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Solubility of Gases in Liquids. 20. Solubility of He, Ne, Ar, Kr, N_2, O_2, CH_4, CF_4, and SF_6 in *n*-Alkanes *n*-C_lH_{2l+2} ($6 \leq l \leq 16$) at 298.15 K†

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The Ostwald coefficients $L_{2,1}$ of He, Ne, Ar, Kr, N_2, O_2, CH_4, CF_4, and SF_6 dissolved in several homologous *n*-alkanes, *n*-C_lH_{2l+2}, $6 \leq l \leq 16$, have been measured at 298.15 K and atmospheric pressure with a modified Ben-Naim/Baer apparatus. Altogether, 99 gas/liquid systems were investigated. Both pressure control and measurement of the volume of gas dissolved in a given volume of solvent were controlled by a microprocessor. This improved, medium-precision apparatus (the imprecision is approximately ±0.5%) combines easy handling with automated data retrieval and is totally mercury-free. Data reduction is presented in some detail, including the estimation of auxiliary quantities, such as second virial coefficients and partial molar volumes at infinite dilution. The effect of chain length *l* upon solubility is shown, and some correlations between $L_{2,1}$, or the derived Henry fugacities $H_{2,1}$, and appropriate molecular and/or bulk properties of the gases and *n*-alkanes are discussed.

Introduction

The solubilities of simple, nonpolar solute molecules in liquids are of profound theoretical interest, and at the same time are needed in many application-oriented areas, such as chemical process design, geochemistry, biomedical technology and biophysics (*1*−*6*). Recently, we measured Ostwald coefficients $L_{2,1}$ of 10 gases (He, Ne, Ar, Kr, Xe, N_2, O_2, CH_4, CF_4, and SF_6) in a series of homologous normal alkan-1-ols, $C_lH_{2l+1}OH$, $1 \leq l \leq 11$, at 298.15 K and atmospheric pressure, and therefrom derived Henry fugacities $H_{2,1}$ (*7*). In fact, it was the largest set of data on this type of system ever obtained by one group with one instrument at one time: 102 gas/alcohol systems were investigated. Solubilities of gases in alcohols have attracted particular attention in connection with studies of bilayers and biological membranes, which relate directly to the mechanism of general anesthesia (*2*, *8*−*11*). In order to see more clearly the role of the alkyl chain in solubility behavior, it seemed desirable and timely to embark on a similarly comprehensive experimental study of gas solubilities in a series of homologous *n*-alkanes. Thus, we present here Ostwald coefficients and derived Henry fugacities of the same set of gaseous solutes—with the exception of xenon—in *n*-C_lH_{2l+2}, with $6 \leq l \leq 16$, at 298.15 K. Altogether, data on 99 gas/liquid systems are reported. The solubility of xenon in *n*-alkanes has been carefully studied by Pollack and co-workers (*12*) and was therefore not remeasured. The temperature dependence of the solubilities of some selected systems will be investigated in a future project.

For the solubility measurements, a synthetic method—essentially a flow equilibration method—was used. The instrument is a Ben-Naim/Baer-type apparatus (*13*) recently presented by us in detail (*7*, *14*). The Ben-Naim/Baer design was modified by incorporating a microprocessor for pressure control and measurement of gas volume. This improved apparatus is for medium-precision work with a maximum imprecision of about ±0.5% or less in most cases. Its assets are easy handling, relatively fast measurements (completion of one run, *i.e.*, dissolution of one gas in a solvent at a given temperature, usually takes less than 3 h), automated data retrieval, and total *absence of mercury*. The measured Ostwald coefficients are converted to Henry fugacities by using the thermodynamically rigorous relations given by Wilhelm (*5*−*7*, *14*−*17*).

Experimental Section

The *n*-hexane was from Fisher Scientific; heptane, nonane, decane, undecane, dodecane, tetradecane, and hexadecane were all from Philips Petroleum. Octane was from Chemical Dynamics, and tridecane and pentadecane were from Alfa Products. The refractive indices of the pure liquid *n*-alkanes were in good agreement with reliable literature values (*18*). The purity of the solvents was also checked by gas chromatography and found to be greater than 99 mol % in all cases. The solvents were stored in brown glass bottles. Prior to actual solubility measurements they were degassed by the method of Battino et al.

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(*19*), and transferred under their own vapor pressure into the apparatus.

All gases were used from the gas tanks as received. They were either from Matheson or from Airco and had the following minimum mole percentage purities: He, 99.999; Ne, 99.994; Ar, 99.9995; Kr, 99.9; N_2, 99.999; O_2, 99.95; CH_4, 99.99; CF_4, 99.7; SF_6, 99.8.

A modified Ben-Naim/Baer apparatus was used for all measurements. It was housed in a large air thermostat, the temperature of which was controlled to better than ±0.05 K with a Yellow Springs Instrument Co. Model 72 proportional controller. Temperatures T are based on IPTS-68 (with negligible difference for this work from ITS-90), and were measured with a Leeds and Northrup knife blade platinum resistance thermometer, which was calibrated with a triple-point-of-water cell and an NBS-certified benzoic acid cell.

Depending on the magnitude of the Ostwald coefficient, several equilibration chambers with volumes ranging from, approximately, (26 to 1650) cm^3 can be used. The equilibration chambers and the gas burets were calibrated with doubly distilled water, and the respective volumes are known to better than ±0.01 cm^3. Gas volumes were determined by having a Motorola microprocessor count the number of steps a stepping motor used to drive a close-fitting piston, with a Teflon seal backed up by O-rings, through a Fischer and Porter 5/8 in. [=(15.875 ± 0.008) mm] precision bore tube. The combination of tube diameter, the pitch of the drive screw, and the number of steps per revolution yields a volume change of about 0.0101 cm^3 per step. Thus, gas volumes can be determined to a few parts per thousand. Before dissolution begins the microprocessor is zeroed. From then on it automatically adjusts the piston to maintain the preselected pressure P. The pressure was determined with a Yellow Springs Instrument Co. Model 2014-27 pressure transducer (calibrated to ±0.2% by YSI) and was kept nulled to within 1 part per thousand. Generally, the dissolution time to a stable equilibration point was about 3 h.

The imprecision of our measurements ranged from ±0.2% to a maximum of ±0.7% for the systems with helium and neon (very small solubilities), the minimum design imprecision of the instrument being ±0.2%. This is in accord with the recent findings of Vosmansky and Dohnal (*20*). The inaccuracy was shown to be roughly of the same order of magnitude via test measurements of $L_{2,1}$ of selected gases dissolved in water (*7*, *14*, *20*).

Data Reduction

The Ostwald coefficient is a convenient and frequently used measure of the solubility of a gas in a liquid. Of the several definitions of the Ostwald coefficient introduced in the literature (*21*), the most appropriate one for a thermodynamically rigorous description of gas solubility is (*5*−*7*, *14*−*17*)

$$L_{2,1}(T,P) = (c_2{}^{L}/c_2{}^{V})_{\mathrm{equil}} \qquad (1)$$

Here, $c_2{}^{L} = x_2/V^{L}$ and $c_2{}^{V} = y_2/V^{V}$ are the amount-of-substance concentrations, at experimental *T and P* of the solute 2 (gas) in the liquid-phase solution (indicated by a superscript L) and in the coexisting vapor-phase solution (indicated by a superscript V), respectively. The mole fraction of gas in the liquid phase is x_2, y_2 is the mole fraction of gas in the vapor phase, and V^{L} and V^{V} are the corresponding molar volumes. The link with the experimentally accessible quantities is established through

$$L_{2,1}(T,P) = v^{V}/v^{L} \qquad (2)$$

where v^{V} is the volume determined through the microprocessor (see above) and v^{L} is the volume of the liquid solution *after* equilibrium is reached.

As indicated, $L_{2,1}(T,P)$ depends on both temperature and total pressure. However, for conditions well below the critical point of the solvent, the pressure dependence is usually very small and can be detected only by measurement techniques of the highest accuracy, that is to say by methods where the experimental error is, roughly, less than 0.1% (see, for instance, refs 15 and 22−24). Thus, given the limits of experimental precision attainable with this apparatus, to an excellent approximation the Henry fugacity $H_{2,1}(T,P_{s,1})$ at temperature T and vapor pressure $P_{s,1}$ of the pure solvent, also known as the Henry coefficient or Henry's law constant, is given by (*5*−*7*, *14*−*17*)

$$H_{2,1}(T,P_{s,1}) = RTZ^{V}\phi_2{}^{V}I_2{}^{-1}/[V^{L}L_{2,1}(T,P)] \qquad (3)$$

where the Poynting term is approximated by

$$I_2 \simeq \exp[(RT)^{-1}V_2^{L,\infty}(P - P_{s,1})] \qquad (4)$$

Here, $Z^{V} = PV^{V}/(RT)$ is the vapor-phase compressibility factor, $\phi_2{}^{V}$ is the vapor-phase fugacity coefficient of the solute, R is the gas constant, and $V_2^{L,\infty}$ is the partial molar volume of the gas at infinite dilution in the liquid phase.

For gas solubility measurements at such low pressures as in this work (P = 101 325 Pa), the virial equation in pressure in the truncated form

$$Z^{V} = 1 + (RT)^{-1}P(y_1B_{11} + y_2B_{22} + y_1y_2\Delta_{12}) \qquad (5)$$

is adequate and convenient for the description of real-gas behavior; hence

$$\phi_i{}^{V} = \exp[(RT)^{-1}P(B_{ii} + y_j{}^2\Delta_{12})], \quad i, j = 1, 2, \quad i \neq j \qquad (6)$$

B_{11} and B_{22} are the second virial coefficients of pure solvent vapor and pure gaseous solute, respectively, B_{12} is the second virial cross-coefficient, and $\Delta_{12} = 2B_{12} - (B_{11} + B_{22})$. The molar volume of the liquid solution is obtained from the asymptotically valid expression

$$V^{L} = x_1V_{s,1}^{L,*} + x_2V_2^{L,\infty} \qquad (7)$$

where $V^{*L,}_{s,1}$ is the molar volume of pure liquid solvent at saturation conditions. At the level of approximation indicated by eq 3, the liquid-phase mole fraction is given by

$$x_2 = P_2V^{L}L_{2,1}(T,P)/(RTZ^{V}) \qquad (8)$$

where $P_2 = y_2P$ is the partial pressure of the gas. For computational details of the rapidly converging iteration procedure used to calculate the mole fractions, the fugacity coefficients, *etc.*, see refs 7, 14, and 15.

Table 1. Vapor Pressures $P_{s,1}$, Densities $\rho_1^{L,*}$, Isobaric Expansivities $\alpha_{P,1}^{L,*}$, Isothermal Compressibilities $\beta_{T,1}^{L,*}$, and Internal Pressures $\Pi_1^{L,*}$ of *n*-Alkanes *n*-C_lH_{2l+2} at T = 298.15 K

n-alkane	$P_{s,1}$/ Pa[a]	$10^{-3}\rho_1^{L,*}$/ (kg·m^{-3})[b]	$10^3\alpha_{P,1}^{L,*}$/ K^{-1} [c]	$10^{12}\beta_{T,1}^{L,*}$/ Pa^{-1} [d]	$10^{-6}\Pi_1^{L,*}$/ Pa [e]
hexane	20179	0.6549	1.387	1669	247.8
heptane	6104	0.6795	1.252	1438	259.6
octane	1875	0.6985	1.155	1282	268.6
nonane	584	0.7138	1.088	1175	276.1
decane	183	0.7264	1.042	1094	284.0
undecane	58	0.7365	1.004	1031	290.3
dodecane	19	0.7452	0.976	988	294.5
tridecane	6	0.7527	0.951	948	299.1
tetradecane	2	0.7592	0.929	910	304.4
pentadecane	<1	0.7649	0.911	882	308.0
hexadecane	<1	0.7699	0.895	857	311.4

[a] Calculated from eq 9 with coefficients a_i taken from Ambrose and Walton;[26] $T_{c,1}$ and $P_{c,1}$ have also been taken from ref 26 (see Table 2). [b] Reference 28. [c] Average values from results reported in refs 29−32. [d] Reference 32. [e] Calculated from eq 18.

Table 2. Acentric Factors ω_1 (*26*), Critical Temperatures $T_{c,1}$ (*26*), Critical Pressures $P_{c,1}$ (*26*), and Critical Molar Volumes $V_{c,1}$ (*39, 43*) of *n*-Alkanes *n*-C_lH_{2l+2}

n-alkane	ω_1	$T_{c,1}$/K	$10^{-6}P_{c,1}$/Pa	$10^6V_{c,1}$/(m^3·mol^{-1})
hexane	0.299	507.90	3.035	369.9
heptane	0.350	540.15	2.735	430.1
octane	0.397	568.95	2.490	492.4
nonane	0.443	594.90	2.290	555.2
decane	0.490	617.65	2.105	624.1
undecane	0.533	638.85	1.955	688.6
dodecane	0.573	658.65	1.830	753.7
tridecane	0.618	676	1.710	823.1
tretradecane	0.654	693	1.610	893.7
pentadecane	0.696	708	1.515	965.5
hexadecane	0.737	722	1.435	1034.0

The vapor pressures of the *n*-alkanes were calculated from a four-constant Wagner-type equation (*25*) as suggested by Ambrose and Walton (*26*):

$$\ln(P_{s,1}/P_{c,1}) = (a_1\tau_1 + a_2\tau_1^{1.5} + a_3\tau_1^{2.5} + a_4\tau_1^{5})/T_{r,1} \qquad (9)$$

where $\tau_1 = 1 - T_{r,1}$, $T_{r,1} = T/T_{c,1}$ is the reduced temperature, and $P_{c,1}$ and $T_{c,1}$ are the critical pressure and the critical temperature of the pure *n*-alkane (component 1), respectively. The Wagner parameters a_i are those recommended by Ambrose and Walton (*26*) and more recently by Magoulas and Tassios (*27*). The densities ρ_1^{L*} of the pure liquid *n*-alkanes were taken from the *TRC Thermodynamic Tables* (*28*) while the isobaric expansivities $\alpha_{P,1}^{L*}$ are average values from results reported in refs 29−32 (expansivities from ref 32 were obtained via polynomial smoothing). The isothermal compressibilities $\beta_{T,1}^{L*}$ are from Diaz Peña and Tardajos (*32*). All these properties of the pure liquid *n*-alkanes are given in Table 1. Relative atomic masses were taken from the table published by IUPAC in 1992 (*33*). The auxiliary quantities necessary for calculating $H_{2,1}(T,P_{s,1})$, that is to say the virial coefficients and the partial molar volumes at infinite dilution, were either obtained from the literature or estimated as follows.

Virial Coefficients. Virial coefficients B_{22} of the pure gases were taken from Dymond and Smith (*34*), while the virial coefficients B_{11} of the pure solvent vapors were estimated using the Tsonopoulos correlation (*35−38*)

$$B_{ii}P_{c,i}/(RT_{c,i}) = B^{(0)}(T_{r,i}) + \omega_i B^{(1)}(T_{r,i}) \qquad (10)$$

$B^{(0)}(T_{r,i})$ and $B^{(1)}(T_{r,i})$ are universal functions of the reduced temperature $T_{r,i}$ of pure *i*, and ω_i is the acentric factor. The critical temperatures, the critical pressures, and the acentric factors of the pure *n*-alkanes (i = 1) are those recommended by Ambrose and Walton (*26*), in accord with recent critical surveys (*27, 39−42*); the critical densities are from Teja et al. (*39, 43*) (see Table 2).

For the estimation of virial cross-coefficients B_{12}, it is assumed that the same relation, eq 10, holds, but with characteristic parameters $T_{c,12}$, $P_{c,12}$, and ω_{12} replacing the corresponding pure-substance quantities (*38, 44*). Thus, reduced virial cross-coefficients $B_{12}(T_{r,12})P_{c,12}/(RT_{c,12})$ are obtained at a reduced temperature $T_{r,12} = T/T_{c,12}$, with

$$T_{c,12} = (1 - k_{12})(T_{c,1}T_{c,2})^{1/2} \qquad (11)$$

$$P_{c,12} = Z_{c,12}RT_{c,12}/V_{c,12} \qquad (12)$$

$$Z_{c,12} = (Z_{c,1} + Z_{c,2})/2 \qquad (13)$$

$$V_{c,12} = 0.125(V_{c,1}^{\ 1/3} + V_{c,2}^{\ 1/3})^3 \qquad (14)$$

$$\omega_{12} = (\omega_1 + \omega_2)/2 \qquad (15)$$

The critical quantities $T_{c,2}$, $P_{c,2}$, and $V_{c,2}$ of the pure gases, as well as their acentric factors ω_2, were taken from Reid *et al.* (*45*). The binary interaction parameter k_{12} is a characteristic constant for each binary.

The most sensitive mixing rule is eq 11, and k_{12} may be estimated by various semiempirical correlations (*38, 44*). For the present purpose we adopted a suggestion of Tsonopoulos (*44*) and used a Fender−Halsey-type (*46*) relation for the interaction parameter:

$$k_{12} = 1 - 2(T_{c,1}T_{c,2})^{1/2}/(T_{c,1} + T_{c,2}) \qquad (16)$$

Agreement with the few relevant experimental data (*38, 44*) is satisfactory.

Partial Molar Volumes. Experimental partial molar volumes at infinite dilution, $V_2^{L,\infty}$, have been reported for quite a number of gas/*n*-alkane systems (*1, 47, 48*). They are well represented, that is to say usually to within 10%, by (*7, 48*)

$$V_2^{L,\infty}P_{c,2}/(RT_{c,2}) = 0.088 + 2.763TP_{c,2}/(T_{c,2}\Pi_1^{L*}) \qquad (17)$$

where Π_1^{L*} is the internal pressure of the pure solvent. This quantity was calculated according to

$$\Pi_1^{L*} = T\alpha_{P,1}^{L*}/\beta_{T,1}^{L*} - P \qquad (18)$$

and is included in Table 1. In this work, all partial molar volumes at infinite dilution were calculated *via* eq 17.

Results and Discussion

Experimental Ostwald coefficients $L_{2,1}(T,P)$ at T = 298.15 K and P = 101 325 Pa are given in Table 3, together with the Henry fugacities $H_{2,1}(T,P_{s,1})$ calculated from eq 3, and the mole fraction solubilities x_2 at P_2 = 101 325 Pa calculated from eq 8. Agreement with reliable literature values (*1, 3, 49, 50*) is in general quite satisfactory. We note, however, the surprisingly small body of literature data on gas/*n*-alkane systems. By way of example, such a comparsion is presented in Table 4 for the Ostwald coefficients of the three solutes argon, nitrogen, and methane dissolved in *n*-alkanes, *n*-C_lH_{2l+2}, $6 \le l \le 16$, at 298.15 K and 101 325 Pa (*51−64*). Our results corroborate the contention of the evaluators of the IUPAC Solubility Data Series (*50*), that the data of Makranczy *et al.* (*52*) are

Table 3. Ostwald Coefficients $L_{2,1}(T,P)$ of Nine Gases Dissolved in *n*-Alkanes n-C_lH_{2l+2}, $6 \leq l \leq 16$, at $T = 298.15$ K and $P = 101\,325$ Pa, Henry Fugacities $H_{2,1}(T,P_{s,1})$, and Mole Fraction Solubilities x_2 at a Partial Pressure $P_2 = 101\,325$ Pa at the Same Temperature

gas	$L_{2,1}(T,P)$	$10^{-6}H_{2,1}$-$(T,P_{s,1})$/Pa	10^4x_2	$L_{2,1}(T,P)$	$10^{-6}H_{2,1}$-$(T,P_{s,1})$/Pa	10^4x_2
		hexane			heptane	
He	0.0479	393.6	2.580	0.0412	408.0	2.482
Ne	0.0691	272.7	3.724	0.0590	284.9	3.555
Ar	0.4694	40.00	25.33	0.4178	40.15	25.18
Kr	1.313	14.27	70.83	1.192	14.06	71.75
N_2	0.2582	72.75	13.93	0.2264	74.06	13.66
O_2	0.3728	50.35	20.13	0.3378	49.64	20.37
CH_4	0.9442	19.84	50.98	0.8409	19.92	50.68
CF_4	0.4328	42.98	23.48	0.3502	47.51	21.20
SF_6	1.971	9.280	107.7	1.687	9.720	102.7
		octane			nonane	
He	0.0352	430.5	2.351	0.0321	429.6	2.356
Ne	0.0543	279.1	3.627	0.0467	295.3	3.427
Ar	0.3652	41.44	24.39	0.3415	40.34	25.05
Kr	1.056	14.33	70.40	0.9736	14.15	71.30
N_2	0.1953	77.48	13.05	0.1817	75.81	13.34
O_2	0.3068	49.31	20.50	0.2908	47.36	21.34
CH_4	0.7669	19.71	51.20	0.7104	19.38	52.08
CF_4	0.2943	51.03	19.73	0.2578	53.04	18.98
SF_6	1.450	10.22	97.68	1.266	10.66	93.63
		decane			undecane	
He	0.0299	423.1	2.392	0.0282	414.0	2.445
Ne	0.0433	292.2	3.464	0.0412	283.4	3.571
Ar	0.3100	40.77	24.79	0.2954	39.49	25.59
Kr	0.9078	13.93	72.45	0.8619	13.54	74.50
N_2	0.1598	79.08	12.78	0.1528	76.33	13.24
O_2	0.2723	46.40	21.78	0.2611	44.67	22.63
CH_4	0.6649	19.00	53.12	0.6292	18.53	54.46
CF_4	0.2331	53.82	18.71	0.2107	54.95	18.32
SF_6	1.098	11.28	88.49	0.9731	11.75	84.96
		dodecane			tridecane	
He	0.0269	403.0	2.512	0.0253	399.9	2.531
Ne	0.0373	290.7	3.482	0.0347	291.6	3.471
Ar	0.2794	38.77	26.07	0.2660	38.01	26.59
Kr	0.8137	13.32	75.73	0.7890	12.83	78.66
N_2	0.1399	77.41	13.06	0.1297	77.93	12.97
O_2	0.2459	44.04	22.95	0.2297	44.00	22.97
CH_4	0.5849	18.51	54.51	0.5649	17.89	56.40
CF_4	0.1914	56.17	17.92	0.1784	56.24	17.90
SF_6	0.8834	12.02	83.06	0.8086	12.26	81.45
		tetradecane			pentadecane	
He	0.0251	377.8	2.679	0.0248	359.8	2.813
Ne	0.0332	285.7	3.543	0.0334	267.2	3.788
Ar	0.2572	36.85	27.43	0.2511	35.52	28.45
Kr	0.7566	12.54	80.46	0.7353	12.15	83.07
N_2	0.1232	76.90	13.15	0.1173	76.00	13.30
O_2	0.2218	42.72	23.66	0.2134	41.78	24.19
CH_4	0.5447	17.40	58.01	0.5288	16.87	59.84
CF_4	0.1667	56.42	17.85	0.1533	56.99	17.67
SF_6	0.7644	12.15	82.13	0.7191	12.16	82.10
		hexadecane				
He	0.0240	351.1	2.883			
Ne	0.0319	264.2	3.832			
Ar	0.2380	35.39	28.56			
Kr	0.6990	12.07	83.62			
N_2	0.1118	75.29	13.43			
O_2	0.2060	40.87	24.73			
CH_4	0.5087	16.56	60.96			
CF_4	0.1515	55.16	18.25			
SF_6	0.6787	12.17	82.05			

unreliable: deviations of their results from ours range from −13% for Ar/n-$C_{16}H_{34}$ to +21% for CH_4/n-C_6H_{14}.

Figure 1 shows the Ostwald coefficients at 298.15 K of He, Ne, Ar, N_2, O_2, and CF_4 dissolved in n-C_lH_{2l+2} as a function of chain length *l*, and Figure 2 shows such a plot for Kr, CH_4, and SF_6. Supplementary results on $L_{2,1}$ of Xe dissolved in *n*-alkanes have been taken from the literature (*12*, *65*), so as to have the same set of gases as in our recent work on gas solubilities in normal alkan-1-ols (*7*) (they are indicated by filled symbols). Of particular note is the absence of any maxima, in contradistinction to what has been observed for some gas/*n*-alkan-1-ol series (*7*): for all the gas/*n*-alkane series investigated, $L_{2,1}$ decreases monotonously with increasing *l*. However, compared to the gas/*n*-alkan-1-ol series, the *l* dependence of the Ostwald coefficient of CF_4 in *n*-alkanes is qualitatively different: a crossover with the curve corresponding to O_2 is observed around $l = 7$, while no crossover for these two solutes is observed in the alkanol series. In addition, the crossover of the SF_6 curve and the Kr curve is shifted from $l = 4$ in the gas/*n*-alkan-1-ol series to a much larger chain length, *i.e.*, $l = 14$, in the gas/*n*-alkane series. The intriguing possibility that the solubility might be influenced in a regular manner by the number of carbons in the alkane chain being even or odd is not borne out by our results. That is to say, any even/odd variation, if existing at all, must be at a level below the measuring precision of the apparatus.

The quantity

$$RT \ln\left[\frac{H_{2,1}V_{s,1}^{L*}}{RT}\right] = W \tag{19}$$

is the reversible work *W* required to dissolve 1 mol of solute in an infinitely large amount of solvent at constant *T* and $P = P_{s,1}$, and is thus well suited to serve as a bona fide measure for the average intermolecular interaction between the solute and the solvent. It is closely related to the second solute−solvent virial coefficient (*67*). According to eq 3 (see also refs 5, 6, and 14−17), for the experimental conditions prevailing in this work to a good approximation

$$\ln\left[\frac{H_{2,1}V_{s,1}^{L*}}{RT}\right] \approx -(\ln L_{2,1}) \tag{20}$$

which justifies the alternative use of $-(\ln L_{2,1})$ in discussing thermodynamic solvation quantities (*68*−*70*). In Figure 3, $\ln[H_{2,1}V_{s,1}^{L*}/(RT)]$ is plotted against the chain length *l* for several selected solutes dissolved in *n*-alkanes ($6 \leq l \leq 16$) at 298.15 K. For the sake of comparison, values referring to Xe dissolved in *n*-alkanes are included (*12*). Essentially similar trends are observed throughout: $W/(RT)$ increases with increasing *l*, with the curvature of the curves suggesting, as intuitively expected, a limiting value as *l* becomes very large. A qualitatively appealing interpretation of this behavior has been given by Ben-Naim and Marcus (*70*) in terms of a simplified segment interaction model (*71*). It is based on the somewhat different interactions between any given solute and the CH_2 groups and CH_3 groups of the *n*-alkanes, as well as packing considerations. The attractive enthalpic interactions become less negative as *l* increases, because of the weaker interactions of the solute gas with the more and more abundant CH_2 groups than with the CH_3 groups. For large *l*, only the gas/CH_2 interactions contribute. Assuming, as a first approximation, the entropic contribution to be independent of *l*, the curvature as well as the limiting values for $l \to \infty$ of the curves $W/(RT)$ *vs* *l* may thus be rationalized. Measuring the temperature dependence of the gas solubilities in the *n*-alkanes will eventually enable us to separate quantitatively the enthalpic and entropic terms, and thereby assess their respective importance.

It is instructive to compare with the situation encountered in the gas/*n*-alkan-1-ol systems (*7*, *72*−*74*). Figure 4 gives the plot $\ln[H_{2,1}V_{s,1}^{L*}/(RT)]$ *vs* *l* for the same six gases He, Ar, Xe, N_2, CH_4, and SF_6 dissolved in *n*-alkan-

Table 4. Comparison with Selected Literature Values: Ostwald Coefficients $L_{2,1}(T,P)$ of Argon, Nitrogen, and Methane Dissolved in n-Alkanes n-C_lH_{2l+2}, $6 \leq l \leq 16$, at T = 298.15 K and P = 101 325 Pa

	$L_{2,1}(T,P)$					
	Ar		N_2		CH_4	
	this work	lit.	this work	lit.	this work	lit.
hexane	0.4694	0.472,[a] 0.477[b]	0.2582	0.263,[e] 0.256,[f] 0.262[b]	0.9442	0.949,[i] 0.935,[j] 1.146,[b] 0.948[k]
heptane	0.4178	0.415,[a] 0.418[b]	0.2264	0.224,[g] 0.229[b]	0.8409	0.840,[j] 0.956,[b] 0.842[k]
octane	0.3652	0.367,[a] 0.373,[b] 0.3502[c]	0.1953	0.196,[g] 0.199,[b] 0.1965[c]	0.7669	0.767,[j] 0.849,[b] 0.7548[c]
nonane	0.3415	0.338,[a] 0.338[b]	0.1817	0.175,[g] 0.178[b]	0.7104	0.762[b]
decane	0.3100	0.311,[a] 0.305,[b] 0.3055[c]	0.1598	0.156,[b] 0.1518[c]	0.6649	0.693,[b] 0.656,[c] 0.685[k]
undecane	0.2954	0.296[b]	0.1528	0.146[b]	0.6292	0.633[b]
dodecane	0.2794	0.275,[a] 0.263[b]	0.1399	0.132[b]	0.5849	0.590,[j] 0.586[b]
tridecane	0.2660	0.247[b]	0.1297	0.124[b]	0.5649	0.541[b]
tetradecane	0.2572	0.250,[a] 0.230[b]	0.1232	0.116[b]	0.5447	0.508[b]
pentadecane	0.2511	0.218[b]	0.1173	0.111[b]	0.5288	0.474[b]
hexadecane	0.2380	0.206,[b] 0.245[d]	0.1118	0.102,[b] 0.105[k]	0.5087	0.500,[j] 0.448,[b] 0.484,[l] 0.486[m]

[a] Reference 51. [b] Reference 52. [c] Reference 53. [d] Calculated, via eq 3, from the average Henry fugacity given in ref 54. [e] Reference 55. [f] Reference 56. [g] Reference 57. [h] Calculated, via eq 3, from the Henry fugacity obtained through extrapolation of data given in ref 58 ($H_{2,1}$ for $300 \leq T \leq 475$). [i] Reference 59. [j] Reference 60. [k] Calculated, via eq 8, from the mole fraction solubility obtained through extrapolation/interpolation of data given in ref 61. [l] Reference 62. This value is nearly the same as that reported in ref 63. [m] Reference 64.

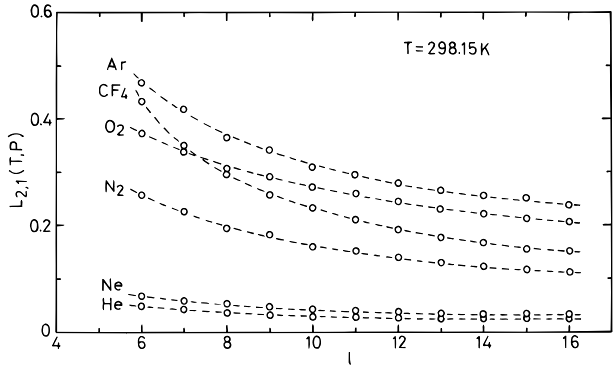

Figure 1. Ostwald coefficients $L_{2,1}(T,P)$ of He, Ne, Ar, N_2, O_2, and CF_4 dissolved in n-alkanes n-C_lH_{2l+2} as a function of chain length l for T = 298.15 K, P = 101 325 Pa, and $6 \leq l \leq 16$: (○) experimental results of this work. The broken curves are only meant to indicate the general trends.

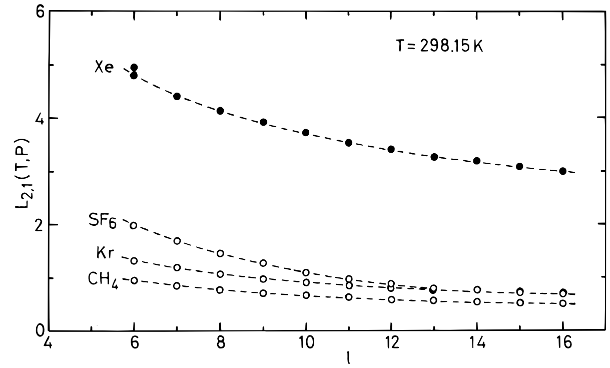

Figure 2. Ostwald coefficients $L_{2,1}(T,P)$ of Kr, Xe, CH_4, and SF_6 dissolved in n-alkanes n-C_lH_{2l+2} as a function of chain length l for T = 298.15 K, P = 101 325 Pa, and $6 \leq l \leq 16$: (○) experimental results of this work; (●) experimental results from the literature (Xe in n-C_lH_{2l+2}, $6 \leq l \leq 16$, ref 12; Xe in n-C_6H_{14} and n-$C_{12}H_{26}$, ref 65). The broken curves are only meant to indicate the general trends.

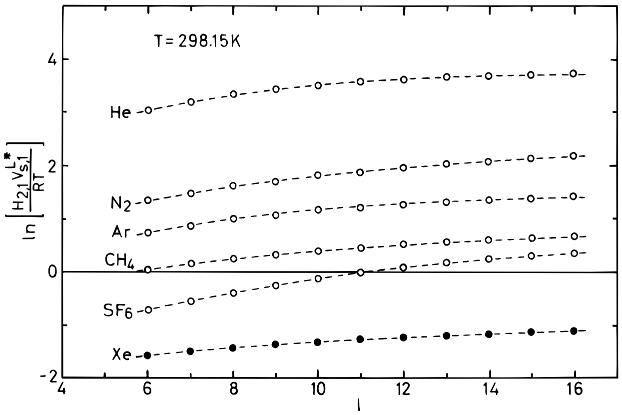

Figure 3. Correlation of $\ln[H_{2,1}V^{L*}_{s,1}/(RT)]$, *i.e.*, the reversible work W divided by RT (see eq 19) required to dissolve 1 mol of gas in an infinitely large amount of solvent (at constant T and $P = P_{s,1}$), for He, Ar, Xe, N_2, CH_4, and SF_6 dissolved in n-alkanes n-C_lH_{2l+2} with the solvent chain length l at T = 298.15 K, $6 \leq l \leq 16$: (○) from experimental results of this work; (●) from experimental results reported in ref 12. The broken curves are only meant to indicate the general trends.

1-ols, n-$C_lH_{2l+1}OH$, $1 \leq l \leq 11$, at 298.15 K. Most of the experimental data are from Bo *et al.* (*7*), with some additional results taken from ref 72 (Ar/CH_3OH) and ref 74 (Xe/CH_3OH, Xe/C_2H_5OH, Xe/n-$C_8H_{17}OH$, Xe/n-$C_9H_{19}OH$, Xe/n-$C_{10}H_{21}OH$, Xe/n-$C_{11}H_{23}OH$). For the solute He and, perhaps, for N_2 the quantity $W/(RT)$ increases with increasing l in a way similar to that observed with n-alkanes. However, already in the Ar curve an inflection point appears, and for the series with Xe, CH_4, and SF_6 *minima* are observed at small values of l. For higher values of l, qualitatively the curves behave in the same way as in the n-alkane series, presumably approaching a limiting value for large l. As compared to their counterparts in the gas/n-alkane systems, all curves are shifted to more *positive* values of $W/(RT)$, which simply reflects the substantially smaller solubility of a gas in an n-alkan-1-ol than in an n-alkane with the same chain length l. Finally, by comparing Figure 3 with Figure 4, we note that the increment

$$\Delta W = W(\text{gas}/n\text{-}C_lH_{2l+1}OH) - W(\text{gas}/n\text{-}C_lH_{2l+2}) \qquad (21)$$

diminishes with increasing l. In fact, this is expected, since for the gas atom or molecule—due to the short-range dispersion forces—only the interactions with the nearest neighbors are significant. Any group further away, such as an OH group on a long-chain alcohol, exerts less and less influence with increasing l. The quantity $\Delta W/(RT)$ is shown in Figure 5 for T = 298.15 K and $6 \leq l \leq 11$. Since $\Delta W/(RT)$ is a *difference* of measured quantities, the experimental scatter is magnified; hence, the broken curves are meant to represent only the general trends.

Scaled particle theory (SPT) has been used successfully by many authors for the prediction and correlation of Henry fugacities, despite the number of approximations involved

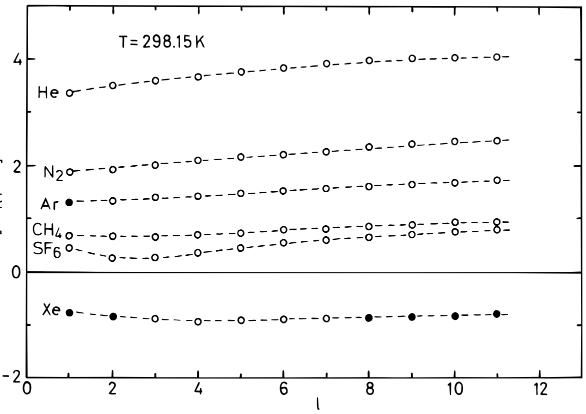

Figure 4. Correlation of $\ln[H_{2,1}V_{s,1}^{L*}/(RT)]$, *i.e.*, the reversible work W divided by RT (see eq 19) required to dissolve 1 mol of gas in an infinitely large amount of solvent (at constant T and $P = P_{s,1}$), for He, Ar, Xe, N_2, CH_4, and SF_6 dissolved in normal alkan-1-ols n-$C_lH_{2l+1}OH$ with the solvent chain length l at $T = 298.15$ K, $1 \le l \le 11$: (○) from experimental results reported by Bo *et al.*;[7] (●) from experimental results reported in refs 72 and 74. The broken curves are only meant to indicate the general trends.

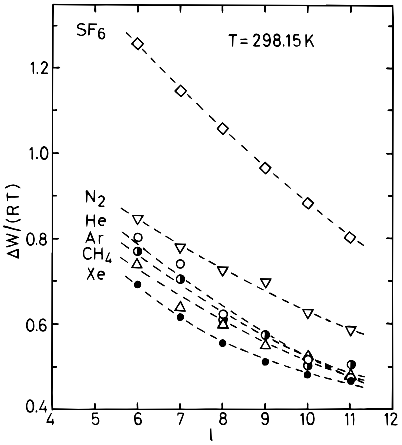

Figure 5. Dependence of the increment $\Delta W/(RT)$, see eq 21, for He, Ar, Xe, N_2, CH_4, and SF_6 dissolved in corresponding solvent pairs $\{n\text{-}C_lH_{2l+1}OH, n\text{-}C_lH_{2l+2}\}$ on chain length l at $T = 298.15$ K, $6 \le l \le 11$. The broken curves are only meant to indicate the general trends.

(*4–6, 8, 14, 15, 17, 22–24, 66, 67, 75–87*). For the suggested two-step dissolution process

$$\ln\left[\frac{H_{2,1}V_{s,1}^{L*}}{RT}\right] = \frac{\mu_{CAV}}{RT} + \frac{\mu_{INT}}{RT} \qquad (22)$$

where μ_{CAV} denotes the partial molar Gibbs energy of cavity formation and μ_{INT} is the partial molar Gibbs energy of interaction. SPT provides a reasonable approximation for μ_{CAV} in that it yields an asymptotic expansion in the radius of the (spherical) cavity to be created in a solvent of compactness $N_A\sigma_1^3\pi/(6V_{s,1}^{L*})$, where N_A is Avogadro's constant and σ_1 is the effective hard sphere diameter of the solvent (*83, 85, 88*). The interactional contribution may, as usual, be approximated by an effective Lennard-Jones term. By way of example, Table 5 shows a comparison between experimental and calculated Henry fugacities of the nine gases plus xenon dissolved in n-heptane at 298.15 K. The necessary effective molecular parameters were taken from Wilhelm and Battino (*83*). For the other n-alkanes, results are of similar quality. Considering the simplicity of the prediction method, the agreement is quite satisfactory. Our comparative studies thus confirm the earlier view of Wilcock *et al.* (*53*) that on a molecular level the decisive factor causing a smaller solubility of a given gas in an n-alkan-1-ol, as compared to its solubility in an n-alkane with the same chain length, is the compactness of the n-alkan-1-ol being larger than that of the n-alkane. Thus, μ_{CAV} is considerably more positive and is only partly compensated by a somewhat more negative μ_{INT}.

Table 5. Comparison of Experimental Values of Henry Fugacities $H_{2,1}(T,P_{s,1})$ for 10 Gases Dissolved in Heptane at T = 298.15 K with Results from the Scaled Particle Theory (SPT)

	ln[H2,1(T,Ps,1)/Pa]			ln[H2,1(T,Ps,1)/Pa]	
gas	exptl	SPT	gas	exptl	SPT
He	19.827	19.498	N_2	18.120	17.949
Ne	19.468	18.552	O_2	17.720	17.286
Ar	17.508	17.172	CH_4	16.807	16.694
Kr	16.459	16.632	CF_4	17.676	17.742
Xe	15.140[a]	15.560	SF_6	16.090	16.427

[a] Calculated from data reported in ref 12.

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