

Solubility of gases in water: Correlation between solubility and the number of water molecules in the first solvation shell

Pirketta Scharlin,^a Rubin Battino,^b Estanislao Silla,^c Iñaki Tuñón^c and Juan Luis Pascual-Ahuir^c

^a Department of Chemistry, University of Turku, FIN-20014 Turku, Finland

^b Department of Chemistry, Wright State University, Dayton, Ohio 45435, USA

^c Departamento de Química Física, Universidad de València, 46100 Burjassot, València, Spain

Abstract: Using a new version of a program called GEPOL, a consistent set of values for areas of three different kinds of surfaces for 53 gaseous solutes was computed by Silla *et al.* These surface areas, together with the volumes of space enclosed by the surfaces, are reported in the present paper. The three surfaces are the van der Waals Surface (WS), the Solvent Accessible Surface (SAS) and the Solvent-Excluding Surface (SES). Values for the number of water molecules (N) in the first solvation shell are estimated by a simple surface area approach from the SAS data. Values of N , as well as literature data on solubilities of gases in water, are used to study various semi-empirical correlations between thermodynamic changes on solution and the number of water molecules in the first solvation shell.

Dilute aqueous solutions of gases have been of continuous experimental and theoretical interest. Reliable solubility data exist for a large variety of gases in water.¹⁻¹⁸ Experimental data have been important for validating the results of theoretical calculations, computer simulations, and various practical applications. There is a continuing search for better equations and better correlations. Studies of the thermodynamics of solution of simple model compounds, such as the rare gases and small alkanes have provided the basic information for various additivity rules to be used in the prediction of changes in the thermodynamic quantities of other, more complex systems. These studies can also be expected to yield useful information on the role that water-solute interactions play in solutions of biological macromolecules.

In water-solute interactions the water molecules in the first layer around the solute differ from the bulk water.^{19,20} Thus, the number of water molecules (N) in the first solvation shell is considered an important quantity in theories of aqueous solutions. However, only a few values of N have been reported in the literature for gaseous solutes, and the gases considered have mainly been rare gases or hydrocarbon gases. Values of N have been estimated from Monte Carlo simulations of solutes in water¹⁹ or from the solute cavity surface areas²¹⁻²⁴. With the development of computers in the last two decades methods for computing molecular surfaces have steadily improved. For the present study, a consistent set of values for areas of three different kinds of surfaces for 53 gaseous solutes was computed by Silla *et al.*, using a new version of a program called GEPOL.²⁵⁻²⁷ The three surfaces are van der Waals Surface (WS), Solvent Accessible Surface (SAS), and Solvent-Excluding Surface (SES). The volumes of space enclosed by WS, SAS and SES were also computed and are reported in this work. Values of N estimated from the SAS data, along with literature values on solubilities, are used to study various semi-empirical correlations between thermodynamic changes on solution and the number of water molecules in the first solvation shell.

*Lecture presented at the 8th International Symposium on Solubility Phenomena, Niigata, Japan, 5–8 August 1998. Other presentations are published in this issue, pp. 1867–1932.

MOLECULAR SURFACES

There are three kinds of molecular surfaces that make use of the van der Waals radius. First, the proper van der Waals surface (WS in Fig. 1) which is the external surface resulting from a set of spheres centered on the atoms or a group of atoms forming the molecule. Second, the surface accessible to the solvent (SAS in Fig. 1), defined by Richards and Lee²⁸ as the surface generated by the center of the solvent, considered as a rigid sphere, when it rolls around the van der Waals surface. Third, the solvent-excluding surface (SES in Fig. 1), which was named by Richards²⁹ as the Molecular Surface, was defined by him as composed of two parts, the contact surface and the reentrant surface. The contact surface is the part of the van der Waals surface of each atom which is accessible to a probe sphere of a given radius. The reentrant surface is defined as the inward-facing part of the probe sphere when this is simultaneously in contact with more than one atom. Silla *et al.*²⁷ suggested the name of Solvent-Excluding Surface which is more specific than Molecular Surface. They define SES as the surface envelope of the volume excluded to the solvent, considered as a rigid sphere (probe sphere), when it rolls around the van der Waals surface.²⁷

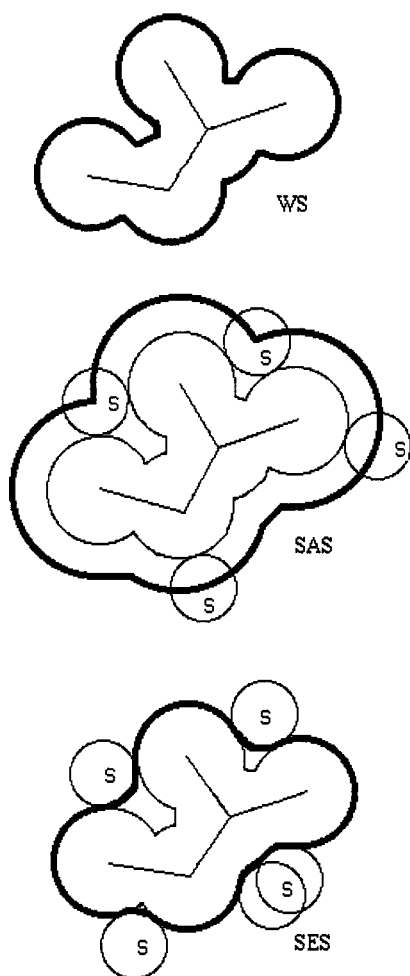


Fig. 1. Three definitions of molecular surface: van der Waals surface (WS), solvent accessible surface (SAS) and solvent-excluding surface (SES).

Many algorithms have been developed for the computation of the area and volume of the WS and SAS but, to our knowledge, only two of them are able to compute the SES.^{30,31} GEPOL,³¹ developed in Silla's laboratory, computes the three types of surface. GEPOL has shown its capability in computing with a high degree of accuracy and precision the WS and SAS for all kinds of systems.^{25-27,32}

The computed values for A_{WS} (the van der Waals Surface area), A_{SAS} (the Solvent Accessible Surface area) and A_{SES} (the Solvent-Excluding Surface area) are listed in Table 1. For the calculations the van der Waals radii were obtained from Bondi's³³ article. Standard bond lengths and bond angles³⁴ were used. Some geometrical values were taken from Ref. 35. The value of $r_w = 0.14$ nm was used for the van der Waals radius of water.³⁶ Values for the three parameters used by GEPOL²⁷ were $NDIV = 5$, $OFAC = 0.8$ and $RMIN = 0.2$.

In Table 1 the values for the number of water molecules (N) are also reported. The value of N was estimated by dividing the area of the Solvent Accessible Surface by the effective area occupied by a water molecule:²³

$$N = A_{SAS} / (2r_w)^2 \quad (1)$$

There are only a few values of N available from Monte Carlo simulations for comparison. A value of 16.84 reported for argon³⁷ is in good agreement with $N = 17.2$ obtained by the simple surface method. Jorgensen¹⁹ reports the following values of N for alkanes: methane 20.3, ethane 23.0, propane 27.3, butane 29.9, isobutane 30.3, pentane 34.0 and neopentane 32.0. These values also agree well with the values given by the surface area approach (Table 1).

TABLE 1. Van der Waals Surface Areas (A_{WS}), Solvent Accessible Surface Areas (A_{SAS}), Solvent-Excluding Surface Areas (A_{SES}) for Gaseous Solutes, and the Number of Water Molecules (N) in the First Solvation Shell

Gas		van der Waals	Solvent Accessible	Solvent-Excluding	N	
		$A_{WS}/(10^{-20} \text{ m}^2)$	$A_{SAS}/(10^{-20} \text{ m}^2)$	$A_{SES}/(10^{-20} \text{ m}^2)$		
1	hydrogen	H ₂	23.7	97.0	23.7	12.4
2	deuterium	D ₂	23.7	97.0	23.7	12.4
3	helium	He	24.6	98.5	24.6	12.6
4	neon	Ne	29.8	108.6	29.8	13.9
5	oxygen	O ₂	39.7	127.7	39.7	16.3
6	nitric oxide	NO	41.5	130.9	41.5	16.7
7	nitrogen	N ₂	43.2	133.6	43.2	17.0
8	carbon monoxide	CO	44.0	135.1	44.0	17.2
9	argon	Ar	44.4	135.2	44.4	17.2
10	methane	CH ₄	48.0	143.8	48.0	18.3
11	krypton	Kr	51.3	147.0	51.3	18.7
12	ozone	O ₃	52.1	150.1	52.1	19.1
13	carbon dioxide	CO ₂	52.4	150.6	52.4	19.2
14	nitrous oxide	N ₂ O	53.1	152.9	53.1	19.5
15	fluoromethane	CH ₃ F	54.4	155.4	54.4	19.8
16	acetylene	HC≡CH	55.4	156.5	55.4	20.0
17	xenon	Xe	58.6	159.3	58.6	20.3
18	ethene	H ₂ C=CH ₂	62.0	168.1	62.0	21.4
19	chloromethane	CH ₃ Cl	65.4	173.2	65.0	22.1
20	trifluoromethane	CHF ₃	67.2	175.9	67.2	22.4
21	cyclopropane (trimethylene)	C ₃ H ₆	68.9	177.4	68.4	22.6
22	bromomethane	CH ₃ Br	70.2	181.1	69.7	23.1
23	ethane	C ₂ H ₆	70.2	182.1	69.6	23.2
24	chlorofluoromethane	CH ₂ ClF	71.6	183.3	71.2	23.4
25	radon	Rn	74.8	185.3	74.8	23.6
26	tetrafluoromethane	CF ₄	73.5	185.5	73.5	23.7
27	chlorodifluoromethane	CHClF ₂	77.8	192.7	77.4	24.6
28	1,1-difluoroethane	CHF ₂ CH ₃	82.6	200.2	81.8	25.5
29	chlorotrifluoromethane	CClF ₃	84.0	201.6	83.5	25.7
30	propene	H ₂ C=CHCH ₃	83.7	202.7	82.5	25.8
31	tetrafluoroethene	F ₂ C=CF ₂	86.4	206.3	84.5	26.3
32	dichlorodifluoromethane	CHCl ₂ F	88.2	208.3	87.0	26.6
33	propane	C ₃ H ₈	91.9	213.2	89.2	27.2
34	sulfurhexafluoride	SF ₆	96.3	215.6	91.9	27.5
35	1,1,1,2-tetrafluoroethane	CH ₂ FCF ₃	94.9	216.5	92.7	27.6
36	dichlorodifluoromethane	CCl ₂ F ₂	94.3	216.6	92.9	27.6
37	1-chloro-1,1-difluoroethane	CH ₃ CClF ₂	99.0	222.9	97.2	28.4
38	1,1,1,2,2-pentafluoroethane	CHF ₂ CF ₃	101.0	224.0	97.6	28.6
39	1,3-butadiene	H ₂ C=CHCH=CH ₂	97.9	224.6	95.9	28.6
40	trichlorofluoromethane	CCl ₃ F	104.4	230.9	101.7	29.5
41	hexafluoroethane	C ₂ F ₆	107.1	231.1	102.4	29.5
42	1,1-dichloro-1-fluoroethane	CH ₃ CCl ₂ F	109.1	236.3	106.0	30.1
43	1-chloro-1,2,2,2-tetrafluoroethane	CHClFCF ₃	110.9	237.6	106.5	30.3
44	2-methylpropane (isobutane)	(CH ₃) ₂ CHCH ₃	112.8	238.2	106.5	30.4
45	1-chloro-1,1,2,2,2-pentafluoroethane	CClF ₂ CF ₃	116.8	244.0	111.1	31.1
46	n-butane	C ₄ H ₁₀	113.5	244.4	108.7	31.2
47	hexafluoropropene	F ₂ C=CF ₂ CF ₃	117.4	250.4	114.2	31.9
48	1,1-dichloro-2,2,2-trifluoroethane	CHCl ₂ CF ₃	120.5	250.5	114.9	32.0
49	1,2-dichloro-1,1,2,2-tetrafluoroethane	CClF ₂ CClF ₂	126.5	256.9	119.5	32.8
50	octafluorocyclobutane	C ₄ F ₈	124.7	258.2	120.9	32.9
51	2,2-dimethylpropane (neopentane)	C(CH ₃) ₄	133.2	258.7	121.0	33.0
52	1,1,1-trichloro-1,2,2-trifluoroethane	CCl ₃ FCF ₂	135.5	268.6	127.6	34.3
53	n-pentane	C ₅ H ₁₂	135.1	275.4	128.3	35.1

In Table 2 volumes of space enclosed by the WS, SAS and SES are given..

TABLE 2. Volumes of Space Enclosed by the van der Waals Surface (V_{WS}), the Solvent Accessible Surface (V_{SAS}), and the Solvent-Excluding Surface (V_{SES}) for Gaseous Solutes

	Gas		van der Waals $V_{WS}/(10^{-30} \text{ m}^3)$	Solvent Accessible $V_{SAS}/(10^{-30} \text{ m}^3)$	Solvent-Excluding $V_{SES}/(10^{-30} \text{ m}^3)$
1	hydrogen	H ₂	10.5	89.3	10.5
2	deuterium	D ₂	10.5	89.3	10.5
3	helium	He	11.5	92.0	11.5
4	neon	Ne	15.3	106.4	15.3
5	oxygen	O ₂	22.3	133.8	22.3
6	nitric oxide	NO	24.1	139.2	24.1
7	nitrogen	N ₂	25.7	143.8	25.7
8	carbon monoxide	CO	26.4	146.1	26.4
9	argon	Ar	27.8	147.8	27.8
10	methane	CH ₄	28.4	157.3	28.4
11	krypton	Kr	34.5	167.6	34.5
12	ozone	O ₃	31.2	167.3	31.2
13	carbon dioxide	CO ₂	32.8	169.3	32.8
14	nitrous oxide	N ₂ O	33.0	171.9	33.0
15	fluoromethane	CH ₃ F	33.3	175.1	33.3
16	acetylene	HC≡CH	35.4	178.4	35.4
17	xenon	Xe	42.2	180.0	42.2
18	ethene	H ₂ C=CH ₂	39.8	195.9	39.8
19	chloromethane	CH ₃ Cl	42.6	204.5	42.8
20	trifluoromethane	CHF ₃	43.1	208.3	43.1
21	cyclopropane (trimethylene)	C ₃ H ₆	47.1	214.4	47.3
22	bromomethane	CH ₃ Br	47.0	217.9	47.3
23	ethane	C ₂ H ₆	45.4	217.5	46.0
24	chlorofluoromethane	CH ₂ ClF	47.5	220.9	47.7
25	radon	Rn	60.9	237.2	60.9
26	tetrafluoromethane	CF ₄	48.0	224.4	48.0
27	chlorodifluoromethane	CHClF ₂	52.4	236.9	52.5
28	1,1-difluoroethane	CHF ₂ CH ₃	55.2	248.8	55.6
29	chlorotrifluoromethane	CClF ₃	57.2	252.3	57.4
30	propene	H ₂ C=CHCH ₃	56.8	252.3	57.2
31	tetrafluoroethene	F ₂ C=CF ₂	58.9	258.8	60.0
32	dichlorofluoromethane	CHCl ₂ F	61.6	264.3	62.4
33	propane	C ₃ H ₈	62.3	271.5	64.2
34	sulfurhexafluoride	SF ₆	68.2	281.0	70.6
35	1,1,1,2-tetrafluoroethane	CH ₂ FCF ₃	64.9	278.3	66.2
36	dichlorodifluoromethane	CCl ₂ F ₂	66.4	279.1	67.2
37	1-chloro-1,1-difluoroethane	CH ₃ CClF ₂	69.2	290.2	69.9
38	1,1,1,2,2-pentafluoroethane	CHF ₂ CF ₃	69.8	292.5	72.0
39	1,3-butadiene	H ₂ C=CHCH=CH ₂	68.2	289.2	69.0
40	trichlorofluoromethane	CCl ₃ F	75.6	305.4	77.3
41	hexafluoroethane	C ₂ F ₆	74.7	306.1	77.7
42	1,1-dichloro-1-fluoroethane	CH ₃ CCl ₂ F	78.4	315.6	79.9
43	1-chloro-1,2,2,2-tetrafluoroethane	CHClFCF ₃	79.0	317.9	81.4
44	2-methylpropane (isobutane)	(CH ₃) ₂ CHCH ₃	79.1	319.8	82.9
45	1-chloro-1,1,2,2,2-pentafluoroethane	CClF ₂ CF ₃	83.9	330.9	87.1
46	n-butane	C ₄ H ₁₀	79.1	325.7	82.3
47	hexafluoropropene	F ₂ C=CFCF ₃	85.1	338.0	87.2
48	1,1-dichloro-2,2,2-trifluoroethane	CHCl ₂ CF ₃	88.1	342.6	91.3
49	1,2-dichloro-1,1,2,2-tetrafluoroethane	CClF ₂ CClF ₂	93.0	355.6	96.7
50	octafluorocyclobutane	C ₄ F ₈	95.8	359.3	98.3
51	2,2-dimethylpropane (neopentane)	C(CH ₃) ₄	95.8	363.3	102.1
52	1,1,1-trichloro-1,2,2-trifluoroethane	CCl ₃ FCClF ₂	102.1	379.0	105.9
53	n-pentane	C ₅ H ₁₂	96.1	379.5	100.6

SOLUBILITY DATA

The solubility data for correlational studies were collected from the literature and are presented in Table 3.

TABLE 3. Mole Fraction Solubility of Gases in Water at 298.15 K and 101.325 kPa Partial Pressure of Gas.

No.	Gas	$x_2 / 10^{-5}$	Ref.	No.	Gas	$x_2 / 10^{-5}$	Ref.
1	H ₂	1.411	5	28	CHF ₂ CH ₃	79.1	15
2	D ₂	1.461	5	29	CClF ₃	1.665	16
3	He	0.70797	13	30	H ₂ C=CHCH ₃	13.36	3
4	Ne	0.82226	13	31	F ₂ C=CF ₂	2.853	3
5	O ₂	2.3011	14	32	CHCl ₂ F	168	2
6	NO	3.477	3	33	C ₃ H ₈	2.732	11
7	N ₂	1.1774	14	34	SF ₆	0.4394	3
8	CO	1.7744	14	35	CH ₂ FCF ₃	26.5	12
9	Ar	2.5319	13	36	CCl ₂ F ₂	5.425	16
10	CH ₄	2.5523	8	37	CH ₃ CClF ₂	25.1	12
11	Kr	4.5463	13	38	CHF ₂ CF ₃	14.56	12
12	O ₃	9.1	6	39	H ₂ C=CHCH=CH ₂	26.01	3
13	CO ₂	61.48	17	40	CCl ₃ F	20.08	9
14	N ₂ O	43.67	7	41	C ₂ F ₆	0.103	4
15	CH ₃ F	106.2	3	42	CH ₃ CCl ₂ F	10.94	12
16	HC≡CH	74.79	3	43	CHClFCF ₃	18.48	12
17	Xe	7.9485	13	44	(CH ₃) ₂ CHCH ₃	1.659	11
18	H ₂ C=CH ₂	8.968	18	45	CClF ₂ CF ₃	0.56	1
19	CH ₃ Cl	187.8	3	46	C ₄ H ₁₀	2.244	11
20	CHF ₃	25	1	47	F ₂ C=CF ₂	0.5298	3
21	C ₃ H ₆	25.32	18	48	CHCl ₂ CF ₃	47.12	12
22	CH ₃ Br	292.8	3	49	CClF ₂ CClF ₂	1.37	2
23	C ₂ H ₆	3.4043	8	50	C ₄ F ₈	0.2373	16
24	CH ₂ ClF	271.2	3	51	C(CH ₃) ₄	1.077	3
25	Rn	16.75	3	52	CCl ₂ FCClF ₂	1.63	2
26	CF ₄	0.3802	15	53	C ₅ H ₁₂	1.43 ^a	10
27	CHClF ₂	60.42	12				

^a Estimated from the ΔG° value given in Ref. 10.

Data for the thermodynamic changes on solution are given in Figures 2-5 as plots against the number of water molecules, N , in the first solvation shell. The data points in Figures 2-5 have been numbered according to the numbering of gases in Tables 1-3.

Until the beginning of eighties, virtually all of the values for ΔG° , ΔH° , ΔS° , and ΔC_p° on solution have been derived from the results of solubility measurements as a function of temperature. Such results can normally be expected to lead to good values for the Gibbs energy changes.³⁸ The ΔG° values plotted in Figure 2 have been calculated from the mole fraction solubilities given in Table 3 (except the ΔG° for C₅H₁₂ which has been taken from Ref. 10). To derive reliable values for the changes of enthalpy and entropy on solution, however, very accurate solubilities over a wide temperature range are needed.³⁸ Precise calorimetric data have become available only quite recently with the development of methods^{23,38-40} which could be used to determine ΔH° for the solubility of gases in water. The number of calorimetric values for ΔH° is still relatively small as compared with the number of ΔH° values obtained by the "traditional" van't Hoff method. The van't Hoff values and the calorimetric values for ΔH° are given as separate plots in Figures 3a and 3b, respectively. For the plot $T\Delta S^\circ$ vs. N (Fig. 4) the values of $T\Delta S^\circ$ have been calculated from the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, using calorimetric values for ΔH° whenever possible. Concerning the heat capacity change on solution, only exceptionally careful solubility studies can lead to good values for ΔC_p° .³⁸ Therefore, in the present work only calorimetric data^{23,24,39-41} have been used for the correlational study on the changes in heat capacity for gases in water (Fig. 5.).

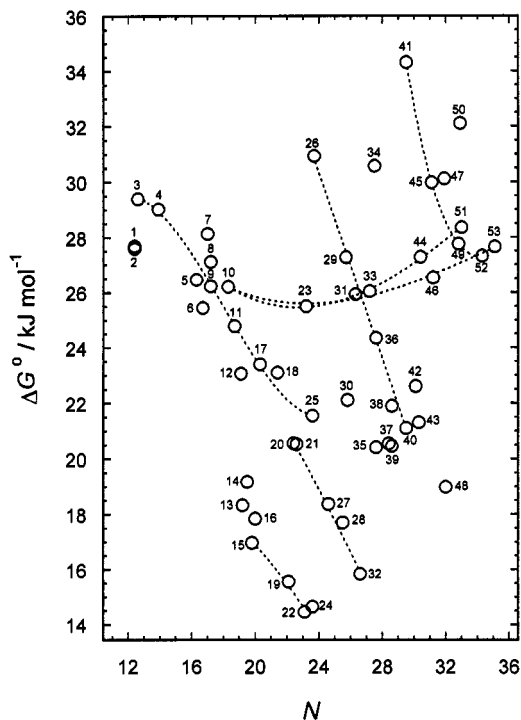


Fig. 2. Gibbs energy change on solution, ΔG° , against the number of water molecules, N , in the first solvation shell. Values of ΔG° are at 298.15 K and 101.325 kPa partial pressure of gas. The numbers next to each point correspond to the numbers in Table 1.

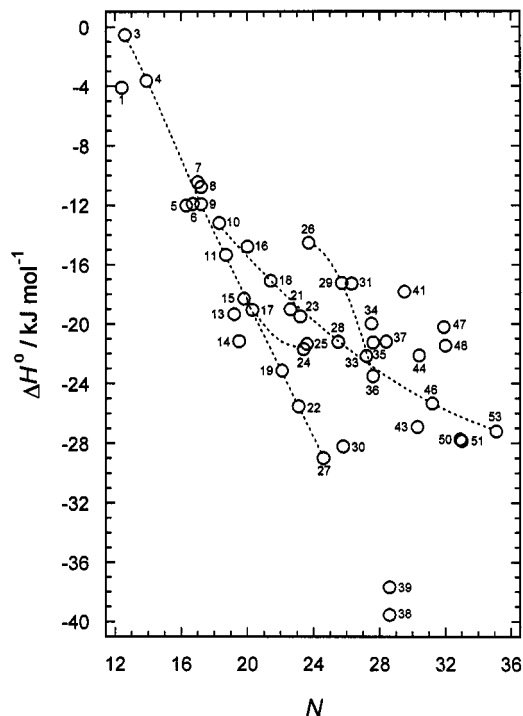


Fig. 3a. Enthalpy change on solution, ΔH° , against the number of water molecules, N , in the first solvation shell. Values of ΔH° at 298.15 K and 101.325 kPa partial pressure of gas have been derived from the solubility measurements as a function of temperature. (Refs 3-5, 7, 8 and 10-18.)

SEMI-EMPIRICAL CORRELATIONS

Despite the continuous search for better equations and better correlations, a really successful general and simple correlation for the solubility of gases in water is still lacking. Studies have mainly been done with the rare gases²³ or simple hydrocarbon gases.^{10,40,41} Some freons²⁴ have also been included. Besides the correlation with the number of water molecules in the first solvation shell^{23,24,41}, the relation between the thermodynamic changes on solution and the number of carbon atoms¹⁰ or hydrogen atoms⁴⁰ in the solute have been studied. In their review article on the low-pressure solubility of gases in water Wilhelm *et al.*³ have studied several semi-empirical correlations for a great variety of gases. The best correlation for the widest range of solute characteristics was for the entropy change on solution *vs.* a parameter related to the surface area of the solute molecules. In the present work our initial hope was that we would find a semi-empirical correlation connecting the number of water molecules in the first solvation shell with

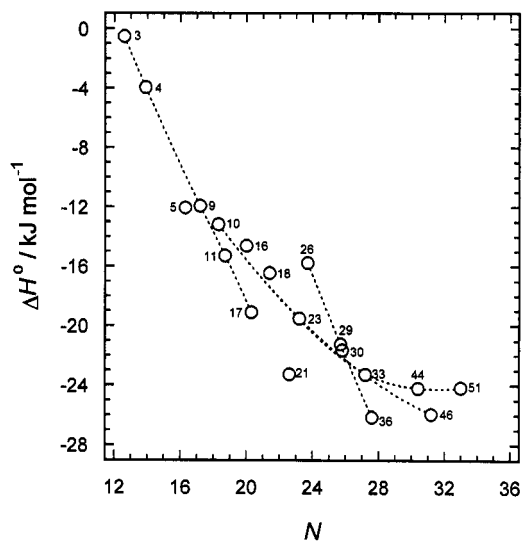


Fig. 3b. Enthalpy change on solution, ΔH° , against the number of water molecules, N , in the first solvation shell. These values of ΔH° are from calorimetric measurements at 298.15 K and 101.325 kPa partial pressure of gas. (Refs 23, 24 and 39-41.)

the equilibrium solubility. A glance at Fig. 2, where ΔG° has been plotted against N , shows that such a simple correlation is not possible. However, a number of better correlations appear if the gases are grouped by class. The dotted lines in Figs 2-4 connect the data points in each group. In Fig. 5 the dotted line presents the best straight line obtained from the fit of ΔC_p° values of all 17 gases vs. N . Regression equations for different groups of gases are given in Tables 4 and 5.

The solubility data for He (3), Ne (4), Ar (9), Kr (11), and Xe (17) are from high precision solubility measurements¹³ whereas the data for Rn (25)³, which originate from Refs 42 and 43, are probably of much poorer precision. If Rn is omitted the correlations become better (Table 4). The regression equations ΔH° vs. N obtained by using either the van't Hoff values or the calorimetric values, which are independent of solubility data, are almost identical for the group He to Xe. This can be considered as an indication of the reliability of these values. As there is a doubt about the precision of the solubility data for Rn, the thermodynamic changes on solution of Rn in water could be estimated from the regression equations for the group He to Xe (Tables 4 and 5). Following estimates are obtained: $\Delta G^\circ = 21 \text{ kJ mol}^{-1}$, $\Delta H^\circ = -27 \text{ kJ mol}^{-1}$, $\Delta S^\circ = -161 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta C_p^\circ = 298 \text{ J K}^{-1} \text{ mol}^{-1}$. The smoothed (van't Hoff) values from Ref. 3 are $\Delta G^\circ = 21.6 \text{ kJ mol}^{-1}$, $\Delta H^\circ = -21 \text{ kJ mol}^{-1}$, $\Delta S^\circ = -144 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta C_p^\circ = 292 \text{ J K}^{-1} \text{ mol}^{-1}$.

Seven alkanes were studied: CH_4 (10), C_2H_6 (23), C_3H_8 (33), $(\text{CH}_3)_2\text{CHCH}_3$ (44), C_4H_{10} (46), $\text{C}(\text{CH}_3)_4$ (51) and C_5H_{12} (53). Besides being part of the n-alkanes group, CH_4 , C_2H_6 and C_3H_8 can be considered to form a homologous series also with the two branched alkanes $(\text{CH}_3)_2\text{CHCH}_3$ and $\text{C}(\text{CH}_3)_4$. Regression equations have been derived for both groups (Table 4). Using the quadratic equations for the group methane to n-butane, following values for n-pentane can be estimated: $\Delta G^\circ = 28 \text{ kJ mol}^{-1}$, $\Delta H^\circ = -27 \text{ kJ mol}^{-1}$, $\Delta S^\circ = -185 \text{ J K}^{-1} \text{ mol}^{-1}$. For ΔC_p° a value of $438 \text{ J K}^{-1} \text{ mol}^{-1}$ is obtained using the equation from Table 5. Values given in the literature are $\Delta G^\circ/\text{kJ mol}^{-1} = 27.3$ (Ref. 10) and 27.8 (Ref. 40), $\Delta H^\circ = -27.2 \text{ kJ mol}^{-1}$ (Ref. 10) and $\Delta S^\circ = -184.1 \text{ J K}^{-1} \text{ mol}^{-1}$ (Ref. 10). For ΔC_p° no literature value was found.

Solubility data for only one alkyne, $\text{HC}\equiv\text{CH}$ (16), and three alkenes, $\text{H}_2\text{C}=\text{CH}_2$ (18), $\text{H}_2\text{C}=\text{CHCH}_3$ (30), and $\text{H}_2\text{C}=\text{CHCH}=\text{CH}_2$ (39) were available. The alkenes and alkynes are more soluble in water than the parent alkane. From Fig. 2 it can be seen that

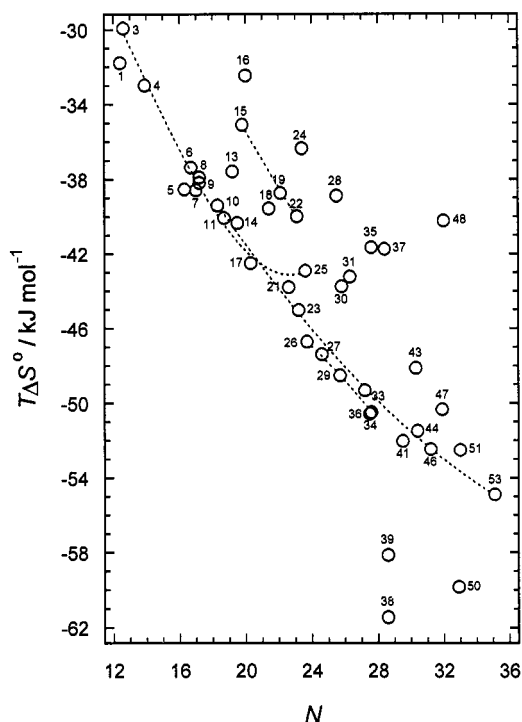


Fig. 4. $T\Delta S^\circ$ against the number of water molecules, N , in the first solvation shell. Values of $T\Delta S^\circ$ are at 298.15 K and 101.325 kPa partial pressure of gas.

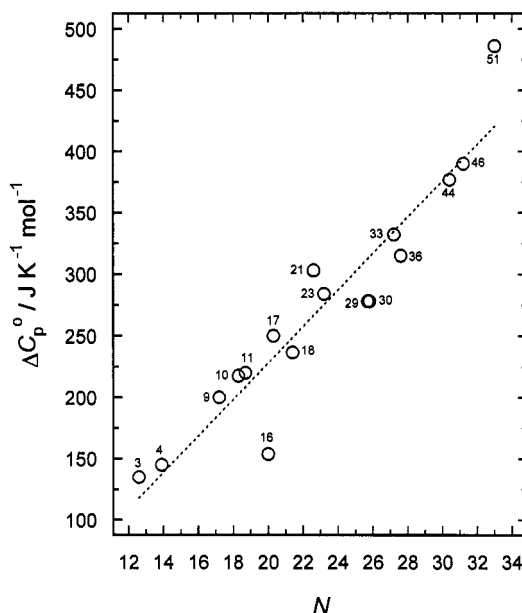


Fig. 5. ΔC_p° against the number of water molecules, N , in the first solvation shell. Values of ΔC_p° at 298.15 K and 101.325 kPa partial pressure of gas are calorimetric values from Refs 23, 24 and 39-41.

TABLE 4. Regression Equations for Thermodynamic Changes on Solution of Gases in H₂O at 298.15 K and 101.325 kPa Partial Pressure of Gas.

Solute range ^a	Regression equation ^b	<i>r</i> ^c	σ ^d	<i>n</i> ^e
<i>Rare gases</i>				
helium to radon (3, 4, 9, 11, 17, and 25)	$\Delta G^\circ = (-0.76 \pm 0.04)N + 39$	0.9951	0.35	6
	$\Delta H^\circ = (-2.0 \pm 0.3)N + 24$ (van't Hoff)	0.9795	1.89	6
	$T\Delta S^\circ = (-1.24 \pm 0.19)N - 16$	0.9576	3.4	6
helium to xenon (3, 4, 9, 11, and 17)	$\Delta G^\circ = (-0.81 \pm 0.05)N + 40$	0.9947	0.32	5
	$\Delta H^\circ = (-2.42 \pm 0.03)N + 29.9$ (van't Hoff)	0.9998	0.159	5
	$\Delta H^\circ = (-2.40 \pm 0.03)N + 29.6$ (calorimetric)	0.9998	0.182	5
	$T\Delta S^\circ = (-1.60 \pm 0.08)N - 10.3$	0.9968	0.49	5
<i>Alkanes</i>				
methane to n-pentane (10, 23, 33, 46, and 53)	$\Delta G^\circ = (0.09 \pm 0.05)N + 24$	0.7445	0.62	5
	$\Delta G^\circ = (0.015 \pm 0.003)N^2 - (0.73 \pm 0.16)N + 34$	0.9857	0.191	5
	$\Delta H^\circ = (-0.82 \pm 0.09)N + 0.7$ (van't Hoff)	0.9836	1.15	5
	$\Delta H^\circ = (0.028 \pm 0.008)N^2 - (2.3 \pm 0.4)N + 19$ (van't Hoff)	0.9980	0.50	5
	$T\Delta S^\circ = (-0.93 \pm 0.07)N - 23$	0.9923	0.88	5
	$T\Delta S^\circ = (0.023 \pm 0.003)N^2 - (2.13 \pm 0.14)N - 7.9$	0.9998	0.169	5
methane to n-butane (10, 23, 33, and 46)	$\Delta G^\circ = (0.03 \pm 0.06)N + 25$	0.4028	0.49	4
	$\Delta G^\circ = (0.017 \pm 0.007)N^2 - (0.8 \pm 0.4)N + 35$	0.9373	0.27	4
	$\Delta H^\circ = (-0.92 \pm 0.11)N + 3.0$ (van't Hoff)	0.9419	0.98	4
	$\Delta H^\circ = (0.032 \pm 0.018)N^2 - (2.5 \pm 0.9)N + 22$ (van't Hoff)	0.9972	0.68	4
	$\Delta H^\circ = (-0.99 \pm 0.11)N + 4.3$ (calorimetric)	0.9891	1.00	4
	$\Delta H^\circ = (0.0375 \pm 0.0012)N^2 - (2.84 \pm 0.06)N + 26.3$ (calorimetric)	0.9999	0.044	4
	$T\Delta S^\circ = (-1.02 \pm 0.06)N - 21$	0.9967	0.57	4
	$T\Delta S^\circ = (0.021 \pm 0.006)N^2 - (2.0 \pm 0.3)N - 9.0$	0.9997	0.22	4
methane to neopentane (10, 23, 33, 44, and 51)	$\Delta G^\circ = (0.15 \pm 0.08)N + 23$	0.7725	0.84	5
	$\Delta G^\circ = (0.029 \pm 0.003)N^2 - (1.31 \pm 0.14)N + 41$	0.9968	0.128	5
	$\Delta H^\circ = (-0.88 \pm 0.13)N + 2.2$ (van't Hoff)	0.9636	1.52	5
	$\Delta H^\circ = (0.007 \pm 0.04)N^2 - (1.2 \pm 1.8)N + 7$ (van't Hoff)	0.9641	1.74	5
	$\Delta H^\circ = (-0.76 \pm 0.16)N - 0.8$ (calorimetric)	0.9429	1.81	5
	$\Delta H^\circ = (0.062 \pm 0.006)N^2 - (3.9 \pm 0.3)N + 38$ (calorimetric)	0.9992	0.27	5
	$T\Delta S^\circ = (-0.91 \pm 0.09)N - 24$	0.9869	1.01	5
	$T\Delta S^\circ = (0.033 \pm 0.007)N^2 - (2.6 \pm 0.4)N - 2.5$	0.9991	0.33	5
<i>Haloalkanes</i>				
fluoromethane to bromomethane (15, 19, and 22)	$\Delta G^\circ = (-0.74 \pm 0.12)N + 32$	0.9885	0.28	3
	$\Delta H^\circ = (-2.23 \pm 0.05)N + 26$ (van't Hoff)	0.9998	0.110	3
	$T\Delta S^\circ = (-1.50 \pm 0.08)N - 5.5$	0.9987	0.185	3
<i>Freons</i>				
CF ₄ to CCl ₃ F (26, 29, 36, and 40) CF ₄ to CCl ₂ F ₂ (26, 29, and 36)	$\Delta G^\circ = (-1.68 \pm 0.04)N + 71$	0.9995	0.165	4
	$\Delta H^\circ = (-2.3 \pm 0.6)N + 41$ (van't Hoff)	0.9712	1.55	3
	$\Delta H^\circ = (-2.66 \pm 0.05)N + 47.2$ (calorimetric)	0.9998	0.129	3
	$T\Delta S^\circ = (-0.97 \pm 0.04)N - 23.8$	0.9993	0.101	3
CHF ₃ to CHCl ₂ F (20, 27, and 32)	$\Delta G^\circ = (-1.12 \pm 0.08)N + 46$	0.9976	0.24	3
C ₂ F ₆ to CCl ₂ FCClF ₂ (41, 45, 49, and 52)	$\Delta G^\circ = (-1.4 \pm 0.4)N + 76$	0.9403	1.34	4
	$\Delta G^\circ = (0.37 \pm 0.03)N^2 - (25.3 \pm 1.7)N + 455$	0.9997	0.132	4

^a Range of homologous solutes covered. See Table 1 for key to numbers. ^b Only linear or quadratic regressions were applied: *Energy* / kJ mol⁻¹ = *aN* + *b* or *Energy* / kJ mol⁻¹ = *cN*² + *dN* + *e*, where *N* = number of water molecules in the first solvation shell. ^c Correlation coefficient. ^d σ / kJ mol⁻¹ = Standard deviation of the fit. ^e Number of solutes.

TABLE 5. Regression Equations for ΔC_p° on Solution of Gases in H₂O at 298.15 K and 101.325 kPa Partial Pressure of Gas.

Solute range ^a	Regression equation ^b	r^c	σ^d	n^e
<i>All gases</i>				
helium to neopentane (3, 4, 9-11, 16-18, 21, 23, 29, 30, 33, 36, 44, 46, and 51)	$\Delta C_p^\circ = (14.8 \pm 1.4)N - 69$	0.9418	32.4	17
<i>Rare gases</i>				
helium to xenon (3, 4, 9, 11, and 17)	$\Delta C_p^\circ = (15.2 \pm 0.8)N - 61$	0.9967	4.7	5
<i>Alkanes</i>				
methane to n-butane (10, 23, 33, and 46)	$\Delta C_p^\circ = (13.2 \pm 0.4)N - 25$	0.9995	2.9	4
methane to neopentane (10, 23, 33, 44, and 51)	$\Delta C_p^\circ = (17 \pm 3)N - 103$	0.9653	30.5	5
<i>All alkanes</i>				
methane to neopentane (10, 23, 33, 44, 46, and 51)	$\Delta C_p^\circ = (16 \pm 3)N - 87$	0.9595	29.3	6

^a Range of solutes covered. The numbers correspond to the numbers in Table 1. ^b Only linear regression was applied: $\Delta C_p^\circ / \text{J K}^{-1} \text{mol}^{-1} = aN + b$, where N = number of water molecules in the first solvation shell. The values of ΔC_p° used for the equations are from calorimetric measurements (Refs 23, 24 and 39-41). ^c Correlation coefficient. ^d $\sigma / \text{J K}^{-1} \text{mol}^{-1}$ = Standard deviation of the fit. ^e Number of solutes.

ΔG° values for alkynes and alkanes do not correlate with N in the same way as ΔG° for alkanes. For the group HC≡CH (16), H₂C=CH₂ (18), and H₃C-CH₃ (23) reasonably good linear relationships exist between the thermodynamic changes on solution and N with the following correlation coefficients: 0.96 for ΔG° vs. N , 0.998 for ΔH° vs. N , 0.99 for ΔS° vs. N , and 0.99 for ΔC_p° vs. N . There are not enough data to see if similar relationships exist for the groups with propane and n-butane as parent alkane.

On the basis of regression equations ΔH° and $T\Delta S^\circ$ vs. N for the freon group CF₄ (26), CClF₃ (29), and CCl₂F₂ (36) (Table 4.) the values of $\Delta H^\circ = -31 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -175 \text{ J K}^{-1} \text{mol}^{-1}$ can be estimated for CCl₃F (40). No literature values were found for comparison. Calorimetric ΔC_p° values²⁴ were available only for CClF₃ [$\Delta C_p^\circ = (278 \pm 22) \text{ J K}^{-1} \text{mol}^{-1}$] and CCl₂F₂ [$\Delta C_p^\circ = (315 \pm 11) \text{ J K}^{-1} \text{mol}^{-1}$]. For CF₄ the following van't Hoff values of $\Delta C_p^\circ / \text{J K}^{-1} \text{mol}^{-1}$ were found in the literature: 380 (Ref. 3), 410 (Ref. 4), and 637 (Ref. 15). Compared with the calorimetric ΔC_p° values reported for the freon homologues²⁴, the above van't Hoff ΔC_p° values for CF₄ seem much too high. As known, relatively large random errors are associated with the experimental ΔC_p° values derived from the temperature dependent solubility data unless the data are of high precision quality.⁴¹ Therefore, more reliable values could perhaps be estimated by utilizing the regression equations given in Table 5 and the calorimetric ΔC_p° values²⁴ of CClF₃ and CCl₂F₂. A reasonably good linear relationship exists between ΔC_p° and N over a wide variety of solute gases (Table 5). On the basis of the slope of regression equations ΔC_p° increases by about $15 \text{ J K}^{-1} \text{mol}^{-1}$ for each additional water molecule in the first solvation shell. Thus, the values of $\Delta C_p^\circ = 248 \text{ J K}^{-1} \text{mol}^{-1}$ for CF₄ and $\Delta C_p^\circ = 345 \text{ J K}^{-1} \text{mol}^{-1}$ for CCl₃F can be estimated. The value predicted by the Scaled Particle Theory^{44,45} for $\Delta C_p^\circ(\text{CF}_4)$ is $210 \text{ J K}^{-1} \text{mol}^{-1}$ (Ref. 15) which is in good agreement with the above estimate of $248 \text{ J K}^{-1} \text{mol}^{-1}$. For $\Delta C_p^\circ(\text{CCl}_3\text{F})$ no literature value was found for comparison.

For all gases taken together, simple semi-empirical correlations between the equilibrium solubility and N were not successful. However, some useful trends for several groupings of the gases have been shown. Values for areas of van der Waals Surface, Solvent Accessible Surface and Solvent-Excluding Surface, as well as values for volumes of space enclosed by these surfaces, for 53 gaseous solutes have been reported for possible further correlational studies where also other factors, like polarity and polarizability should be taken into account.

REFERENCES

1. H. M. Parmelee, *Refriger. Eng.* **61**, 1341 (1953).
2. Du Pont Freon Product Information B-2. "Freon" Fluorocarbons, Properties and Applications, p. 9. E. I. Du Pont de Nemours & Co. (Inc.) "Freon" Products Division, Wilmington, Delaware (1969).
3. E. Wilhelm, R. Battino and R. J. Wilcock, *Chem. Rev.* **77**, 219 (1977).
4. W-Y. Wen and J. A. Muccitelli, *J. Solution Chem.* **8**, 225 (1979).
5. C. L. Young, Ed., IUPAC Solubility Data Series, Vol. 5/6. *Hydrogen and Deuterium*, p. 1. Pergamon Press, Oxford, England (1981).
6. R. Battino, Ed., IUPAC Solubility Data Series, Vol. 7. *Oxygen and Ozone*, Pergamon Press, Oxford, England (1981).
7. C. L. Young, Ed., IUPAC Solubility Data Series, Vol. 8. *Oxides of Nitrogen*, p. 1. Pergamon Press, Oxford, England (1981).
8. T. R. Rettich, Y. P. Handa, R. Battino and E. Wilhelm, *J. Phys. Chem.* **85**, 3230 (1981).
9. T. Park, T. R. Rettich, R. Battino, D. Peterson and E. Wilhelm, *J. Chem. Eng. Data* **27**, 324 (1982).
10. M. H. Abraham, *J. Chem. Soc., Faraday Trans. 1*, **80**, 153 (1984).
11. W. Hayduk, Ed., IUPAC Solubility Data Series, Vol. 24. *Propane, Butane and 2-Methylpropane*, a) p. 1, b) p. 16, c) p. 34. Pergamon Press, Oxford, England (1986).
12. World Meteorological Organization Global Ozone research and Monitoring project - Report No. 20. Scientific Assessment of Stratospheric Ozone: 1989. Volume II. Appendix: AFEAS Report. M.O. McLinden, *Physical Properties of Alternatives to the Fully Halogenated Chlorofluorocarbons* pp. 11-38 (1989).
13. D. Krause, Jr. and B.B. Benson, *J. Solution Chem.* **18**, 823 (1989).
14. R. Battino, *Rev. Anal. Chem.* **9**, 131 (1989).
15. P. Scharlin and R. Battino, *J. Solution Chem.* **21**, 67 (1992).
16. P. Scharlin and R. Battino, *Fluid Phase Equilib.* **94**, 137 (1994).
17. P. Scharlin, Ed., IUPAC Solubility Data Series, Vol. 62. *Carbon Dioxide in Water and Aqueous Electrolyte Solutions*, p. 2. Oxford University Press, Oxford, England (1996).
18. P. Scharlin and R. Battino, Unpublished results.
19. W. L. Jorgensen, J. Gao and C. Ravimohan, *J. Phys. Chem.* **89**, 3470 (1985).
20. N. Matubayasi, *J. Am. Chem. Soc.* **116**, 1450 (1994).
21. R. B. Hermann, *J. Phys. Chem.*, **76**, 2754 (1972).
22. S. J. Gill, S. F. Dec, G. Olofsson and I. Wadsö, *J. Phys. Chem.* **89**, 3758 (1985).
23. S. F. Dec and S. J. Gill, *J. Solution Chem.* **14**, 417 (1985).
24. H. Naghibi, D. W. Ownby and S. J. Gill, *J. Solution Chem.* **16**, 171 (1987).
25. J. L. Pascual-Ahuir and E. Silla, *J. Comput. Chem.*, **11**, 1047 (1990).
26. E. Silla and I. Tuñón, *J. Comput. Chem.*, **12**, 1077 (1991).
27. J. L. Pascual-Ahuir, E. Silla and I. Tuñón, *J. Comput. Chem.*, **15**, 1127 (1994).
28. B. Lee and F. M. Richards, *J. Mol. Biol.*, **55**, 379 (1971).
29. F. M. Richards, *Ann. Rev. Biophys. Bioeng.*, **6**, 151 (1977).
30. M. L. Connolly, QCPE Program No. 75 (1981).
31. J. L. Pascual-Ahuir, E. Silla and I. Tuñón, QCPE Program No. 554 (1988, 1992, 1994).
32. J. L. Pascual-Ahuir and E. Silla, in R. Carbó, Ed., *Studies in Physical and Theoretical Chemistry*, **62**, 597 (1989).
33. A. Bondi, *J. Phys. Chem.* **68**, 441 (1966).
34. J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*, Table 4.16. McGraw-Hill Book Company, New York (1970).
35. L. E. Sutton, Ed. *Tables of Interatomic Distances and Configuration in Molecules and Ions*. The Chemical Society, London (1958).
36. F. Franks, *Water*, p. 21. The Royal Society of Chemistry, London (1983).
37. G. Alagona and A. Tani, *J. Chem. Phys.* **72**, 580 (1980).
38. G. Olofsson, A.A. Oshojd, E. Qvarnström and I. Wadsö, *J. Chem. Thermodynamics* **16**, 1041 (1984).
39. S. J. Gill and I. Wadsö, *J. Chem. Thermodynamics* **14**, 905 (1982).
40. S. F. Dec and S. J. Gill, *J. Solution Chem.* **13**, 27 (1984).
41. S. F. Dec and S. J. Gill, *J. Solution Chem.* **14**, 827 (1985).
42. M. Kofler, *Sitzungsber. Akad. Wiss. Wien, Math.-Naturwiss. Kl.*, **121**, 2169 (1912); *Monatsh. Chem.*, **34**, 389 (1923).
43. M. Szeperowicz, *Sitzungsber. Akad. Wiss. Wien, Math.-Naturwiss. Kl.*, **129**, 437 (1920).
44. R. A. Pierotti, *J. Phys. Chem.* **69**, 281 (1965).
45. E. Wilhelm and R. Battino, *J. Chem. Thermodynamics* **3**, 379 (1971).