COMPONENTS:

(1) Methane; CH_4; [74-82-8]

(2) Water; H_2O; [7732-18-5]

EVALUATOR:

Rubin Battino
Department of Chemistry
Wright State University
Dayton, OH 45435 USA

1984, December

CRITICAL EVALUATION:

THE SOLUBILITY OF METHANE IN WATER BETWEEN 298 AND 627 K AT A TOTAL PRESSURE BETWEEN 0.5 AND 200 MPa.

There were thirteen papers (1-13) that reported on the solubility of methane in water as a function of pressure. Of these, several reported additional data on methane, ethane, and propane mixtures (1), methane and butane mixtures (6), aqueous electrolyte solutions (2), and brine solutions (13) as a function of temperature and pressure.

The table below summarizes the ranges of temperature and pressure studied for the methane + water system for each paper. Also listed are the number of data points from each study and the *estimated* per cent precision of the data in terms of the mole fraction solubility of methane in water.

Reference Number	Temperature Range T/K	Total Pressure Range p/MPa	Number of Experimental Points	Estimated Precision, Percent Mol Fraction
1	311 - 344	4.1 - 34.5	8	2
2	373	15 - 154	9	5
3	298 - 518	1.3 - 6.5	7	1-2
4	298 - 444	2.3 - 68.9	71	3
5	298 - 303	0.3 - 5.2	17	1-2
6	311 - 411	0.3 - 13	Graphs	8
7	298 -423	4.1 - 46.9	39	3-5
8	325 - 398	10.1 - 61.6	18	1
9	427 - 627	3.5 - 197	71	3-5
10	298	2.4 - 5.2	6	1-2
11	423 - 633	9.9 - 113.3	58	5
12	277 -573	1.1 - 13.2	16	6
13	298	3.6 - 66.7	11	5

Although the studies covered widely varying ranges of temperature and pressure, they report data of roughly comparable precision. Initially, all the data from references 1-11 (304 data points) were fit as a function of temperature and pressure. (References 12 and 13 were found later and will be treated separately below - this omission did not affect the analysis.) The temperature was expressed as the function $\tau = T/100\ \mathrm{K}$, since this gives regression coefficients of comparable magnitude. Since the papers report *total* pressure and not partial pressure, the total pressures were converted to MPa and then fit. Initially, four equations were tested and they are:

$$\ln x_1 = A_0 + A_1/\tau + B_0 \ln (p/\mathrm{MPa}) \tag{1}$$

$$\ln x_1 = A_0 + A_1 \ln \tau + B_0 \ln (p/\mathrm{MPa}) \tag{2}$$

$$\ln x_1 = A_0 + A_1/\tau + A_2 \ln \tau + B_0 \ln (p/\mathrm{MPa}) \tag{3}$$

$$\ln x_1 = A_0 + A_1/\tau + A_2 \ln \tau + B_0 \ln (p/\mathrm{MPa}) + B_1 (p/\mathrm{MPa}) \tag{4}$$

Equation (3) gave the best fit in all tests. The precision of the fit was not significantly improved by the addition of the linear pressure term in equation (4).

An additional seven equations were fit in an attempt to find a form related to the Kasarnovsky-Kritchevsky and Kritchevsky-Ilinskaya equations. These equations follow:

$$\ln x_1 = A_0 + A_1 \ln \tau + C_0 \tau \ln (p/\mathrm{MPa}) \tag{5}$$

$$\ln x_1 = A_0 + A_1/\tau + C_0 \tau \ln (p/\mathrm{MPa}) \tag{6}$$

$$\ln x_1 = A_0 + A_1/\tau + A_2 \ln \tau + C_0 \tau \ln (p/\mathrm{MPa}) \tag{7}$$

$$\ln x_1 = A_0 + A_1/\tau + A_2 \ln \tau + B_0 \ln (p/\mathrm{MPa}) + C_0 \tau (p/\mathrm{MPa}) \tag{8}$$

$$\ln x_1 = A_0 + A_1/\tau + A_2 \ln \tau + B_0 \ln (p/\mathrm{MPa}) + C_0 \ln (\tau p/\mathrm{MPa}) \tag{9}$$

$$\ln x_1 = A_0 + A_1/\tau + A_2 \ln \tau + B_0 \ln (p/\mathrm{MPa}) + C_0 \ln (\tau p/\mathrm{MPa}) + D_0 (1 - x_2^2) \tag{10}$$

$$\ln x_1 = A_0 + A_1/\tau + A_2 \ln \tau + B_0 \ln (p/\mathrm{MPa}) + C_0 \tau (p/\mathrm{MPa}) + D_0 (1 - x_2^2) \tag{11}$$

The degree of fit for equations (8-11) was of the same order as that of equation (3), while the fit to equations (5-7) was significantly poorer. Thus, there appears to be no reason to prefer any other equation over equation (3).

If Henry's law is obeyed exactly, the coefficient B_0 in equation (3) would be unity. B_0 is not unity, so methane in water solubilities are not accurately described by Henry's law, although plots of $\ln x_1$ *vs.* $\ln(p/\mathrm{MPa})$ are *linear*. Since we are using total pressure rather than partial pressures (due to the difficulty in calculating the later), any discussion of Henry's law is not meaningful.

In the evaluation procedure used all points which deviated from the smoothed curve by about two or more standard deviations were deleted and the linear regression repeated. This procedure was carried out three times for equation (3) with the results shown below:

Number of points	304	275	242	192
Standard deviation in $\ln x_1$	0.27	0.15	0.11	0.081

COMPONENTS:	EVALUATOR:
(1) Methane; CH_4; [74-82-8] (2) Water; H_2O; [7732-18-5]	Rubin Battino Department of Chemistry Wright State University Dayton, OH 45435 USA 1984, December

CRITICAL EVALUATION:

The process could be continued until any desired precision were attained, but this does some violence to the original data set. Also, the further one goes, the more the pressure and temperature ranges narrow, and the larger deviations accumulate at the extremes.

After studying the individual papers and the results from combining their data, we recommend as a most reasonable choice the results obtained with 242 data points and their associated standard deviation of 0.11 in ln x_1. These 242 data points fall in the 298 to 627 K and 0.6 to 192 MPa ranges. The error in mole fraction is a function of pressure at each temperature. At a represenative temperature of 479 K the per cent errors in x_1 at (p/MPa) are: 0.11 % (5 MPa); 1.3 % (95 MPa); and 12 % (192 MPa). It is reasonable to expect poorer precision as pressure increases.

Taking into consideration the discussion in the previous paragraph the *recommended* smoothing equation is:

$$\ln x_1 = -55.8111 + 74.7884/\tau + 20.6794 \ln \tau + 0.753158 \ln (p/\mathrm{MPa}) \qquad (12)$$

where $\tau = T/100$ K and p/MPa is the *total* pressure. Smoothed values of the mole fraction solubility at 25 K intervals between 300 and 625 K are given at seven pressures in Table 1. Several isotherms of ln x_1 *vs.* ln (p/MPa) are shown in Figure 1. At all pressures there appears to be a minimum in the mole fraction solubility at a temperature of about 350 K.

An important characteristic to keep in mind at these elevated temperatures and pressures is the vapor pressure of the solvent water. Ambrose and Lawrenson (14) provided a smoothing equation for the vapor pressure of pure water using Chebyshev polynomials. We provide in Table 2 for reference at 10 K intervals the vapor pressure of water calculated from their equation. We have added to Figure 1 a line showing the vapor pressure of water. In Table 1 the water vapor pressure exceeds the total pressure heading of 0.5 MPa at 425 K, 1.0 MPa at 475 K, and 10 MPa at 600 K.

TABLE 1. The *tentative* mole fraction solubility of methane in water as a function of temperature between 300 and 625 K at total pressures between 0.5 and 200 MPa.

T/K	Mol Fraction Solubility, 10^3x_1, at a Total Pressure of:						
	0.5 MPa	1.0 MPa	10 MPa	50 MPa	100 MPa	150 MPa	200 MPa
300	0.1691	0.2850	1.614	5.43	9.14	12.41	15.41
325	0.1301	0.2192	1.242	4.17	7.03	9.55	11.86
350	0.1164	0.1962	1.111	3.73	6.29	8.54	10.61
375	0.1166	0.1966	1.114	3.74	6.31	8.56	10.63
400	0.1274	0.2147	1.216	4.09	6.89	9.35	11.61
425	0.1486	0.2504	1.418	4.77	8.03	10.90	13.54
450	-	0.3072	1.740	5.85	9.86	13.38	16.61
475	-	-	2.220	7.46	12.57	17.08	21.19
500	-	-	2.918	9.81	16.53	22.43	27.86
525	-	-	3.925	13.19	22.23	30.18	37.48
550	-	-	5.376	18.07	30.45	41.33	51.33
575	-	-	7.463	25.08	42.27	57.37	71.25
600	-	-	-	35.17	59.28	80.46	99.92
625	-	-	-	49.69	83.76	113.7	141.2

Table 2. The vapor pressure of water (14).

T/K	p/kPa	T/K	p/MPa
273.15	0.6107	470	1.4538
280	0.9912	480	1.7890
290	1.9191	490	2.1814
300	3.5352	500	2.6372
310	6.2280	510	3.1633
320	10.540	520	3.7665
330	17.202	530	4.4540
340	27.167	540	5.2336
350	41.647	550	6.1134
360	62.138	560	7.1019
370	90.451	570	8.2084
380	128.73	580	9.4427
390	179.48	590	10.816
400	245.54	600	12.339
410	330.15	610	14.026
420	436.90	620	15.892
430	569.74	630	17.958
440	733.00	640	20.256
450	931.36	647.31[a]	22.106
460	1169.9		

[a] critical temperature

After the above analysis was completed we found two more papers (12, 13). Their points were added to the 242 used for this analysis. Eleven out of the sixteen of the points of Cramer (13) reported were off the smoothing curve by 1.5 σ or more, while half of Culberson *et al*.'s (12) points showed the same deviation. The Cramer paper (13) is important and needs further study since his reported pressures are fugacities which may account for some of the discrepency reported above.

ACKNOWLEDGMENT: The evaluator thanks Professor H. L. Clever for many helpful suggestions in the preparation of this evaluation.

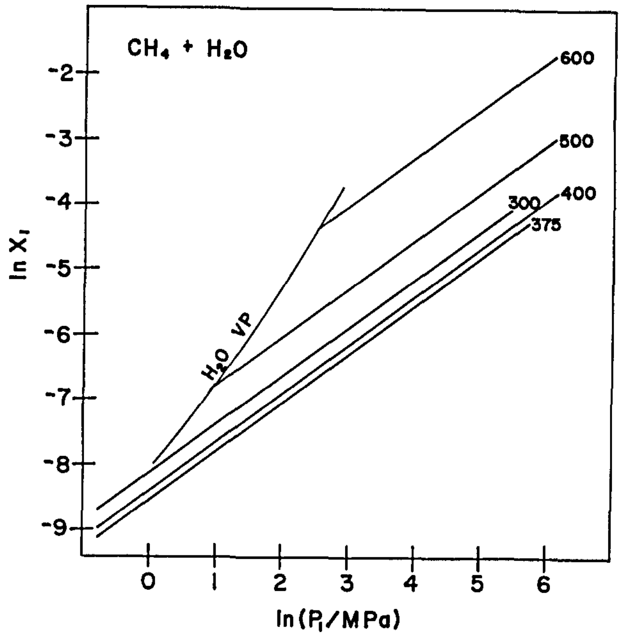


Figure 1. Methane + Water. ln x_1 *vs.* ln (p_t/MPa) at five temperatures between 300 and 600 K.

The water vapor pressure curve is shown crossing the 500 and 600 K isotherms.

The solubility minimum shows in the order of the 300, 375 and 400 K isotherms.

REFERENCES:

1. Amirijafari, B.; Campbell, J. M. *Soc. Pet. Engnrs. J.* 1972, *12*, 21-7.
2. Blount, C. W.; Price, L. C.; Wenger, L. M.; Tarullo, M. *DOE Contract Report DE-AS08-78ET12145.*
3. Crovetto, R.; Fernandez-Prini, R.; Japas, M. L. *J. Chem. Phys.* 1982, *76*, 1077-86.
4. Culberson, O. L.; McKetta, J. J. *J. Petrol. Tech.* 1951, *3*, 223-6; *AIME Trans.* 1951, *192*, 223-6.
5. Duffy, J. R.; Smith, N. O.; Nagy, B. *Geochim. Cosmochim. Acta* 1961, *24*, 23-31.
6. McKetta, J. J.; Katz, D. L. *Ind. Eng. Chem.* 1948, *40*, 853-62.
7. Michels, A.; Gerver, J.; Biji, A. *Physica* 1936, *3*, 797-808.
8. O'Sullivan, T. D.; Smith, N. O. *J. Phys. Chem.* 1970, *74*, 1460-6.
9. Price, L. C. *Am. Assn. Petr. Geol. Bull.* 1979, *63*, 1527-33.
10. Stoessell, R. K.; Byrne, P. A. *Clays Clay Miner.* 1982, *30*, 67-72; *Geochim. Cosmochim. Acta* 1982, *46*, 1327-32.
11. Sultanov, R. G.; Skripka, V. G.; Namiot, A. Yu. *Zh. Fiz. Khim.* 1972, *46*, 2160; *VINITI*, 4387-72; *Gazov. Prom.* 1972, *17*, 6-7.
12. Culberson, O. L.; Horn, A. B.; McKetta, J. J. *J. Petrol. Tech.* 1950, *2*, 1-6; or *AIME, Petrol. Trans.* 1950, *189*, 1-6.
13. Cramer, S. D. *Ind. Eng. Chem. Process Des. Dev.* 1984, *23*, 533-8.
14. Ambrose, D.; Lawrenson, I. J. *J. Chem. Thermodynamics* 1972, *4*, 755-61.

See also Larsen, E. R.; Prausnitz, J. M. *AIChE J.* 1984, *30*, 732-8.

COMPONENTS:

1. Methane; CH_4; [74-82-8]
2. Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Michels, A.; Gerver, J.; Biji, A.

Physica

1936, *3*, 797-808.

VARIABLES:

Temperature, pressure

PREPARED BY:

C. L. Young

EXPERIMENTAL VALUES:

T/K	$P/10^5$Pa	10^3 Mole fraction of methane in liquid, $10^3x_{CH_4}$	T/K	$P/10^5$Pa	10^3 Mole fraction of methane in liquid, $10^3x_{CH_4}$
298.15	40.6	0.81	348.15	176.2	1.74
	46.0	0.90		208.0	1.93
	81.3	1.28	373.15	49.0	0.66
	112.0	1.58		82.2	1.01
	145.9	1.87		113.0	1.27
	176.5	2.10		148.3	1.52
	204.9	2.28		180.5	1.71
	330.8	2.68		209.2	1.84
	469.1	2.97	398.15	49.0	0.64
323.15	49.6	0.72		82.1	0.98
	82.3	1.12		113.0	1.24
	113.1	1.42		150.0	1.50
	145.6	1.69		181.1	1.66
	176.5	1.90		212.3	1.79
	208.2	2.07	423.15	47.1	0.62
348.15	44.3	0.61		81.7	0.93
	79.2	1.01		110.8	1.19
	114.5	1.33		145.4	1.42
	148.1	1.57		177.8	1.60
				206.1	1.73

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Simple rocking equilibrium cell. Amount of gas absorbed calculated from volume and pressure change of charging vessel. Details in source.

SOURCE AND PURITY OF MATERIALS:

No details given.

ESTIMATED ERROR:

$\delta T/K = \pm 0.1$; $\delta P/10^5$ Pa $= \pm 0.05$ to 0.5%; $\delta x_{CH_4} = \pm 3\text{-}5\%$ (estimated by compiler).

REFERENCES:

COMPONENTS:

(1) Methane; CH_4; [74-82-8]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Culberson, O. L.; Horn, A. B.;
McKetta, J. J.

J. Pet. Technol. 1950, *2*, 1-6.
or
AIME, Pet. Trans. 1950, *189*, 1-6.

VARIABLES:

$T/K = 298.15$
$p_t/MPa = 3.62 - 66.74$

PREPARED BY:

H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Total Pressure		Mole Ratio
$t/^0F$	T/K	p/psia	p/MPa	$10^3 (n_1/n_2)$
77	298.15	525	3.62	0.770
		1000	6.89	1.10
		1450	10.00	1.80
		1845	12.72	2.02
		1930	13.31	2.27
		2535	17.48	2.31
		3615	24.92	2.88
		4435	30.58	3.28
		6342	43.72	4.07
		7935	54.71	3.91
		9680	66.74	4.51

The mole fraction solubility is $x_1 = n_1/(1 + n_1)$, when n_2 is assumed one.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The sample is equilibrated in a large rocking autoclave. Samples are analyzed by removing water and measuring the gas volumetrically.

The temperature is measured with a thermocouple and the pressure with a Bourdon gage.

SOURCE AND PURITY OF MATERIALS:

(1) Methane. Phillips Petroleum Co. The purity was 99.0 mole per-cent minimum.

(2) Water. Distilled water was boiled to degass.

ESTIMATED ERROR:

$\delta T/K = \pm 0.5$; $\delta n_1/n_2 = \pm 5$ %
$\delta p/MPa = \pm 0.02$; less than 10 MPa
$\delta p/MPa = \pm 0.07$; 10 to 35 MPa
$\delta p/MPa = \pm 0.14$; over 35 MPa

REFERENCES:

COMPONENTS:

1. Methane; CH_4; [74-82-8]
2. Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Culberson, O. L.; McKetta, J. J.
J. Petrol. Tech. 1951, *3*, 223-226
or
AIME Petrol. Trans. 1951, *192*, 223-226.

VARIABLES:

PREPARED BY:

C. L. Young

EXPERIMENTAL VALUES:

T/K	p/psia	P/MPa	Mole fraction of methane in liquid, x_{CH_4}
298.2	341	2.35	0.000497
(77)	459	3.16	0.000717
	659	4.54	0.001000
	934	6.44	0.001317
	1290	8.89	0.001678
	1930	13.31	0.002235
	2495	19.20	0.002585
	3515	24.24	0.003110
	4810	33.16	0.003660
	6440	44.40	0.004170
310.9	330	2.28	0.000440
(100)	477	3.29	0.000619
	664	4.58	0.000839
	950	6.55	0.001123
	1270	8.76	0.001440
	1900	13.10	0.001890
	2575	17.75	0.002290
	3535	24.37	0.002760
	4910	33.85	0.003330
	6525	44.99	0.00391
	7870	54.26	0.00417
	9895	68.22	0.00465

(cont.)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Sample equilibrated in large rocking autoclave. Samples of liquid analysed by removing water and estimating the gas volumetrically cally. Temperature measured with thermocouple and pressure with Bourdon gauge. Details in ref. (1).

SOURCE AND PURITY OF MATERIALS:

1. Phillips Petroleum Co. sample, purity 98.72 mole per cent.
2. Distilled and degassed.

ESTIMATED ERROR:

$\delta T/K = \pm 0.5$; $\delta P/MPa = \pm 1\%$;
$\delta x_{CH_4} = \pm 3\%$ (estimated by compiler).

REFERENCES:

1. Culberson, O. L.; Horn, A. B.; McKetta, J. J.
   J. Petr. Technol. Trans AIME Pet. Div.
   1950, *189*, 1.

COMPONENTS:

1. Methane; CH_4; [74-82-8]

2. Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Culberson, O. L.; McKetta, J. J.
J. Petrol. Tech. 1951, *3*, 223-226
or
AIME, Petrol. Trans. 1951, *192*, 223-226.

EXPERIMENTAL VALUES:

T/K (T/°F)	p/psia	P/MPa	Mole fraction of methane in liquid, x_{CH_4}
344.3	331	2.28	0.000340
(160)	467	3.22	0.000470
	659	4.54	0.000632
	943	6.50	0.000909
	1320	9.10	0.001183
	1880	12.96	0.001500
	2555	17.62	0.001924
	3535	24.37	0.002385
	4925	33.96	0.002770
	6525	44.99	0.00342
	8220	56.67	0.00375
	9865	68.02	0.00424
377.6	333	2.30	0.000323
(220)	466	3.21	0.000432
	468	3.23	0.000472
	652	4.50	0.000611
	945	6.52	0.000886
	1310	9.03	0.001188
	1900	13.10	0.001560
	2535	17.48	0.001980
	3570	24.61	0.002510
	4965	34.23	0.00314
	6525	44.99	0.00361
	8190	56.47	0.00408
	9875	68.09	0.00451
410.9	336	2.32	0.000326
(280)	464	3.20	0.000460
	654	4.51	0.000673
	941	6.49	0.000938
	1310	9.03	0.001326
	1900	13.10	0.001857
	2480	17.10	0.002346
	3555	24.51	0.003015
	4975	34.30	0.003805
	6525	44.99	0.00449
	8270	57.02	0.00518
	9835	67.81	0.00574
444.3	323	2.23	0.000323
(340)	475	3.28	0.000535
	662	4.56	0.000789
	949	6.54	0.001150
	1360	9.38	0.001725
	1920	13.24	0.002355
	2580	17.79	0.003025
	3580	24.68	0.003835
	5045	34.78	0.004875
	6525	44.99	0.00595
	8210	56.61	0.00680
	9995	68.91	0.00775

COMPONENTS:

1. Methane; CH_4; [74-82-8]

2. Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Duffy, J. R.; Smith, N. O.; Nagy, B.

Geochim. Cosmochim. Acta 1961, *24*, 23-31.

VARIABLES:

Temperature, pressure

PREPARED BY:

C. L. Young

EXPERIMENTAL VALUES:

T/K	P/MPa	Mole fraction of methane in liquid phase, $10^4\ x_{CH_4}$
298.15	1.103	2.14
	1.482	2.73
	1.586	3.76
	2.965	7.08
	3.068	7.03
	3.544	8.00
	4.033	9.39
	4.688	9.79
	5.171	11.30
303.15	0.317	0.60
	0.552	1.15
	0.793	1.84
	0.938	2.32
	1.972	4.90
	2.048	4.93
	2.744	6.12
	3.606	7.64

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Rocking equilibrium cell. Pressure measured with a Bourdon gauge. Cell charged with boiled water; gas admitted to known pressure. Cell contents allowed to equilibrate. Final pressure measured and used to calculate amounts of gas dissolved. Details in source ref.

SOURCE AND PURITY OF MATERIALS:

1. C.P. grade - no other details given.

2. Degassed.

ESTIMATED ERROR:

$\delta T/K = \pm 1$; $\delta P/MPa = \pm 0.03$;

$\delta x_{CH_4} = \pm 5 \times 10^{-6}$.

REFERENCES:

COMPONENTS:

(1) Methane; CH_4; [74-82-8]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Schröder, W.

Z. Naturforsch. 1969, *24b*, 500-8.

Chem.-Ing.-Tech. 1973, *45*, 603-8.

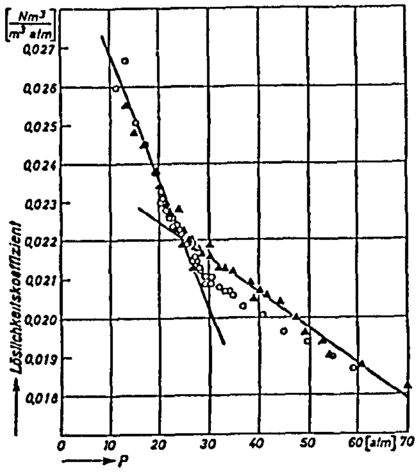
VARIABLES:

$T/\mathrm{K} = 303.15 - 373.15$
$p_1/\mathrm{MPa} = 1.013 - 6.080$

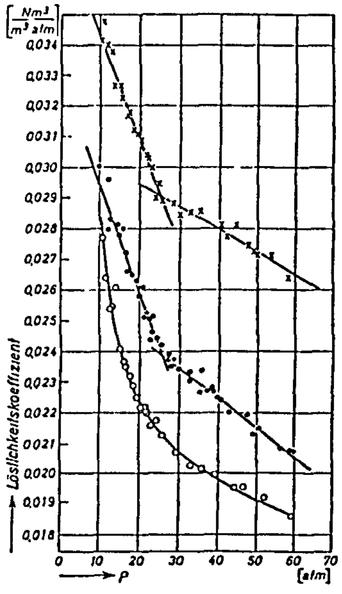
PREPARED BY:

H. L. Clever

EXPERIMENTAL VALUES:



Löslichkeit von Methan in Wasser. ▲: 70 °C, ⊙: 80 °C.



Löslichkeit von Methan in Wasser. ×: 30 °C, ●: 50 °C, o: 100 °C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The apparatus was a bubbling-type autoclave of the type described by Wiebe, Gaddy and Heins (ref 1).

The Bunsen coefficient was calculated from the experimental data.

The data were presented in the graphs above.

The data were discussed briefly in an earlier paper (ref 2).

The second paper gives the equation

$$\ln(\alpha/\mathrm{m}^3(\mathrm{STP})\,\mathrm{m}^{-3}\mathrm{atm}^{-1}) = 4.211 - 5821/(T/\mathrm{K}) + 1.019 \times 10^6/(T/\mathrm{K})^2$$

for the 303 - 373 temperature interval at a methane pressure of 100 atm (10.133 MPa). The temperature of minimum solubility is 350 K at this pressure, it increases to 377 K at 20 atm partial pressure methane.

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

1. Wiebe, R.; Gaddy, V.L.; Heins, C. *Ind. Eng. Chem.* 1932, *24*, 823; *J. Am. Chem. Soc.* 1933, *55*, 947.
2. Schröder, W. *Naturwissenschaften* 1968, *55*, 542.

COMPONENTS:

1. Methane; CH_4; [74-82-8]
2. Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

O'Sullivan, T.D.; Smith, N.O.

J. Phys. Chem., 1970, *74*, 1460-1466.

VARIABLES:

Temperature, pressure

PREPARED BY:

C.L. Young

EXPERIMENTAL VALUES:

T/K	P/MPa	10^3 Mole fraction of methane in liquid, $10^3 x_{CH_4}$
324.65	10.13	1.427
	20.26	2.279
	30.40	2.87
	40.53	3.34
	50.63	3.73
	60.79	4.09
375.65	10.23	1.355
	20.37	2.205
	30.60	2.87
	40.83	3.33
	50.97	3.85
	61.20	4.19
398.15	10.44	1.434
	20.67	2.321
	30.90	2.96
	41.04	3.43
	51.37	3.96
	61.61	4.30

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Large steel stirred equilibrium cell. Pressure measured with Bourdon gauge. Temperature measured with iron-constantan thermocouple. Cell charged with liquid, compressed gas added. After equilibrium obtained samples removed and analysed using volumetric techniquies. Details in ref. (1).

SOURCE AND PURITY OF MATERIALS:

1. Matheson Co., sample purity 99.95 mole per cent.
2. Distilled and de-ionised, air removed.

ESTIMATED ERROR:

$\delta T/K = \pm 0.5$; $\delta P/MPa = \pm 0.05\%$; $\delta x_{CH_4} = \pm 0.4\%$.

REFERENCES:

1. O'Sullivan, T.D.; Smith, N.O.

Geochim. Cosmochim. Acta, 1966, *30*, 617.

COMPONENTS: 1. Methane; CH_4; [74-82-8] 2. Water; H_2O; [7732-18-5]	ORIGINAL MEASUREMENTS: Sultanov, R. G.; Skripka, V. G.; Namoit, A. Yu. *Zh. Fiz. Khim.* 1972, *46*, 2160; VINITI, *4387-72.*
VARIABLES:	PREPARED BY: C. L. Young

EXPERIMENTAL VALUES:

T/K	P/kg cm^{-2}	P/MPa	Mole fraction of methane in liquid, x_{CH_4}	Mole fraction of methane in vapor, y_{CH_4}
423.2	100	9.81	0.0010	0.9400
	200	19.61	0.0018	0.9630
	400	39.23	0.0030	0.9780
	600	58.84	0.0046	0.9830
	800	78.45	0.0056	0.9835
	1000	98.07	0.0056	0.9850
473.2	100	9.81	0.0020	0.8100
	200	19.61	0.0038	0.8915
	400	39.23	0.0067	0.9350
	600	58.84	0.0087	0.9480
	800	78.45	0.0100	0.9545
	1000	98.07	0.0104	0.9630
523.2	100	9.81	0.0025	0.5300
	200	19.61	0.0063	0.7330
	400	39.23	0.0117	0.8325
	600	58.84	0.0140	0.8720
	800	78.45	0.0146	0.8980
	1000	98.07	0.0151	0.9100
573.2	100	9.81	0.0015	0.0950
	200	19.61	0.0078	0.4360
	400	39.23	0.0185	0.6260
	600	58.84	0.0265	0.6790
	800	78.45	0.0340	0.7150
	1000	98.07	0.0407	0.7500

(cont.)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Static equilibrium cell fitted with magnetic stirrer, details in ref. (1). Samples of coexisting phases analysed by freezing out water and estimating methane volumetrically.

SOURCE AND PURITY OF MATERIALS:

1. Purity 99.95 volume per cent.
2. No details given.

ESTIMATED ERROR:

$\delta T/K = \pm 0.3$; $\delta P/MPa = \pm 0.1$;

δx_{CH_4}, δy_{CH_4} = ±0.0005 (estimated by compiler).

REFERENCES:

1. Sultanov, R. G.; Skripka, V. G.; Namoit, A. Yu. *Gazov. Prom.* 1971, *16*, 6.

COMPONENTS:

1. Methane; CH_4; [74-82-8]

2. Water; H_2O; [-732-18-5]

ORIGINAL MEASUREMENTS:

Sultanov, R. G.; Skripka, V. G.; Namoit, A. Yu.

Zh. Fiz. Khim.

1972, *46*, 2160; VINITI, *4387-72*.

EXPERIMENTAL VALUES:

T/K	P/kg cm^{-2}	P/MPa	Mole fraction of methane in liquid, x_{CH_4}	in vapor, y_{CH_4}
603.2	200	19.61	0.0100	0.1950
	400	39.23	0.0325	0.4170
	600	58.84	0.0464	0.5040
	800	78.45	0.0572	0.5540
	1000	98.07	0.0635	0.5850
	1050	102.97	0.0650	-
623.2	200	19.61	0.0053	0.0800
	400	39.23	0.0414	0.2350
	600	58.84	0.0707	0.2980
	800	78.45	0.0955	0.3150
	1000	98.07	0.1230	0.3350
	1050	102.97	0.1300	-
	1100	113.27	0.1365	-
625.2	250	24.52	0.0135	0.1390
	300	29.42	0.0230	0.1850
	400	39.23	0.0410	0.2280
	500	49.03	0.0550	0.2490
	600	58.84	0.0660	0.2660
	700	68.65	0.0800	0.2780
	800	78.45	0.1050	0.2750
	900	88.26	0.1250	0.2310
	935*	91.69	0.1800	0.1800
	992**	97.28	0.1730	0.1730
	1000	98.07	0.1250	0.2000
	1050	102.97	0.0820	0.2400
	1100	113.27	0.0680	0.2470
628.2	250	24.52	0.0165	0.1050
	300	29.42	0.0275	0.1530
	400	39.23	0.0540	0.2050
	500	49.03	0.0830	0.2150
	600	58.84	0.1200	0.2140
	650	63.74	0.1430	0.2040
	680*	66.69	0.1720	0.1720
633.2	250	24.52	0.0160	0.0820
	300	29.42	0.0260	0.1190
	400	39.23	0.0500	0.1590
	500	49.03	0.0700	0.1710
	600	58.84	0.0960	0.1570
	620*	60.80	0.1280	0.1280

* gas-liquid critical point

** gas-gas critical point

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Methane; CH_4; [74-82-8] 2. Water; H_2O; [7732-18-5]	Amirijafari, B.; Campbell, J. M. *Soc. Pet. Engnrs. J.* 1972, 12, 21-27.
VARIABLES:	PREPARED BY: C. L. Young

EXPERIMENTAL VALUES:

T/K (T/°F)	P/psi	P/MPa	10^3 × Mole fraction of methane in water-rich phase $10^3x_{CH_4}$
310.93	600	4.14	0.759
(100)	2000	13.79	1.956
	3000	20.68	2.519
	5000	34.47	3.350
344.26	600	4.14	0.602
(160)	2000	13.79	1.612
	3000	20.68	2.150
	5000	34.47	2.800

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Static stainless steel equilibrium vessel of approximately 75 mL capacity. Pressure measured with Bourdon gauge and temperature measured with thermocouple. Samples of liquid and vapor analysed using a gas chromatograph equipped with a flame ionisation detector. Poropak R column used.

SOURCE AND PURITY OF MATERIALS:

1. Pure grade sample, purity 99.9 mole per cent.
2. No details given.

ESTIMATED ERROR:

$\delta T/K = \pm 0.03$; $\delta P/MPa = \pm 1\%$; $\delta x_{CH_4} = \pm 2\%$.

REFERENCES:

COMPONENTS:

1. Methane; CH_4; [74-82-8]

2. Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Price, L. C.

Am. Assn. Pet. Geol. Bull.

1979, *63*, 1527-33.

VARIABLES:

PREPARED BY:

C. L. Young

EXPERIMENTAL VALUES:

T/K (T/°C)	*P*/psi	*P*/MPa[a]	Solubility[c] SCF/bbl	Mole per cent of methane,[b] x_{CH_4}
427	514	3.54	5.65 ± 0.3	0.0741
(154)	2205	15.20	21.81 ± 2.69	0.2859
	4645	32.03	34.43 ± 1.66	0.4514
	6790	46.82	42.03 ± 0.36	0.5510
	9760	67.29	46.72 ± 1.28	0.6125
	12670	87.36	49.78 ± 0.70	0.6526
	15260	105.21	58.76 ± 1.33	0.7703
	18260	125.90	67.37 ± 0.15	0.8832
	23780	163.96	78.76 ± 1.83	1.0325
479	750	5.17	9.51 ± 0.80	0.1247
(206)	2323	16.02	30.82 ± 0.75	0.4041
	4270	29.44	48.12 ± 1.92	0.6309
	7923	54.63	72.36 ± 0.22	0.9486
	13759	94.86	98.11 ± 2.19	1.286
	18906	103.35	116.5 ± 1.5	1.527
	23652	163.07	127.0 ± 7.6	1.665
	27915	192.47	143.5 ± 0.5	1.881
494	583	4.02	9.73 ± 0.19	0.1276
(221)	5331	36.76	62.87 ± 0.35	0.8242
	9109	62.80	101.7 ± 1.90	1.333
	12670	87.36	116.4 ± 2.9	1.526
	15020	103.56	131.4 ± 9.7	1.723

(cont.)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Static equilibrium cell filled with water, vessel sealed and brought to temperature, excess water being allowed to bleed out. Some water removed and compressed methane added. Samples for analysis removed, methane being added simultaneously so that the total pressure remained constant. Samples analysed by measuring equilibrium pressure when sample injected into an evacuated flask. Duplicate samples taken.

SOURCE AND PURITY OF MATERIALS:

1. Matheson gas, purity 99.99 mole per cent.

2. Distilled and degassed.

ESTIMATED ERROR:

T/K = ±1.0.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Methane; CH_4; [74-82-8]	Price, L. C. *Am. Assn. Pet. Geol. Bull.*
2. Water; H_2O; [7732-18-5]	1979, *63*, 1527-33.

EXPERIMENTAL VALUES:

T/K (T/°C)	*P*/psi	*P*/MPa[a]	Solubility[c] SCF/bbl	Mole per cent of methane,[b] x_{CH_4}
494	17940	123.69	135.3 ± 1.6	1.774
(221)	20530	141.55	139.4 ± 4.1	1.828
507	1176	8.11	19.92 ± 0.09	0.2612
(234)	2160	14.89	34.91 ± 1.41	0.4577
	3014	20.78	54.75 ± 1.03	0.7178
	4027	27.77	63.97 ± 0.82	0.8386
	6836	47.13	108.2 ± 1.84	1.419
	8658	59.69	117.3 ± 0.3	1.538
	11330	78.12	140.0 ± 0.5	1.835
	13540	93.36	150.8 ± 4.9	1.977
	15690	108.18	161.9 ± 0.4	2.123
	15770	108.73	159.2 ± 2.6	2.087
	19230	132.59	169.3 ± 3.0	2.220
	21340	147.13	172.1 ± 1.9	2.256
	23830	164.30	181.0 ± 4.4	2.373
553	2866	19.76	65.0 ± 3.70	0.8522
(280)	4616	31.83	101.6 ± 6.4	1.332
	6953	47.94	160.0 ± 2.1	2.098
	10170	70.12	206.3 ± 9.2	2.705
	14490	99.91	252.3 ± 0.7	3.308
	18330	126.38	264.9 ± 4.6	3.473
	22020	151.82	282.8 ± 8.8	3.708
	23120	159.41	292.5 ±19.6	3.835
	27400	188.92	308.4 ± 8.9	4.043
565	1566	10.80	22.59 ± 0.08	0.2962
(292)	2770	19.10	67.26 ± 0.59	0.8818
	4337	29.90	115.2 ± 6.4	1.510
	13130	90.53	278.3 ± 1.2	3.649
	15940	109.90	293.9 ± 3.9	3.853
	22050	152.03	336.1 ± 4.6	4.406
	24500	168.92	349.9 ± 8.5	4.587
589	1632	11.25	11.2 ± 1.5	0.1468
(316)	3631	25.03	132.2 ± 3.7	1.733
	7747	53.41	321.2 ± 1.5	4.211
	10440	71.98	377.9 ± 4.5	4.954
	13390	92.32	421.1 ± 8.3	5.521
	17010	117.28	474.0 ± 6.5	6.214
	23990	165.41	509.1 ± 7.3	6.674
	27750	191.33	527.6 ± 5.7	6.917
627	2837	19.56	46.79 ± 0.71	0.6134
(354)	3631	25.03	134.7 ± 3.45	1.766
	4689	32.33	268.5 ± 2.2	3.520
	6174	42.57	422.1 ±12.0	5.534
	7688	53.01	488.7 ± 5.5	6.407
	15820	109.08	669.7 ± 8.1	8.780
	18460	127.28	700.3 ±11.3	9.181
	24650	169.96	775.9 ± 1.8	10.17
	26940	185.74	803.0 ± 1.7	10.53
	28610	197.26	828.8 ± 2.0	10.87

[a] Calculated by compiler.

[b] Calculated by compiler by multiplying solubility by conversion factor stated by author in original.

[c] Unit of standard cubic feet per barrel of water.

COMPONENTS:

(1) Methane; CH_4; [74-82-8]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Crovetto, R.; Fernández-Prini, R.; Japas, M. L.

J. Chem. Phys. 1982, *76*, 1077-86.

VARIABLES:

T/K = 297.5 - 518.3
p/MPa = 1.327 - 6.451

PREPARED BY:

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]
297.5	1.861	0.9983	1.798	4.351	1.419
333.7	1.327	0.9840	1.286	2.124	1.801
385.3	2.092	0.9226	1.908	2.985	1.855
388.4	2.156	0.9166	1.954	3.085	1.846
430.6	2.131	0.7147	1.531	3.025	1.621
473.2	3.210	0.4873	1.618	4.146	1.362
518.3	6.451	0.3875	2.697	10.337	0.959

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

The smoothing equation was obtained from the data and the values of H for 288, 298, and 308 K given in reference (1).

$$\ln(H/\text{GPa}) = -8.681 + 7.837/(T/1000\ \text{K}) - 1.509/(T/1000\ \text{K})^2 + 0.0206/(T/1000\ \text{K})^3 \qquad (\sigma = 0.017)$$

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	26.28	-13.32	132.6	244
400.0	36.58	5.63	77.4	141
520.0	43.89	18.80	48.1	85

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

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.

SOURCE AND PURITY OF MATERIALS:

(1) Methane. Matheson (UHP) 99.97 mol %.

(2) Water. Conductivity water.

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

REFERENCES:

1. Wilhelm, E.; Battino, R.; Wilcock, R. J. *Chem. Rev.* 1977, *77*, 219.

COMPONENTS:

(1) Methane; CH_4; [74-82-8]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Stoessell, R. K.; Byrne, P. A.

Clays Clay Miner. 1982, *30*, 67-72.

Geochim. Cosmochim. Acta 1982, *46*, 1327-32.

VARIABLES:

$T/K = 298.15$

$p_1/\text{kPa} = 2410 - 5170$

PREPARED BY:

H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Pressure		Methane	
$t/^{\circ}C$	T/K	p_1/psia	p_1/kPa	$m_1/\text{mol kg}^{-1}$	Mol Fraction 10^4x_1
25	298.15	350	2410	0.0318[a] 0.0319[b]	5.73 5.74
		550	3790	0.0473[a] 0.0483[b]	8.51 8.69
		750	5170	0.0623[a] 0.0617[b]	11.21 11.10

[a] Values from first reference above.

[b] Values from second reference above.

The kPa pressure and the mole fraction values were calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubility determinations were made using a titanium-lined chamber within a stainless-steel reaction vessel jacketted by a water bath for temperature control. The system pressure was set by controlling the input and output of methane within the chamber headpiece. The vessel was rocked for 3 h to allow equilibration between the methane and water.

The amount of gas in the saturated solution was measured by transfer of a sample volume to a loop at the system pressure, followed by flashing the sample in an expansion loop and measuring the gas pressure in a known volume. The total gas volume and pressure change were used to compute the moles of methane assuming ideal behavior. A correction was made for the gas not released on flashing.

SOURCE AND PURITY OF MATERIALS:

(1) Methane. Matheson Co., Inc. Ultra high purity grade. Stated to have a minimum purity of 99.97 mole percent.

(2) Water. Distilled.

ESTIMATED ERROR:

$\delta T/K = \pm 0.1$

$\delta p_1/\text{psia} = \pm 1$

$\delta m_1/\text{mol kg}^{-1} = \pm 0.0003$ Av.

± 0.0005 Max.

REFERENCES:

COMPONENTS:

(1) Methane; CH_4; [74-82-8]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Cramer, S. D.

Ind. Eng. Chem. Process Des. Dev. 1984, *23*, 533-8.

VARIABLES:

T/K = 277.2 - 573.2
p_t/MPa = 1.1 - 13.2

PREPARED BY:

H. L. Clever

EXPERIMENTAL VALUES:

Temperature $t/^\circ C$	Temperature T/K	Total Pressure p/MPa	Henry's Constant k/MPa
0	*273.2*		*2460*
4.0	277.2	3.0	2580
12.6	285.8	3.0	3430
20	*293.3*		*3950*
40	*313.2*		*5370*
42.0	315.2	1.1	5800
60	*333.2*		*6420*
61.0	334.2	1.1	6260
80	*353.2*		*6940*
90.4	363.6	1.1	6610
100	*373.2*		*6930*
111.0	384.2	1.2	6310
120	*393.2*		*6510*
140	*413.2*		*5850*
159.3	432.5	1.1	4890
160	*433.2*		*5070*
180	*453.2*		*4290*
184.3	457.5	5.7	4050
187.7	460.9	7.2	3990
193.3	466.5	6.9	3120
200	*473.2*		*3580*
210.7	483.9	6.9	3080
220	*493.2*		*2950*
239.7	512.9	6.9	2580
240	*513.2*		*2430*
260	*533.2*		*2010*
264.4	537.6	10.5	2040
269.2	542.4	8.0	2240
280	*553.2*		*1670*
281.0	554.2	12.0	1780
300.0	573.2	13.2	1130
300	*573.2*		*1400*

The values in *italic* are the author's smoothed values. Six additional values from ref 1 were included in the smoothing.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Methane solubilities were determined from pvT measurements by the gas extraction technique. The measuring apparatus consisted of: (*i*) a high pressure, thermostated, stirred reactor for dissolving gas in the solvent; (*ii*) a heat exchanger for bringing the gas saturated solvent to room temperature; and (*iii*) a low pressure, thermostated gas buret for making pvT measurements on collected samples of vapor and liquid. The apparatus and its operation were described earlier (ref 2).

Four to eight gas-saturated solution samples were taken and analyzed at 15 - 30 minute intervals after the time determined necessary for saturation. Henry's constants were computed (ref 2) and smoothed by a specially developed equation (ref 3).

Henry's constant, $k^0 = f/a = (\phi p_1)/(\gamma x_1)$. $p_1 = p_t - p_2$; ϕ from reduced properties chart. See paper.

SOURCE AND PURITY OF MATERIALS:

(1) Methane.
No information.
(2) Water.

Henry's constants from (ref 1) corrected by author for H_2O vapor presure. (T/k)(unit as above).

298.2/4550; 311.0/5360; 344.3/6900
377.6/7320; 411.0/6320; 444.3/5040

ESTIMATED ERROR:

$\delta k/k = \pm 0.058$ (author's est exp. error)
Rel std error of estimate 5.1-10.5 %.

REFERENCES:

1. Culbertson, O.L.; McKetta, J.J., Jr. *Pet. Trans. AIME* 1951, *192*, 223.
2. Cramer, S. D. *Ind. Eng. Chem. Process Des. Dev.* 1980, *19*, 300.
3. Cramer, S. D. *Ind. Eng. Chem. Process Des. Dev.* 1984, *23*, 618.

COMPONENTS:

1. Methane; CH_4; [74-82-8]

2. Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Yarym-Agaev, N. L.;
Sinyavskaya, R. P.; Koliushko, I.L.;
Levinton, L. Ya.;
Zh. Prikl. Khim., 1985, *58(1)*, 165-8.

VARIABLES:

Temperature, pressure

PREPARED BY:

C. L. Young

EXPERIMENTAL VALUES:

T/K	P/MPa	Mole fraction of methane in liquid	Mole fraction of methane in vapour
298.2	2.5	0.000599	0.99746
	5.0	0.00112	0.99854
	7.5	0.00146	0.999066
	10.0	0.00190	0.999180
	12.5	0.00221	0.999416
313.2	2.5	0.000490	0.99697
	5.0	0.000929	0.99813
	7.5	0.00127	0.99866
	10.0	0.00164	0.99888
	12.5	0.00187	0.999074
338.2	2.5	0.000405	0.99017
	5.0	0.000771	0.99391
	7.5	0.00110	0.99552
	10.0	0.00136	0.99652
	12.5	0.00162	0.99702

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Flow method: dry methane passed through a series of six saturators containing water, each fitted with a diffuser. gas then passed through a demister fitted with packed gauze. Flow rate of methane was about 200 cm^3 hr. Gas then passed through a heated needle valve to near atmospheric pressure. Samples of gas analysed either GC or by freezing out water and estimating gravimetrically and estimating methane volumetrically.

SOURCE AND PURITY OF MATERIALS:

1. Purity 99.95 mass per cent.
2. Distilled.

ESTIMATED ERROR:

$\partial T/K = \pm 0.1$; $\partial p/MPa = \pm 0.05$;
∂x, $\partial y = \pm 0.003$ (estimated by compiler)

REFERENCES: