_1/MPa	Mol Fraction $10^4 x_1$	ln(H/GPa)[1]
298.2	1.852	0.9984	1.789	4.515	1.377
323.2	1.803	0.9935	1.749	3.187	1.702
355.2	1.773	0.9716	1.696	2.565	1.885
393.3	2.062	0.9021	1.843	2.983	1.821
446.1	2.504	0.6479	1.639	3.562	1.527
474.4	4.115	0.5852	2.473	6.740	1.300
479.9	4.465	0.5704	2.625	7.374	1.270
517.5	7.220	0.4510	3.485	13.440	0.953

[1] Henry's constant, H/GPa = $(f_1$/GPa$)/x_1$.

$$\ln(H/\text{GPa}) = -9.062 + 8.148/(T/1000\text{ K}) - 1.5808/(T/1000\text{ K})^2$$
$$+ 0.0236/(T/1000\text{ K})^3 \qquad (\sigma = 0.010)$$

Thermodynamic quantities for the process CH$_4$(g, 0.1 MPa, T) →
CH$_4$(l, x_1 = 1, T) are below:

T/K	ΔG_1°/kJ mol^{-1}	ΔH_1°/kJ mol^{-1}	ΔS_1°/J (K mol)$^{-1}$	ΔC_{p1}°/J (K mol)$^{-1}$
298.2	26.20	-13.81	134.3	251
400.0	36.56	5.71	77.0	146
520.0	43.77	19.37	46.9	89

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The method involved the equilibration of the gas with the liquid and the determination of the gas mole fraction by sampling the equilibrated liquid phase. Henry's constant was obtained for each temperature by employing second virial coefficients for pure components and mixture in order to correct for non-ideal behavior in the gas phase. The gas was equilibrated in a thermostated stainless steel vessel which was continuously rocked. Weighed samples of the liquid phase were withdrawn and the amount of dissolved gas determined with a gas buret. The system was then taken to a new temperature. Pressures were measured with calibrated Bourdon gauges.	(1) Methane. Matheson (UHP) 99.97 mol %. (2) Water-d$_2$. CNEA, 99.8 mol%

	ESTIMATED ERROR: δT/K = ± 0.2 (Authors') $\quad \delta p/p$ = ± 0.003 $\qquad\qquad \delta x_1/x_1$ = ± 0.005 (T/K⩽520) $\quad \delta H/H$ = ± 0.01 - 0.02
	REFERENCES: