The Solubility of Hydrogen, Nitrogen, Oxygen and Ethane in Normal Hydrocarbons

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The solubilities of four gases in some normal hydrocarbons have been determined. The values found for the Bunsen absorption coefficients at 25°C are as follows (with the solvent in brackets): *Hydrogen* 0.0864 (nonane); *nitrogen* 0.206 (heptane), 0.179 (octane) and 0.160 (nonane); *oxygen* 0.330 (heptane), 0.286 (octane) and 0.264 (nonane); *ethane* 5.12 (heptane), 4.71 (octane) and 4.28 (nonane).

It is shown that there are some systematic differences between the experimental values and values calculated according to the existing theory.

The solubilities of non-polar gases in non-polar liquids [1-6] can be accounted for by the equation

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

In this equation x_2 denotes the solubility in mole fraction, $x_2{}^i$ the "ideal" solubility, $\overline{V}_2$ the partial molar volume of the gas in the saturated solution, V_1 the molar volume of the solvent, δ_1 the "solubility parameter" of the solvent defined as the square root of the energy of vaporization (ΔE_1) per ml, *i.e.*

$$\delta_1 = \sqrt{\Delta E_1/V_1} \qquad (2)$$

δ_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 [7].

Hildebrand [8] has shown that the solubility relations of heptane with perfluoroheptane, iodine, sulphur, stannic iodide and phosphorus are accounted for with better agreement, if the solubility parameter of heptane $\delta_1 = 7.45$ — calculated from eqn. (2) — is replaced by the empirical value 8.1. Similarly the empirical value 7.45 for 2,2,4-trimethylpentane should be used instead of the theoretical value 6.85. In order to get a more detailed knowledge of this

problem we carried out several solubility determinations in heptane, octane and nonane. It will be shown that the solubilities calculated from eqns. (1) and (2) deviate still more in octane and nonane than in heptane.

APPARATUS, PROCEDURE AND MATERIALS

Apparatus. The solubility determinations of hydrogen, nitrogen and oxygen were carried out (cf. Table 1) in an apparatus with a solvent container of either about 90 ml (app. I) or about 20 ml (app. II). The apparatus and the procedure for the solubility determinations are described in previous papers [3,5].

Using app. II it turned out not to be possible to get reproducible results with ethane as the dissolving gas; in heptane we got values of the Bunsen coefficient between 3.9 and 4.7 and in octane values between 3.7 and 4.3. We therefore constructed a new apparatus (III), which is described in the following (cf. Fig. 1).

The apparatus was made of glass and the tubes B, C and K were calibrated by weighing with mercury. The stopcocks 5 − 10 are capillary cocks.

The dimensions of the apparatus can be seen from Fig. 1. The volumes of the tubes B, C and K are 1.20, 0.81 and 0.029 ml/cm, respectively. In each experiment 1 − 2 ml solvent was used of which about 0.5 ml was introduced into K, after which about 55 ml of gas was introduced, about 40 ml into B and about 15 ml into C.

This apparatus − in which Bunsen coefficients higher than two can be determined − is a modification of an apparatus described by Lannung [9]. Our modification has the disadvantage, that one of the stopcocks (No. 6) is in contact with the gas during the experiment. Experiments carried out over long periods of time proved that the solubility of the gas in the stopcock grease made no errors in the solubility determinations.

Procedure. The whole apparatus was filled under vacuum whith mercury; the solvent was introduced through cock 5 letting mercury run out through 8. The solvent was thoroughly degassed by evacuating the space above it. Gas was let in through 7 in such a way that B was totally and C only half filled; then mercury was introduced to the mark a. Cock 6 was closed and a string of solvent − closed in both ends with mercury − was introduced into K. The apparatus was brought to constant temperature in a thermostatically controlled air bath; the volume of the solvent in K and the gas volumes and pressures in B and C were read using tube A as a manometer.

The string of solvent was now introduced into C and the mercury in K was drawn back to the mark c. During the dissolving process the mercury rises in C. To assure a definite volume of solvent an amount of gas was introduced quickly from B into C, which was such that the level of mercury in C was a little below its original level (*i.e.* the level before the introduction of solvent). Before the introduction of gas from B into C, the pressure in B was increased and that in C decreased; this was done to prevent vapour of the solvent from going from C into B. To ensure equilibrium the apparatus was moved mechanically forward and backward for about 12 h at constant temperature. Pressures and volumes of the gas in B and C were read, and the Bunsen coefficient, a, calculated from

$$\alpha = \frac{(A - B)\ 760}{V\ P}$$

where A is the total volume of gas before the experiment and B the total volume of gas after the equilibrium has been established, both volumes expressed in ml and reduced to 1 atm. and 0°C. V is the volume of solvent (ml) in C, and P the partial pressure of the gas (mm Hg) in C after the equilibrium has been established.

The experimental values were corrected for the pressure of the solvent over the mercury in C, the vapour pressure of the solvent and the volume of the solvent; we also took into account the small diminution of the solvent volume due to the evaporation of the solvent; this last correction was only necessary for solvents with higher vapour pressure than about 10 mm Hg at 25°C.

Materials. The solvents were distilled in a wire gauze column having about 35 theoretical plates (Klit [10]). The boiling point determinations were carried out in an apparatus
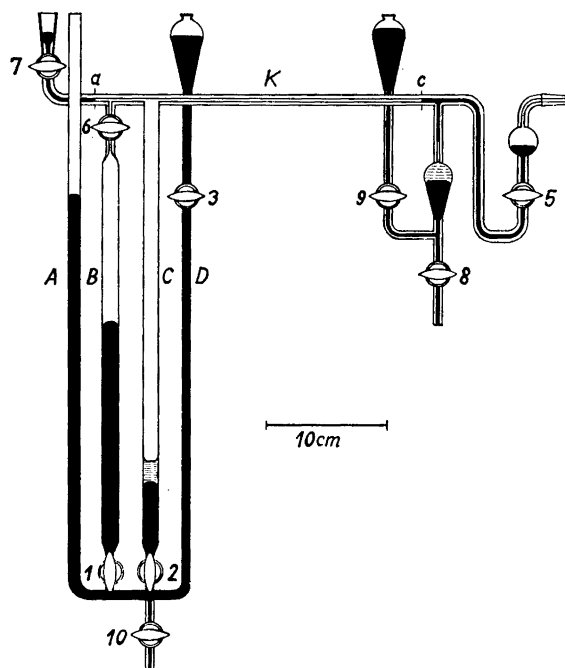
Fig. 1.

described by Baggesgaard Rasmussen and Reimers [11]. At least 75 % of each solvent distilled within the temperature intervals given below.

The solvents and the gases were analysed for impurities on a Perkin-Elmer gaschromatograph (model 154B). The adsorbent or the absorbing liquid phase and the temperature for the analyses are given in parenthesis. The supporting solid in the one metre long columns were "Sil−o−cel 22". The carrier gas was helium except where otherwise stated.

Heptane (Merck) distilled within 0.09°C and showed n_D^{25} = 1.3854 (Timmermans [12] states 1.3851−1.3852). Gaschromatographic analysis (tricresyl phosphate, 52°C) showed only one component, so that the heptane was used without further purification.

Octane. Most of the experiments were carried out in an octane, which was purified in the following way. 500 ml octane (British Drug House) was distilled and the middle fractions (430 ml) were redistilled. Nine fractions were collected; of these the five middle fractions (180 ml) were mixed and called octane A.

Octane A distilled within 0.02°C and showed n_D^{25} = 1.3955 (Timmermans [12] states 1.3951−1.3953). Gaschromatographic analysis (tricresyl phosphate, 100°C) showed an impurity with retention time 1.50 relative to octane. The amount of the impurity was estimated from the relative areas of the peaks to be about 1 %. The impurity could neither be removed by bases nor dilute acids and gave no reaction with iodine and sodium permanganate.

One of the solubility experiments with oxygen was carried out in an octane made by treating octane A with concentrated sulphuric acid and nitric acid followed by distillation. Gaschromatographic analysis showed that this sample (octane B) did not contain the impurity. In octane A we found a = 0.289 and in octane B, a = 0.282. Since the difference between these two values is so small, we considered octane A to be pure enough for the solubility measurements.

600 g *Nonane* (purum, Fluka) was distilled and the middle fractions (450 ml) were redistilled; ten fractions were collected from which seven middle fractions (240 ml) were

mixed and used for the experiments. The sample distilled within 0.08°C and showed $n_D^{25} = 1.4035$ (Timmermans [12] states $1.4034-1.4035$). Gaschromatographic analysis (tricresyl phosphate, 97°C) showed only one component.

Perfluoro-n-heptane was of the same origin and purity as described in an earlier paper [5].

Nitrogen was freed from oxygen and water by an alkaline solution of pyrogallol and silicagel, respectively. Gaschromatographic analysis ("Molecular Sieve 5A", 30°C, carrier gas oxygen) showed a content of 0.2 volume per cent argon. It was superfluous to make any correction for this small amount of argon since the solubilities of argon and nitrogen in the solvents used are of the same order of magnitude.

Oxygen was shown to contain 0.2 volume per cent nitrogen ("Molecular Sieve 5A", 29°C) and was used directly in the solubility experiments. No corrections for the impurity were made, *cf.* the remarks under nitrogen.

Hydrogen. Gaschromatographic analysis ("Molecular Sieve 5A", 29°C) showed as impurities only traces of oxygen (0.02 volume per cent) and nitrogen (0.03 volume per cent), so that the hydrogen was used without any purification.

Table 1. Solubilities of hydrogen, nitrogen and oxygen. Experimental values expressed in Bunsen absorption coefficients.

Gas and apparatus	Solvent	$t°C$	α	Mean of α at 25°C	$x_2 \times 10^4$ at 25°C
H$_2$ App. I	Nonane	25.0 24.9 34.9	0.0870 0.0857 0.0898	0.0864	6.93
N$_2$ App. II	Heptane	25.0 25.0 25.1 25.1 35.0 35.2	0.208 0.206 0.206 0.205 0.207 0.206	0.206	13.5
	Octane	25.0 25.1 25.3 25.1 25.1 34.9	0.179 0.176 0.178 0.180 0.181 0.181	0.179	13.1
	Nonane	25.0 25.0 25.0 25.1	0.160 0.160 0.161 0.160	0.160	12.8
O$_2$ App. II	Heptane	25.0 25.1 34.8	0.331 0.328 0.328	0.330	21.6
	Octane	25.1 25.0 35.0	0.289 0.282 0.281	0.286	20.9
	Nonane	24.9 25.0	0.266 0.261	0.264	21.2

Table 2. Solubilities of ethane. Experimental values expressed in Bunsen absorption coefficients. (All experiments carried out in apparatus III).

Solvent	$t°C$	a	Mean of a at 25°C
Heptane	24.9 25.0	5.08 5.15	5.12
Octane	25.3 25.1 25.0 25.1	4.64 4.70 4.71 4.79	4.71
Nonane	25.0 25.0 25.0	4.23 4.30 4.30	4.28
Perfluoroheptane	25.0 25.0 25.0	2.17 2.12 2.18	2.16

Ethane (research grade, Phillips Petroleum Company) was also used directly. Gas-chromatographic analysis (silicagel, 39°C) showed as impurities about 0.2 volume per cent atmospheric air and a not identified impurity with retention time about 0.13 calculated relative to ethane. The order of magnitude of this impurity was 0.1 %.

EXPERIMENTAL RESULTS

A survey of the results is given in Tables 1 and 2. A comparison with older experiments of the Bunsen coefficients in heptane at 25°C is given in the following table:

	older measurements	this paper
Nitrogen	0.189 Guerry [13]	0.206
Oxygen	0.300 —	0.330
Ethane	4.12 McDaniel [14]	5.12

The solubility of ethane in perfluoroheptane was earlier [5] found to be $a = 2.03$, *i.e.* 6 % lower than in this paper.

The Bunsen coefficient for hydrogen in nonane is about 4 % higher at 35°C than at 25°C, while the values of the solubilities of nitrogen and oxygen in the solvents used showed no temperature dependence between 25° and 35°C.

CORRELATION WITH THEORY

In an earlier paper [5] on the solubility of ethane the value $x_2^i = 0.0242$ was used; this value was not corrected for deviations from an ideal gas; furthermore the molar volume of liquid ethane at 25°C ($V_2 = 88$ ml) was used. It was possible to account for the experiments using eqn. (1) together with these two values and the empirical value $\delta_2 = 5.43$.

In this paper we want to use the ideal solubility at 25°C calculated from

$$x_2{}^i = f_2/f_2{}^\circ$$

where f_2 is the fugacity of ethane at 1 atm. and $f_2{}^\circ$ the fugacity of ethane at the vapour pressure of liquid ethane at 25°C (41.45 atm.).

The calculation is given in an earlier paper [15] and the result is $x_2{}^i = 0.988/30.24 = 0.0327$.

Horiuti [17] has determined the partial molar volume of ethane in benzene and carbon tetrachloride to be 66 ml. Using eqn. (1), $x_2{}^i = 0.0327$, $\overline{V}_2 = 66$ ml/mole and the solubility experiments we have evaluated the empirical value $\delta_2 = 6.60$. The differences between experimental and calculated values are given in Table 3. In an earlier paper on the solubility of chlorine [2] it was shown that the solubilities calculated from eqn. (1) are higher than the experimental values; using

$$\log x_2 = \log x_2{}^i - \frac{V_2 \Phi_1{}^2}{2.303\ RT}\ (\delta_1 - \delta_2)^2 \tag{3}$$

the calculated solubilities are lower than the experimental ones. It can be seen from Table 3 that eqn. (3) represents somewhat better than eqn. (1) the solubilities of ethane; in perfluoroheptane, perfluorotributylamine and in trimethylpentane the differences are serious.

A survey of the differences between experimental and calculated solubilities for several gases is given in Table 4. The differences calculated from eqn. (1) increase in each solvent examined in the order hydrogen, oxygen, nitrogen, ethane, and for each gas with increasing number of carbon atoms in the solvents. The differences for propane in hexane and octane [18] are included; it was a surprise to find that these are smaller than for ethane.

In the derivation of eqn. (3) the free molar volumes (V^f) of the two components are assumed to be equal and in eqn. (1) they are assumed to be proportional to the molar volumes of the liquid components, *i.e.*

$$V_1{}^f/V_2{}^f = V_1/V_2 \tag{4}$$

Table 3. Solubilities of ethane at 25°C. Comparison of experimental and calculated values of $x_2 \times 10^4$. $x_2{}^i = 327 \times 10^{-4}$, $\overline{V}_2 = 66$ ml/mole, $\delta_2 = 6.60$.

Solvent	V_1 ml/mole	δ_1	exptl.	calculated eqn. (1)	calculated eqn. (3)	% difference eqn. (1)	% difference eqn. (3)
n-C_7F_{16}	226	5.85	216	519	306	+ 140	+ 42
$(C_4F_9)_3N$	358	5.95	333 [a]	748	312	+ 120	− 6
2,2,4-trimethyl pentane	166	6.85	294 [a]	448	324	+ 53	+ 10
n-C_7H_{16}	147	7.45	329	387	302	+ 17	− 8
n-C_8H_{18}	164	7.55	337	401	295	+ 19	− 12
n-C_9H_{20}	180	7.65	336	420	289	+ 25	− 14
CCl_4	97.1	8.60	213 [b]	224	209	+ 5	− 2
C_6H_6	89.3	9.15	151 [b]	165	158	+ 9	+ 5
CS_2	60.6	10.0	107	90.8	90.2	− 15	− 16

[a] Kobatake and Hildebrand [16], [b] Horiuti [17].

Table 4. Percentage differences between experimental and calculated values of the solubilities (x_2).

	H_2	O_2	N_2	C_2H_6	C_3H_8 [b]	
$x_2^i \times 10^4$	5.5	17.6	16	327	1200	
$\bar{V}_2$ ml/mole	37	46	53	66	89	
δ_2	5.1	5.7	5.2	6.6	6.65	
Hexane			5 [a]		3	
Heptane		3	10	17		Eqn. (1)
Octane		12	18	19	3	
Nonane	15	15	23	25		
Hexane			− 4		− 2	
Heptane		− 36	− 24	− 8		Eqn. (3)
Octane		− 35	− 26	− 12	− 10	
Nonane	− 47	− 34	− 29	− 14		

[a] see Ref.[1], [b] see Ref.[18]

The following two assumptions were tried successively

$$V_1^f/V_2^f = k(V_1/V_2) \qquad (5)$$

$$V_1^f/V_2^f = (V_1/V_2)^n \qquad (6)$$

By empirical determination of the new constants k and n we succeeded in fitting the experiments for most of the solvents, but the calculated results for solubilities in the fluorocarbons were still bad (errors up to 55 %). Since the new assumptions do not amount to a real improvement, detailed results of the calculations will not be given.

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