The Solubility of Argon and Ethane in Perfluoro-*n*-Heptane and Carbon Disulfide

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Solubility experiments carried out at 25°C resulted in the following values expressed as Bunsen coefficients: Argon in perfluoro-*n*-heptane 0.528, argon in carbon disulfide 0.180; ethane in perfluoro-*n*-heptane 2.03, ethane in carbon disulfide 3.94. From these values together with existing data in other solvents the solubility parameters for argon and ethane have been calculated to 5.43 and 7.55, respectively.

For a subsequent investigation of the solubility of gases in alcohols and water we needed values for the solubility parameters of argon and ethane. Concerning the concept "solubility parameter" the reader is referred to Hildebrand and Scott's monograph [1, p. 129].

Preliminary values for these parameters (argon 5.4 and ethane 6.45) have been published in an earlier paper [2, p. 56]. These values were considered to be rather inaccurate since the calculation was based on only two solvents for each gas. For the new experiments we have chosen a solvent with a very low and one with a very high solubility parameter, *viz.* perfluoro-*n*-heptane (5.85) and carbon disulfide (10.0).

EXPERIMENTAL AND RESULTS

The solubility determinations of argon were carried out in an apparatus and by a procedure described in an earlier paper [3]. The solubility determinations of ethane were carried out in an analogous apparatus having a 20 ml container for both the solvent and the gas.

Argon (from "L'air liquide") was identified by its emission spectrum. A sample of the gas was filled in a Geissler tube and the wave lengths of about fifty lines in the red and the blue spectrum were measured and found to be in accordance with values given in the literature. The gas was dried over phosphorus pentoxide and proved to contain less than 0.05 % water.

Ethane (Research Grade from Phillips Petroleum-Company) was analyzed in a gas-chromatograph; 25 ml of the gas (measured at 20°C and 1 atm) was adsorbed on a column of silica gel. The length of the column was 25 cm and the cross section about 0.8 cm².
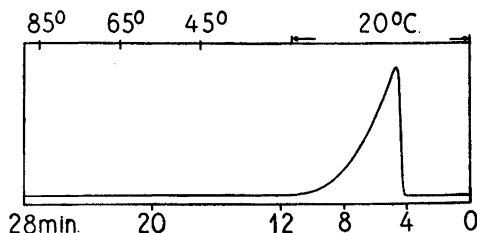
Fig. 1.

The speed of the supporting gas, hydrogen, was about 50 ml per minute. The detector was a thermal conductivity cell. The resulting curve is reproduced in Fig. 1, where the abscissa is the time in minutes. The first part of the analysis was carried out at 20°C. The sharp front after about 4 min shows that the gas contains no methane. 11 min after the beginning of the experiment the temperature was gradually increased to 85°C as shown in Fig. 1. Butane and higher hydrocarbons must be absent, since the curve shows only one peak.

To prove that lower hydrocarbons were absent the gas was analyzed in a Beckman spectrograph; the length of the cuvette was 10 cm and the pressure about 530 mm; the wave length was varied from 15 to 3 μ corresponding to wave numbers from 670 to 3 300 cm^{-1}.

The curve showed three characteristic bands for ethane at about 820, 1 450 and 2 934 cm^{-1}. A weak band at 949 cm^{-1} was interpreted as originating from ethene, the content of which was estimated to be less than 0.5 and possibly as low as 0.1 %. A very weak band at about 1 250 cm^{-1} was not identified.

By combustion analysis in an apparatus, as described by Christiansen and Wulff[4], we found results between 99.6 and 100.4 % ethane.

Perfluoro-n-heptane was fractionated in a 35-plate column (boiling point from 82.44 to 82.53°C at 760 mm). The fractions were analyzed in a Beckman spectrophotometer DU and showed a strong absorption in ultraviolet with maximum at about 216 mμ. Using the purification method of Glew and Reeves[5] we passed the fluoroheptane through a column of dry silica gel. After this purification we found the extinction coefficient to be about 0.02 at 216 mμ. The boiling point was now 82.55—82.56° ± 0.02 at 760 mm.

Carbon disulfide (analytical reagent) was fractionated in the distillation column and showed a boiling point of 46.03°C (760 mm).

The experimental results are given in Table 1 and expressed as Bunsen coefficients. The calculated means are considered to be reliable to within one per cent. The experiments were finished in June 1956. Since then Reeves and Hildebrand[6] have published a value for the solubility of argon in carbon disulfide; their value differs less than 1 % from our value.

CALULCATION OF THE SOLUBILITY PARAMETERS FOR ARGON AND ETHANE

The solubilities of argon and ethane are given in Tables 2 and 3 together with existing values for the solubilities in other solvents; the values are given in mole fractions ($x_2 \times 10^4$).

The solubility parameter (δ_2) for argon has been calculated from the equation

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

Table 1. Solubilities of argon and ethane expressed in Bunsen coefficients at 25°C.

	Argon		Ethane	
	singel determi- nations	mean	singel determi- nations	mean
CS$_2$	0.1815 0.179 0.1796	0.180	3.927 3.944	3.94
n-C$_7$F$_{16}$	0.5286 0.5275	0.528	(1.922) * 2.032 2.027	2.03

* this result is regarded to be too low.

in such a way that the equation reproduces the experimental values as closely as possible. With regard to the derivation of eqn. (1) reference should be made to Hildebrand and Scott [1, p. 131]. The ideal solubility, x_2^i, of argon has been calculated from

$$-\log x_2^i = -\frac{\Delta H \cdot 0.4343}{R}\left(\frac{1}{T} - \frac{1}{T_b}\right)$$

using $\Delta H = 1\,500$ cal/mole (*Int. Crit. Tables* V, p. 135) at the boiling point for argon $T_b = 87°$K. The result is $x_2^i = 21.6 \times 10^{-4}$ at $T = 298.1°$K. Since the partial molal volume ($\overline{V}_2$) of argon is not determined we have used the value for oxygen ($\overline{V}_2 = 46$ ml), see *Gjaldbæk* [2, p. 57].

From eqn. (1) we have calculated $\delta_2 = 5.43$. The accuracy with which this value represents the experimental data appears from Table 2.

The ideal solubility of ethane has been calculated from

$$x_2^i = \frac{1}{41.37} = 0.0242$$

where 41.37 atm is the vapour pressure of ethane at 25°C, confer Beattie et al.[9]

The density 0.338 of liquid ethane at 25°C has been interpolated using densities given in *Int. Crit. Tables* (III, p. 230); from this density we calculated the molal volume of liquid ethane to be 88 ml.

The accuracy with which the empirical value $\delta_2 = 7.55$ represents the experimental data appears in Table 3.

McDaniel [11] has measured the solubilities of ethane in n-hexane and n-heptane. If we recalculate his values into mole fractions we get 0.0177 and 0.0266, respectively. From equation (1) we calculate 0.026 and 0.0268.

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Table 2. Solubilities of argon in non-polar solvents at 25°C. Comparison of experimental and calculated values.

$$x_2^i = 21.6 \times 10^{-4} \qquad \bar{V}_2 = 46 \text{ ml} \qquad \delta_2 = 5.43$$

	V_1	δ_1	$x_2 \times 10^4$		exp.	$-\log x_2$ calc.	Δ
$n\text{-}C_7F_{16}$	226	5.85	53.0		2.276	2.326	+ 0.05
$c\text{-}C_7F_{14}$	195	6.0	46.0	a)	2.337	2.381	+ 0.04
$i\text{-}C_8H_{18}$	166	6.85	29.1	b)	2.536	2.490	− 0.05
$n\text{-}C_6H_{14}$	132	7.3	25.3	b)	2.597	2.609	+ 0.01
$n\text{-}C_7H_{16}$	147	7.45	25.0	b)	2.602	2.597	− 0.01
$c\text{-}C_7H_{14}$	128	7.85	18.55	a)	2.732	2.697	− 0.04
$c\text{-}C_6H_{12}$	109	8.2	1^4.8	c)	2.830	2.801	− 0.03
CCl_4	97.1	8.6	13.44	a)	2.872	2.909	+ 0.04
C_6H_6	89.3	9.15	8.85	c)	3.053	3.055	0.00
CS_2	60.6	10.0	4.87		3.313	3.355	+ 0.04

a) Reeves and Hildebrand [6], b) Clever *et al.* [7], c) Lannung [8].

Table 3. Solubilities of ethane in non-polar solvents at 25°C. Comparison of experimental and calculated values.

$$x_2^i = 242 \times 10^{-4} \qquad V_2 = 88 \text{ ml} \qquad \delta_2 = 7.55$$

	V_1	δ_1	$x_2 \times 10^4$		exp.	$-\log x_2$ calc.	Δ
$n\text{-}C_7F_{16}$	226	5.85	203		1.693	1.658	− 0.04
CCl_4	97.1	8.6	213	a)	1.672	1.685	+ 0.01
C_6H_6	89.3	9.15	151	a)	1.821	1.781	− 0.04
CS_2	60.6	10.0	107		1.971	1.969	0.00

a) Horiuti [10].

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