COMPONENTS:	EVALUATOR:
(1) Methane; CH_4; [74-82-8]	H. Lawrence Clever Chemistry Department
(2) Octamethylcyclotetrasiloxane; $C_8H_{24}O_4Si_4$; [556-67-2]	Emory University Atlanta, GA 30322 USA
	1985, April

CRITICAL EVALUATION:

Chappelow and Prausnitz (ref 1) report Henry's constants for the system at 25 degree intervals from 300 to 425 K. The Henry's constants were converted to mole fraction solubilities at a methane pressure of 0.101325 MPa assuming a linear relationship between pressure and mole fraction. The solubilities go through a minimum between 375 and 400 K. Wilcock *et al.* (ref 2) report solubilities at three temperatures between 292.15 and 313.15 K. Both laboratories used a volumetric method. The smoothed mole fraction solubilities from the two papers agree within 0.5 percent over the 292 to 325 K range.

The data from both papers are classed as tentative. The data have been treated in two ways. First, the mole fraction solubilities between 292.15 and 350 K were fit by a linear regression to the two constant equation

$$\ln x_1 = -6.04961 + 4.12303/(T/100 \text{ K})$$

with a standard error about the regression line of 5.37 x 10^{-5}. Second, all of the data from both papers were treated by a linear regression to obtain a four constant equation that gives a minimum solubility near 393 K.

$$\ln x_1 = 52.96522 - 77.0211/(T/100 \text{ K}) - 50.6322 \ln (T/100 \text{ K}) + 7.8863(T/100)$$

with a standard error about the regression line of 5.73 × 10^{-5}.

The two equations give mole fraction solubilities over the 292.15 to 348.15 K interval that agree within 0.2 percent. The thermodynamic changes for the transfer of one mole of methane from the gas at a methane pressure of 0.101325 MPa to the infinitely dilute solution are

$$\Delta H_1^0/\text{kJ mol}^{-1} = -3.43 \quad \text{and} \quad \Delta S_1^0/\text{J K}^{-1}\text{ mol}^{-1} = -50.3$$

from the two constant equation. The four constant equation gives values of ΔH_1^0, ΔS_1^0, and ΔC_{p1}^0 which are functions of temperature of

T/K	$\Delta H_1^0/\text{J mol}^{-1}$	$\Delta S_1^0/\text{J K}^{-1}\text{ mol}^{-1}$	$\Delta C_{p1}^0/\text{J K}^{-1}\text{ mol}^{-1}$
293.15	-3.02	-48.9	-36.5
308.15	-3.42	-50.3	-16.9
323.15	-3.53	-50.6	+ 2.8
373.15	-1.75	-45.6	68.4
398.15	+0.37	-40.1	101.2
423.15	3.31	-33.0	133.9

It is unusual to find solubility data that requires more than a three constant equation to represent the temperature dependence, but this is such a case. Smoothed values of the mole fraction solubility from both equations are in Table 1.

Table 1. The solubility of methane in octamethylcyclotetrasiloxane. Tentative values of the mole fraction solubility as a function of temperature at a methane partial pressure of 0.101325 MPa.

T/K	$10^3 x_1$		T/K	$10^3 x_1$
	2 const eqn	4 const eqn		4 const eqn
293.15	9.63	9.61	353.15	7.61
298.15	9.40	9.40	363.15	7.43
303.15	9.19	9.20	373.15	7.29
308.15	8.99	9.00	383.15	7.21
313.15	8.80	8.81	393.15	7.18
318.15	8.62	8.63	403.15	7.20
323.15	8.45	8.45	413.15	7.27
			423.15	7.40
348.15	7.71	7.72		

REFERENCES:

1. Chappelow, C. C.; Prausnitz, J. M. *Am. Inst. Chem. Eng. J.* <u>1974</u>, *20*, 1097 - 1104.
2. Wilcock, R. J.; McHale, J. L.; Battino, R.; Wilhelm, E. *Fluid Phase Equilib.* 1978, *2*, 225 - 30.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methane; CH_4; [74-84-8] (2) Octamethylcyclotetrasiloxane; $C_8H_{24}O_4Si_4$; [556-67-2]	Wilcock, R. J.; McHale, J. L.; Battino, B.; Wilhelm, E. *Fluid Phase Equilib.* 1978, 2, 225-230.

VARIABLES:	PREPARED BY:
T/K: 292.15 - 313.04 p/kPa: 101.325 (1 atm)	H. L. Clever

EXPERIMENTAL VALUES:

T/K	Mol Fraction $10^3 x_1$	Bunsen Coefficient α/cm^3(STP)cm^{-3}atm^{-1}	Ostwald Coefficient L/cm^{3}cm^{-3}
292.15	9.647	0.7032	0.7521
298.01	9.346	0.6764	0.7380
313.04	8.880	0.6310	0.7231

The solubility values were adjusted to a gas partial pressure of 101.325 kPa by Henry's law.

The Bunsen coefficients were calculated by the compiler.

Smoothed Data: For use between 292.15 and 313.04 K.

$$\ln x_1 = -5.8575 + 3.5442/(T/100K)$$

The standard error about the regression line 5.46 x 10^{-5}.

T/K	Mol Fraction $10^3 x_1$
298.15	9.384
308.15	9.029

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The apparatus is based on the design of Morrison and Billett (1), and the version used is described by Battino, Evans, and Danforth (2). The degassing apparatus and procedure are described by Battino, Banzhof, Bogan, and Wilhelm (3). Degassing. Up to 500 cm^3 of solvent is placed in a flask of such size that the liquid is about 4 cm deep. The liquid is rapidly stirred, and vacuum is applied intermittently through a liquid N$_2$ trap until the permanent gas residual pressure drops to 5 microns. Solubility Determination. The degassed solvent is passed in a thin film down a glass spiral tube containing the solute gas plus the solvent vapor at a total pressure of one atm. The volume of gas absorbed is found by difference between the initial and final volumes in the buret system. The solvent is collected in a tared flask and weighed.	(1) Methane. Matheson Co., Inc. Stated to be 99.97 mole percent minimum purity. (2) Octamethylcyclotetrasiloxane. General Electric Co. Distilled, density at 298.15 K was 0.9500 g cm^{-3}.

	ESTIMATED ERROR: δT/K = 0.03 δP/mmHg = 0.5 $\delta x_1/x_1$ = 0.1

REFERENCES:
1. Morrison, T. J.; Billett, F.
   J. Chem. Soc. 1948, 2033.
2. Battino,R.;Evans,F.D.;Danforth,W.F.
   J.Am.Oil Chem.Soc. 1968, 45, 830.
3. Battino, R.; Banzhof, M.;
   Bogan, M.; Wilhelm, E.
   Anal. Chem. 1971, 43, 806.

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Methane; CH_4; [74-82-8] 2. Octamethylcyclotetrasiloxane; $C_8H_{24}O_4Si_4$; [556-67-2]	Chappelow, C.C.; Prausnitz, J.M. *Am. Inst. Chem. Engnrs. J.* <u>1974</u>, *20*, 1097-1104.

VARIABLES:
   Temperature
	PREPARED BY:
	   C.L. Young

EXPERIMENTAL VALUES:

T/K	Henry's Constant[a] /atm	Mole fraction[b] of methane at 1 atm partial pressure, x_{CH_4}
300	107	0.00935
325	119	0.00840
350	131	0.00763
375	138	0.00725
400	138	0.00725
425	135	0.00741

a. Authors stated measurements were made at several pressures
and values of solubility used were all within the Henry's
Law region.

b. Calculated by compiler assuming linear relationship between
mole fraction and pressure.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Volumetric apparatus similar to that described by Dymond and Hildebrand (1). Pressure measured with a null detector and precision gauge. Details in ref . (2).	Solvent degassed, no other details given.

ESTIMATED ERROR:

$\delta T/K = \pm 0.1$; $\delta x_{CH_4} = \pm 1\%$

REFERENCES:

1. Dymond, J.; Hildebrand, J.H.
Ind.Chem.Eng.Fundam.<u>1967</u>,*6*,130.
2. Cukor, P.M.; Prausnitz, J.M.
Ind.Chem.Eng.Fundam.<u>1971</u>,*10*,638.

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Methane; CH_4; [74-82-8] 2. Esters of phosphoric acid	Lenoir, J-Y.; Reanult, P.; Renon, H. *J. Chem. Eng. Data*, <u>1971</u>, *16*, 340-2.
VARIABLES: Temperature	PREPARED BY: C. L. Young

EXPERIMENTAL VALUES:

T/K	Henry's constant H_{CH_4}/atm	Mole fraction at 1 atm* x_{CH_4}
Phosphoric acid, triethyl ester; $C_6H_{15}O_4P$; [78-40-0]		
325.2	705	0.00142
Phosphoric acid, tripropyl ester; $C_9H_{21}O_4P$; [513-08-6]		
298.2	257	0.00389
323.2	306	0.00327
343.2	325	0.00308
Phosphoric acid, tributyl ester; $C_{12}H_{27}O_4P$; [126-73-8]		
325.2	224	0.00446
Phosphoric acid, tris(2-methylpropyl)ester; $C_{12}H_{27}O_4P$; [126-71-6]		
325.2	190	0.00526

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

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
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.	(1) L'Air Liquide sample, minimum purity 99.9 mole per cent. (2) Touzart and Matignon or Serlabo sample, purity 99 mole per cent.
	ESTIMATED ERROR: $\delta T/K = \pm 0.1$; $\delta H/atm = \pm 6\%$ (estimated by compiler).
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Methane; CH_4; [74-82-8] 2. Phosphoric acid tributyl ester (Tributyl phosphate); $(C_4H_9)_3PO_4$; [126-73-8]	Shakhova, S.F.; Zubchenko, Yu.P. *Khim. Prom.* 1973, *49*, 595-6.

VARIABLES:	PREPARED BY:
Temperature, pressure	C.L. Young

EXPERIMENTAL VALUES:

T/K	$P/10^5$Pa	Mole fraction of methane in liquid, x_{CH_4}	α^+ vol/vol
298.15	37.49	0.1475	14.9
	47.52	0.1760	18.4
	58.36	0.2194	24.2
	67.38	0.2305	25.8
	74.58	0.2400	27.2
	90.02	0.2854	34.4
	100.72	0.3005	37.0
323.15	38.81	0.1372	13.7
	48.03	0.1600	16.4
	72.14	0.2186	24.1
	93.22	0.2653	31.1
	95.14	0.2678	31.5
	103.15	0.2848	34.3
	105.48	0.2913	35.4
	110.64	0.2901	35.2
343.15	43.37	0.1346	13.4
	53.50	0.1591	16.3
	66.27	0.1915	20.4
	82.38	0.2326	26.1
	96.16	0.2577	29.9
	98.29	0.2603	30.3
	104.97	0.2715	32.1

+ values quoted in original paper, appear to be the volume of gas at T/K = 273.15 and P = 1 atmosphere absorbed by unit volume of liquid at room temperature.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Rocking autoclave. Mixture stirred by ball in rocking autoclave. Sample of liquid analysed by volumetric method. Details in source.	1. Purity 97.8 mole per cent. 2. No details given.

ESTIMATED ERROR:

$\delta T/K = \pm 0.1$; $\delta P/10^5$Pa $= \pm 0.1$;

$\delta x_{CH_4} = \pm 5\%$.

(estimated by compiler)

REFERENCES:

1. Shakhova, S.F. Zubchenko, Yu.P. Kaplan, L.K.

   Khim. Prom. 1973, *5*, 102.

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Methane; CH_4: [74-82-8] 2. Hexamethylphosphoric triamide; $C_8H_{24}N_3OP$; [680-31-9]	Lenoir, J-Y.; Renault, P.; Renon, H. *J. Chem. Eng. Data*, 1971, *16*, 340-2.

VARIABLES:	PREPARED BY:
	C. L. Young

EXPERIMENTAL VALUES:

T/K	Henry's constant H_{CH_4}/atm	Mole fraction at 1 atm* x_{CH_4}
298.2	471	0.00212

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

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
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.	(1) L'Air Liquide sample, minimum purity 99.9 mole per cent. (2) Touzart and Matignon or Serlabo sample, purity 99 mole per cent.
	ESTIMATED ERROR: $\delta T/K = \pm 0.1$; δH/atm $= \pm 6\%$ (estimated by compiler).
	REFERENCES: