COMPONENTS:	EVALUATOR:
(1) Methane; CH ₄ ; [74-82-8] (2) Alkanes	H. Lawrence Clever Chemistry Department Emory University Atlanta, GA 30322 USA
	1984. January

CRITICAL EVALUATION:

The Solubility of Methane in Alkanes at Partial

Pressures up to 200 kPa (ca. 2 atm).

The solubility of methane in normal alkanes.

The two methods most commonly used to determine the solubility of methane in alkanes are volumetric methods used at a total pressure of about one atmosphere and gas liquid chromatography methods in which retention times or volumes are measured when the solvent is the stationary phase. Also used was a gas pressure change method at very low methane partial pressure and a gas stripping method with the GLC used as a detector.

With two exceptions the volumetric methods used since 1960 give consistent results which appear to be reliable within several percent. The GLC methods used since 1974 also appear to give reliable results. Earlier work by both methods gave solubility values that appear to be too small sometimes by as much as 40 percent.

The volumetric methods used cover a variety of degassing and equilibration techniques. The solubility values from the early work of McDaniel (ref. 1) are consistently too small. This may be because of poor equilibration in the hand shaken apparatus or incomplete degassing of the solvent.

Guerry (ref. 2) used a modified van Slyke method. The small solvent volumes and large solvent vapor pressure gave problems which resulted in too small solubility values. Tilquin $et\ al.$ (ref. 5) measured pressure changes at low methane partial pressures when degassed solvent and gas were contacted. When the methane solubility is calculated for 101.325 kPa partial pressure, the value appears to be too small for the normal alkane and too large for the branched alkane. It is possible that Henry's Law is not obeyed between the low partial pressure of the measurement and atmospheric pressure, but Henry's law is supported by the GLC results on solvents of higher carbon number. The results of Makranczy $et\ al.$ (ref. 11) are often too large. Their volumetric technique appears to have problems when solvents of relatively large vapor pressure are studied. Both Lannung and Gjaldbaek (ref. 3) and Wilcock $et\ al.$ (ref. 12) usually report reliable solubility values. However, both find a smaller temperature coefficient of solubility and enthalpy of solution for methane in hexane and octane than do most other workers which casts some doubts on their results for these systems. The other solubility values by volumetric methods (ref. 7, 9, 10, and 13) appear to show a consistent and reliable pattern of results.

The GLC retention time studies of Ng $et\ al$. (ref. 6) and Lenoir $et\ al$. (ref. 8) give methane solubility values that appear to be too small. The results obtained by Lin and Parcher (ref. 15) from GLC retention volume studies and by Richon and Renon (ref. 14) by gas stripping and GLC detector method appear to give reasonable methane solubility values.

The mole fraction solubility values at 298.15 K and 101.325 kPa methane pressure are given as a function of normal alkane carbon number in Fig. 1. Although the values show considerable scatter, we believe that there are enough reliable values measured by traditional volumetric methods near atmospheric pressure to allow a reliable line to be placed through the data. Octadecane melts at 301.33 K, thus the normal alkanes of C_{18} and larger melt at temperatures greater than 298.15 K. The solubility values of methane in hydrocarbons of carbon number 18 and greater are for a hypothetical liquid hydrocarbon. The values were estimated from solubility data at higher temperatures by assuming $\ln x_1$ vs 1/(T/K) is linear. The

- (1) Methane; CH₄; [74-82-8]
- (2) Alkanes

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CRITICAL EVALUATION:

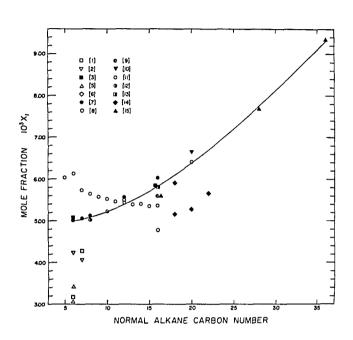


Figure 1. The mole fraction solubility of methane at 298.15 K and 0.1013 MPa partial pressure in the normal alkanes.

The ${\rm C}_{18}$ and above hydrocarbons are solids at 298.15 K. The solubility values are extrapolated from experimental values in the liquid state at higher temperatures.

The numbers refer to the references at the end of the evaluation.

solubility of Tilquin $et\ al.$ (ref. 5) in hexane was adjusted assuming Henry's law and an average enthalpy of solution to estimate a 298 K value from the experimental value at 288 K.

The line drawn in Fig. 1 must be considered as only an approximation as to how the methane mole fraction solubility at 298.15 K and 101.325 kPa methane pressure changes with carbon number. The steady increase in solubility as the carbon number increases seems reasonable. The mole fraction solubility does increase more rapidly with carbon number than does the contact surface of the hydrocarbon.

The partial molal enthalpy of solution of methane in normal alkanes averages (-4.1 \pm 0.5) kJ mol⁻¹ at 298.15 K for hydrocarbons C₆ through C₂₀. The enthalpy values in heptane and hexadecane indicate the methane solubility values in these solvents are not quite consistent with the data on the other systems.

The work of Cukor and Prausnitz (ref. 9) and Chappelow and Prausnitz (ref. 10) indicate the enthalpy of solution decreases in magnitude as the temperature increases. Values of the partial molal enthalpies of solution of methane in normal alkanes from a three constant equation fitted to the data are about

$$T/K$$
 298 323 373 473 $\Delta \overline{H}_1^{\circ}/kJ \text{ mol}^{-1}$ -4.1 -3.1 -2.2 -0.4

The individual systems are discussed in more detail below.

Methane + Pentane; C₅H₁₂; [109-66-0]

The mole fraction solubility of 6.02×10^{-3} at 298.15 K and 101.32 101.325 kPa methane pressure of Makranczy et~al. (ref. 11) is the only experimental value for the system. Although it is classed as tentative, we believe it may be as much as 15-20 percent too large.

Methane + Hexane; $C_{6}H_{14}$; [110-54-3]

The solubility of methane in hexane is reported from six laboratories. The early work of McDaniel (ref. 1) and Guerry (ref. 2) is rejected. Their solubility values at temperatures between 293 and 333 K are much too small. The single value of Tilquin et al. (ref. 5) at 288.15 is also rejected, however, it may have some validity as a distribution coefficient at small methane partial pressures. The single value of Makranczy et al. (ref. 11) at 298.15 K is classed as doubtful. It may be 15-20 percent too large.

The values of Lunnung and Gjaldbaek (ref. 3) at 291.15, 298.15, and 310.15 K and of Hayduk and Buckley (ref. 7) over the 273.15 to 323.15 K interval are classed as tentative. There is an inconsistency in the two data sets in that the Lannung and Gjaldbaek data gives an enthalpy of solution of -2.1 kJ mol⁻¹ while the Hayduk and Buckley data gives a value of -4.7 kJ mol⁻¹. The Lannung, Gjaldbaek data extends over a much shorter temperature interval. The two studies appear internally consistent. Although the temperature coefficients of solubility differences casts some doubts on the results, the mole fraction solubility values from the two papers were combined in a linear regression to obtain the tentative equation for the mole fraction solubility over the 273.15 to 323.15 K interval.

$$\ln x_1 = -6.92496 + 4.85402/(T/100 \text{ K})$$

With a standard error about the regression line of 1.60 \times 10⁻⁴. From the equation, the temperature independent thermodynamic quantities are

$$\Delta \overline{H}_{1}^{\circ}$$
 / kJ mol⁻¹ = -4.04 and $\Delta \overline{S}_{1}^{\circ}$ / J K⁻¹ mol⁻¹ = -57.6

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- (1) Methane; CH_A; [74-82-8]
- (2) Alkanes

EVALUATOR:

H. Lawrence Clever Chemistry Department Emory University Atlanta, GA 30322 USA

1984, January

CRITICAL EVALUATION:

Smoothed values of the mole fraction solubility and partial molar Gibbs energy of solution are in Table 1.

Table 1. Solubility of methane in hexane at a methane partial pressure of 101.325 kPa (1 atm). Tentative mole fraction solubility and partial molal Gibbs energy of solution as a function of temperature.

T/K	Mol Fraction	$\Delta \overline{G}_1^{\circ}/kJ \text{ mol}^{-1}$
	10 ³ x ₁	-
273.15 283.15 293.15	5.81 5.46 5.15	11.691 12.267 12.843
298.15	5.01	13.131
303.15 313.15 323.15	4.87 4.63 4.41	13.418 13.994 14.570

Methane + Heptane; C₇H₁₆; [142-82-5]

McDaniel (ref. 1) reports the solubility of methane in heptane at 295.35, 303.25, and 313.15 K, Guerry (ref. 2) at 293.15 and 298.15 K, Hayduk and Buckley (ref. 7) at 298.15, 323.15 and 348.15 K, and Makranczy et al. (ref. 11) at 298.15 K. Again the McDaniel and the Guerry data are rejected as too small. The other data are classed as tentative, but the data of Hayduk and Buckley are preferred.

The tentative data below are based entirely on the three measurements of Hayduk and Buckley. The mole fraction solubility values were fitted by a linear regression to obtain the tentative equation for the 298.15 to 348.15 K temperature interval

$$\ln x_7 = -7.28446 + 5.95159/(T/100 K)$$

with standard error about the regression line of 2.18×10^{-5} . From the equation the temperature independent thermodynamic changes are

$$\Delta \overline{H}_1^{\circ}/kJ \text{ mol}^{-1} = -4.95 \text{ and } \Delta \overline{S}_1^{\circ}/J \text{ K}^{-1} \text{ mol}^{-1} = -60.6$$

Smoothed values of the mole fraction solubility and partial molar Gibbs energy of solution are in Table 2.

Table	2.	Solubility of methane in heptane at a partial pressure of
		101.325 kPa (1 atm) methane. Tentative mole fraction
		solubility and partial molal Gibbs energy as a function
		of temperature.

Mol Fraction	$\Delta \overline{G}_1^{\circ}/\text{kJ mol}^{-1}$
10 ³ x ₁	
5.05	13.109
4.89	13.412
4.59	14.017 14.623
4.09	15.229 15.835
	10 ³ x ₁ 5.05 4.89 4.59 4.33

Methane + Octane; C_8H_{18} ; [111-65-9]

Hayduk and Buckley (ref. 7) report the solubility of methane in octane at four temperatures between 273.15 and 348.15 K, Makranczy $et\ al.$ (ref. 11) report one solubility value at 298.15 K and Wilcock $et\ al.$ (ref. 12) report values 298.15 and 313.35 K. All are classed as tentative but the data from (ref. 7 and 12) are preferred.

The temperature coefficients of solubility differ in the two studies. Wilcock $et\ al.$ data are consistent with an enthalpy of solution of -2.97 kJ mol⁻¹ and the Hayduk and Buckley a value of -4.16 kJ mol⁻¹. The Wilcock $et\ al.$ enthalpy is based on only two experimental points 15 degrees apart and thus subject to some error.

The six experimental values from Hayduk and Buckley and from Wilcock \it{et} \it{al} . were combined in a linear regression to obtain the tentative equation

$$\ln x_1 = -6.94961 + 4.95903/(T/100 K)$$

with a standard error around the regression line of 5.37×10^{-5} . The temperature independent thermodynamic changes from the equation are

$$\Delta \overline{H}_{1}^{\circ}/kJ \text{ mol}^{-1} = -4.12$$
 and $\Delta \overline{S}_{1}^{\circ}/J \text{ K}^{-1} \text{ mol}^{-1} = -57.8$

Smoothed values of the mole fraction solubility and partial molar Gibbs energy of solution are in Table 3.

Table 3. Solubility of methane in octane. Tentative values of the mole fraction solubility at 101.325 kPa (1 atm) partial pressure methane and partial molal Gibbs energy as a function of temperature.

T/K	Mol Fraction	$\Delta \overline{G}_1^{\circ}/\text{kJ mol}^{-1}$
	10 ³ x ₁	
273.15	5.89	11.660
283.15	5.53	12.238
293.15	5.21	12.815
298.15	5.06	13.104
303.15	4.92	13.393
313.15	4.67	13.971
323.15	4.45	14.549
333.15	4.25	15.127
343.15	4.07	15.705

COMPONENTS:	EVALUATOR:
(1) Methane; CH ₄ ; [74-82-8]	H. Lawrence Clever Chemistry Department
(2) Alkanes	Emory University Atlanta, GA 30322 USA
	1984, January

CRITICAL EVALUATION:

Methane + Nonane; C₉H₂₀; [111-84-2]

The mole fraction solubility of 5.57×10^{-3} at 298.15 K and 101.325 kPa methane pressure of Makranczy et al. (ref. 11) is the only experimental value reported for the system. Although it is classed as tentative, the evaluator believes it may be as much as 10 percent too large.

Methane + Decane; $C_{10}H_{22}$; [124-18-5]

Makranczy et al. (ref. 11) report the solubility of methane in decane at 298.15 K, Wilcock et al. (ref. 12) report the solubility at 282.80 and 313.15 K. Both sets of data are classed as tentative but the Wilcock et al. data are preferred.

The tentative values are based on the Wilcock et αl . data. The equation for the mole fraction solubility between 282.80 and 313.15 K is

$$\ln x_1 = -7.0050 + 5.2154/(T/100 K)$$

and the corresponding temperature independent thermodynamic changes are

$$\Delta \overline{H}_{1}^{\circ}/kJ \text{ mol}^{-1} = -4.34$$
 and $\Delta \overline{S}_{1}^{\circ}/J \text{ K}^{-1} \text{ mol}^{-1} = -58.2$

Tentative values of the mole fraction solubility and partial molal Gibbs energy are given in Table 4.

Table 4. The solubility of methane in decane. Tentative values of the mole fraction solubility at 101.325 kPa (1 atm) partial pressure methane and partial molal Gibbs energy of solution as a function of temperature.

T/K	Mol Fraction $10^3 x_1$	$\Delta \overline{G}_1^{\circ}/\mathrm{kJ~mol}^{-1}$
283.15	5.72	12.135
293.15	5.37	12.737
298.15	5.22	13.029
303.15	5.07	13.320
313.15	4.80	13.902

Methane + Undecane; $C_{11}^{H}_{24}$; [1120-21-4]

The mole fraction solubility of 5.46×10^{-3} at 298.15 K and 101 101.325 kPa (1 atm) methane pressure of Makranczy et al. (ref. 11) is the only experimental value reported for the system. It is classed as tentative.

Methane + Dodecane; C₁₂H₂₆; [112-40-3]

Hayduk and Buckley (ref. 7) report four solubility values at temperatures between 273.15 and 348.15 K. Makranczy $et\ al.$ (ref. 11) report one value at 298.15 K. All of the data are classed as tentative.

The data were fitted by a linear regression to obtain the equation for the 273.15 to 348.15 K temperature interval

$$\ln x_1 = -6.76819 + 4.63437/(T/100 \text{ K})$$

with a standard deviation about the regression line of 4.3 \times $10^{-5}\,.$ The temperature independent thermodynamic changes from the equation are

$$\Delta \overline{H}_{1}^{\circ}/kJ \text{ mol}^{-1} = -3.85$$
 and $\Delta \overline{S}_{1}^{\circ}/J \text{ K}^{-1} \text{ mol}^{-1} = -56.3$

Smoothed values of the mole fraction solubility and partial molal Gibbs energy of solution are in Table 5.

Table 5. Solubility of methane in dodecane. Tentative values of the mole fraction solubility at 101.325 kPa (1 atm) methane partial pressure and partial molal Gibbs energy of solution as a function of temperature.

T/K	Mol Fraction	$\Delta \overline{G_1^{\circ}}/kJ \text{ mol}^{-1}$
	10 ³ x ₁	
273.15	6.27	11.518
283.15 293.15	5.91 5.59	12.080 12.643
298.15	5.44	12.925
303.15	5.30	13.206
313.15 323.15	5.05 4.82	13.769 14.331
333.15 343.15	4.62 4.44	14.894 15.457

Methane + Tridecane; C₁₃H₂₈; [629-50-5]

Methane + Tetradecane; C₁₄H₃₀; [629-59-4]

Methane + Pentadecane; C₁₅H₃₂; [629-62-9]

Only Makranczy $et\ \alpha l$. (ref. 11) have reported data on these systems. They report the solubility at 298.15 K. The mole fraction solubility at 298.15 K and 101.325 kPa (1 atm) methane pressure from their measurements is as follows:

Tridecane	5.39 x	10-3
Tetradecane	5.40 x	10-3
Pentadecane	5.35 x	10-3

The data are classed as tentative.

Methane + Hexadecane; $C_{16}H_{34}$; [544-76-3]

Seven papers report solubility data on the $\mathrm{CH_4}$ + $\mathrm{C_{16}^H_{34}}$ system. The mole fraction solubility values at 298.15 K and 101.325 kPa methane pressure are

COMPONENTS:	EVALUATOR:
(1) Methane; CH ₄ ; [74-82-8] (2) Alkanes	H. Lawrence Clever Chemistry Department Emory University Atlanta, GA 30322 USA
	1984, January

CRITICAL EVALUATION:	
6.02×10^{-3}	Hayduk, Buckley (ref. 7)
5.841×10^{-3}	Richon, Renon (ref. 14)
5.824 x 10 ⁻³	Rivas, Prausnitz (ref. 13)
5.75×10^{-3} (300K)	Cukor, Prausnitz (ref. 9)
5.59×10^{-3}	Lin, Parcher (ref. 15)
5.36 x 10 ⁻³	Makranczy et al. (ref. 11)
4.78×10^{-3}	Lenoir et al. (ref. 8)

CRITICAL EVALUATION.

The larger five values average a mole fraction solubility of 5.81 x 10^{-3} with standard deviation 0.16 x 10^{-3} .

The data of Hayduk and Buckley, Richon and Renon, Rivas and Prausnitz, and Lin and Parcher were combined in a linear regression to obtain the equation

$$\ln x_1 = -10.68231 + 9.91533/(T/100 K) + 2.02051 \ln (T/100 K)$$
 for the 298.15 to 473.15 K temperature interval.

The equation gives the following thermodynamic changes for the solution process:

T/K	$\Delta \overline{H}_1^{\circ}/kJ \text{ mol}^{-1}$	$\Delta \overline{S}_{1}^{\circ}/J$ K ⁻¹ mol ⁻¹	$\Delta \overline{c}_{p_1}^{\circ}/J K^{-1} mol^{-1}$
298.15	-3.24	-53.7	16.8
323.15	-2.82	-52.3	16.8
348.15	-2.40	-51.1	16.8
373.15	-1.98	-49.9	16.8
398.15	-1.56	-48.8	16.8
423.15	-1.14	-47.8	16.8
448.15	-0.72	-46.8	16.8
473.15	-0.30	-45.9	16.8

The smoothed mole fraction solubility and partial molar Gibbs energy values are in Table 6.

Table 6. Solubility of methane in hexadecane. Tentative values of the mole fraction solubility at 101.325 kPa (1 atm) methane partial pressure partial molal Gibbs energy of solution as a function of temperature.

T/K	Mol Fraction $10^3 x_{ extit{1}}$	$\Delta \overline{G}_1^{\circ}/kJ \text{ mol}^{-1}$
298.15	5.80	12.765
323.15	5.28	14.089
348.15	4.92	15.381
373.15	4.68	16.643
398.15	4.52	17.877
423.15	4.41	19.084
448.15	4.34	20.267
473.15	4.31	21.425

The smoothed solubility values differ only a few percent from the values of Cukor and Prausnitz and the enthalpies of solution are 3.5 to 7 percent less negative than the Cukor and Prausnitz values up to 400 K. The present evaluation does not show the change to a positive enthalpy of solution at 475 K. The Cukor and Prausnitz data are a good alternative to the tentative data presented here.

Methane + Octadecane; C₁₈H₃₈; [593-45-3]

Ng, Harris and Prausnitz (ref. 6) used gas liquid chromatography retention times to estimate the solubility of methane in octadecane at six temperatures between 308.2 and 423.2 K. Richon and Renon (ref. 14) report a mole fraction solubility value of 5.079 x 10^{-3} at 323.15 K and 101.325 kPa methane pressure. The Richon and Renon value is classed as tentative and the Ng $et\ al.$ data as doubtful. Unfortunately there is some problem with the Ng $et\ al.$ experiment and their results for this system as well as the methane + eicosane and docosane systems appear to be too small mole fraction solubilities by 15 to 30 percent.

Both Ng et al. (ref. 6) and Chappelow and Prausnitz (ref. 10) report solubility data as a function of temperature. As discussed for the previous system the Ng et al. data are doubtful. The Chappelow and Prausnitz data are classed as tentative.

The Chappelow and Prausnitz data were treated by a linear regression to obtain the equation †

$$\ln x_{\gamma} = -11.65137 + 11.01303/(T/100 \text{ K}) + 2.41842 \ln (T/100 \text{ K})$$

with a standard error about the regression line of 9.1×10^{-6} for the 323.15 to 473.15 K temperature interval.

The equation gives the following thermodynamic changes for the solution process:

T/K	$\Delta \overline{H}_1^{\circ}/kJ \text{ mol}^{-1}$	$\Delta \overline{S}_{1}^{\circ}/J K^{-1} mol^{-1}$	$\Delta \overline{C}_{p_1}^{\circ}/J K^{-1} mol^{-1}$
298.15	-3.91 ^a	-54.8 ^a	20.1 ^a
323.15	-3.41	-53.2	20.1
348.15	-2.90	-51.7	20.1
373.15	-2.40	-50.3	20.1
398.15	-1.90	-49.0	20.1
423.15	-1.40	-47.8	20.1
448.15	-0.88	-46.6	20.1
473.15	-0.39	-45.5	20.1

a Hypothetical liquid state. Eicosane melts at 310.0 K.

The smoothed mole fraction solubilities and partial molal Gibbs energy values are in Table 7.

Table 7. Solubility of methane in eicosane. Tentative mole fraction solubility at 101.325 kPa (1 atm) methane pressure and partial molal Gibbs energy of solution as a function of temperature.

T/K	Mol Fraction	$\Delta \overline{G}_1^{\circ}/\text{kJ mol}^{-1}$
	10 3 x 1	
298.15	6.65 ^a	12.429 ^a
323.15	5.93	13.778
348.15	5.45	15.089
373.15	5.12	16.363
398.15	4.90	17.358
423.15	4.76	18.813
448.15	4.67	19.992
473.15	4.63	21.143

For hypothetical liquid state. Eicosane melts at 310.0 K.

COMPONENTS:	EVALUATOR:
(1) Methane; CH ₄ ; [74-82-8] (2) Alkanes	H. Lawrence Clever Chemistry Department Emory University Atlanta, GA 30322 USA 1984, January

CRITICAL EVALUATION:

Methane + Docosane; C₂₂H₄₆; [629-98-0]

The only data on this system is from the work of Ng $et\ al.$ (ref. 6) which appears to give mole fraction values 15 to 30 percent too small with the octadecane and eicosane systems discussed earlier. Although the data are doubtful, they are presented because they are the only data on the system.

The data were fitted to a two constant equation by a linear regression

$$\ln x_1 = -7.29746 + 6.32687/(T/100 \text{ K})$$

with a standard error about the regression line at 1.50×10^{-4} .

The corresponding temperature independent thermodynamic changes are

$$\Delta H_1^{\circ}/kJ \text{ mol}^{-1} = -5.26$$
 and $\Delta S_1^{\circ}/J K^{-1} \text{ mol}^{-1} = -60.8$

Smoothed values of the mole fraction solubility and partial molal Gibbs energy are given in Table 8. The values are probably 15 to 30 percent smaller than the true values.

Table 8. The solubility of methane in docosane. Smoothed values of the mole fraction solubility at 101.3 kPa (1 atm) and partial molal Gibbs energy of solution as a function of temperature.

T/K	Mol Fraction	$\Delta \overline{G}_{1}^{\circ}/\text{kJ mol}^{-1}$
	10 ³ x ₁	
298.15	5.65 ^a	12.829 ^a
323.15	4.80	14.346
348.15	4.17	15.863
373.15	3.69	17.380
398.15	3.32	18.897
423.15	3.02	20.414
448.15	2.78	21.930
473.15	2.58	23.447

a For hypothetical liquid state. Docosane melts at 317.6 K.

Methane + Octacosane; C₂₈H₅₈; [630-02-4]

Only Lin and Parcher (ref. 15) have reported solubility data on the system. They report three solubility values between 353.2 and 393.2 K by a GLC method. The three points were fitted to the two constant equation by linear regression

$$\ln x_1 = -6.06004 + 3.55025/(T/100 K)$$

with a standard error about the regression line of 2.00×10^{-5} . The equation gives the temperature independent thermodynamic changes

$$\Delta \overline{H}_{1}^{\circ}/kJ \text{ mol}^{-1} = -2.95$$
 and $\Delta \overline{S}_{1}^{\circ}/J \text{ K}^{-1} \text{ mol}^{-1} = -50.4$

The smoothed values of the mole fraction solubility and partial molal Gibbs energy are given in Table 9.

T/K	Mol Fraction	$\Delta \overline{G}_1^{\circ}/\text{kJ mol}^{-1}$
	10³x ₁	-
298.15	7.68 ^a	12.071 ^a
353.15	6.38	14.842
363.15 373.15	6.20 6.04	15.346 15.849
383.15 393.15	5.90 5.76	16.353 16.857

Table 9. Solubility of methane in octacosane. Tentative values of the mole fraction solubility at 101.325 kPa (1 atm) and partial molal Gibbs energy of solution as a function of temperature.

Methane + Hexatriacontane; C₃₆H₇₄; [630-06-8]

The system at temperatures between 353.2 and 413.2 K by a GLC method. The results are classed as tentative. The data of Lin and Parcher were treated by a linear regression to obtain the equation.

$$\ln x_1 = -5.93818 + 3.77226/(T/100 K)$$

with a standard error about the regression line of 5.5 x 10^{-5} . The temperature independent thermodynamic changes are

$$\Delta H_{1}^{\circ}/kJ \text{ mol}^{-1} = -3.14$$
 and $\Delta S_{1}^{\circ}/J \text{ K}^{-1} \text{ mol}^{-1} = -49.4$.

Smoothed values of the mole fraction solubility and partial molal Gibbs energy of solution are in Table $10. \,$

Table 10. Solubility of methane in hexatriacontane. Tentative mole fraction solubility at 101.325 kPa (1 atm) methane partial pressure and partial molal Gibbs energy of solution as a function of temperature.

T/K	Mol Fraction	$\Delta \overline{G}_1^{\circ}/\text{kJ mol}^{-1}$
	10 3 x 1	
298.15	9.34 ^a	11.584
353.15 363.15 373.15 383.15 393.15 403.15 413.15	7.67 7.45 7.25 7.06 6.88 6.72 6.57	14.299 14.793 15.287 15.780 16.274 16.768 17.202

a Extrapolated hypothetical liquid state. Hexatriacontane melts at 349.

II. The solubility of methane in branched alkanes.

The solubility of methane is reported for only four branched chain alkanes. All of the available data are consistent with a larger solubility of methane in the branched chain alkane than in the linear alkane of the same number of carbon atoms. The data for the $\rm C_6$ and $\rm C_{16}$ branched hydrocarbon gives a branched/normal methane solubility ratio of greater than 2 while the $\rm C_8$ and $\rm C_{30}$ solubility branched/normal ratio is 1.06-1.12. The smaller ratio appears to be more reasonable.

a Extrapolated hypothetical liquid state. Octacosane melts at 337.7 K.

COMPONENTS:	EVALUATOR:
(1) Methane; CH ₄ ; [74-82-8]	H. Lawrence Clever Chemistry Department
(2) Alkanes	Emory University Atlanta, GA 30322 USA
	1984, January

CRITICAL EVALUATION:

Methane + 2,2-Dimethylbutane; C_6H_{14} ; [75-83-2]

Tilquin et al. (ref. 5) report measurements at low methane partial pressures from which we calculate a mole fraction solubility of 12.7 x 10^{-3} at 101.325 kPa methane pressure at 288.15 K. The C_6 branched/normal solubility ratio is 2.4 using the tentative hexane solubility value from this evaluation. Since there is no other value to compare with the present value, it is classed as tentative, but we believe the value is probably too large and that it should be used with caution.

Methane + 2,2,4-Trimethylpentane; C_9H_{18} ; [540-84-1]

Hiroka and Hildebrand report the solubility of methane at four temperatures between 277.51 and 308.22 K. The data are classed as tentative. At 298.15 K the branched/normal solubility ratio is 1.06.

The solubility data were fitted by a linear regression to the equation $\ensuremath{\mathsf{T}}$

$$\ln x_1 = -7.29405 + 6.14129/(T/100 K)$$

with a standard error about the regression line of 3.3×10^{-5} .

The temperature independent thermodynamic changes are

$$\Delta \overline{H}_{1}^{\circ}/kJ \text{ mol}^{-1} = 5.11$$
 and $\Delta \overline{S}_{1}^{\circ}/J \text{ K}^{-1} \text{ mol}^{-1} = -60.6$

Table 11. Solubility of methane in 2,2,4-trimethylpentane. Tentative values of the mole fraction solubility at 101.325 kPa methane partial pressure and partial molal Gibbs energy of solution as a function of temperature.

T/K	Mol Fraction	$\Delta \overline{G}_1^{\circ}/\mathrm{kJ\ mol}^{-1}$
	10 ³ x ₁	
283.15	5.95	12.066
293.15	5.52	12.672
298.15	5.33	12.975
303.15	5.15	13.278

Methane + 2,2,4,4,6,8,8-Heptamethylnonane; $C_{16}^{H}_{34}$; [4390-04-9]

Richon and Renon (ref. 14) report measurements from which a mole fraction solubility of 30.5 x 10^{-3} at 101.325 kPa methane pressure at 298.15 K can be calculated. The branched/normal C_{16} methane solubility ratio is 5.3. Since there is no other value with which to compare the solubility value it is classed as tentative. However, it is suspected that the value is too large and it should be used with caution.

Methane + 2,6,10,15,19,23-Hexamethyltetracosane; $C_{30}H_{62}$; [111-01-3]

Chappelow and Prausnitz (ref. 10) report eight solubility values over the 300 to 475 K temperature interval for this system. Taking the linear $\rm C_{30}$ hydrocarbon solubility from Fig. 1, the branched/normal methane solubility ratio is 1.12. The data are classed as tentative.

The data were fitted to a three constant equation by a linear regression

 $\ln x_1 = -10.32638 + 10.42056/(T/100 K) + 1.9508 \ln (T/100 K)$

The equation reproduces the experimental data so closely that there is reason to believe the data are smoothed data rather than experimental points.

The equation gives the following values of the thermodynamic functions:

T/K	$\Delta \overline{H}_1^{\circ}/\text{kJ mol}^{-1}$	$\Delta \overline{S}_{1}^{\circ}/J K^{-1} mol^{-1}$	$\Delta \overline{C}_{p_1}^{\circ}/J K^{-1} mol^{-1}$
298.15	-3.83	-51.9	16.2
323.15	-3.42	-50.6	16.2
348.15	-3.02	-49.4	16.2
373.15	-2.61	-48.2	16.2
398.15	-2.21	-47.2	16.2
423.15	-1.80	-46.2	16.2
448.15	-1.40	-45.3	16.2
473.15	-0.99	-44.4	16.2

The smoothed mole fraction solubility and partial molal Gibbs energy of solution are in Table 12.

Table 12. Solubility of methane in 2,6,10,15,19,23-Hexamethylnonane.

Tentative values of the mole fraction solubility at 101.325 kPa
methane pressure and the partial molal Gibbs energy of solution
as a function of temperature.

T/K	Mol Fraction	$\Delta \overline{G}_{1}^{\circ}/\text{kJ mol}^{-1}$
	10 ³ x ₁	1
298.15	9.09	11.651
323.15	8.12	12.933
348.15	7.45	14.183
373.15	6.98	15.404
398.15	6.65	16.597
423.15	6.41	17.766
448.15	6.25	18.910
473.15	6.15	20.031

- 1. McDaniel, A. S. J. Phys. Chem. 1911, 15, 587.
- Guerry, D. Jr. Ph. D. Thesis, <u>1944</u>, Vanderbilt University, Nashville, TN.
- 3. Lannung, A.; Gjaldbaek, J. C. Acta Chem. Scand. 1960, 14, 1124.
- 4. Hiraoka, H.; Hildebrand, J. H. J. Phys. Chem. 1964, 68, 213.
- 5. Tilquin, B.; Decannière, L.; Fontaine, R.; Claes, P. Ann. Soc. Sc. Bruxelles (Belgium) 1967, 81, 191.
- Ng, S.; Harris, H. G.; Prausnitz, J. M. J. Chem. Eng. Data, 1969, 14, 482.
- 7. Hayduk, W.; Buckley, W. D. Can. J. Chem. Eng. 1971, 49, 667.
- Lenoir, J-Y.; Renault, P.; Renon, H. J. Chem. Eng. Data <u>1971</u>, 16, 340.
- 9. Cukor, P. M.; Prausnitz, J. M. J. Phys. Chem. 1972, 76, 598.

COMPONENTS: (1) Methane; CH₄; [74-82-8] (2) Alkanes EVALUATOR: H. Lawrence Clever Chemistry Department Emory University Atlanta, GA 30322 USA 1984, January

CRITICAL EVALUATION:

- Chappelow, C. C.; Prausnitz, J. M. Am. Inst. Chem. Engnrs. J. 1974, 20, 1097.
- Makranczy, J.; Megyery-Balog, K.; Rusz, L.; Patyi, L. Hung. J. Ind. Chem. <u>1976</u>, 4, 269.
- Wilcock, R. J.; Battino, R.; Danforth, W. F.; Wilhelm, E. J. Chem. Thermodyn. 1978, 10, 817.
- 13. Rivas, O. R.; Prausnitz, J. M. Ind. Eng. Chem. Fundam. 1979, 18, 289.
- 14. Richon, D.; Renon, H. J. Chem. Eng. Data 1980, 25, 59.
- 15. Lin, P. J.; Parcher, J. F. J. Chromatog. Sci. 1982, 20, 33.

The evaluation of the solubility of methane in hydrocarbons at high pressure is given in separate sections later in the volume.

A useful paper to consult for additional information on methane + hydrocarbons systems is

Legret, D.; Richon, D.; Renon, H. Fluid Phase Equilib. 1984, 17, 323-50.

COMPONENTS: ORIGINAL MEASUREMENTS: (1) Methane; CH₄; [74-82-8] Makranczy, J.; Megyery-Balog, K.; Rusz, L.; Patyi, L. (2) Pentane; C₅H₁₂; [109-66-0] Hung. J. Ind. Chem. 1976, 4, 269 - 280. Hexane; C₆H₁₄; [110-54-3] VARIABLES: PREPARED BY: T/K: 298.15 p/kPa: 101.325 (1 atm) S. A. Johnson H. L. Clever

EXPERIMENTAL	VALUES:			
	T/K	Mol Fraction $10^3 x_1$	Bunsen Coefficient α/cm³(STP)cm-³atm-1	Ostwald Coefficient L/cm ³ cm ⁻³
	Pentane			
	298.15	6.03	1.172	1.279
	Hexane			
1	298.15	6.13	1.050	1.146

The Bunsen coefficient and mole fraction values were calculated by the compiler assuming that the gas is ideal and that Henry's law is obeyed.

AUXILIARY INFORMATION

SOURCE AND PURITY OF MATERIALS: METHOD/APPARATUS/PROCEDURE: Volumetric method. The apparatus Both the gas and the liquid were described by Bodor, Bor, Mohai and analytical grade reagents of Hungarian or foreign origin. No Sipos was used (1). further information. ESTIMATED ERROR: $\delta L/L = \pm 0.03$ REFERENCES: Bodor, E.; Bor, Gy.; Mohai, B.; Sipos, G. Veszpremi Vegyip. Egy. Kozl. 1957, 1, 55. Chem. Abstr. 1961, 55, 3175h.

- (1) Methane; CH₄; [74-82-8]
- (2) Hexane; C₆H₁₄; [110-54-3]

ORIGINAL MEASUREMENTS:

McDaniel, A. S.

J. Phys. Chem. 1911, 15, 587-610.

VARIABLES:

T/K = 295.35 - 333.15 $p_1/kPa = 101.3 (1 atm)$

PREPARED BY:

H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Mol Fraction	Bunsen Coefficient ^a	Ostwald Coefficient ^b
t/°C	T/K	10 ³ x ₁	a	L/cm ³ cm ⁻³
22.2	295.35	3.25	0.5585	0.6035
25.0	298.15	3.17	0.5422	0.5918 ^C
40.2	313.35	2.77	0.4639	0.5320
49.7	322.85	2.66	0.4380	0.5180
60.0	333.15	2.51	0.4068	0.4964

a Bunsen coefficient, α/cm^3 (STP) cm^{-3} atm⁻¹.

EVALUATOR'S COMMENT: McDaniel's data should be used with caution. His values are often 20 percent or more too small when compared with more reliable data.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The apparatus is all glass. It consists of a gas buret connected to a contacting vessel. The solvent is degassed by boiling under reduced pressure. Gas pressure or volume is adjusted using mercury displacement. Equilibration is achieved at atm pressure by hand shaking, and incrementally adding gas to the contacting chamber. Solubility measured by obtaining total uptake of gas by known volume of the solvent.

SOURCE AND PURITY OF MATERIALS:

- Methane. Prepared by reaction of methyl iodide with zinccopper. Passed through water and sulfuric acid.
- (2) Hexane.

ESTIMATED ERROR:

 $\delta L/L \geq -0.20$

b Listed as absorption coefficient in the original paper. Interpreted to be equivalent to Ostwald coefficient by compiler.

C Ostwald coefficient (absorption coefficient) estimated as 298.15 K value by author.

d Mole fraction and Bunsen coefficient values calculated by compiler assuming ideal gas behavior.

- (1) Methane; CH₄; [74-82-8]
- (2) Hexane; C₆H_{1.4}; [110-54-3]

ORIGINAL MEASUREMENTS:

Lannung, A.; Gjaldbaek, J. C.

Acta Chem. Scand. 1960, 14, 1124 - 1128.

VARIABLES:

T/K = 291.15 - 310.15 $p_1/kPa = 101.325$ (1 atm) PREPARED BY:

J. Chr. Gjaldbaek

EXPERIMENTAL VALUES:

T/K	Mol Fraction	Bunsen	Ostwald
	10 ³ x ₁	Coefficient α/cm³(STP)cm-³atm-1	Coefficient L/cm³cm-3
291.15	5.14	0.884	0.942
291.15	5.15	0.886	0.944
298.15	5.06	0.865	0.944
298.15	5.10	0.872	0.952
310.15	4.87	0.813	0.923
310.15	4.90	0.818	0.929

Smoothed Data: For use between 291.15 and 310.15 K.

 $\ln x_{\tau} = -6.1312 + 2.5167/(T/100 \text{ K})$

The standard error about the regression line is 2.75×10^{-5} .

T/K	Mol Fraction
	$10^{3}x_{1}$
298.15	
308.15	5.06 4.92
500.15	4.52

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

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 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.

SOURCE AND PURITY OF MATERIALS:

- (1) Methane. Generated from magnesium methyl iodide. Purified by fractional distillation. Specific gravity corresponds with mol wt 16.08.
- (2) Hexane. Kahlbaum. "Hexan aus
 petroleum". Fractionated by
 distillation. B.p. (760 mmHg)/
 °C = 68.85, vapor pressure
 (25°C)/mmHg = 154.

ESTIMATED ERROR:

$$\delta T/K = \pm 0.05$$

 $\delta x_1/x_1 = \pm 0.015$

REFERENCES:

Lannung, A.
 J. Am. Chem. Soc. 1930, 52, 68.

- (1) Methane; CH₄; [74-82-8]
- (2) Alkanes; C_6H_{14} and C_7H_{16}

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:

T/K	Mol Fraction $x_1 \times 10^4$	Bunsen Coefficient a	Ostwald Coefficient L
Не	xane; C ₆ H ₁₄ ;	[110-54-3]	
293.15	43.4	0.748	0.803
298.15	42.4	0.726	0.792
Не	ptane; C7H16;	[142-82-5]	
293.15	46.7	0.718	0.771
298.15	40.7	0.622	0.679

The Ostwald coefficients were calculated by the compiler.

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:

- (1) Methane. Prepared by hydrolysis of crystaline methyl Grignard reagent. Passed through conc. H₂SO₄, solid KOH, and Dririte.
- (2) Alkanes. Distilled from sodium in air. In addition to the solubility data the thesis contains data of the refractive index, density, vapor pressure, and b.p.

SOURCE AND PURITY OF MATERIALS:

Hexane. Eastman Kodak Co. B.p. (760.3 mmHg) t/°C 68.85 - 68.90.

Heptane. B.p. (753.9 mmHg) t/°C 98.27 - 98.28 (corr.).

ESTIMATED ERROR:

 $\delta T/K = 0.05$

- Van Slyke, D. D.
 J. Biol. Chem. 1939, 130, 545.
- 2. Ijams, C. C. Ph.D. thesis, <u>1941</u> Vanderbilt University

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Methane; CH₄;]74-82-8] Hexane; C₆H₁₄; [110-54-3] 	Tilquin, B.; Decannière, L.; Fontaine, R.; Claes, P. Ann. Soc. Sc. Bruxelles (Belgium) 1967, 81, 191-199.
VARIABLES: T/K: 288.15 P/kPa: 4.11-8.13	PREPARED BY: C. L. Young

EXPERIMENTAL VALUES:

t/C	T/K	Ostwald coefficient, a	Mole b fraction $f(x)$	Henry's constant b H/atm
15.0	288.15	0.56	0.00306	326

- Original data at low pressure reported as distribution coefficient; but if Henry's law and ideal gas law apply, distribution coefficient is equivalent to Ostwald coefficient as shown here.
- b Calculated by compiler for a gas partial pressure of 101.325 kPa assuming that Henry's law and ideal gas law apply.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

All glass apparatus used at very low gas partial pressures, containing a replaceable degassed solvent ampule equipped with a breakable point which could be broken by means of a magnetically activated plunger. Quantity of gas fed into system determined by measuring the pressure change in a known volume. Quantity of liquid measured by weight. Pressure change observed after solvent released. Experimental details described by Rzad and Claes, ref. (1).

SOURCE AND PURITY OF MATERIALS:

- Source not given; minimum purity specified as 99.0 mole per cent.
- Fluka pure grade; minimum purity specified as 99.0 mole per cent.

ESTIMATED ERROR:

 $\delta T/K = 0.05;$ $\delta x_1/x_1 = 0.01$ (estimated by compiler).

REFERENCES:

Rzad, S.; Claes, P.
 Bull. Soc. Chim. Belges
 1964, 73, 689.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Methane; CH ₄ ; [74-82-8]	Hayduk, W.; Buckley, W.D.
(2) Hexane; C ₆ H ₁₄ ; [110-54-3]	Can. J. Chem. Eng. <u>1971</u> , 49, 667-671.
VARIABLES: T/K: 273.15-323.15 P/kPa: 101.325	PREPARED BY: W. Hayduk

EXPERIMENTAL VALUES:

<i>T</i> /K		¹ Bunsen Coefficient ² α/cm ³ (STP) cm ⁻³ atm ⁻¹	Mole Fraction $\frac{10^4 x_1}{}$
273.15	1.004	1.004	57.1 (58.1) ³ 50.2 (48.7) 41.3 (41.9)
298.15	0.935	0.857	
323.15	0.801	0.677	

- Original data
- ² Calculated by compiler
- 3 The original mole fraction solubility data were used to determine the following equations for ΔG° and $\ln x_{1}$ and table of smoothed values: $\Delta G^{\circ}/J \text{ mol}^{-1} = -RT \ln x_1 = 60.361 T - 4795.3$ $\ln x_1 = 576.8/T^2 - 7.260$

Std. deviation for $\Delta G^{\circ} = 66.9 \text{ J mol}^{-1}$; Correlation coefficient = 0.9991

T/K	10 ⁻⁴ ΔG°/J mo1 ⁻¹	10 4x 1	
273.15 283.15	1.169 1.230	58.1 53.9	
293.15 298.15	1.290 1.320	50.3 48.7	
303.15 313.15	1.350 1.411	47.1	
323.15	1.471	44.3 41.9	

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A volumetric method using a glass apparatus was employed. Degassed solvent contacted the gas while flowing as a thin film, at a constant rate, through an absorption spiral into a solution buret. A constant solvent flow was obtained by means of a calibrated syringe pump. The solution at the end of the spiral was considered saturated. Dry gas was maintained at atmospheric pressure in a gas buret by mechanically raising the mercury level in the buret at an adjustable rate. Volumes of solvent injected and residual gas were obtained for regular time intervals. The solubility was calculated from the constant slope of volume of gas dissolved and volume of solvent injected.

Degassing was accomplished using a two stage vacuum process described by Clever et al. (1).

SOURCE AND PURITY OF MATERIALS:

- 1. Matheson Co. Specified as ultra high purity grade of 99.97 per cent.
- 2. Canlab. Chromatoquality grade of specified minimum purity of 99.0 per cent.

ESTIMATED ERROR:

 $\delta T/K$ = 0.1 $\delta x_1/x_1 = 0.01$

REFERENCES:

Clever, H.L.; Battino, R.; Saylor, J.H.; Gross, P.M. J. Phys. Chem. 1957, 61, 1078.

COMPONENTS: ORIGINAL MEASUREMENTS: (1) Methane; CH₄; [74-82-8] (2) Hexane; C₆H₁₄; [110-54-3]

Yokoyama, C.; Masuoka, H. Aral, K.; Saito, S.

J. Chem. Eng. Data 1985, 30, 177-9.

VARIABLES:

T/K = 311.0 $p_{+}/\text{MPa} = 0.57 - 1.98$ PREPARED BY:

H. L. Clever

EXPERIMENTAL VALUES:

Temperature		Total	Mol Fraction	
t/°C	T/K	Pressure	Liquid	Vapor
		p _t /MPa	$\frac{x_1}{}$	<u> </u>
37.8	311.0	0.57		0.9264
		0.59		0.9256
		0.83		0.9468
		1.06		0.9468
		1.20	0.0567	0.9607
		1.30	0.0616	0.9627
		1.53	0.0734	0.9680
		1.58	0.0757	
		1.77	0.0860	0.9696
		1.79	0.0892	
		1.81	0.0880	0.9724
		1.98	0.0965	

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The equipment consists of an equilibration system and an analysis system. The procedures are essentially the same as those used by King et al. (ref 1) and Kubota et al. (ref 2). The equilibration system is in a thermostated water bath. The analysis system is in an air bath at 100 C to avoid condensation problems.

Details of the degassing, equilibration, and sampling procedures are not given in the paper. The composition analysis was made by a gas chromatograph and digital integrator. Calibration curves were obtained from mixtures of known composition.

SOURCE AND PURITY OF MATERIALS:

- (1) Methane. Takachio Kagaku Co., Ltd. Used as received.
- (2) Hexane. Takachio Kagaku Co., Ltd. Used as received.

A trace analysis of the components found no measurable impurities. The samples were used without further purification.

ESTIMATED ERROR:

 $\delta T/K = \pm 0.05$ $\delta p_t/\text{MPa} = \pm 0.01$ $\delta x_1/x_1 = \pm 0.015$

REFERENCES:

1.King,M.B.;Alderson,D.A.;Fallah,F.; Kassim, D.M.; Sheldon, J.R.; Mahmud, R. "Chemical Engineering at Supercritical Conditions "Paulatis, M.E.; Penninger, J.M.L.; Gray, R.D., Jr.; Davidson,P, Editors; Ann Arbor Sci. Ann Arbor, MI 1983, p. 31.

REFERENCES: (continued)

- 2. Kubota, H.; Inatome, H.; Tanaka, Y.; Makita, T.
 - J. Chem. Eng. Jpn. 1983, 16, 99.

ORIGINAL MEASUREMENTS: 1. Methane; CH4; [74-82-8] 2. 2,2'-Dimethylbutane (Neo-hexane); Fontaine, R.; Claes, P. C6H14; [75-83-2] VARIABLES: T/K: 288.15 P/kPa: 2.05-2.11 ORIGINAL MEASUREMENTS: Tilquin, B.; Decannière, L.; Fontaine, R.; Claes, P. Ann. Soc. Sc. Bruxelles (Belgium) 1967, 81, 191-199. C. L. Young

EXPERIMENTAL VALUES:

t/C	T/K	Ostwald coefficient, a	Mole fraction b	Henry's b constant
15.0	288.15	2.30	0.01266	79.0

- Original data at low pressure reported as distribution coefficient; but if Henry's law and ideal gas law apply, distribution coefficient is equivalent to Ostwald coefficient as shown here.
- b Calculated by compiler for a gas partial pressure of 101.325 kPa assuming that Henry's law and ideal gas law apply.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

All glass apparatus used at very low gas partial pressures, containing a replaceable degassed solvent ampule equipped with a breakable point which could be broken by means of a magnetically activated plunger. Quantity of gas fed into system determined by measuring the pressure change in a known volume. Quantity of liquid measured by weight. Pressure change observed after solvent released. Experimental details described by Rzad and Claes, ref. (1).

SOURCE AND PURITY OF MATERIALS:

- Source not given; minimum purity specified as 99.0 mole per cent.
- Fluka pure grade; minimum purity specified as 99.0 mole per cent.

ESTIMATED ERROR:

 $\delta T/K = 0.05$; $\delta x_1/x_1 = 0.01$ (estimated by compiler).

REFERENCES:

1. Rzad, S.; Claes, P.

Bull. Soc. Chim. Belges

1964, 73, 689.

- (1) Methane; CH_A ; [74-82-8]
- (2) Heptane; C₇H₁₆; [142-82-5]

ORIGINAL MEASUREMENTS:

McDaniel, A. S.

J. Phys. Chem. 1911, 15, 587-610.

VARIABLES:

T/K = 295.35 - 313.15 $p_1/kPa = 101.3$ (1 atm) PREPARED BY:

H. L. Clever

EXPERIMENTAL VALUES:

Tempe	erature	Mol Fraction	Bunsen Coefficient ^a	Ostwald Coefficient ^b
t/°C	<i>T</i> /K	10 ³ x ₁	α	L/cm ³ cm ⁻³
22.2	295.35	4.37	0.6720	0.7242
25.0 30.1	298.15 303.25	4.27 4.10	0.6519 0.6221	0.7116 ^C 0.6906
40.0	313.15	3.89	0.5820	0.6675

- a Bunsen coefficient, α/cm^3 (STP) cm⁻³ atm⁻¹.
- b Listed as absorption coefficient in the original paper. Interpreted to be equivalent to Ostwald coefficient by compiler.
- C Ostwald coefficient (absorption coefficient) estimated as 298.15 K value by author.
- d Mole fraction and Bunsen coefficient values calculated by compiler assuming ideal gas behavior.

EVALUATOR'S COMMENT: McDaniel's data should be used with caution. His values are often 20 percent or more too small when compared with more reliable data.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The apparatus is all glass. It consists of a gas buret connected to a contacting vessel. The solvent is degassed by boiling under reduced pressure. Gas pressure or volume is adjusted using mercury displacement. Equilibration is achieved at atm pressure by hand shaking, and incrementally adding gas to the contacting chamber. Solubility measured by obtaining total uptake of gas by known volume of the solvent.

SOURCE AND PURITY OF MATERIALS:

- (1) Methane. Prepared by reaction of methyl iodide with zinccopper. Passed through water and sulfuric acid.
- (2) Heptane.

ESTIMATED ERROR:

 $\delta L/L \geq -0.20$

- (1) Methane; CH₄; [74-82-8]
- (2) Heptane; C₇H₁₆; [142-82-5] Octane; C₈H₁₈; [111-65-9]

ORIGINAL MEASUREMENTS:

Makranczy, J.; Megyery-Balog, K.; Rusz, L.; Patyi, L.

Hung. J. Ind. Chem. 1976, 4, 269 - 280.

VARIABLES:

T/K: 298.15 p/kPa: 101.325 (1 atm)

PREPARED BY:

S. A. Johnson H. L. Clever

EXPERIMENTAL VALUES:

_	***************************************			
	<i>T</i> /K	Mol Fraction	Bunsen Coefficient α/cm³(STP)cm-³atm-1	Ostwald Coefficient L/cm³cm-3
	Heptane			
	298.15	5.73	0.876	0.956
	Octane			
	298.15	5.64	0.778	0.849

The Bunsen coefficient and mole fraction values were calculated by the compiler assuming that the gas is ideal and that Henry's law is obeyed.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Volumetric method. The apparatus described by Bodor, Bor, Mohai and Sipos was used (1).

SOURCE AND PURITY OF MATERIALS:

Both the gas and the liquid were analytical grade reagents of Hungarian or foreign origin. No further information.

ESTIMATED ERROR:

 $\delta L/L = \pm 0.03$

REFERENCES:

Bodor, E.; Bor, Gy.;
 Mohai, B.; Sipos, G.
 Veszpremi Vegyip. Egy. Kozl.
 1957, 1, 55.
 Chem. Abstr. 1961, 55, 3175h.

- (1) Methane; CH_A ; [74-82-8]
- (2) Heptane; C₇H₁₆; [142-82-5]

ORIGINAL MEASUREMENTS:

Hayduk, W.; Buckley, W.D.

Can. J. Chem. Eng. 1971, 49, 667-671.

VARIABLES:

T/K: 273.15-348.15

P/kPa: 101.325

PREPARED BY:

W. Hayduk

EXPERIMENTAL VALUES:

<i>T</i> /K	Ostwald Coefficient ¹ L/cm ³ cm ⁻³	Bunsen Coefficient ² α/cm^3 (STP) cm^{-3} atm ⁻¹	Mole Fraction ¹ 10 ⁴ x ₁
273.15	0.894	0.894	57.1 (58.1) ³
298.15	0.840	0.770	50.6 (49.4)
323.15	0.752	0.636	43.1 (43.1)
348.15	0.688	0.540	38.0 (38.3)

¹Original data.

 $^3{\rm The}$ mole fraction solubility of the original data was used to determine the following equations for $\Delta{\rm G}^\circ$ and ln x_1 and table of smoothed values:

$$\Delta G^{\circ}/J \text{ mol}^{-1} = -RT \ln x_1 = 58.916 T - 4401.9$$

 $\ln x_1 = 529.5/T - 7.086$

Std. deviation for $\Delta G^{\circ} = 43.2 \text{ J mol}^{-1}$; Correlation coefficient = 0.9997

T/K	$10^{-4}\Delta G^{\circ}/J \text{ mol}^{-1}$	10 4 x ₁	T/K	$10^{-4}\Delta G^{\circ}/J \text{ mol}^{-1}$	104 x ₁
273.15	1.169	58.1	313.15	1.404	45.4
283.15	1.228	54.2	323.15	1.464	43.1
293.15	1.287	50.9	333.15	1.523	41.0
298.15	1.316	49.4	343.15	1.582	39.1
303.15	1.346	48.0	348.15	1.611	38.3

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A volumetric method using a glass apparatus was employed. Degassed solvent contacted the gas while flowing as a thin film, at a constant rate, through an absorption spiral into a solution buret. A constant solvent flow was obtained by means of a calibrated syringe pump. The solution at the end of the spiral was considered saturated. Dry gas was maintained at atmospheric pressure in a gas buret by mechanically raising the mercury level in the buret at an adjustable The solubility was calculated from the constant slope of volume of gas dissolved and volume of solvent injected.

Degassing was accomplished using a two stage vacuum process described by Clever et al. (1).

SOURCE AND PURITY OF MATERIALS:

- Matheson Co. Specified as ultra high purity grade of 99.97 per cent.
- Canlab. Chromatoquality grade of specified minimum purity of 99.0 per cent.

ESTIMATED ERROR:

$$\delta T/K = 0.1$$

$$\delta x_1/x_1 = 0.01$$

REFERENCES:

 Clever, H.L.; Battino, R.; Saylor, J.H.; Gross, P.M.
 J. Phys. Chem. 1957, 61, 1078.

²Calculated by compiler

- (1) Methane; CH₄; [74-82-8]
- (2) Octane; C_RH_{1R}; [111-65-9]

ORIGINAL MEASUREMENTS:

Wilcock, R. J.; Battino, R.; Danforth, W. F.; Wilhelm, E.

J. Chem. Thermodyn. 1978, 10, 817 - 822.

VARIABLES:

T/K: 298.25, 313.35 p/kPa: 101.325 (1 atm) PREPARED BY:

H. L. Clever

EXPERIMENTAL VALUES:

T/K	Mol Fraction 10 ³ x ₁	Bunsen Coefficient α/cm³(STP) cm ⁻³ atm ⁻¹	Ostwald Coefficient L/cm³ cm-3
298.25	5.026	0.6913	0.7548
313.35	4.744	0.6410	0.7353

The Bunsen coefficients were calculated by the compiler.

It is assumed that the gas is ideal and that Henry's law is obeyed.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility 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 is that described by Battino, Banzhof, Bogan, and Wilhelm (3).

Degassing. Up to 500 cm³ 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 intermittently applied through a liquid N2 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 helical tube containing 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.

SOURCE AND PURITY OF MATERIALS:

- (1) Methane. Matheson Co., Inc. Minimum mole percent purity stated to be 99.97.
- (2) Octane. Phillips Petroleum Co. 99 mole per cent, distilled, density at 298.15 K, ρ/g cm⁻³ 0.6988.

ESTIMATED ERROR:

 $\delta T/K = 0.02$ $\delta P/mmHg = 0.5$ $\delta x_1/x_1 = 0.01$

- Morrison, T. J.; Billett, F. J. Chem. Soc. 1948, 2033.
- Battino, R.; Evans, F. D.; Danforth, W. F. J. Am. Oil Chem. Soc. 1968, 45, 830.
- Battino, R.; Banzhof, M.; Bogan, M.; Wilhelm, E. Anal. Chem. <u>1971</u>, 43, 806.

- (1) Methane; CH₄; [74-82-8]
- (2) Octane; C₈H₁₈; [111-65-9]

ORIGINAL MEASUREMENTS:

Hayduk, W.; Buckley, W.D.

Can. J. Chem. Eng. <u>1971</u>, 49, 667-671.

VARIABLES:

T/K: 273.15-348.15 P/kPa: 101.325

PREPARED BY:

W. Hayduk

EXPERIMENTAL VALUES:

т/к	Ostwald Coefficient ¹ L/cm ³ cm ⁻³	Bunsen Coefficient ² α/cm^3 (STP) cm ⁻³ atm ⁻¹	Mole Fraction ¹
273.15	0.826	0.826	58.6 (58.9) ³
298.15	0.767	0.703	51.1 (50.5)
323.15	0.696	0.588	44.1 (44.4)
348.15	0.653	0.512	39.7 (39.7)

¹Original data.

³The mole fraction solubility of the original data was used to determine the following equations for ΔG° and $\ln x_{1}$ and table of smoothed values: $\Delta G^{\circ}/J \text{ mol}^{-1} = -RT \ln x_{1} = 57.958 \ T - 4172.4$

 $\ln x_1 = 501.9/T - 6.971$

Std. deviation for $\Delta G^{\circ} = 20.0 \text{ J mol}^{-1}$; Correlation coefficient = 1.000

<i>T</i> /K	10-4ΔG°/J mol-1	104 x1	<i>T</i> /K	10 ⁻⁴ ΔG°/J mol ⁻¹	104 x ₁
273.15	1.166	58.9	303.15	1.340	49.1
283.15	1.224	55.2	313.15	1.398	46.6
293.15	1.282	52.0	323.15	1.456	44.4
298.15	1.311	50.5	348.15	1.601	39.7

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A volumetric method using a glass apparatus was employed. Degassed solvent contacted the gas while flowing as a thin film, at a constant rate, through an absorption spiral into a solution buret. A constant solvent flow was obtained by means of a cabibrated syringe pump. The solution at the end of the spiral was considered saturated. Dry gas was maintained at atmospheric pressure in a gas buret by mechanically raising the mercury level in the buret at an adjustable The solubility was calculated rate. from the constant slope of volume of gas dissolved and volume of solvent injected. Degassing was accomplished using a

two stage vacuum process described

by Clever et al. (1).

SOURCE AND PURITY OF MATERIALS:

- Matheson Co. Specified as ultra high purity grade of 99.97 per cent.
- Canlab. Chromatoquality grade of specified minimum purity of 99.0 per cent.

ESTIMATED ERROR:

 $\delta T/K = 0.1$ $\delta x_1/x_1 = 0.01$

REFERENCES:

 Clever, H.L.; Battino, R.; Saylor, J.H.; Gross, P.M.
 J. Phys. Chem. 1957, 61, 1078.

²Calculated by compiler

- (1) Methane; CH_A ; [74-82-8]
- (2) 2,2,4-Trimethylpentane or isooctane; C₈H₁₈; [540-84-1]

ORIGINAL MEASUREMENTS:

Hiraoka, H.; Hildebrand, J. H.

J. Phys. Chem. 1964, 68, 213-214.

VARIABLES:

$$T/K = 277.51 - 308.22$$

 $p_1/kPa = 101.325$ (1 atm)

PREPARED BY:

M. E. Derrick H. L. Clever

EXPERIMENTAL VALUES:

FD:			
erature	Mol Fraction	Bunsen	Ostwald
<i>T</i> /K	10 ³ x ₁	Coefficient α/cm^3 (STP) cm^{-3} atm ⁻¹	Coefficient L/cm3cm-3
277.51	6.236	0.868	0.882
288.12	5.688	0.781	0.824
297.92	5.351	0.726	0.792
308.22	4.989	0.669	0.755
	T/K 277.51 288.12 297.92	erature Mol Fraction $ \frac{T/K}{277.51} = \frac{10^3 x_1}{6.236} $ 288.12 5.688 297.92 5.351	erature Mol Fraction Bunsen Coefficient $\alpha/\text{cm}^3 (\text{STP}) \text{ cm}^{-3} \text{ atm}^{-1}$ 277.51 6.236 0.868

The Bunsen and Ostwald coefficients were calculated by the compiler assuming ideal gas behavior.

Smoothed Data: For use between 277.51 and 308.22 K.

 $\ln x_1 = -7.2940 + 6.1413/(T/100 \text{ K})$

The standard error about the regression line is 3.32×10^{-4} .

T/K	Mol Fraction 10 ² x ₁
278.15	6.182
288.15	5.726
298.15	5.331
308.15	4.986

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

- SOURCE AND PURITY OF MATERIALS:
- (1) Methane. Phillips Petroleum Co. Gas passed through a cold trap.
- (2) Isooctane. Source not given. Distilled, purity checked by ultraviolet absorbance.

ESTIMATED ERROR:

$$\delta T/K = 0.02$$

 $\delta x_1/x_1 = 0.003$

- Kobatake, Y.; Hildebrand, J. H. J. Phys. Chem. <u>1961</u>, 65, 331.
- introduction of the gas into the pipet. The stirrer is set in motion. Equilibrium is attained within 24 hours.

COMPONENTS: (1) Methane; CH₄; [74-82-8] (2) Nonane; C₉H₂₀; [111-84-2] Decane; C₁₀H₂₂; [124-18-5] VARIABLES: T/K: 298.15 p/kPa: 101.325 (1 atm) ORIGINAL MEASUREMENTS: Makranczy, J.; Megyery-Balog, K.; Rusz, L.; Patyi, L. Hung. J. Ind. Chem. 1976, 4, 269 - 280. PREPARED BY: S. A. Johnson H. L. Clever

The Bunsen coefficient and mole fraction values were calculated by the compiler assuming that the gas is ideal and that Henry's law is obeyed.

0.635

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: Volumetric method. The apparatus described by Bodor, Bor, Mohai and Sipos was used (1).

Decane

298.15

5.52

SOURCE AND PURITY OF MATERIALS:
Both the gas and the liquid were
analytical grade reagents of
Hungarian or foreign origin. No
further information.

0.693

ESTIMATED ERROR:

 $\delta L/L = \pm 0.03$

REFERENCES:

Bodor, E.; Bor, Gy.;
 Mohai, B.; Sipos, G.
 Veszpremi Vegyip. Egy. Kozl.
 1957, 1, 55.
 Chem. Abstr. 1961, 55, 3175h.

COMPONENTS: (1) Methane; CH₄; [74-82-8] (2) Decane; C₁₀H₂₂; [124-18-5] J. Chem. Thermodyn. 1978, 10, 817 - 822.

VARIABLES: T/K: 282.80, 313.35

p/kPa: 101.325 (1 atm)

PREPARED BY:

H. L. Clever

EXPERIMENTAL VALUES:

282.80 5.737 0.6693 0.6929 313.35 4.798 0.5420 0.6218	<i>T/</i> K	Mol Fraction 10 ³ x ₁	Bunsen Coefficient α/cm³ (STP) cm ⁻³ atm ⁻¹	Ostwald Coefficient L/cm³ cm-3

The Bunsen coefficients were calculated by the compiler.

It is assumed that the gas is ideal and that Henry's law is obeyed.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility 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 is that described by Battino, Banzhof, Bogan, and Wilhelm (3).

Degassing. Up to $500~\rm{cm^3}$ 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 intermittently applied 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 helical tube containing 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.

SOURCE AND PURITY OF MATERIALS:

- (1) Methane. Matheson Co., Inc. Minimum mole percent purity stated to be 99.97.
- (2) Decane. Phillips Petroleum Co. 99 mol %, distilled, density at 298.15 K, ρ/g cm⁻³ 0.7264.

ESTIMATED ERROR:

 $\delta T/K = 0.02$ $\delta P/mmHg = 0.5$ $\delta x_1/x_1 = 0.01$

- Morrison, T. J.; Billett, F. J. Chem. Soc. <u>1948</u>, 2033.
- Battino, R.; Evans, F. D.; Danforth, W. F. J. Am. Oil Chem. Soc. 1968, 45, 830.
- Battino, R.; Banzhof, M.; Bogan, M.; Wilhelm, E. Anal. Chem. <u>1971</u>, 43, 806.

(1) Methane; CH₄; [74-82-8] (2) Dodecane; C₁₂H₂₆; [112-40-3]

ORIGINAL MEASUREMENTS:

Hayduk, W.; Buckley, W.D. Can. J. Chem. Eng. 1971, 49, 667-671.

VARIABLES:

T/K: 273.15-348.15 P/kPa: 101.325

PREPARED BY:

W. Hayduk

EXPERIMENTAL VALUES:

T/K	Ostwald Coefficient 1 L/cm3 cm-3	Bunsen Coefficient ² α/cm ³ (STP)cm ⁻³ atm ⁻¹	Mole Fraction ¹ $10^4 x_1$
273.15	0.627	0.627	62.4 (62.8) ³
298.15	0.590	0.540	54.9 (54.4)
323.15	0.547	0.462	48.2 (48.2)
348.15	0.517	0.406	43.4 (43.5)

¹Original data.

$$\ln x_1 = 465.4/T - 6.775$$

Std. deviation for $\Delta G^{\circ} = 15.3 \text{ J mol}^{-1}$; Correlation coefficient = 0.9999

<i>T/</i> K	10-4ΔG°/J mol-1	10 4 x ₁	<i>T</i> /K	10 ⁻⁴ ΔG°/mol ⁻¹	10 4 x ₁
273.15	1.152	62.8	303.15	1.321	53.0
283.15	1.208	59.1	313.15	1.377	50.5
293.15	1.264	55.9	323.15	1.433	48.2
298.15	1.292	54.4	348.15	1.574	43.5

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A volumetric method using a glass apparatus was employed. Degassed solvent contacted the gas while flowing as a thin film, at a constant rate, through an absorption spiral into a solution buret. A constant solvent flow was obtained by means of a calibrated syringe pump. The solution at the end of the spiral was considered saturated. Dry gas was maintained at atmospheric pressure in a gas buret by mechanically raising the mercury level in the buret at an adjustable rate. The solubility was calculated from the constant slope of volume of gas dissolved and volume of solvent injected.

Degassing was accomplished using a two stage vacuum process described by Clever et al. (1).

SOURCE AND PURITY OF MATERIALS:

- Matheson Co. Specified as ultra high purity grade of 99.98 per cent.
- Canlab. Chromatoquality grade of specified minimum purity of 99.0 per cent.

ESTIMATED ERROR:

 $\delta T/K = 0.1$ $\delta x_1/x_1 = 0.01$

REFERENCES:

 Clever, H.L.; Battino, R.; Saylor, J.H.; Gross, P.M.
 J. Phys. Chem. 1957, 61, 1078.

²Calculated by compiler

³The mole fraction solubility of the original data was used to determine the following equations for ΔG° and $\ln x_{1}$ and table of smoothed values: $\Delta G^{\circ}/J$ mol⁻¹ = -RT ln x_{1} = 56.325 T - 3869.4

COMPONENTS: (1) Methane; CH₄; [74-82-8] (2) Undecane; C₁₁H₂₄; [1120-21-4] Dodecane; C₁₂H₂₆; [112-40-3] VARIABLES: T/K: 298.15 p/kPa: 101.325 (1 atm) ORIGINAL MEASUREMENTS: Makranczy, J.; Megyery-Balog, K.; Rusz, L.; Patyi, L. Hung. J. Ind. Chem. 1976, 4, 269 - 280. PREPARED BY: S. A. Johnson H. L. Clever

EXPERIMENTAL VALUES:

T/K	Mol Fraction 10 ³ x ₁	Bunsen Coefficient α/cm³(STP)cm-3atm-1	Ostwald Coefficient L/cm³cm-3
Undecan	ie		
298.15	5.46	0.580	0.633
Dodecan	ie		
298.15	5.45	0.537	0.586

The Bunsen coefficient and mole fraction values were calculated by the compiler assuming that the gas is ideal and that Henry's law is obeyed.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Volumetric method. The apparatus described by Bodor, Bor, Mohai and Sipos was used (1).

SOURCE AND PURITY OF MATERIALS:

Both the gas and the liquid were analytical grade reagents of Hungarian or foreign origin. No further information.

ESTIMATED ERROR:

 $\delta L/L = \pm 0.03$

REFERENCES:

Bodor, E.; Bor, Gy.; Mohai, B.; Sipos, G.
 Veszpremi Vegyip. Egy. Kozl.
 1957, 1, 55.
 Chem. Abstr. 1961, 55, 3175h.

COMPONENTS: ORIGINAL MEASUREMENTS: (1) Methane; CH₄; [74-82-8] Makranczy, J.; Megyery-Balog, K.; Rusz, L.; Patyi, L. (2) Tridecane; C₁₃H₂₈; [629-50-5] Hung. J. Ind. Chem. 1976, 4, 269 - 280. Tetradecane; C₁₄H₃₀; [629-59-4] PREPARED BY: VARIABLES: T/K: 298.15 S. A. Johnson p/kPa: 101.325 (1 atm) H. L. Clever

EXPERIMENTAL	VALUES:			
1	T/K	Mol Fraction 10^3x_1	Bunsen Coefficient α/cm³(STP)cm-3atm-1	Ostwald Coefficient L/cm³cm-3
	Trideca	ne		
	298.15	5.39	0.496	0.541
	Tetrade	cane		
	298.15	5.40	0.465	0.508

The Bunsen coefficient and mole fraction values were calculated by the compiler assuming that the gas is ideal and that Henry's law is obeyed.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: Volumetric method. The apparatus described by Bodor, Bor, Mohai and Sipos was used (1).	SOURCE AND PURITY OF MATERIALS: Both the gas and the liquid were analytical grade reagents of Hungarian or foreign origin. No further information.
	ESTIMATED ERROR:
	$\delta L/L = \pm 0.03$

REFERENCES:

1. Bodor, E.; Bor, Gy.;
Mohai, B.; Sipos, G.
Veszpremi Vegyip. Egy. Kozl.
1957, 1, 55.
Chem. Abstr. 1961, 55, 3175h.

- (1) Methane; CH₄; [74-82-8]
- (2) Pentadecane; C₁₅H₃₂; [629-62-9] Hexadecane; C₁₆H₃₄; [544-76-3]

ORIGINAL MEASUREMENTS:

Makranczy, J.; Megyery-Balog, K.; Rusz, L.; Patyi, L.

Hung. J. Ind. Chem. 1976, 4, 269 - 280.

VARIABLES:

T/K: 298.15 p/kPa: 101.325 (1 atm)

PREPARED BY:

S. A. Johnson H. L. Clever

EXPERIMENTAL VALUES:

<i>T</i> /K	Mol Fraction $10^3 x_1$	Bunsen Coefficient α/cm^3 (STP) cm^{-3} atm ⁻¹	Ostwald Coefficient L/cm³cm-3
Pentade	cane		
298.15	5.35	0.434	0.474
Hexadeo	ane		
298.15	5.36	0.410	0.448

The Bunsen coefficient and mole fraction values were calculated by the compiler assuming that the gas is ideal and that Henry's law is obeyed.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Volumetric method. The apparatus described by Bodor, Bor, Mohai and Sipos was used (1).

SOURCE AND PURITY OF MATERIALS:

Both the gas and the liquid were analytical grade reagents of Hungarian or foreign origin. No further information.

ESTIMATED ERROR:

 $\delta L/L = \pm 0.03$

REFERENCES:

Bodor, E.; Bor, Gy.;
 Mohai, B.; Sipos, G.
 Veszpremi Vegyip. Egy. Kozl.
 1957, 1, 55.
 Chem. Abstr. 1961, 55, 3175h.

ORIGINAL MEASUREMENTS: 1. Methane; CH₄; [74-82-8] 2. Hexadecane; C₁₆H₃₄; [544-76-3] VARIABLES: ORIGINAL MEASUREMENTS: Lenoir, J-Y.; Renault, P.; Renon, H. J. Chem. Eng. Data, 1971, 16, 340-2.

EXPERIMENTAL VALUES:

* 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:

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 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).

- (1) Methane; CH₄; [74-82-8]
- (2) Hexadecane; C₁₆H₃₄; [544-76-3]

ORIGINAL MEASUREMENTS:

Hayduk, W.; Buckley, W.D. Can. J. Chem. Eng. 1971, 49,

667-671.

VARIABLES:

T/K: 298.15-348.15

P/kPa: 101.325

PREPARED BY:

W. Hayduk

EXPERIMENTAL VALUES:

T/K	Ostwald Coefficient ¹ L/cm ³ cm ⁻³	Bunsen Coefficient ² α/cm^3 (STP) cm ⁻³ atm ⁻¹	Mole Fraction ¹
298.15	0.500	0.458	60.2 (59.9) ³
323.15	0.475	0.401	53.7 (55.2)
348.15	0.464	0.364	49.9 (49.7)

¹Original data.

³The mole fraction solubility of the original data was used to determine the following equations for ΔG° and $\ln x_{1}$ and table of smoothed values: $\Delta G^{\circ}/J \text{ mol}^{-1} = -RT \ln x_{1} = 53.380 \ T - 3229.7$

 $\ln x_1 = 388.5/T - 6.420$

Std. deviation for $\Delta G^{\circ} = 20.4 \text{ J mol}^{-1}$; Correlation coefficient = 0.9999

T/K	$10^{-4}\Delta G^{\circ}/mol^{-1}$	104 x ₁
298.15	1.269	59.9
303.15	1,295	58.6
313.15	1.349	56.3
323.15	1.375	55.2
333.15	1,455	52.3
348.15	1.535	49.7

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A volumetric method using a glass apparatus was employed. Degassed solvent contacted the gas while flowing as a thin film, at a constant rate, through an absorption spiral into a solution buret. A constant solvent flow was obtained by means of a calibrated syringe pump. The solution at the end of the spiral was considered saturated. Dry gas was maintained at atmospheric pressure in a gas buret by mechanically raising the mercury level in the buret at an adjustable rate. The solubility was calculated from the constant slope of volume of gas dissolved and volume of solvent injected.

Degassing was accomplished using a two stage vacuum process described by Clever et al. (1).

SOURCE AND PURITY OF MATERIALS:

- Matheson Co. Specified as ultra high purity grade of 99.97 per cent.
- Canlab. Olefin-free grade of specified minimum purity of 99.0 per cent.

ESTIMATED ERROR:

$$\delta T/K = 0.1$$

$$\delta x_1/x_1 = 0.01$$

REFERENCES:

 Clever, H.L.; Battino, R.; Saylor, J.H.; Gross, P.M.
 J. Phys. Chem. 1957, 61, 1078.

²Calculated by compiler.

238	Alkanes: Partial Pressure	of Methane up to 0.2 MPa
COMPONENTS:		ORIGINAL MEASUREMENTS:
1. Methane; C	H ₄ ; [74-82-8]	Cukor, P.M.; Prausnitz, J.M.
2. Hexadecane [544-76-3]	; C ₁₆ H ₃₄ ;	J. Phys. Chem. <u>1972</u> , 76, 598-601
VARIABLES:		PREPARED BY:
Temperature		C.L. Young
EXPERIMENTAL VALUE	ES:	
т/к		onstant ^a Mole fraction of methane ^b atm in liquid, $x_{\mathrm{CH_4}}$
300		0.00575
325		0.00524
350		0.00485
375		0.00459
400		0.00439
425	233	0.00429
450		0.00426
475	233	0.00429
a.	Quoted in supplementary	y material for original paper
b.	Calculated by compiler	for a partial pressure of 1 atmosphere
	AUXILIARY	INFORMATION
METHOD/APPARATUS/	PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
to that desc Hildebrand (with a null	pparatus similar ribed by Dymond and l). Pressure measured detector and precision ils in ref. (2).	No details given
		ESTIMATED EDDOR
		ESTIMATED ERROR: $\delta T/K = \pm 0.05$; $\delta x_{CH_4} = \pm 2\%$
		REFERENCES:
		1. Dymond, J.; Hildebrand, J.H. Ind. Eng. Chem. Fundam. 1967, 6, 130.
		2. Cukor, P.M.; Prausnitz, J.M. Ind. Eng. Chem. Fundam. 1971, 10 638.

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Methane; CH4; [74-82-8]	Rivas, O.R.; Prausnitz, J.M.
2. Hexadecane; C ₁₆ H ₃₄ ; [544-76-3]	Ind. Eng. Chem. Fundam. <u>1979</u> ,18, 289-292.
VARIABLES: Temperature	PREPARED BY: C.L. Young
EXPERIMENTAL VALUES:	
T/K Henry's con / atm	stant Mole fraction at 1 atm partial pressure*, **CH4
298.15 171.7 373.15 216.1 473.15 231.7	0.005824 0.004627 0.004316
* Calculated by compiler ass solubility linear with pre	
	INFORMATION
METHOD/APPARATUS/PROCEDURE: Volumetric apparatus with a fused quartz precision bourdon pressure gauge. Solubility apparatus carefully thermostatted. Solvent degassed in situ. Apparatus described in source and similar to that described in ref (1).	INFORMATION SOURCE AND PURITY OF MATERIALS: No details given.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Methane; CH₄; [74-82-8] Hexadecane; C₁₆H₃₄; [544-76-3] or Octadecane; C₁₈H₃₈; [593-45-3] 	Richon, D.; Renon, H. J. Chem. Eng. Data <u>1980</u> , 25, 59-60.
VARIABLES:	PREPARED BY: C. L. Young
EXPERIMENTAL VALUES:	we of Mole fraction of

T/K	Limiting value of Henry's constant, H / /atm	Mole fraction of methane, * ²⁰ CH,
298.15	Hexadecane 171.2	0.005841
	Octadecane	
323.15	196.9	0.005079

^{*} Calculated by compiler assuming mole fraction is a linear function of pressure up to 1 atm.

AUXILIARY INFORMATION

METHOD /APPARATUS / PROCEDURE:

Inert gas stripping plus gas chromatographic method. Details given in ref. (1). Method based on passing constant stream of inert gas through dissolved gas-solvent mixture and periodically injecting mixture into gas chromatograph. Henry's law constant determined from variation of gas peak area with time.

SOURCE AND PURITY OF MATERIALS:

- L'Air Liquide sample, purity
 99.95 mole per cent.
- Hexadecane was a Merck sample, Octadecane was a Fluka sample, both had purities of not less than 99 mole per cent.

ESTIMATED ERROR:

 $\delta T/K = \pm 0.05$; $\delta H^{\infty} = \pm 4\%$ (estimated by compiler).

REFERENCES:

1. Leroi, J. C.; Masson, J. C.;
Renon, H.; Fabries, J. F.;
Sannier, H. Ind. Eng. Chem.
Process. Des. Develop. 1977, 16,
139.

COMPONENTS:		ORIGINAL MEASUREMENTS:
1. Methane;	CH ₄ ; [74-82-8]	Lin, P. J.; Parcher, J. F.
2. Alkanes		J. Chromatog. Sci.
		<u>1982</u> , <i>20</i> , 33-38.
VARIABLES:		PREPARED BY:
		C. L. Young
EXPERIMENTAL VALU	JES:	
	Henry's law	Mole fraction at a partial
T/K		pressure of 1 atmosphere **CH4
	/atm	Cn ₄
	Hexadecane; C ₁₆ H ₃₄ ;	[544-76-3]
298.2	179	0.00559
313.2 328.2	189 192	0.00529 0.00521
320.2	192	0.00321
	Octacosane; C28H58;	[630-02-4]
353.2 373.2	157 165	0.00637 0.00606
393.2	174	0.00575
	Howatuingontone. G	W - 1620 06 01
353.2	Hexatriacontane; C ₃₆	0.00763
373.2 393.2	137 145	0.00730
413.2	153	0.00690 0.00654
	AUXILIARY	INFORMATION
METHOD/APPARATUS	/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
	constant determined on volume of gas on	
a chromatogr	aphic column. Helium a carrier gas and a	No details given.
mass spectro	meter was used as a	
law constant	The measured Henry's s were independent of	
	flow rate and composicted sample. The dead	
volume was d	etermined by two methods and the values	ESTIMATED ERROR:
	n experimental error.	$\delta T/K = \pm 0.1; \delta x_{CH_4} = \pm 5\%$
		(estimated by compiler).
		REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
 Methane; CH₄; [74-82-8] 2,2,4,4,6,8,8-Heptamethyl nonane; C₁₆H₃₄; [4390-04-9] 	Richon, D.; Renon, H. J. Chem. Eng. Data 1980, 25, 59-60.
VARIABLES:	PREPARED BY: C. L. Young

T/K

Limiting value of Henry's Mole fraction of constant, H^{∞}/atm

methane, xCH4

298.15

32.8

0.0305

AUXILIARY INFORMATION

METHOD /APPARATUS / PROCEDURE:

Inert gas stripping plus gas chromatographic method. given in ref. (1). Method based on passing constant stream of inert gas through dissolved gas-solvent mixture and periodically injecting mixture into gas chromatograph. Henry's law constant determined from variation of gas peak area with time.

SOURCE AND PURITY OF MATERIALS:

- 1. L'Air Liquide sample, purity 99.95 mole per cent.
- 2. Sigma sample, purity not less than 99 mole per cent.

ESTIMATED ERROR:

 $\delta T/K = \pm 0.05; \quad \delta x_{CH_L} = \pm 4\%$ (estimated by compiler).

REFERENCES:

1. Leroi, J. C.; Masson, J. C.; Renon, H.; Fabries, J. F.; Ind. Eng. Chem. Sannier, H. Process. Des. Develop. 1977, 16, 139.

Calculated by compiler assuming mole fraction is a linear function of pressure up to 1 atm.

COMPONENTS:	ORIGINAL MEASUREMENTS:
	Ng, S.; Harris, H.G.; Prausnitz,
1. Methane; CH4; [74-82-8]	J.M.;
2. Octadecane; C ₁₈ H ₃₈ ;	
[593-45-3]	J. Chem. Engng. Data, 1969, 14,
	482-3.
VARIABLES:	PREPARED BY:
	1
Temperature	C.L. Young
EXPERIMENTAL VALUES:	<u> </u>
T/K Henry's Const	ant, H Mole fraction +
/atm.	of methane in
	liquid, x_{CH_4}
308.2 209 323.2 239	0.00478 0.00418
323.2 239 343.2 272	0.00368
363.2 255	0.00392
373.2 423.2 306	0.00327 0.00253
423.2 395	0.00233
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Gas chromatographic method. Solvent supported on Chromosorb P in 6 m	1. Matheson sample purity greater than 99 mole per cent.
column. Gas injected as sample,	-
helium used as carrier gas. Henry's	2. Matheson, Coleman and Bell
law constant calculated from know- ledge of retention time and flow	sample, m.pt. 27-28.5°C.
rate.	
	ESTIMATED ERROR:
	$\delta T/K = \pm 0.1$; $\delta H/atm = \pm 5\%$.
	DEFENDING
	REFERENCES:

COMPONENTS:		ORIGINAL MEASUREMENTS:
1. Methane; CH ₄ ; [74-82-8]	Ng. S.; Harris, H.G.; Prausnitz, J.M.
2. Eicosane; C ₂₀ H ₄₂	; [112-95-8]	J. Chem. Engng. Data, <u>1969</u> , 14, 482-3
VARIABLES:		PREPARED BY:
Temperature		C. L. Young
EXPERIMENTAL VALUES:		
T/K Her	nry's Constant, /atm	H Mole fraction of methane in liquid, $x_{\mathrm{CH_{i_q}}}$
323.2 373.2	226 286	0.00442 0.00350
I	201	1711111

* At 1 atmosphere partial pressure, calculated by compiler assuming mole fraction equals $1/{\it H}$

301

356

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

393.2

413.2

Gas chromatographic method. Solvent supported on Chromosorb P in 6 m column. Gas injected as sample, helium used as carrier gas. Henry's law constant claculated from knowledge of retention time and flow rate.

SOURCE AND PURITY OF MATERIALS:

1. Matheson sample, purity greater than 99 mole per cent.

0.00332

0.00281

2. Matheson, Coleman and Bell sample, m.pt. 35-36.5°C.

ESTIMATED ERROR:

 $\delta T/K = \pm 0.1$; $\delta H/atm = \pm 5$ %

ORIGINAL MEASUREMENTS: COMPONENTS: Methane; CH4; [74-82-8] Chappelow, C.C.; Prausnitz, J.M. Am. Inst. Chem. Engnrs. J. 1974, 2. Eicosane; C₂₀H₄₂; [112-95-8] 20, 1097-1104. VARIABLES: PREPARED BY: Temperature C.L. Young EXPERIMENTAL VALUES: Henry's Constant^a Mole fraction^b of methane T/K at 1 atm. partial pressure, /atm $x_{\text{CH}_{1}}$ 325 170 0.00588 184 0.00543 350 375 196 0.00510 400 205 0.00488 425 210 0.00476 450 214 0.00467 475 0.00463 216 Authors stated measurements were made at several pressures a. and values of solubility used were all within the Henry's Law region. Calculated by compiler assuming linear relationship between b. mole fraction and pressure. AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: SOURCE AND PURITY OF MATERIALS: Volumetric apparatus similar to that Solvent degassed, no other details described by Dymond and Hildebrand (1). Pressure measured with a null given. detector and precision gauge. Details in ref. (2). ESTIMATED ERROR: $\delta T/K = \pm 0.1; \ \delta x_{CH_h} = \pm 1$ % REFERENCES: 1. Dymond, J.; Hildebrand, J.H. Ind. Eng. Chem. Fundam. 1967, 6, 130. 2. Cukor, P.M.; Prausnitz, J.M. Ind. Eng. Chem. Fundam. 1971, 10, 638.

COMPONENTS:		ORIGINAL MEASUREMENTS:
1. Methane; CH	; [74-82-8]	Ng, S.; Harris, H.G.; Prausnitz, J.M.
2. Docosane; C ₂	₂ H ₄₆ [629-97-0]	J. Chem. Engng. Data, <u>1969</u> , 14, 482-3
VARIABLES:	····	PREPARED BY:
Temperatu:	re	C. L. Young
EXPERIMENTAL VALUES:		*
T/K	Henry's Constant, /atm	<pre>Mole fraction of methane in liquid, x_{CH₄}</pre>
333.2	229	0.00437
383.2	269	0.00372
408.2 433.2	314	0.00318
433.2	338 355	0.00296 0.00282
453.2		0.00202

* At 1 atmosphere partial pressure, calculated by compiler assuming mole fraction equals $1/{\it H}$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Gas chromatographic method. Solvent supported on Chromosorb P in 6 m column. Gas injected as sample, helium used as carrier gas. Henry's law constant calculated from knowledge of retention time and flow rate.

SOURCE AND PURITY OF MATERIALS:

- 1. Matheson sample, purity greater than 99 mole per cent.
- 2. Matheson, Coleman and Bell sample, m.pt . 43-45°C.

ESTIMATED ERROR:

 $\delta T/K = \pm 0.1$; $\delta H/atm = \pm 5$ %

COMPONENTS:	_		ORIGINAL MEASUREMENTS:	
		H ₄ ; [74-82-8]	Chappelow, C.C.; Prausnitz, J.M.	
			,	
2. 2,6,10 tetrac [111-	cosan	19,23,-Hexamethyl- e,(Squalane); C ₃₀ H ₆₂ ;	Am. Inst. Chem. Engnrs. J. 1974, 20, 1097-1104.	
VARIABLES:		· · · · · · · · · · · · · · · · · · ·	PREPARED BY:	
Tempera	ature		C.L. Young	
EXPERIMENTAL	VALUE	S:		
	T/K		Constant ^a Mole fraction ^b of methane at 1 atm. partial pressure,	
	300	111	0.00901	
	325	124	0.00806	
	350	135	0.00741	
	375	144	0.00694	
	400	151	0.00662	
	425	156	0.00641	
	450	160	0.00625	
	475	163	0.00613	
	a.	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 compile mole fraction and pre	assuming linear relationship between ssure.	
	······································	AUXILIAR	INFORMATION	
METHOD/APPARATUS/PROCEDURE: Volumetric apparatus similar to that described by Dymond and Hildebrand (1). Pressure measured with a null detector and precision gauge. Details in ref. (2).				
			ESTIMATED ERROR: δT/K = ±0.1; δx _{CH4} = ±1% REFERENCES: 1. Dymond, J.; Hildebrand, J.H. Ind. Chem. Eng. Fundam. 1967, 6, 130. 2. Cukor, P.M.; Prausnitz, J.M. Ind. Chem. Eng. Fundam. 1971, 10, 638.	