

## COMPONENTS:

1. Methane; CH<sub>4</sub>; [74-82-8]
2. Methanol; CH<sub>4</sub>O; [67-56-1]

## EVALUATOR:

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University of Melbourne.  
Parkville, Victoria, 3052  
Australia.  
February 1986.

## EVALUATION:

This system has been investigated at elevated pressures by five groups (1-5). The most detailed study has been undertaken by Francesconi et al. (4) and their data are classified as tentative over the temperature range 303 K to 513 K for pressures up to 300 MPa. There are large differences between the early work of Kritchevsky and Koroleva (1) and the data reported in ref (4). At 70 MPa deviations up to 20 per cent in the gas phase mole fraction of methanol are evident. The data Shenderei et al. (2) were determined at high pressure but these workers only reported Henry's law constants. These data which cover the temperature range 213 K to 250 K are classified as tentative.

Yarym-Agaev et al. (5) investigated this system in the temperature range 298 K to 338 K at pressures up to 12.5 MPa. However there is virtually no overlap with the pressure range of the data reported by Francesconi et al. (4). The data of Yarym-Agaev et al (5) is classied as tentative. Hemmaplardh and King (3) have investigated the solubility of methanol in compressed methane up to 6 MPa. but detailed consideration of this data falls outside the scope of the present work.

References

1. Kritchevsky, I. and Koroleva, M.  
*Acta Physicochim. USSR*, 1941, *15*, 327.
2. Shenderei, E. P.; Zelvinski, Y. D.; Ivanovsky, F. P.  
*Gazov. Prom.*, 1961, *6(3)*, 42.
3. Hemmaplardh, B.; King, A. D.;  
*J. Phys. Chem.*, 1972, *76*, 2170.
4. Francesconi, A. Z.; Lentz, H.; Franck, E. U.  
*J. Phys. Chem.*, 1981, *85*, 3303.
5. Yarym-Agaev, N. L.; Sinyavskaya, R. P.; Koliushko, I. L.;  
Levinton, L. Ya.  
*Zh. Prikl. Khim.*, 1985, *58(1)*, 165.

<b>COMPONENTS:</b> 1. Methane; CH <sub>4</sub> ; [74-82-8] 2. Methanol; CH <sub>4</sub> O; [67-56-1]	<b>ORIGINAL MEASUREMENTS:</b> Shenderei, E. P.; Zelvinski, Y. D.; Ivanovsky, F. P. <i>Gazov. Prom.</i> , <u>1961</u> , 6(3), 42-45.															
<b>VARIABLES:</b> Temperature	<b>PREPARED BY:</b> C. L. Yung															
<b>EXPERIMENTAL VALUES:</b>																
<table border="1"> <thead> <tr> <th data-bbox="153 586 561 707">T/K</th> <th data-bbox="561 586 857 707">Henry's constant atm</th> <th data-bbox="857 586 1264 707">Mole fraction of methane<sup>a</sup></th> </tr> </thead> <tbody> <tr> <td data-bbox="153 707 561 747">248</td> <td data-bbox="561 707 857 747">800.0</td> <td data-bbox="857 707 1264 747">0.00125</td> </tr> <tr> <td data-bbox="153 747 561 778">238</td> <td data-bbox="561 747 857 778">756.0</td> <td data-bbox="857 747 1264 778">0.00132</td> </tr> <tr> <td data-bbox="153 778 561 808">223</td> <td data-bbox="561 778 857 808">662.0</td> <td data-bbox="857 778 1264 808">0.00151</td> </tr> <tr> <td data-bbox="153 808 561 838">213</td> <td data-bbox="561 808 857 838">610.0</td> <td data-bbox="857 808 1264 838">0.00164</td> </tr> </tbody> </table> <p data-bbox="153 858 1264 943"><sup>a</sup> extrapolated to 1 atm pressure, calculated by compiler</p>		T/K	Henry's constant atm	Mole fraction of methane <sup>a</sup>	248	800.0	0.00125	238	756.0	0.00132	223	662.0	0.00151	213	610.0	0.00164
T/K	Henry's constant atm	Mole fraction of methane <sup>a</sup>														
248	800.0	0.00125														
238	756.0	0.00132														
223	662.0	0.00151														
213	610.0	0.00164														
<b>AUXILIARY INFORMATION</b>																
<b>METHOD/APPARATUS/PROCEDURE:</b> Static equilibrium cell fitted with a magnetic stirrer. Temperature measured with a copper-constantan thermopile. Pressure measured with Bourdon gauge. Sample analysed by separating components by freezing out methanol. Details in ref. (1).	<b>SOURCE AND PURITY OF MATERIALS:</b> 1. Obtained from fermentation, free from higher hydrocarbons carbon dioxide removed by passing through potassium hydroxide solution. 2. No details given  <b>ESTIMATED ERROR:</b> $\partial T/K = \pm 0.1$ ; $\partial x/x = \pm 0.04$ (compiler)  <b>REFERENCES:</b> 1. Shenderei, E. R.; Zelvenski, Ya. D.; Ivanovskii, F. P.; <i>Khim. Prom.</i> , <u>1959</u> , 50.															

COMPONENTS:		ORIGINAL MEASUREMENTS:	
1. Methane; CH <sub>4</sub> ; [74-82-8] 2. Methanol; CH <sub>4</sub> O; [67-56-1]		Yarym-Agaev, N. L.; Sinyavskaya, R. P.; Koliushko, I.L.; Levinton, L. Ya.; Zh. Prikl. Khim., 1985, 58(1), 165-8.	
VARIABLES:		PREPARED BY:	
Temperature, pressure		C. L. Young	
EXPERIMENTAL VALUES:			
T/K	P/MPa	Mole fraction of methane in liquid                  in vapour	
298.2	2.5	0.02277	0.99192
	5.0	0.04404	0.99487
	7.5	0.06615	0.99574
	10.0	0.08080	0.99608
	12.5	0.09437	0.99564
313.2	2.5	0.02279	0.98477
	5.0	0.04164	0.98830
	7.5	0.06043	0.99011
	10.0	0.07793	0.99134
	12.5	0.09200	0.99276
338.2	2.5	0.02211	0.95433
	5.0	0.03934	0.97068
	7.5	0.05771	0.97567
	10.0	0.07239	0.97759
	12.5	0.08650	0.97956
AUXILIARY INFORMATION			
METHOD/APPARATUS/PROCEDURE:		SOURCE AND PURITY OF MATERIALS:	
Flow method: dry methane passed through a series of six saturators containing methanol, each fitted with a diffuser. gas then passed through a demister fitted with packed gauze. Flow rate of methane was about 200 cm <sup>3</sup> /hr. Gas then passed through a heated needle valve to near atmospheric pressure. Samples of gas analysed either GC or by freezing out methanol and estimating gravimetrically and estimating methane volumetrically.		1. Purity 99.95 mass per cent. 2. Contained 0.05 mass per cent water.	
		ESTIMATED ERROR: $\partial T/K = \pm 0.1$ ; $\partial p/MPa = \pm 0.05$ ; $\partial x/x = \pm 0.003$ (estimated by compiler)	
		REFERENCES:	

COMPONENTS:			ORIGINAL MEASUREMENTS:
1. Methane; CH <sub>4</sub> ; [74-82-8]			Francesconi, A. Z.; Lentz, H.;
2. Methanol; CH <sub>4</sub> O; [67-56-1]			Franck, E. U.
			<i>J. Phys. Chem.</i>
			<u>1981</u> , 85, 3303-7.
VARIABLES:			PREPARED BY:
			C. L. Young
EXPERIMENTAL VALUES:			
T/K	t/°C	P/MPa	Mole fraction of methane, $x_{\text{CH}_4}$
502.2	229.0	11.7	0.997
500.2	227.0	11.9	
495.2	222.0	12.2	
482.2	209.0	13.2	
468.2	195.0	13.9	
435.2	162.0	14.4	
317.2	44.0	18.4	
485.2	212.0	14.0	0.110
471.2	198.0	14.6	
426.7	153.5	15.4	
338.7	65.5	18.0	
318.2	45.0	21.9	
468.2	195.0	22.2	0.290
463.2	190.0	23.5	
457.7	184.5	25.4	
438.2	165.0	28.3	
409.2	136.0	32.6	
379.7	106.5	37.7	
373.2	100.0	40.6	
351.7	78.5	44.8	
328.2	55.0	49.0	
322.2	49.0	61.5	
(cont.)			
AUXILIARY INFORMATION			
METHOD/APPARATUS/PROCEDURE:		SOURCE AND PURITY OF MATERIALS:	
Static equilibrium cell fitted with a magnetic stirrer and movable piston and single colorless sapphire indow. PVT data obtained for mixtures of fixed and known compositions. Details of apparatus and procedure in source and ref. (1).		1. Messer-Griesheim sample, purity 99.95 mole per cent or better.	
		2. Research grade Merck sample, contained less than 0.01 mole per cent water.	
		ESTIMATED ERROR:	
		$\delta T/K = \pm 1.0$ ; $\delta x_{\text{CH}_4} = \pm 0.002$ .	
		REFERENCES:	
		1. Lentz, H.	
		<i>Rev. Sci. Instrum.</i>	
		<u>1969</u> , 40, 341.	

COMPONENTS:		ORIGINAL MEASUREMENTS:	
1. Methane; CH <sub>4</sub> ; [74-82-8]		Francesconi, A. Z.; Lentz, H.;	
2. Methanol; CH <sub>4</sub> O; [67-56-1]		Franck, E. U.	
		<i>J. Phys. Chem.</i>	
		1981, 85, 3303-7.	
EXPERIMENTAL VALUES:			
T/K	t/°C	P/MPa	Mole fraction of methane, x <sub>CH<sub>4</sub></sub>
457.2	184.0	9.2	0.359
471.2	198.0	10.7	
481.2	208.0	13.4	
483.2	210.0	16.6	
479.2	206.0	18.1	
476.2	203.0	19.8	
467.2	194.0	23.7	
458.2	185.0	25.1	
453.2	180.0	26.0	
450.2	177.0	28.3	
443.7	170.5	30.1	
436.2	163.0	32.5	
427.2	154.0	35.7	
430.2	157.0	9.3	0.464
445.7	172.5	11.7	
455.2	182.0	15.5	
464.2	191.0	19.4	
465.2	192.0	22.9	
458.2	185.0	26.0	
442.8	169.6	29.8	
435.2	162.0	32.8	
425.8	152.6	35.8	
417.2	144.0	39.6	0.464
406.2	133.0	44.4	
392.8	119.6	51.0	
381.7	108.5	58.0	
373.7	100.5	64.3	
364.2	91.0	71.3	
345.4	72.2	80.6	
336.0	62.8	88.9	
324.0	50.8	101.1	
418.2	145.0	12.2	0.549
433.2	160.0	15.2	
443.2	170.0	18.0	
451.7	178.5	22.5	
451.2	178.0	26.6	
442.2	169.0	30.3	
433.7	160.5	33.4	
419.9	146.7	40.0	
395.2	122.0	50.8	
376.7	103.5	63.7	
356.8	83.6	76.8	
341.2	68.0	94.2	
322.2	49.0	126.8	
314.8	41.6	141.9	
305.2	32.0	168.7	
297.2	24.0	198.6	
433.2	160.0	21.5	0.700
437.2	164.0	23.9	
437.2	164.0	24.7	
432.2	159.0	28.9	
422.2	149.0	34.0	
402.2	129.0	44.5	
391.7	118.5	51.4	

(cont.)

COMPONENTS:		ORIGINAL MEASUREMENTS:	
1. Methane; CH <sub>4</sub> ; [74-82-8]		Francesconi, A. Z.; Lentz, H.;	
2. Methanol; CH <sub>4</sub> O; [67-56-1]		Franck, E. U.	
		<i>J. Phys. Chem.</i>	
		<u>1981, 85, 3303-7.</u>	
EXPERIMENTAL VALUES:			
T/K	t/°C	P/MPa	Mole fraction of methane, $x_{\text{CH}_4}$
381.7	108.5	58.6	0.700
366.8	93.6	71.5	
354.5	81.3	86.5	
344.0	70.8	102.1	
336.4	63.2	115.0	
325.6	52.4	145.0	
321.6	48.4	164.9	
317.6	44.4	190.4	
313.8	40.6	208.0	
311.7	38.5	227.8	
309.4	36.2	245.8	
308.2	35.0	270.5	
305.8	32.6	292.3	
410.2	137.0	22.8	0.816
413.2	140.0	25.2	
415.2	142.0	30.0	
410.2	137.0	32.6	
398.7	125.5	37.0	
391.2	118.0	42.3	
378.2	105.0	50.0	
364.2	91.0	61.0	
349.2	76.0	78.3	
337.2	64.0	101.3	
328.7	55.5	121.5	
320.2	47.0	159.0	
313.5	40.3	186.1	
312.3	39.1	220.6	
309.2	36.0	247.5	
308.7	35.5	275.0	
307.0	33.8	293.5	
380.2	107.0	34.0	0.9158
373.2	100.0	40.5	
363.2	90.0	53.0	
349.2	76.0	65.3	
342.2	69.0	88.5	
327.2	54.0	99.5	
322.2	49.0	121.6	
318.2	45.0	141.5	
303.2	30.0	248.0	

COMPONENTS: 1. Methane; CH <sub>4</sub> ; [74-82-8] 2. Ethanol; C <sub>2</sub> H <sub>6</sub> O; [64-17-5]		ORIGINAL MEASUREMENTS: Frolich, P.K.; Tauch, E.J.; Hogan, J.J.; Peer, A.A.  <i>Ind. Eng. Chem.</i> <u>1931</u> , <i>23</i> , 548-550	
VARIABLES:  Pressure		PREPARED BY:  C.L. Young	
EXPERIMENTAL VALUES:			
T/K	P/MPa	Solubility* ,S	Mole fraction of methane in liquid, x <sub>CH<sub>4</sub></sub>
298.15	1.0	4	0.0095
	2.0	8	0.019
	3.0	12	0.028
	4.0	16	0.037
	5.0	20	0.046
	6.0	24	0.054
	7.0	27.5	0.062
	8.0	31.2	0.070
	9.0	36.5	0.081
	10.0	40.5	0.089
	11.0	45	0.097
	12.0	49	0.105
* Data taken from graph in original article. Volume of gas measured at 101.325 kPa and 298.15 K dissolved by unit volume of liquid measured under the same conditions.			
+ calculated by compiler.			
AUXILIARY INFORMATION			
METHOD/APPARATUS/PROCEDURE:  Static equilibrium cell. Liquid saturated with gas and after equilibrium established samples removed and analysed by volumetric method. Allowance was made for vapor pressure of liquid and the solubility of the gas at atmospheric pressure. Details in source.		SOURCE AND PURITY OF MATERIALS:  Stated that the materials were the highest purity available.	
		ESTIMATED ERROR:  $\delta T/K = \pm 0.1$ ; $\delta x_{CH_4} = \pm 5\%$	
		REFERENCES:	

COMPONENTS: 1. Methane; CH <sub>4</sub> ; [74-82-8] 2. 2-Propanol; C <sub>3</sub> H <sub>8</sub> O; [67-63-0]		ORIGINAL MEASUREMENTS: Frolich, P.K.; Tauch, E.J.; Hogan, J.J.; Peer, A.A.  <i>Ind. Eng. Chem.</i> <u>1931</u> , 23, 548-550	
VARIABLES:  Pressure		PREPARED BY:  C.L. Young	
EXPERIMENTAL VALUES:			
T/K	P/MPa	Solubility <sup>*,S</sup>	Mole fraction of methane in liquid, <sup>+</sup> x <sub>CH<sub>4</sub></sub>
298.15	1.0	4	0.012
	2.0	9	0.028
	3.0	14	0.042
	4.0	19	0.056
	5.0	25	0.073
	6.0	30.5	0.088
	7.0	36.5	0.103
	8.0	42.5	0.118
	9.0	48	0.131
* Data taken from graph in original article. Volume of gas measured at 101.325 kPa pressure and 298.15K dissolved by unit volume of liquid measured under the same conditions.			
+ calculated by compiler.			
AUXILIARY INFORMATION			
METHOD/APPARATUS/PROCEDURE:  Static equilibrium cell. Liquid saturated with gas and after equilibrium established samples removed and analysed by volumetric method. Allowance was made for vapor pressure of liquid and the solubility of the gas at atmospheric pressure. Details in source.		SOURCE AND PURITY OF MATERIALS:  Stated that the materials were the highest purity available.	
		ESTIMATED ERROR:  $\delta T/K = \pm 0.1$ ; $\delta x_{CH_4} = \pm 5\%$	
		REFERENCES:	

<p>COMPONENTS:</p> <p>(1) Methane; CH<sub>4</sub>; [74-82-8]</p> <p>(2) Cyclohexanol; C<sub>6</sub>H<sub>12</sub>O; [108-93-0]</p>	<p>EVALUATOR:</p> <p>H. Lawrence Clever Chemistry Department Emory University Atlanta, GA 30322 USA</p> <p>1985, April</p>
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## CRITICAL EVALUATION:

Cauquil (ref 1) and Lannung and Gjaldbaek (ref 2) have measured the solubility of methane in cyclohexanol. The single solubility value of Cauquil is rejected because it is only about one-half the magnitude of the values reported by Lannung and Gjaldbaek, workers whose solubility data are usually reliable.

The mole fraction solubility values of Lannung and Gjaldbaek were treated by a linear regression to obtain the equation

$$\ln x_1 = -7.8296 + 3.4376/(T/100 \text{ K})$$

with a standard error about the regression line of  $1.12 \times 10^{-5}$ .

The equation was treated to obtain the thermodynamic changes for the transfer of one mole of methane from the gas at a pressure of 0.101325 MPa to the infinitely dilute solution of

$$\Delta H_1^0/\text{kJ mol}^{-1} = -2.86 \text{ and } \Delta S_1^0/\text{J K}^{-1} \text{ mol}^{-1} = -65.1.$$

Smoothed values of the mole fraction solubility are in Table 1.

Table 1. The solubility of methane in cyclohexanol. Tentative values of the mole fraction solubility and partial molal Gibbs energy of solution as a function of temperature at a methane partial pressure of 0.101325 MPa.

$T/\text{K}$	$10^3 x_1$	$\Delta G_1^0/\text{kJ mol}^{-1}$
298.15	1.26	16.551
303.15	1.24	16.876
308.15	1.21	17.202

1. Cauquil, G. *J. Chim. Phys.* 1927, 24, 53-5.
2. Lannung, A.; Gjaldbaek, J. C. *Acta Chem. Scand.* 1960, 14, 1124-8.

<p>COMPONENTS:</p> <p>(1) Methane; CH<sub>4</sub>; [74-82-8]</p> <p>(2) Cyclohexanol; C<sub>6</sub>H<sub>12</sub>O; [108-93-0]</p>	<p>ORIGINAL MEASUREMENTS:</p> <p>Cauquil, G. <i>J. Chim. Phys.</i> <u>1927</u>, <i>24</i>, 53-55.</p>
<p>VARIABLES:</p> <p style="text-align: center;"><math>T/K = 299</math> <math>p_1/kPa = 102</math></p>	<p>PREPARED BY:</p> <p style="text-align: center;">H. L. Clever</p>
<p>EXPERIMENTAL VALUES:</p> <p>The author states that one liter of cyclohexanol absorbs 133 cm<sup>3</sup> methane at 26 °C and 765 mmHg.</p> <p>The compiler calculates an Ostwald coefficient of <math>L/cm^3cm^{-3} = 0.133</math> and a mole fraction solubility at 101.325 kPa of <math>x_1 = 5.6 \times 10^{-4}</math> at 299 K.</p>	
<p>AUXILIARY INFORMATION</p>	
<p>METHOD/APPARATUS/PROCEDURE:</p> <p>The apparatus appears to be of the Bunsen type.</p> <p>The initial and final volumes of gas in contact with the liquid were measured at 26 °C and a known pressure. The liquid vapor pressure was ignored.</p>	<p>SOURCE AND PURITY OF MATERIALS:</p> <p>(1) Methane. No information.</p> <p>(2) Cyclohexanol. Distilled, boiling point 160.9 °C at 766 mmHg. Degassed and tested to be air free.</p> <p>ESTIMATED ERROR:</p> <p style="text-align: center;"><math>\delta L/L = \pm 0.05</math> (compiler)</p> <p>REFERENCES:</p>

<b>COMPONENTS:</b> (1) Methane; CH <sub>4</sub> ; [74-82-8] (2) Cyclohexanol; C <sub>6</sub> H <sub>12</sub> O; [108-93-0]	<b>ORIGINAL MEASUREMENTS:</b> Lannung, A.; Gjaldbaek, J. C. <i>Acta Chem. Scand.</i> <u>1960</u> , <i>14</i> , 1124 - 1128.																										
<b>VARIABLES:</b> $T/K = 298.15 - 310.15$ $p_1/kPa = 101.325$ (1 atm)	<b>PREPARED BY:</b> J. Chr. Gjaldbaek																										
<b>EXPERIMENTAL VALUES:</b> <table border="1" data-bbox="237 519 1078 717"> <thead> <tr> <th>T/K</th> <th>Mol Fraction <math>10^3 x_1</math></th> <th>Bunsen Coefficient <math>\alpha/cm^3</math> (STP) <math>cm^{-3} atm^{-1}</math></th> <th>Ostwald Coefficient <math>L/cm^3 cm^{-3}</math></th> </tr> </thead> <tbody> <tr> <td>298.15</td> <td>1.25</td> <td>0.263</td> <td>0.287</td> </tr> <tr> <td>298.15</td> <td>1.27</td> <td>0.268</td> <td>0.292</td> </tr> <tr> <td>310.15</td> <td>1.20</td> <td>0.251</td> <td>0.285</td> </tr> <tr> <td>310.15</td> <td>1.21</td> <td>0.253</td> <td>0.287</td> </tr> </tbody> </table> <p>Smoothed Data: For use between 298.15 and 310.15 K.</p> $\ln x_1 = -7.8296 + 3.4376/(T/100 \text{ K})$ <p>The standard error about the regression line is <math>1.12 \times 10^{-5}</math>.</p> <table border="1" data-bbox="467 880 817 1030"> <thead> <tr> <th>T/K</th> <th>Mol Fraction <math>10^3 x_1</math></th> </tr> </thead> <tbody> <tr> <td>298.15</td> <td>1.26</td> </tr> <tr> <td>308.15</td> <td>1.22</td> </tr> </tbody> </table>		T/K	Mol Fraction $10^3 x_1$	Bunsen Coefficient $\alpha/cm^3$ (STP) $cm^{-3} atm^{-1}$	Ostwald Coefficient $L/cm^3 cm^{-3}$	298.15	1.25	0.263	0.287	298.15	1.27	0.268	0.292	310.15	1.20	0.251	0.285	310.15	1.21	0.253	0.287	T/K	Mol Fraction $10^3 x_1$	298.15	1.26	308.15	1.22
T/K	Mol Fraction $10^3 x_1$	Bunsen Coefficient $\alpha/cm^3$ (STP) $cm^{-3} atm^{-1}$	Ostwald Coefficient $L/cm^3 cm^{-3}$																								
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308.15	1.22																										
<b>AUXILIARY INFORMATION</b>																											
<b>METHOD/APPARATUS/PROCEDURE:</b> A calibrated all-glass combined manometer and bulb containing degassed solvent and the gas was placed in an air thermostat and shaken until equilibrium (1).  The absorbed volume of gas is calculated from the initial and final amounts, both saturated with solvent vapor. The amount of solvent is determined by the weight of displaced mercury.  The values are at 101.325 kPa (1 atm) pressure assuming Henry's law is obeyed.	<b>SOURCE AND PURITY OF MATERIALS:</b> (1) Methane. Generated from magnesium methyl iodide. Purified by fractional distillation. Specific gravity corresponds with mol wt 16.08. (2) Cyclohexanol. Poulenc Frères. "pur." Fractionated twice <i>in vacuo</i> . M.p./°C = 23.6 - 23.9.  <b>ESTIMATED ERROR:</b> $\delta T/K = \pm 0.05$ $\delta x_1/x_1 = \pm 0.015$																										
	<b>REFERENCES:</b> 1. Lannung, A. <i>J. Am. Chem. Soc.</i> <u>1930</u> , <i>52</i> , 68.																										