

## The Solubility of Methane in Hydrocarbons, Alcohols, Water and Other Solvents

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The solubility of methane in a series of solvents has been determined. For each solvent used, the values found for the Bunsen absorption coefficients at 18°, 25° and 37°C are, respectively, as follows: *n*-hexane 0.885, 0.869, 0.816; cyclohexane 0.701, 0.675, 0.643; acetone 0.594, 0.564, 0.547; benzene 0.535, 0.523, 0.510; ethanol 0.512, 0.489, 0.455; methanol 0.500, 0.479, 0.446; water 0.0352, 0.0313, 0.0260 and cyclohexanol 0.266 at 25°C and 0.252 at 37°C.

The experimental values obtained are in agreement with values calculated from equations derived on a semiempirical basis, and are compared with values found by other authors.

The experiments presented in this paper have previously been carried out by the first author in the *Chemical Laboratory of the Royal Veterinary and Agricultural College, Copenhagen*.

### MATERIALS AND PROCEDURE

*Methane* was generated from magnesium methyl iodide in a gasometer with airfree water and ethyl ether as blocking liquid; the methane was led slowly through a trap cooled with solid carbon dioxide, dried over concentrated sulphuric acid and phosphorus pentoxide, and condensed in a container cooled with liquid air. The methane was freed from atmospheric air by repeated distillations at a pressure of about 35 mm Hg, the air being pumped out after each distillation. It was finally purified by fractional distillation. The fraction used in the experiments showed by determination of the specific gravity an apparent molecular weight of 16.08 (22.40 l 0°C) in accordance with the corresponding value of the literature.

The solvents used were of the same origin and purity as described in a previous paper<sup>1</sup>. *Normal hexane* was fractionated by distillation of "*n*-Hexan aus Petroleum, Kahlbaum"; the fractions used in the experiments showed boiling point 68.85°C (760 mm) and vapour pressure 154 mm Hg at 25°C. The solubility determinations were carried out as previously described<sup>1</sup>.

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## RESULTS

The results of the solubility determinations are shown in Table 1; the calculated mean is considered to be reliable to within 1 %.

Table 2 shows that most of the present solubility determinations are higher than found by other authors; exceptions are the solubility determinations in acetone and benzene. In these solvents the present results are in strict accordance with Horiuti's results.

Table 1. Solubilities of methane expressed as Bunsen absorption coefficients. Experimental values.

Solvent	18°C			25°C			37°C		
	Single determination		Mean	Single determination		Mean	Single determination		Mean
<i>n</i> -Hexane	0.884	0.886	0.885	0.865	0.872	0.869	0.813	0.818	0.816
Cyclohexane	0.702	0.699	0.701	0.677	0.673	0.675	0.645	0.641	0.643
Acetone	0.593	0.594	0.594	0.566	0.562	0.564	0.548	0.546	0.547
Benzene	0.537	0.533	0.535	0.523	0.523	0.523	0.506	0.514	0.510
Ethanol	0.511	0.512	0.512	0.487	0.490	0.489	0.454	0.456	0.455
Methanol	0.500	0.500	0.500	(0.467)	0.479	0.479	0.440	0.451	0.446
Cyclohexanol				0.263	0.268	0.266	0.251	0.253	0.252
Water	0.0350	0.0354	0.0352	0.0315	0.0310	0.0313	0.0259	0.0261	0.0260

Table 2. Solubilities of methane expressed as Ostwald absorption coefficients at 25°C. Comparison with other measurements.

Solvent			Present investigation
<i>n</i> -Hexane	0.584 d)	0.794 g)	0.949
Cyclohexane	0.640 g)		0.737
Acetone	0.409 b)	0.615 f)	0.616
Benzene	0.483 d)	0.568 f)	0.571
Ethanol	0.477 a)	0.458 d)	0.534
Methanol	0.423 b)	0.438 d)	0.523
Cyclohexanol	0.132 (26°) e)		0.290
Water	0.0328 c)	0.0336 h)	0.0342

a) Bunsen, R. *Z. physik. Chem.* **9** (1892) 439.

b) Levi, M. G. *Z. physik. Chem.* **41** (1902) 110.

c) Winkler, L. W. *Ber.* **34** (1901) 1409, 1421.

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e) Cauquill, G. *J. chim. phys.* **24** (1927) 53.

f) Horiuti, J., see Ref.<sup>4</sup>, p. 125.

g) Guerry, D. *Thesis*, Vanderbilt Univ. Nashville Tennessee 1944.

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## CORRELATION WITH THEORY

In a previous paper,<sup>2,p.54</sup> it was shown that eqn (1) can account for the solubility of methane in non-polar solvents.

$$\log x_2 = \log x_2^i - \frac{\bar{V}_2}{2.303 RT} (\delta_1 - \delta_2)^2 - \left[ \log \frac{\bar{V}_2}{V_1} + 0.4343 \left( 1 - \frac{\bar{V}_2}{V_1} \right) \right] \quad (1)$$

In this equation  $x_2$  denotes the solubility in mole fraction,  $x_2^i$  the "ideal" solubility,  $\bar{V}_2$  the partial molal volume of the gas in the saturated solution,  $V_1$  the molal volume of the solvent,  $\delta_1$  the "solubility parameter" of the solvent defined as the square root of the energy of vaporization ( $\Delta E_1$ ) per ml, *i.e.*

$$\delta_1 = \sqrt{\frac{\Delta E_1}{V_1}}$$

$\delta_2$  the "solubility parameter" of the gas (see below) and  $T$  the absolute temperature. With regard to the derivation of eqn (1) reference should be made to Hildebrand and Scott<sup>3</sup>.

The ideal solubility at 25°C was calculated by means of the equation

$$\log x_2^i = \frac{\Delta H}{2.303 R} \left( \frac{1}{T} - \frac{1}{T_b} \right)$$

where  $\Delta H$  is the heat of vaporization of methane (1 955 cal/mole) at the boiling point  $T_b = 112^\circ\text{K}$ . The value for the ideal solubility was calculated to be  $39.8 \times 10^{-4}$ .

When a gas is dissolved in a liquid the volume of the solution is always greater than the volume of the solvent. From this expansion — which is only to a slight degree dependent on the solvent — one can calculate the partial molal volume of the gas in the solvent. Using the measurements of Horiuti<sup>4</sup> we get the value 52 ml for methane in benzene. The solubility parameter for methane,  $\delta_2$ , was calculated from eqn (1) to be 6.20, using Horiuti's values for the solubility of methane in benzene and in carbon tetrachloride.

In Table 3 the experimental values of the solubility have been compared with values calculated by means of eqn (1).

In Table 3 we have included the calculated values for the solubility of methane in some polar solvents, listed in the order of their increasing dielectric constant. It can be seen that the experimental values are higher than the values calculated from eqn (1). It should be emphasized that this equation is derived on the assumption that the molecules are non-polar and that chemical reactions are absent. Deviations of the same order of magnitude have previously been found for the calculated solubility of carbon dioxide, oxygen, carbon monoxide and nitrogen in polar solvents<sup>5</sup>.

In a recent paper<sup>6</sup> it is shown that eqn (1) can account for the solubility at 25°C of nitrogen, argon and ethane in alcohols, if  $\delta_1$  is substituted by  $\delta_1^*$  calculated from

$$\delta_1^* = \delta_1 - (\epsilon - 1)(0.165 - 0.00143\alpha \times 10^{25}) \quad (2)$$

In this equation,  $\delta_1$  is calculated from

$$\delta_1 = \sqrt{\frac{\Delta E_1}{V_1}} = \sqrt{\frac{\Delta H_1 - RT}{V_1}}$$

where  $\Delta H_1$  is the heat of vaporization of the solvent at the absolute temperature  $T$  and  $V_1$  the molal volume of the solvent. In eqn (2)  $\epsilon$  is the dielectric constant of the solvent and  $\alpha$  the polarizability of the gas.

Table 4 shows that the solubilities of methane in ethanol, methanol and in cyclohexanol can also be calculated by the same procedure. For methane we have used  $\alpha \times 10^{25} = 26.0$ . Included in Table 4 is a calculation of the solubility of methane in water; such a calculation gives only a rough estimate<sup>6</sup>, and the fair agreement with the experimental value for this solvent is regarded to be casual.

If we use the  $\delta_1^*$  values in the calculation of the solubility in the solvents mentioned in Table 3, we get no improvement. The deviations between calculated and experimental values turn out to be nearly the same. For acetone on the contrary we get a much greater deviation; using for this solvent a value

Table 3. Solubilities of methane at 25°C expressed in mole fractions  $x_2$ . Comparison of experimental and calculated values.

Solvent	$V_1$	$\delta_1$	$x_2 \times 10^4$		per cent deviation
			exptl.	calc.	
<i>n</i> -Hexane	132	7.27	50.8	49.7	+ 2.2
Cyclohexane	109	8.20	32.7	34.8	- 6.4
Carbon tetrachloride	97.1	8.60	28.6	28.2	+ 1.4
Benzene	89.3	9.15	20.9	21.0	- 0.5
Dioxane	86.1	10.0	12.9 g)	12.6	+ 0.2
Diethyl ether	105	7.42	45.4 f)	42.6	+ 6.5
Chlorobenzene	102	9.6	20.0 f)	17.4	+ 15
Methyl acetate	79.9	9.5	19.5 f)	16.6	+ 17
Acetone	74.0	9.65	18.6	14.4	+ 29

g) Guerry, D., see Ref. in Table 2.

f) Horiuti, J., see Ref.<sup>4</sup>

Table 4. Solubilities of methane at 25°C in some alcohols and in water. Comparison of experimental and calculated values.

Solvent	$V_1$	$\delta_1$	$\epsilon$	$x_2 \times 10^4$		per cent deviation
				exptl.	calc.	
Ethanol	58.7	12.8	24.3	12.8	12.7	+ 0.8
Cyclohexanol	106	11.7	15.0	12.6	14.5	- 13
Methanol	40.7	14.35	32.8	8.71	9.31	- 6
Water	18.1	23.4	78.0	0.253	0.292	- 13

for the dielectric constant of 20.9, we obtain  $x_2 = 39 \times 10^{-4}$  a value much higher than the experimental one,  $x_2 = 18.6 \times 10^{-4}$ . It should be mentioned that eqn (2) has been evaluated for alcohols all having nearly equal dipole moments.

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