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Group Contributions to the Thermodynamic Properties of Non-Ionic Organic Solutes in Dilute Aqueous Solution

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The thermodynamic properties ΔG_h^o, ΔH_h^o, and $\Delta C_{p,h}^o$ associated with the transfer of non-ionic organic compounds from gas to dilute aqueous solution and the limiting partial molar properties $\overline{C}_{p,2}^o$ and $\overline{V}_2^o$ of these compounds in water are described through a simple scheme of group contributions. A distinction is made between groups made only of carbon and hydrogen, and functional groups i.e. groups containing at least one atom different from carbon and hydrogen. Each group is assigned a contribution, for each property, through a least squares procedure which utilizes only molecules containing at most one functional group. Finally, for compounds containing more than one functional group, correction parameters are evaluated as the differences between the experimental values and those calculated by means of the group contributions. The different behavior of hydrophilic compared with hydrophobic groups is discussed for the various properties. A rationale for the correction parameters, i.e. for the effects of the interactions among hydrophilic groups on the thermodynamic properties, is attempted.

KEY WORDS: Group contributions; partial molar heat capacity; partial molar volume; free energy of hydration; enthalpy of hydration; dilute aqueous solutions; non-electrolytes.

1. INTRODUCTION

For some time considerable interest has been shown in such properties as gas solubility in water, structure of water and aqueous solutions of non-electrolytes, the effect of water in determining the

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conformation of biological molecules, and the role of solvation in equilibria and kinetics of reactions. This interest, coupled with the development of apparatus which permit the rapid measurement of highly precise data, explains the large number of recent data for the standard thermodynamic functions of hydration $\Delta G_{\mathrm{h}}^{\circ}$, $\Delta H_{\mathrm{h}}^{\circ}$, $\Delta S_{\mathrm{h}}^{\circ}$, $\Delta C_{\mathrm{p,h}}^{\circ}$ and the partial molar properties $\overline{C}_{\mathrm{p,2}}^{\circ}$ and $\overline{V}_{2}^{\circ}$ (of non-charged organic compounds) in water. Data are presently known for the following number of compounds: 350 for $\Delta G_{\mathrm{h}}^{\circ}$, 197 for $\Delta H_{\mathrm{h}}^{\circ}$, 272 for $\overline{C}_{\mathrm{p,2}}^{\circ}$, and 425 for $\overline{V}_{2}^{\circ}$.

These data represent a substantial reservoir of information on water-organic solutes interactions. Unfortunately, in the absence of a rigorous statistical thermodynamic theory for aqueous solutions to provide a rationale for these interactions, it is not easy to predict how the changes of the thermodynamic properties of water are related to the molecular structure of the solute molecules. Thus it appears justified to search for such a correlation adopting empirical procedures.

Three methods can be identified for this purpose. In the most commonly used, the contribution of a repetitive unit to each molar thermodynamic property is calculated as a difference between the property values for two consecutive members of a homologous series. In the second method, the molecules are subdivided into groups, each of which is assumed to contribute a constant amount to the thermodynamic quantity. These contributions are calculated using a least squares method. Finally, in a third procedure the hydrocarbons are selected as reference molecules and the effects of substituting some hydrocarbon surface area (or volume) with a like surface area (or volume) of hydrophilic nature are evaluated.(1-4)

The second method was used some years ago by Hine and Mookerjee(5) and by Guthrie(6) to rationalize the free energies of hydration and the partial molar heat capacities, respectively. In this paper we apply such a procedure to the partial molar volumes and to the enthalpies of hydration. For the sake of homogeneity, the calculations are also performed for $\Delta G_{\mathrm{h}}^{\circ}$ and $\overline{C}_{\mathrm{p,2}}^{\circ}$, including recent experimental data. Heat capacities of hydration $\Delta C_{\mathrm{p,h}}^{\circ}$ and partial molal volumes $\overline{V}_{2}^{\circ}$ are also considered.

The aim of this work is to give a compact picture of the state of our present knowledge of the main thermodynamic properties of dilute aqueous solutions of non-electrolytes and to test to what extent these properties can be reproduced by means of a simple scheme of group contributions.

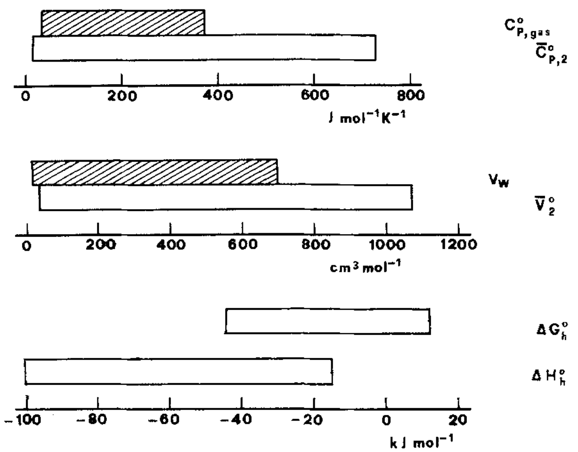

Fig. 1. Ranges of experimental $\overline{C}^{o}_{p,2}$, $\overline{V}^{o}_{2}$, ΔG^{o}_{h}, and ΔH^{o}_{h} for non-electrolytes in water at 25°C and ranges of corresponding gas molar heat capacities ($C^{o}_{p,g}$) and van der Waals volumes (V_W).

2. MEASURED PROPERTIES AND EXPERIMENTAL DATA

In general, each value of $\overline{C}^{o}_{p,2}$, $\overline{V}^{o}_{2}$, ΔG^{o}_{h}, or ΔH^{o}_{h} was found in a single literature source and was converted, where necessary, to the units and standard states used in this paper. Some values were obtained by combining data from different literature sources. In particular, a few $\overline{C}^{o}_{p,2}$ data were evaluated from the heat capacity of hydration $\Delta C^{o}_{p,h}$ and the molar heat capacity of the gas, or from the heat capacity of solution of the pure condensed substance, $\Delta C^{o}_{p,s}$, and its molar heat capacity. Many ΔG^{o}_{h} were calculated from data for water solubility and vapor pressure of the pure compounds. Finally, some ΔH^{o}_{h} values were obtained from solution and vaporization heats.

The standard free energy changes for the isothermal transfer of molecules from gas to water were calculated assuming as standard states the ideal gas at 1*M* concentration and the hypothetical 1*M* ideal aqueous solution. SI units were used except for volumes which were expressed in cm^{3}-mol^{-1}. The factor of 4.184 was used to convert calories to joules. In Fig. 1 are illustrated the ranges of known experimental data for $\overline{C}^{o}_{p,2}$, $\overline{V}^{o}_{2}$, ΔG^{o}_{h}, and ΔH^{o}_{h} of non-ionic organic compounds in water at 25°C.

We wish to emphasize that a substantial difference exists between the transfer properties, ΔG^{o}_{h} and ΔH^{o}_{h}, and the partial molar properties, $\overline{C}^{o}_{p,2}$ and $\overline{V}^{o}_{2}$. While the former are determined essentially by the changes the solvent structure undergoes in the vicinity of the solute molecule, the latter also include internal contributions due to atoms and bonds of the molecule. The ranges of these internal contributions *i.e.* gas molar heat capacities, $C^{o}_{p,g}$, and intrinsic volumes, as measured by van der Waals volumes, V_W, are also shown for comparison in Fig. 1. For the single molecules, $C^{o}_{p,g}$ ranges from 20 to 60% of $\overline{C}^{o}_{p,2}$, whereas V_W represents 50 to 80% of $\overline{V}^{o}_{2}$.

Because of this large internal contribution, the heat capacity of hydration $\Delta C^{o}_{p,h} = \overline{C}^{o}_{p,2} - C^{o}_{p,g}$ and the volume function $\Delta V^{*} = \overline{V}^{o}_{2} - V_W$ were also examined as more significant quantities. The gas heat capacities and the van der Waals volumes were estimated by group contributions according to Benson(7) and to Bondi,(8) respectively.

The quantity ΔV^{*} has no evident thermodynamic meaning. Moreover, its value depends on the model chosen to evaluate the intrinsic volume. Nevertheless, we deemed it interesting to correlate this quantity with the solute molecular structure, since it should be more sensitive than $\overline{V}^{o}_{2}$ to the changes that the solute molecule induces in the structure of the surrounding water.

The full list of experimental data for $\overline{C}^{o}_{p,2}$, $\overline{V}^{o}_{2}$, ΔG^{o}_{h}, and ΔH^{o}_{h} with the corresponding sources is given in the Appendix together with $C^{o}_{p,g}$ and V_W used for calculating $\Delta C^{o}_{p,h}$ and ΔV^{*}, respectively.

3. STRUCTURAL PARAMETERS

The molecular structures were described through a scheme of group contributions as follows:

1) A group is defined as an arrangement of one or more atoms containing no carbon-carbon bond, except for multiple bonds of alkenes and alkynes. The contribution the j^{th} group gives to a thermodynamic property Z is indicated as $B_Z(j)$. A group containing at least one atom different from carbon and hydrogen is called a functional group and is indicated as Y.

2) Each group is characterized only by its constituent atoms, *i.e.* is independent of the nature of neighboring atoms. Thus, the propane methylene group is considered equal to the methylene of ethanol. Y groups directly attached to an aromatic or heteroaromatic ring are the only exceptions in that they are distinguished from the corresponding groups bonded to aliphatic or alicyclic frames.

3) Groups which are part of the ring skeleton of cyclic compounds are

Table IA. Group Contributions B_Z to the Partial Molar Heat Capacity and Partial Molar Volume of Non-Ionic Organic Compounds in Water at 25°C[a,†]

	B_Z Contribution			B_Z Contribution	
Group[b]	$\bar{C}^{o}_{p,2}$ J-mol^{-1}-K^{-1}	$\bar{V}^{o}_{2}$ cm^{3}-mol^{-1}	Group[b]	$\bar{C}^{o}_{p,2}$ J-mol^{-1}-K^{-1}	$\bar{V}^{o}_{2}$ cm^{3}-mol^{-1}
CH_3	110.1 (68)	19.06 (86)	$^{*}NH$	-27.0 (6)	7.76 (7)
CH_2	87.5 (49)	15.80 (62)	$^{*}N$	-35.0 (2)	8.04 (2)
CH	71.4 (10)	12.33 (18)	N_{ar}	4.0 (5)	7.19 (5)
C	28.3 (7)	9.54 (4)	O	-51.9 (1)	7.28 (1)
C=C	89.1 (4)	20.51 (2)	OH	-10.1 (24)	6.74 (31)
C≡C	74.0 (2)	-	$^{*}O$	-68.4 (4)	7.23 (6)
$H(C_{\pi})^{c}$	22.4 (7)	2.78 (7)	S	-	16.38 (1)
$^{*}CH_2$	71.9 (15)	14.09 (33)	SO	-114.1 (1)	17.40 (1)
$^{*}CH$	79.6 (7)	11.76 (17)	F	-0.1 (1)	3.44 (1)
$^{*}C$	-	9.54^{d}	Cl	35.4 (1)	13.74 (1)
$^{*}C=C$	65.9 (1)	-	Br	53.5 (1)	19.04 (3)
CH_{ar}	45.6 (15)	11.46 (9)	I	272.0 (1)	31.24 (1)
C_{ar}	-0.6 (13)	8.28 (7)	NH_2CONH	-	30.84^{e}(3)
C_{cond}	8.6 (1)	7.37 (1)	NHCONH	-52.0 (1)	28.52 (1)
CHO	-43.7 (1)	-	NH_2CON	-25.4 (1)	27.36 (1)
CO	-52.0 (3)	15.18 (4)	NCON	-85.5 (1)	25.67 (1)
COO	3.8 (2)	21.39 (3)	OCOO	-	28.02 (2)
COOH	-23.1 (7)	20.34 (8)	$^{*}OCOO$	-	20.71 (1)
$CONH_2$	-24.4 (3)	23.11 (5)	$^{*}CONHCO$	-	30.71 (1)
CONH	-47.1 (12)	22.31 (9)	NH_2COO	-	30.61 (1)
CON	-97.1 (1)	19.83 (8)	CHO(ϕ)	-	17.11 (1)
$CSNH_2$	-	33.95 (1)	COOH(ϕ)	65.3 (1)	19.81 (1)
$^{*}CO$	-	15.58 (6)	$NH_2(\phi)$	0.3 (1)	10.34 (1)
$^{*}COO$	-	18.61 (2)	$NO_2(\phi)$	-	18.74 (1)
$^{*}CONH$	-71.4 (2)	20.84 (2)	OH(ϕ)	9.4^{e}(3)	7.20 (1)
$^{*}CON$	-98.9 (2)	15.66 (1)	SH(ϕ)	-	15.13 (1)
CN	-	14.94 (1)			
NH_2	-33.8 (12)	9.89 (15)	A_Z	79.6 (93)	13.41 (118)
NH	9.3 (3)	8.57 (4)			
N	-42.5 (3)	3.77 (2)	σ^{f}	13.2	0.70

[†] See Table IB for footnotes.

Table IB. Group Contributions B_z to the Hydration Functions of Non-Ionic Organic Compounds at 25°C

Group[b]	B_Z Contribution			
	$\Delta G_h^{o\,g}$ kJ-mol^{-1}	ΔH_h^o kJ-mol^{-1}	$\Delta C_{p,h}^o$ J-mol^{-1}-K^{-1}	ΔV^* cm^3-mol^{-1}
CH_3	3.17 (186)	-2.39 (80)	66.4 (68)	6.01 (86)
CH_2	0.74 (131)	-3.24 (45)	64.5 (49)	5.57 (62)
CH	-1.06 (38)	-3.07 (17)	67.8 (10)	4.90 (18)
C	-3.87 (9)	-4.56 (6)	44.7 (7)	4.95 (4)
C=C	-9.81 (22)	-6.63 (3)	100.8 (4)	9.17 (2)
C≡C	-8.68 (8)	0.10 (4)	44.3 (2)	-
$H(C_\pi)^c$	3.60 (38)	1.18 (7)	-0.2 (7)	-0.03 (7)
$^*CH_2$	0.75 (22)	-3.07 (16)	47.3 (15)	4.45 (33)
$^*CH$	-1.58 (8)	-5.23 (7)	74.1 (7)	5.04 (17)
$^*C=C$	-8.64 (3)	-	64.3 (1)	-
CH_{ar}	-0.83 (26)	-2.92 (19)	26.0 (15)	3.60 (9)
C_{ar}	-3.92 (24)	-5.70 (17)	0.0 (13)	2.33 (7)
C_{cond}	-2.59^e(9)	-3.57^e(4)	0.1 (1)	2.43 (1)
CHO	-18.83 (12)	-	-91.0 (1)	-
CO	-23.06 (14)	-23.18 (13)	-79.5 (3)	3.48 (4)
COO	-20.34 (27)	-22.77 (7)	-37.0 (2)	6.24 (3)
COOH	-32.21 (3)	-35.46 (5)	-84.7 (7)	1.43 (8)
$CONH_2$	-44.85 (1)	-	-84.6 (3)	1.72 (5)
CONH	-	-59.93 (1)	-87.4 (12)	3.32 (9)
CON	-	-45.42 (1)	-112.4 (1)	3.42 (8)
$^*CO$	-	-25.08 (2)	-	4.55 (6)
$^*COO$	-	-	-	5.65 (2)
$^*CONH$	-	-	-108.2 (2)	3.83 (2)
$^*CON$	-	-	-109.3 (2)	1.49 (1)
CN	-20.83 (3)	-19.31 (2)	-	0.83 (1)
NH_2	-24.13 (6)	-33.21 (8)	-75.5 (12)	-0.01 (15)
NH	-25.67 (4)	-39.46 (5)	-7.7 (3)	1.08 (4)
N	-24.79 (2)	-38.92 (1)	-39.0 (3)	-1.17 (2)
$^*NH$	-25.97 (6)	-36.54 (4)	-45.1 (6)	1.54 (7)
$^*N$	-24.08 (2)	-34.52 (2)	-33.7 (2)	4.64 (2)
N_{ar}	-17.02 (13)	-20.57 (12)	-12.0 (5)	2.23 (5)
NO_2	-19.88 (3)	-19.47 (1)	-	-
O	-15.77 (6)	-21.88 (1)	-62.6 (1)	3.59 (1)
OH	-25.95 (25)	-36.38 (16)	-44.4 (24)	-0.67 (31)
$^*O$	-18.29 (4)	-20.62 (4)	-90.6 (4)	5.00 (6)
S	-14.36 (2)	-	-	5.59 (1)
SH	-9.91 (2)	-	-	-
SO	-	-53.07 (1)	-152.0 (1)	1.84 (1)

Table IB. (Continued)

Group[b]	B_Z Contribution			
	ΔG_h^{o}[g] kJ-mol^{-1}	ΔH_h^{o} kJ-mol^{-1}	$\Delta C_{p,h}^{o}$ J-mol^{-1}-K^{-1}	ΔV^{*} cm^3-mol^{-1}
F	-5.14 (1)	-1.87 (1)	-30.3 (1)	-1.67 (1)
Cl	-7.26 (8)	-6.90 (1)	2.0 (1)	2.73 (1)
Br	-7.75 (7)	-9.27 (1)	18.4 (1)	5.26 (3)
I	-7.98 (5)	-9.64 (1)	235.2 (1)	12.63 (1)
NH_2CONH	-	-	-	1.93[e](3)
NHCONH	-	-	-81.0 (1)	2.06 (1)
NH_2CON	-	-	-99.9 (1)	1.00 (1)
NCON	-	-	-88.4 (1)	4.30 (1)
CHO(ϕ)	-9.83 (1)	-	-	2.68 (1)
CO(ϕ)	-15.34 (1)	-	-	-
COO(ϕ)	-14.08 (1)	-	-	-
COOH(ϕ)	-	-	22.8 (1)	0.67 (1)
NH_2(ϕ)	-	-	-47.2 (1)	0.40 (1)
NO_2(ϕ)	-8.60[e](3)	-	-	2.61 (1)
O(ϕ)	-0.50 (1)	-	-	-
OH(ϕ)	-19.35[e](4)	-21.94[e](4)	-32.3[e](3)	-0.23 (1)
S(ϕ)	-7.58 (1)	-	-	-
SH(ϕ)	-3.66 (1)	-	-	0.90 (1)
Cl(ϕ)	2.32 (1)	-	-	-
Br(ϕ)	1.13[e](4)	-	-	-
A_Z	1.06 (209)	-13.87 (97)	115.9 (93)	12.17 (118)
σ[f]	0.51	1.63	13.4	0.71

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[a] The parameters A_Z and B_Z were obtained by solving Eq. (2) by a linear least squares analysis which considered only monofunctional compounds including hydrocarbons. Within the parentheses are indicated the number of compounds in which the group is present. When this number was less than 3, the corresponding compounds were not included in the regression analysis and the B_Z value was calculated as a difference (see text). [b] An asterisk indicates a group inserted in a cyclic non-aromatic structure, while the subscript ar indicates a group which is a part of an aromatic or heteroaromatic ring. The subscript cond was added to a C group to indicate a carbon atom common to two or more aromatic rings. The symbol ϕ denotes a group directly bonded to an aromatic or heteroaromatic ring. [c] Hydrogen atom on olefinic or acetylenic carbon and hydrogen atom of formic acid and its derivatives. [d] Assumed equal to the corresponding non-cyclic parameter. [e] Calculated from compounds not included in the regression analysis. [f] Standard deviation $\sigma^2 = \Sigma\,[Z(\text{calc}) - Z(\text{exp})]^2/\,(N\text{-}P)$, N and P being the number of compounds and parameters, respectively. [g] Standard states: 1M ideal gas and hypothetical 1M ideal solution. A_Z depends on the standard states chosen while B_Z does not. For example, a value $A_{\Delta G}$ = 18.94 kJ-mol^{-1}, instead of 1.06 kJ-mol^{-1}, should be used when the standard states are ideal gas at 1 atm and the hypothetical ideal solution at unit mole fraction.

distinguished from the corresponding groups in open chains. They are marked with an asterisk; for example, ${}^{*}CH_2$ represents the methylene group of cyclohexane. This distinction eliminates any need for ring corrections.

4) A constant A_Z is introduced, common to all molecules, whose value depends only on the Z property.

5) Molecules containing more than one Y group, *i.e.* polyfunctional, were described by adding one correction parameter $C_Z\,(Y_1,Y_2 \cdots Y_m)$.

Following the above rules, the Z property of any $RY_1Y_2 \cdots Y_m$ molecule, R being its hydrocarbon moiety, can be expressed as

$$Z = A_Z + \Sigma_j\, n_j B_Z\,(j) + C_Z\,(Y_1,Y_2 \cdots Y_m) \qquad (1)$$

where n_j is the number of times the j^{th} group appears in the molecule under consideration.

The A_Z constant term was introduced by Traube(9) in a scheme of atomic additivities for partial molar volumes of organic compounds in water. It was suggested here by the non-zero intercept of a plot of the thermodynamic properties for a homologous series of organic compounds against any extensive quantity characterizing the solute such as molecular weight or intrinsic volume.(10) A non-zero value of the thermodynamic functions of solvation as well as of some of the partial molar properties (for point like inert molecules) are predicted by theories such as the SPT.(11) Introduction of the A_Z term leads to a description of the experimental data which is better than can be obtained by addition of any other type of parameter, as shown by a few preliminary calculations. One further advantage is the fact that this term includes all information concerning standard states, thereby permitting $B_{\Delta G}$ *e.g.* to be calculated independent of the choice of standard states.

As far as the near-nearest effect is concerned, we think that a scheme of group contributions which also takes into account this effect should be recommended for the description of thermodynamic properties which are directly related to the internal structure of the molecules, such as heats of formation. The different nature of the properties we are dealing within this paper, mostly determined by the changes that the solute surface induces in the structure of surrounding water, should justify our simplification.

4. CALCULATION PROCEDURE

Parameters of Eq. (1) were determined in successive steps using the following procedure. First, only hydrocarbons and monofunctional compounds were considered, for which Eq. (1) reduces to

$$Z = A_Z + \Sigma_j n_j B_Z(j) \tag{2}$$

A least squares procedure applied to this equation yielded a first set of B_Z values and the constant term A_Z. In this step, groups contained in less than three compounds were not considered. Compounds for which the least squares value differed from the experimental value by more than three times the standard deviation σ were discarded.

In the second step, the B_Z contributions of the groups not considered in the regression analysis were calculated, one at a time, as a difference between the experimental value and that calculated by inserting into Eq. (2) the set of B_Z values already determined.

Finally, an analogous procedure was applied to determine the correction terms C_Z $(Y_1, Y_2 \cdots Y_m)$ for polyfunctional compounds. Their values were in fact calculated by fitting, one parameter at a time, the differences

$$\Delta = Z(\mathrm{exp}) - Z(\mathrm{calc}) \tag{3}$$

where $Z(\mathrm{calc})$ is calculated through Eq. (2) using all the B_Z values previously determined.

5. RESULTS

Table I summarizes the values of the A_Z constant and B_Z parameters for all properties examined in this work. Table IA refers to partial molar properties $\overline{C}^{\circ}_{p,2}$ and $\overline{V}^{\circ}_2$, while Table IB refers to the hydration functions ΔG°_h, ΔH°_h, and $\Delta C^{\circ}_{p,h}$, including also ΔV^*. The standard deviation σ relative to the compounds which entered the regression analysis is finally reported for each property. Standard deviations of single B_Z values determined through the regression analysis and the average deviations of the remaining B_Z parameters are generally lower than the standard deviation σ reported in the table. In particular their values range as follows: $0.5\sigma - 1\sigma$ for the A_Z constant and terminal groups; $0.1\sigma - 0.2\sigma$ for CH_2, $^*CH_2$ and CH_{ar}; intermediate values for other groups.

A comparison with similar studies by Hine$^{(5)}$ and by Guthrie$^{(6)}$ is not straightforward owing to the different schemes used for group contributions and because of the different number and type of compounds taken into consideration. However, we would like to mention that Hine handled 212 ΔG_h° values using 51 parameters, with a standard deviation of 0.7, while we described 209 compounds (hydrocarbons and monofunctional molecules) using 28 parameters, with a σ value of 0.5 kJ-mol^{-1}. Moreover, Guthrie obtained a weighted σ value of 6 using 12 parameters for 48 $\overline{C}_{p,2}^\circ$ values, while our scheme required 21 structural parameters in order to reproduce $\overline{C}_{p,2}^\circ$ values of 93 compounds with an unweighted σ value of 13 J-mol^{-1}-K^{-1}.

Though the ability to reproduce experimental data is comparable in our and Hine's or Guthrie's schemes, quite different contributions are reported for the same groups, particularly terminal groups such as CH_3, OH, COOH, *etc.* This is mainly due to the presence in our scheme of the constant term A_Z which does not produce the anomalous large values attributed to these groups by the additivity schemes so far adopted.(12) For repetitive internal groups, such as CH_2, our scheme yields practically the same value found by others.

Table II summarizes some typical correction parameters $C_Z(Y_1,Y_2)$ for bifunctional saturated compounds of the type Y_1-$(C)_n$-Y_2, aliphatic as well as alicyclic. We choose to report parameters determined by several compounds or defined for many Z properties. The majority of the values reported refer to $n=2$, which is the most frequent case. Values for $n\neq 2$ can be satisfactorily calculated through the relationship

$$\ln C_{Z,n} = \ln C_{Z,2} - \gamma_Z(n\text{-}2) \tag{4}$$

where γ_Z is a constant depending only on the Z property. Equation (4) was found not to hold for $Z = \overline{C}_{p,2}^\circ$. In this case, the deviations Δ of the experimental data from those calculated using Eq. (2) show no regular trend when plotted against the number n of intermediate carbon atoms. Correction parameters for this property, for each Y_1,Y_2 pair, were computed as the average Δ value over the various $Y_1 \cdots Y_2$ distances.

The reliability of $C_Z(Y_1,Y_2)$, as well as of B_Z, in cases where they are defined by a single compound, cannot obviously be ascertained. These numbers may only be accepted as provisional.

A few C_Z parameters for selected classes of polyfunctional compounds having particular structures, are finally collected in Table III. These correction terms may be constants (see for example the C_Z value

Table II. Selected Correction Parameters $C_Z(Y_1,Y_2)$ for Saturated Bifunctional Compounds Y_1-$(C)_n$-Y_2[a]

Groups		C_Z Correction Parameter			
Y_1	Y_2	$\overline{C}^{o}_{p,2}$ [b] J-mol^{-1}-K^{-1}	$\overline{V}^{o}_{2}$ [b] cm^3-mol^{-1}	ΔG^{o}_{h} kJ-mol^{-1}	ΔH^{o}_{h} kJ-mol^{-1}
OH	OH	-54.9[c] (6)	-3.83[d] (6)	17.33 (1)	20.82 (1)
OH	O	-13.3 (5)	-2.76 (4)	7.65 (4)	17.81 (5)
OH	NH_2	-44.1[c] (5)	-2.38[d] (1)	-	-
OH	NH	-70.2 (2)	-2.28 (2)	-	-
OH	N	-65.3 (2)	-2.18 (1)	-	-
OH	COOH	-	-2.58[e] (7)	-	-
OH	$CONH_2$	17.4[e] (2)	-1.64[f] (4)	-	-
OH	SO	-	-0.69[d] (2)	-	-
O	O	4.2[c] (8)	-1.90[d] (2)	4.42[d] (2)	6.10 (6)
O	NH_2	-26.4[c] (3)	-1.64[d] (1)	6.80[d] (1)	14.32[d] (1)
NH_2	NH_2	-22.5[c] (3)	-2.09[d] (2)	13.94 (1)	10.67[d] (1)
CO	CO	-14.1 (1)	-1.87 (1)	-	-
COOH	COOH	16.6 (1)	-2.74[d] (1)	-	-
$CONH_2$	$CONH_2$	-	-2.43[d] (1)	-	-
X[g]	X′	-	-	4.41 (5)	-
*O	OH	-36.6 (2)	-3.31 (2)	-	20.72 (2)
*O	*O	6.5[c] (4)	-3.52[e] (3)	11.36 (1)	19.43 (1)
*O	*NH	-37.2 (1)	-2.20 (1)	10.18 (1)	13.86 (1)
*O	*N	-55.7 (1)	-2.82 (1)	8.62 (1)	15.02 (1)
*NH	*NH	-72.4 (3)	-1.76 (1)	17.02 (1)	8.85 (1)
*NH	*N	-72.0 (1)	-2.32 (1)	10.29 (1)	9.18 (1)
*N	*N	-77.9 (1)	-2.96 (1)	6.05 (1)	9.26 (1)
γ_Z[h]		-	0.25 (31)	0.44 (10)	0.73 (4)

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[a] Unless otherwise indicated, the data refer to molecules with Y_1 and Y_2 groups separated by two carbon atoms (n=2). The number of compounds which determined each parameter is indicated within parentheses. [b] Values of the parameters listed for $\overline{C}^{o}_{p,2}$ and $\overline{V}^{o}_{2}$ are also valid for $\Delta C^{o}_{p,h}$ and ΔV^{*}, respectively (see text). [c] Average over different *n* values. [d] Data are also available for n≠2. They have been used to estimate the γ_Z parameter of Eq. (4). [e] The value refers to compounds with n=1. [f] The value refers to compounds with n=3. Data are also available for n≠3. They have been used to estimate the γ_Z parameter of Eq. (4). [g] X,X′= F, Cl, Br. [h] Decay constant of Eq. (4).

for $\overline{C}^{\circ}_{p,2}$ of polyols) or linear functions of the number of Y groups characterizing the considered class of compounds (see for example the C_Z for $\overline{V}^{\circ}_2$ of polyols). Parameters of Table III are not to be used in addition to parameters of Table II, *i.e.* compounds with three or more functional groups have been characterized by a single correction parameter $C_Z(Y_1,Y_2 \cdots Y_m)$, all the interactions among Y groups being included in this parameter according to Eq. (1).

We would like to note that the correction parameters C_Z reported for the partial molar properties $\overline{C}^{\circ}_{p,2}$ and $\overline{V}^{\circ}_2$ in Tables II and III are also valid for $\Delta C^{\circ}_{p,h}$ and ΔV^{*}, respectively. This is a consequence of the fact that the intrinsic terms ($C^{\circ}_{p,g}$ and V_W) are additive quantities.

The degree of success with which parameters reported in Tables I to III describe the thermodynamic properties of organic compounds in water, may be appreciated by observing the differences between experimental and calculated values reported in the Appendix.

The number of compounds utilized as well as the corresponding structural parameters determined in each single step of the calculation procedure are summarized in Table IV for all properties. Since several parameters were calculated from only one compound, we thought it useful to specify, in the same table, the total number of parameters which offer a mimimum of reliability, *i.e.* parameters determined by at least two compounds. The number of compounds they are generated from, and the corresponding standard deviation, are also indicated. It may be noticed that the σ value practically equals the value observed in the regression analysis (see Table I).

6. DISCUSSION

Table IV shows that the group additivity scheme proposed here is valid for ΔG°_h and $\overline{V}^{\circ}_2$, for which properties the standard deviation over a large number of compounds is of the order of magnitude of the disagreement which may be found among different authors or even comparable to the experimental error. A lower reproducibility is obtained for ΔH°_h and $\overline{C}^{\circ}_{p,2}$ data. Poor precision of many experimental data, expecially for hydrocarbons, is possibly responsible in the case of $\overline{C}^{\circ}_{p,2}$.

Although the values of the parameters have a purely empirical meaning owing to the way they were calculated, we nevertheless wish to comment on their values since they seem indicative of the kind of influence that different solutes exert on the structure of the surrounding solvent. In this respect, B_Z may yield a relative estimate of the thermodynamic effects involved in the interaction of hydrophobic

Table III. Correction Parameters $C_Z(Y_1, Y_2 \cdots Y_m)$ for Selected Classes of Polyfunctional Compounds and for Compounds with Particular Structures

Z Property	Class of Compounds	C_Z	No. of Cpds
$\overline{C}^{\circ}_{p,2}$ [a] $(J\text{-}mol^{-1}\text{-}K^{-1})$	Polyols: $C_nH_{n+2}(OH)_n$ (n=3-6)	-48.4	8
	Diazines[b]	-59.7	3
	2,4-Pyrimidinediones	79.4	8
	2,5-Piperazinediones	45.8	3
$\overline{V}^{\circ}_{2}$ [a] $(cm^3\text{-}mol^{-1})$	$RO(CHR'CH_2O)_nR''$ $(R,R',R'' = H,CH_3;\ n=2\text{-}8)$	-1.84·n	17
	Polyols: $C_nH_{n+2}(OH)_n$ (n=3-6)	-2.52·n	8
	$NH_2(CH_2CH_2NH)_nH$ (n=2-4)	-2.34·n	4
	Carbohydrates $(n_{OH}=3\text{-}20)$[c]	$-3.71 \cdot n_{OH}$	38
	Benzenediols[b]	-1.98	3
	Pyridinamines[b]	-2.46	3
	Diazines[b]	-2.80	4
	Adamantane ring system	-12.98	3
ΔG°_{h} $(kJ\text{-}mol^{-1})$	$RCX_1X_2X_3$ $(R=H,R;\ X_i=F,Cl,Br)$	17.27	5
	$CX_1X_2X_3X_4$ $(X_i=F,Cl,Br)$	34.58	5
	$CX_1X_2X_3-CX_4X_5X_6$ $(X_i=F,Cl)$	51.23	5
	2-Alkylpyrazines	12.67	3

[a] Values of the parameters listed for $\overline{C}^{\circ}_{p,2}$ and $\overline{V}^{\circ}_{2}$ are also valid for $\Delta C^{\circ}_{p,h}$ and ΔV^*, respectively (see text). [b] The correction parameter is valid independently of the relative position of the two Y groups. [c] This class includes mono- and polysaccharides as well as glycosides. The value of the correction parameter is obtained by multiplying -3.71 by the number of hydroxyl groups (n_{OH}), independently of the number of ether oxygens.

and hydrophilic groups with water. C_Z, derived from differences between experimental data and data calculated for hypothetical molecules containing functional groups completely independent of each other, give an idea of the extra effects which arise from the interactions between two or more functional groups.

6.1. Hydrophobic and Hydrophilic Groups

Values of main group contributions, B_Z, found for the various properties, are represented in Fig. 2. The entropy of hydration was here also considered. Group contributions to this property were calculated through the relationship $B_{T\Delta S} = B_{\Delta H} - B_{\Delta G}$. The internal consistency

Table IV. Summary of the Number of Compounds Examined and Parameters Determined[a]

Compound		$\overline{C}^{\circ}_{p,2}$	$\overline{V}^{\circ}_{2}$	ΔG°_{h}	ΔH°_{h}
Monofunctional - in the regression analysis		93 (22)	118 (24)	209 (29)	97 (21)
Monofunctional - for calculation of B_Z		28 (21)	37 (29)	37 (17)	24 (15)
Polyfunctional - for calculation of C_Z		73 (22)	55 (30)	48 (17)	26 (13)
Not utilized[b]	- monofunctional	33	15	21	19
	- polyfunctional	45	100	35	31
Total		272	425	350	197
Compounds which generated 'reliable' parameters[c]		174 (45)	277 (50)	276 (45)	128 (30)
σ[d]		13.6	0.91	0.72	1.66

[a] The number of parameters determined in each calculation step are in parentheses. [b] Here are included compounds for which $|Z(\exp) - Z(\text{calc})| > 3\sigma$ and compounds which may be considered as a single group or which contain one or more structural features not included in Tables I-III. [c] The term 'reliable' is used to indicate a parameter determined by at least two compounds. [d] Standard deviation obtained for 'reliable' parameters. Units as in Table I.

of ΔH°_{h}, ΔG°_{h}, and ΔS°_{h} functions is thus preserved.

Fig. 2 shows the most important features of the thermodynamic behavior of monofunctional compounds in water:

i) A sharp separation exists between the values of the B_Z parameters relative to the hydration functions ΔH°_{h}, ΔG°_{h} and $\Delta C^{\circ}_{p,h}$, according to whether a hydrophobic or hydrophilic group is involved. The separation is not found for ΔS°_{h}, and is feebly shown by ΔV^{*}. When the $\overline{C}^{\circ}_{p,2}$ and $\overline{V}^{\circ}_{2}$ properties are considered, the above separation is reduced compared to the corresponding transfer quantities. This appears to be due to the intrinsic term which contributes a large amount to the partial molar properties (see Fig. 1) and thus may mask solvation effects.

ii) Hydration enthalpies clearly distinguish hydrophilic groups containing hydrogen atoms from other hydrophilic groups, the former

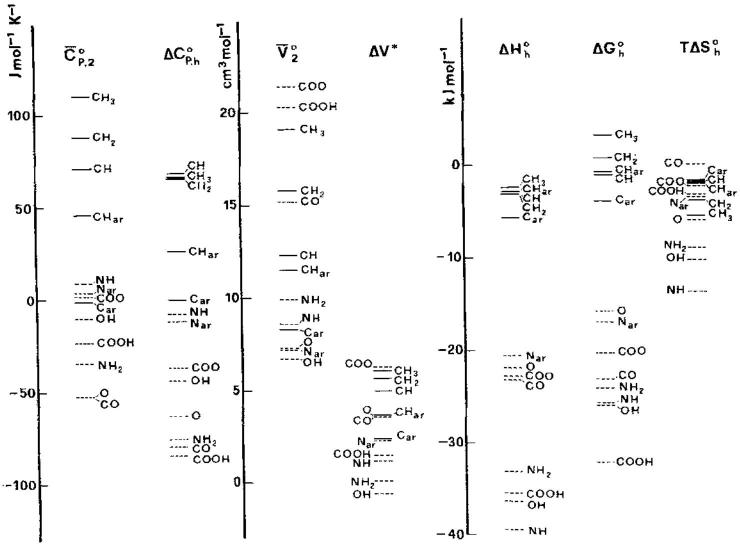

Fig. 2. Selected values of group contributions, B_Z, to the thermodynamic properties of non-ionic organic compounds in water at 25°C. (Hydrophobic groups: --------; hydrophilic groups: - - - - -).

being characterized by far more negative $B_{\Delta H}$ values. This distinction may also be observed for ΔG_h°, ΔV^* and, to a lesser extent, for $T\Delta S_h^\circ$, but is absent in $\bar{C}_{p,2}^\circ$, $\Delta C_{p,h}^\circ$ and $\bar{V}_2^\circ$.

iii) The contributions of CH_3, CH_2 and CH groups fall in a narrow range for all transfer quantities. The number of hydrogen atoms would thus seem to deserve a negligible importance in hydrophobic hydration contrary to the opinion expressed elsewhere.(13)

iv) The hydration entropy is always negative whatever group is considered and its value is not significantly dependent on the nature of the group. Therefore, entropy does not appear the proper function to characterize the behavior of organic compounds in dilute aqueous solution. It seems the importance given to the entropy term in order to explain the thermodynamics of nonpolar solutes in water is exaggerated.(14) In fact, the enthalpy is the most suitable function to distinguish polar from nonpolar groups.

6.2. Interaction Between Hydrophilic Centers

For saturated bifunctional compounds of the type $Y_1\text{-}(C)_n\text{-}Y_2$ the

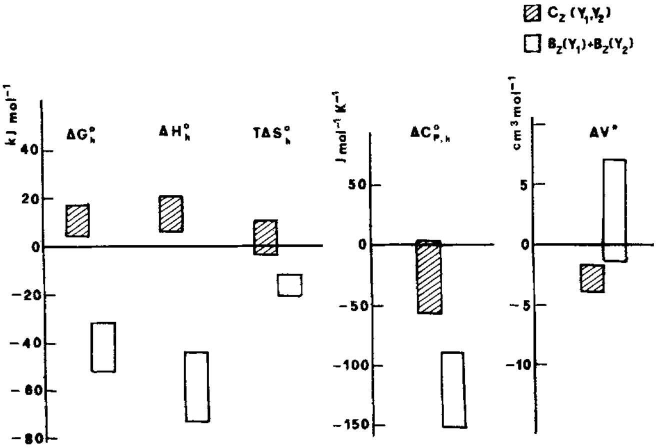

Fig. 3 Comparison between the ranges of values of correction parameters $C_Z(Y_1,Y_2)$ and the ranges of the sums $B_Z(Y_1) + B_Z(Y_2)$ for bifunctional saturated aliphatic compounds of the type Y_1-C-C-Y_2 (Y_1,Y_2 = O,OH,NH_2).

values of correction parameters C_Z are always large and for each property generally possess the same sign independent of the nature of the Y_1,Y_2 pair. As seen in Fig. 3, where the cases of Y_1,Y_2 =O,OH,NH_2 and $n=2$ are taken into consideration, the interactions give a systematically positive contribution ($C_Z > 0$) to ΔG_h^o, ΔH_h^o, and $T\Delta S_h^o$,[3] but a negative contribution to $\Delta C_{p,h}^o$ and ΔV^*. If the C_Z values are compared with the sum $B_Z(Y_1)+B_Z(Y_2)$, it may be noticed (Fig. 3) that the interactions enhance the action of the hydrophilic groups in the case of $\Delta C_{p,h}^o$, while they generally oppose it for other properties. The C_Z values decrease with increasing distance between Y_1 and Y_2 groups following an exponential law. The values of the decay constant γ_Z are not large (see Table II) indicating a slow rate of decrease: particularly for partial molar volumes, the interactions are still clearly appreciable, as observed by others,(15) when Y_1 and Y_2 are separated by 5 or 6 carbon atoms.

No general behavior may be identified when the Y_1 and Y_2 groups are inserted in an unsaturated backbone (olefines, aromatics, and heteroaromatics). This is possibly due to the insufficient number of experimental data and also, perhaps, to a higher sensitivity of solvation to the internal structure of these molecules. Examination of the differences between experimental values and those calculated under the hypothesis of no interference between the hydrophilic groups (see Δ

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[3] Entropy effects were calculated, analogously to $B_{T\Delta S}$ values, from the corresponding enthalpy and free energy parameters.

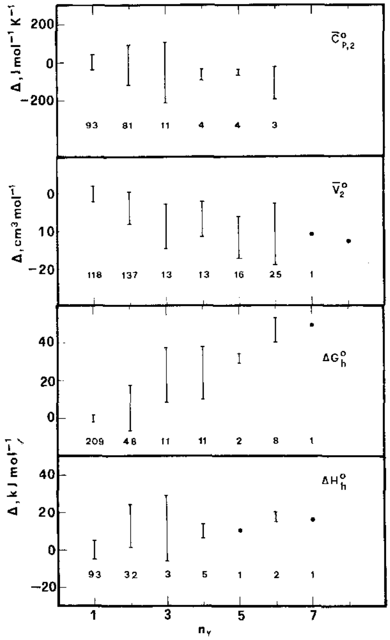

Fig. 4. Range of Δ from [Eq. (3)] *vs.* the number of functional groups for polyfunctional molecules $RY_1Y_2 \cdots Y_m$. The number of compounds yielding each range is indicated. For $n_Y = 1$, the number of compounds entering the regression analysis, and the corresponding range $\pm 3\sigma$, are reported.

values of the Appendix) permits recognition of 'singular' effects of interaction such as, for example: *i*) contrary to the general trend shown in Table II, the free energy of hydration of most disubstituted benzene derivatives is lower than that calculated considering Y_1 and Y_2 as independent groups; *ii*) the relative position of the hydrophilic groups proves sometimes unimportant thus allowing the definition of a single correction parameter for a certain Y_1, Y_2 couple (see the C_Z values reported in Table III for benzenediols, pyridinamines, and diazines). Importance seems instead to be given to the overall structure of the unsaturated hydrocarbon moiety. The Δ values observed in the case of $\overline{V}_2^o$ and $\overline{C}_{p,2}^o$ for quinazoline and quinoxaline result in fact sensibly different from the corresponding C_Z values of simple diazines mentioned above.

When the molecules contain more than two functional groups the situation may be very complex. Fig. 4 shows the ranges of Δ values [Eq. (3)] for polyfunctional molecules plotted against the number of functional groups n_Y. Despite the large spread of data at a fixed n_Y, it may be qualitatively observed that the interaction effects, inside each property, have generally the same sign and increase in magnitude with increasing number of functional groups. General rules which permit the description of the thermodynamic behavior in water of all these molecules taking into account the number, type and relative position of the Y groups are evidently not possible at this time. A quantitative description appears to be possible only when the molecules contain some repetitive structural feature. For instance, the $\overline{V}_2^\circ$ values of polymers such as poly(ethylene glycols) may be predicted by use of a single correction parameter (Table III).

7. CONCLUSION

This analysis of thermodynamic data for non-ionic organic molecules in aqueous solution reveals that water reacts in a very specific way with respect to organic solutes and, as a consequence, the thermodynamic properties in water of molecules showing many different structural features differ appreciably from those calculated as a sum of the contributions of each single feature. Therefore, the hope of achieving a good knowledge of the thermodynamic state in water of very complex molecules by using the information obtained from the study of small and simple molecules should be abandoned. However, the knowledge of group contributions is still useful in order to *i*) give a quantitative, although relative, estimate of the thermodynamic effects arising from the interaction of hydrophobic and hydrophilic groups with water, and *ii*) give a qualitative estimate of the effects caused by the presence of two or more functional groups.

Therefore, even in the absence of an accepted theory of hydration at the molecular level, the above information may assist studies of solvation of organic compounds in water, and thus may shed some light on the role played by solvation in equilibria and in rates of reactions in aqueous solution.

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APPENDIX

Tables V-VIII summarize the experimental data for the thermodynamic properties $\overline{C}^{\circ}_{P,2}$, $\overline{V}^{\circ}_{2}$, ΔG°_{h}, and ΔH°_{h}. In each table monofunctional and polyfunctional compounds are considered separately and are given in the order: hydrocarbons, alcohols and phenols, ethers, amines and pyridines, ketones, aldehydes, carboxylic acids, esters, amides, hydroxyethers, hydroxyamines, hydroxyacids, hydroxyamides, aminoethers, halo-compounds, thio-compounds, sugars, and miscellaneous compounds. Inside each class the compounds are subdivided into aliphatic, alicyclic, unsaturated, aromatic and ordered according to the number of carbon atoms. IUPAC nomenclature[(47)] has been generally used, except in a few cases where the common name was reported for the sake of simplicity.

The tables provide for each compound the experimental value, the relative source, and the difference $\Delta = Z(\text{exp})\text{-}Z(\text{calc})$, where the calculated value is obtained from the group contributions of Table I. In the case of polyfunctional compounds, one more Δ value is reported, where Z(calc) was computed using the data of Tables I to III. For reasons of uniformity, Δ values are sometimes reported with a number of figures which are inconsistent with the actual precision of the experimental data. In Tables V and VI values of the gas molar heat capacities, $C^{\circ}_{p,g}$, and van der Waals volumes, V_W, utilized to calculate $\Delta C^{\circ}_{p,h}$ and ΔV^{*} values are also given.

Sources of additional experimental data, not utilized in the calculations, are given within parentheses. The bibliography covers all literature up to December 1979.

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TABLE V. Molar Heat Capacities of Gases ($C^{\circ}_{p,gas}$) and Partial Molar Heat Capacities ($\bar{C}^{\circ}_{p,2}$) in Water at 25°C [a]

	MONOFUNCTIONAL COMPOUND	$C^{\circ}_{p,gas}$ [b]	$\bar{C}^{\circ}_{p,2}$(exp)	Ref.[c]	Δ[d]
1.	Methane	35.7^{e}	243.2^{f}	183 (4,181)	g
2.	Ethane	52.6^{e}	303.5^{f}	4 (181,183)	3.5
3.	Propane	73.5^{e}	368.3^{f}	4 (181,183)	-19.1
4.	Butane	97.5^{e}	470.5^{f}	183 (181)	-4.3
5.	2-Methylpropane	96.8^{e}	-47.6^{f}	183	-529.2^{h}
6.	Pentane	120.2^{e}	572	80	9.9
7.	2,2-Dimethylpropane	121.6^{e}	636.2^{f}	183	87.7^{h}
8.	Hexane	143.1^{e}	635	80	-14.4
9.	Cyclopropane	55.9^{e}	-367.3^{f}	183	-662.4^{h}
10.	Cyclohexane	106.3^{e}	516	80	5.3
11.	Ethene	43.6^{e}	243.0^{f}	4 (181,183)	-15.3
12.	1-Propene	63.9^{e}	-85.9^{f}	183	-432.1^{h}
13.	2-Methyl-1-propene	89.1^{e}	362.6^{f}	183	-71.6^{h}
14.	1,3-Butadiene	79.5^{e}	660.2^{f}	183	267.7^{h}
15.	Ethyne	43.9^{e}	221.9^{f}	183	23.5
16.	1-Propyne	60.7^{e}	393.5^{f}	183	107.2^{h}
17.	1-Butyne	81.4^{e}	-41.9^{f}	183	-415.6^{h}
18.	1-Buten-3-yne	73.2^{e}	118.8^{f}	183	-213.7^{h}
19.	Benzene	81.7^{e}	361	80 (104,181)	7.9
20.	Methylbenzene	103.6^{e}	430	80 (181)	12.8
21.	Ethylbenzene	128.4^{e}	504	80 (181)	-0.5
22.	1,3-Dimethylbenzene	127.6^{e}	538^{f}	181	56.7^{h}
23.	1,4-Dimethylbenzene	126.9^{e}	462^{f}	181	-19.3^{h}
24.	Propylbenzene	152.3^{e}	606	80	14.1
25.	(1-Methylethyl)benzene	151.7^{e}	488.9^{f}	181	-109.9^{h}
26.	9H-Fluorene	172.9	1244^{f}	181	730.1^{h}
27.	Naphthalene	132.6^{e}	476^{f}	181	14.5^{h}
28.	Acenaphthene	169.5	559^{f}	181	46.0^{h}
29.	Anthracene	191.3	392^{f}	181	-178.0^{h}
30.	Phenathrene	191.3	1292^{f}	181	722.0^{h}
31.	Pyrene	219.2	763^{f}	181	175.7^{h}
32.	Methanol	43.9^{e}	158.2	105 (3,7,8,67)	-21.4
33.	Ethanol	65.4^{e}	260.3	105 (3,7,8,67)	-6.6
34.	1-Propanol	87.1^{e}	352.9	105 (3,8,67)	-1.4
35.	2-Propanol	88.7^{e}	361^{i}	3,165 (7,8,142)	-0.2
36.	1-Butanol	110.0^{e}	437.0	105 (3,8)	-4.7
37.	2-Methyl-1-propanol	109.8	432.5	105 (8)	-16.0
38.	2-Butanol	113.3^{e}	449.1	105 (8,50)	0.6
39.	2-Methyl-2-propanol	113.4^{e}	464.0	105 (3,7,8,61, 167)	35.9
40.	1-Pentanol	132.9^{e}	523.8	105 (8,167)	-5.2
41.	3-Pentanol	136.0	539.8	105 (50)	3.9
42.	2-Methyl-2-butanol	136.9	520^{i}	8,165 (8)	4.6
43.	2,2-Dimethyl-1-propanol	134.9	503.5	105	-11.9
44.	1-Hexanol	155.8^{e}	606^{i}	93,165	-12.4
45.	3-Hexanol	159.0	653	50	29.8
46.	1-Heptanol	178.7^{e}	729^{i}	93,165	25.3
47.	2-Propen-1-ol	76.0^{e}	325^{i}	8,165 (8)	8.8
48.	2-Buten-1-ol	98.2	406^{i}	8,165 (86)	4.9
49.	3-Buten-1-ol	99.2	400^{i}	8,165 (86)	-0.5
50.	4-Penten-1-ol	122.2	433^{i}	8,165 (86)	-54.9^{h}
51.	3-Pentyn-1-ol	111.8	405^{i}	8,165	-23.5
52.	Cyclopentanol	103.1	448	50 (8)	11.7
53.	Cyclohexanol	127.2^{e}	515	50 (8)	6.8
54.	Cycloheptanol	152.0	561	50 (8)	-19.0
55.	2-Cyclohexen-1-ol	123.9	475^{i}	8,165	0.0^{j}
56.	Phenol	103.6^{e}	315	147 (101,140)	-1.1
57.	4-Methylphenol	124.5^{e}	384	140	3.8
58.	Benzenemethanol	112.6	396	140 (8)	11.9
59.	4-Ethylphenol	150.0	465	140	-2.6
60.	Benzeneethanol	142.4	462	140	-9.5
61.	Benzenepropanol	165.4	530	140	-28.8
62.	1,1'-Oxybisethane (Ethyl ether)	107.8	423	44	0.0^{j}
63.	Oxetane	59.8^{k}	209	44	-17.6
64.	Tetrahydrofuran	84.2	294.6	35 (21)	-3.9
65.	Tetrahydro-2H-pyran	107.1	373.2	35 (112)	2.9
66.	2-Methyltetrahydrofuran	109.3	435.1	35	18.7
67.	Ammonia	35.9^{k}	75	35	g
68.	Methanamine	50.1^{e}	155	35	-1.1
69.	1-Propanamine	95.8^{e}	327	114	-3.9
70.	2-Propanamine	95.3	342	114	4.3
71.	1-Butanamine	118.5^{e}	422	114	3.8
72.	2-Methyl-1-propananime	116.7	416	114	-9.1
73.	2-Methyl-2-propanamine	120.0^{e}	403	114	-1.6
74.	1-Pentanamine	140.8	515	114	9.4
75.	1-Hexanamine	163.9	603	114 (16)	10.1
76.	Cyclohexanamine	134.3	481	16	-3.7
77.	Benzenamine	108.4^{e}	307	140	0.0^{j}
78.	Benzenemethanamine	126.4	375	140	14.3
79.	Benzeneethanamine	149.3	445	140	-3.0
80.	Benzenepropanamine	172.3	516	140	-19.4
81.	N-Methylmethanamine	69.0^{e}	262.8	35	-46.9^{h}
82.	N-Methylethanamine	91.3	331.4	35	-65.6^{h}
83.	N-Ethylethanamine	115.7^{e}	486.6	35 (114)	2.3
84.	N-Ethyl-1-propananime	136.3	569.9	35	-1.8
85.	N-Propyl-1-propanamine	159.3	658.6	35	-0.4
86.	N-(1-Methylethyl)-2-propanamine	160.3	515^{i}	77,151	-158.8^{h}
87.	N-Butyl-1-butanamine	205.4	602^{i}	77,151	-231.7^{h}
88.	2-Methyl-N-(2-methylpropyl)-1-propanamine	203.1	643^{i}	77,151	-204.5^{h}
89.	N-(1-Methylpropyl)-2-butanamine	206.3	679^{i}	77,151	-168.5^{h}
90.	Pyrrolidine	81.1^{e}	333.5	35	-6.4
91.	Piperidine	106.2$^{\ell}$	424.7	35 (112)	12.9
92.	Hexahydro-1H-azepine	130.3$^{\ell}$	493.7	35	10.1
93.	2-Methylpiperidine	126.6$^{\ell}$	531	39	1.3
94.	4-Methylpiperidine	126.6$^{\ell}$	515	39	-14.7
95.	Octahydroazocine	154.4$^{\ell}$	552	35	-3.5
96.	N,N-Dimethylmethanamine	91.8^{e}	397	35 (21)	29.3
97.	N-Ethyl-N-methylethanamine	136.2	533.5	35	-9.0
98.	N,N-Diethylethanamine	160.9^{e}	609	16	-20.8
99.	1-Methylpyrrolidine	104.1$^{\ell}$	450	35	8.0
100.	1-Methylpiperidine	128.9$^{\ell}$	506	35	-8.0
101.	Pyridine	78.1^{e}	305.7	70	-5.5
102.	2-Methylpyridine	100.0^{e}	370.0	70	-5.3
103.	3-Methylpyridine	99.6^{e}	380.2	70	4.9
104.	4-Methylpyridine	102.2	378.9	70	3.6
105.	2,6-Dimethylpyridine	125.7	441.8	70	2.4
106.	Quinoline	133.6	419.6	71	0.0^{j}
107.	2-Propanone	74.9^{e}	241.3	113 (7)	-6.8
108.	2-Butanone	102.9^{e}	336.6	155	1.2
109.	3-Pentanone	127.1	428.3	155	5.6
110.	4-Methyl-2-pentanone	146.0	426	86	91.0^{h}
111.	2-Heptanone	170.2	438	86	-159.5^{h}
112.	4-Heptanone	173.1	416	86	-181.5^{h}
113.	2,4-Dimethyl-3-pentanone	178.9	422	86	-189.2^{h}
114.	Acetaldehyde	54.6^{e}	146	86	0.0^{j}
115.	Formic acid	45.2^{e}	95.5	114 (67,157)	16.7
116.	Acetic acid	66.5^{e}	165	114 (67,157,177)	-1.8
117.	Propanoic acid	92.8	253	114 (67,157)	-1.1
118.	Butanoic acid	115.8	337	114 (67,157)	-4.5
119.	2-Methylpropanoic acid	118.7	334	114	-14.3
120.	Pentanoic acid	138.8	432	114	3.2
121.	2,2-Dimethylpropanoic acid	139.8	417	114	1.8
122.	Benzoic acid	103.5^{e}	372	86	0.0^{j}
123.	Acetic acid methyl ester	93.1	298.2	155	-5.5
124.	Acetic acid ethyl ester	113.6^{e}	396.6	155 (168)	5.5
125.	Formamide	46.4^{e}	82	167 (21)	4.5
126.	Acetamide	65.4^{e}	160	167 (113)	-5.4
127.	Propanamide	92.6	253.6	155	0.9
128.	N-Methylformamide	71.5	164	167 (21,63)	-1.1
129.	N-Methylacetamide	90.5	258	167	5.0
130.	N-Ethylacetamide	112.4	343	114	2.7
131.	N-Methylpropanamide	116.4	334	114	-6.3
132.	N-Propylacetamide	135.4	437	114	9.3
133.	N-(1-Methylethyl)acetamide	135.9	441	114	6.5
134.	N-Methylbutanamide	139.4	434	114	6.3
135.	2-Methyl-N-methylpropanamide	142.0	431	114	-3.5
136.	N-Butylacetamide	158.5	516	167 (114)	1.0
137.	N-(1,1-Dimethylethyl)acetamide	160.5	498	114	-3.4
138.	2,2-Dimethyl-N-methylpropanamide	163.5	476	114	-25.4
139.	N-Methylpentanamide	162.4	524	167 (114)	9.0
140.	N,N-Dimethylformamide	88.9	225.1	62 (21)	0.0^{j}
141.	2-Pyrrolidinone	73.9	218.4	45	-5.3
142.	2-Piperidinone	98.7	300.8	45	5.3
143.	1-Methyl-2-pyrrolidinone	91.3	306.7	45	0.4
144.	1-Methyl-2-piperidinone	116.1	377.8	45	-0.4
145.	Fluoromethane	37.5^{e}	189.5^{f}	4 (183)	0.0^{j}
146.	Chloromethane	40.8^{e}	225.1^{f}	4 (183)	0.0^{j}
147.	Chloroethene	53.7^{e}	183.0^{f}	183	-88.4^{h}
148.	Bromomethane	42.4^{e}	243.2^{f}	4 (183)	0.0^{j}
149.	Iodomethane	44.1^{e}	461.7^{f}	4	0.0^{j}
150.	Sulfinylbismethane (Dimethylsulfoxide)	89.0^{k}	185.7	113 (7)	0.0^{j}
151.	Urea	56.5	87.5	149 (67,83)	g
152.	N,N-Dimethylurea	99.0	247.8	148	0.0^{j}
153.	N,N'-Dimethylurea	106.7	274.4	148	0.0^{j}
154.	Tetramethylurea	141.4	434.6	148	0.0^{j}

	POLYFUNCTIONAL COMPOUND	$C^{\circ}_{P,gas}$ [b]	$\bar{C}^{\circ}_{P,2}$(exp)	Ref.[c]	Δ[d]	Δ[m]
155.	1,2-Ethanediol	78.0	191.9	105 (65,141)	-42.0	12.1
156.	1,2-Propanediol	103.1	312.9	65	-15.2	38.9[h]
157.	1,3-Propanediol	101.0	269	141 (65)	-52.2	1.9
158.	1,4-Butanediol	124.0	346.8	105 (141)	-61.8	-7.7
159.	1,5-Pentanediol	147.0	439	141	-56.9	-2.8
160.	2,2-Dimethyl-1,3-propanediol	148.1	432.3	105	-50.0	4.1
161.	1,6-Hexanediol	170.0	521.6	105 (141)	-61.7	-7.6
162.	1,2,3-Propanetriol	116.2	240.2	65 (67)	-54.8	-7.4
163.	2-(Hydroxymethyl)-2-methyl-1,3-propanediol	161.2	373.3	105	-76.0	-28.9[n]
164.	(R^*,S^*)-1,2,3,4-Butanetetrol (Mesoerythritol)	154.4	310.0	65	-46.2	1.2
165.	2,2-Bis(hydroxymethyl)-1,3-propanediol (Pentaerythritol)	174.3	328.8	105	-87.4	-40.0[n]
166.	D-Arabinitol	192.6	374.6	65	-42.7	4.7
167.	L-Arabinitol	192.6	372.8	65	-44.5	2.9
168.	Ribitol	192.6	375.6	65	-41.7	5.7
169.	D-Xylitol	192.6	346.4	65	-70.9	-23.5
170.	D-Mannitol	230.8	455.4	65	-23.1	24.3
171.	Glucitol	230.8	423.1	65	-55.4	-8.0
172.	Dimethoxymethane	92.1	272	44	-11.9	-16.2
173.	Diethoxymethane	133.9	469	44	10.4	6.1
174.	1,2-Dimethoxyethane	122.0	364	44 (115)	-7.3	-11.6
175.	1-Ethoxy-2-methoxyethane	142.9	463	115	4.4	0.1
176.	1,2-Diethoxyethane	163.8	569	115	23.0	18.7
177.	1-(2-Methoxyethoxy)propane	165.9	563	115	17.0	12.7
178.	1-(2-Methoxyethoxy)butane	188.9	652	115	18.7	14.4
179.	1-(2-Propoxyethoxy)propane	209.8	701	115	-19.7	-24.0
180.	1,3-Dioxolane	71.6	174.9	35	16.7	10.1
181.	1,3-Dioxane	94.6	239	44	9.0	2.4
182.	1,4-Dioxane	94.6[e]	222.4	112 (21,35)	-7.6	-14.2
183.	1,3-Dioxepane	117.6	310	44	8.2	1.6
184.	1,1'-Oxybis(2-ethoxyethane)	219.7	697.8	155	28.8	—
185.	1,3,5-Trioxane	85.7	180	44	90.3	—
186.	2,4,6-Trimethyl-1,3,5-trioxane	191.4	406	44	-37.5	—
187.	2,5-Dimethoxytetrahydrofuran	165.1	410	44	-20.9	—
188.	1,2-Ethanediamine	91.8	160	44 (141)	-27.0	-4.7
189.	1,3-Propanediamine	114.8	256	141	-18.3	4.0
190.	1,4-Butanediamine	137.8	340	141	-21.7	0.6
191.	Piperazine	98.6[l]	276	39 (112)	-36.7	35.6
192.	2-Methylpiperazine	119.0[l]	356	39	-75.1	-2.8
193.	2,5-Dimethylpiperazine	139.4[l]	444	39	-105.2	-32.8
194.	1-Methylpiperazine	121.4[l]	343	39	-71.9	0.0[j]
195.	1,4-Dimethylpiperazine	144.2[l]	439	39	-77.9	0.0[j]
196.	Pyrazole	67.5	210.2	71	17.2	—
197.	Imidazole	67.5	182.1	71	-10.9	—
198.	Pyridazine	76.0	201.5	71	-67.9	-8.6
199.	Pyrimidine	76.0	211.3	71	-58.1	1.2
200.	Pyrazine	76.0	217.4	71	-52.0	7.3
201.	4-Phenylpyrimidine	158.1	461.9	71	11.3	70.6[h]
202.	2,2'-Bipyridine	158.1	498.3	71	47.7	—
203.	4,4'-Bipyridine	158.1	445.9	71	-4.7	—
204.	1H-Benzimidazole	125.1	302.8	71	1.3	—
205.	Quinazoline	131.0	365.1	71	-12.7	46.6[h]
206.	Quinoxaline	131.0	391.7	71	13.9	73.2[h]
207.	1,10-Phenanthroline	185.9	537.9	71	51.6	—
208.	1,3,5-Triazine	73.3	13.9	71	-213.6	—
209.	1H-Benzotriazole	122.4	314.8	71	55.2	—
210.	1H-Purin-6-amine (Adenine)	139.7	226.0	110	72.7	—
211.	Propanedioic acid	105.3	0.8	109	-120.0	—
212.	Butanedioic acid	133.7	225	141	16.8	0.0[j]
213.	Pentanedioic acid	156.7	271	141 (109)	-24.5	—
214.	Hexanedioic acid	179.4	336	141	-46.9	—
215.	Heptanedioic acid	202.8	410	141	-60.3	—
216.	2-Methoxyethanol	100.0	286.7	156 (115)	-15.9	-2.9
217.	2-Ethoxyethanol	120.9	383.5	156 (115)	-6.4	6.6
218.	2-Propoxyethanol	143.9	470.9	156 (115)	-6.4	6.6
219.	2-(1-Methylethoxy)ethanol	146.0	457	115	-27.2	-14.2
220.	2-Butoxyethanol	166.9	555.6	156 (115)	-9.0	4.0
221.	Tetrahydro-2-furanmethanol	122.4	333	21	-50.4	-14.1
222.	Tetrahydro-2H-pyran-2-methanol	145.3	433	21	-22.2	14.1
223.	2-Phenoxyethanol	158.2	459	140	[o]	—
224.	2-Aminoethanol	84.9	176	44	-34.4	9.3
225.	3-Amino-1-propanol	107.9	243	44	-54.8	-11.1
226.	4-Amino-1-butanol	130.9	343.2	106	-42.1	1.5
227.	5-Amino-1-pentanol	153.9	423.3	106	-49.4	-5.7
228.	6-Amino-1-hexanol	176.9	522.2	106	-37.9	5.8
229.	2-(Methylamino)ethanol	104.4	289	44	-74.9	-4.8
230.	2-(Ethylamino)ethanol	126.4	386	44	-65.3	4.8
231.	2-(Dimethylamino)ethanol	127.3	360	44	-62.0	2.9
232.	2-(Diethylamino)ethanol	171.3	529	44	-67.7	-2.9
233.	2,2'-Iminobisethanol	139.5	334.2	106	-84.2	—
234.	2,2'-(Ethylimino)bisethanol	184.4	482.3	106	-81.6	—
235.	2-Amino-2-(hydroxymethyl)-1,3-propanediol (TRIS)	159.1	268	86	-37.4	—
236.	2,2',2''-Nitrilotrisethanol	197.4	438.0	106	-92.9	—
237.	3-Hydroxybenzoic acid	124.8	306	86	-29.1	—
238.	4-Hydroxybenzoic acid	124.8	337	86	1.9	—
239.	2-Hydroxyacetamide	77.1	149.6	84	17.3	-0.2
240.	2-Hydroxypropanamide	98.8	244.3	85	17.7	0.2
241.	2-Methoxyethanamine	106.9	250	44	-29.1	-2.7
242.	2-Ethoxyethanamine	127.8	358	44	-8.5	17.9
243.	3-Methoxy-1-propanamine	129.9	325	44	-41.5	-15.1
244.	Morpholine	95.2[l]	234	39 (112)	-37.1	0.0[j]
245.	4-Methylmorpholine	117.9[l]	318	39	-55.6	0.0[j]
246.	Tetrafluoromethane	61.1[k]	440.8[e]	183	334.2	—
247.	Tetrafluoroethene	80.8[k]	377.1[e]	183	209.1	—
248.	1,1,2,3,3,3-Hexafluoro-1-propene	122.6	180.0[e]	183	-15.5	—
249.	Chlorofluoromethane	49.1[l]	203.3[e]	183	1.4	—
250.	Chlorodifluoromethane	53.2[l]	403.0[e]	183	217.3	—
251.	D-Glucose	208.2	251	67	-194.2	—
252.	Sucrose	375.2	649.4	65 (67,82)	-86.5	—
253.	2,5-Hexanedione	150.5	357	45	-13.9	0.0[j]
254.	1,4-Cyclohexanedione	116.6	310	45	[o]	—
255.	3-Nitrophenol	124.5	373.6	104	[o]	—
256.	4-Nitrophenol	124.5	357.7	104	[o]	—
257.	3-Hydroxybenzonitrile	96.9	362.8	104	[o]	—
258.	4-Hydroxybenzonitrile	96.9	363.6	104	[o]	—
259.	2,4(1H,3H)-Pyrimidinedione (Uracyl)	75.1	137	174	89.4	10.1
260.	1-Methyl-2,4(1H,3H)-pyrimidinedione	90.4	205.0	174	74.8	-4.5
261.	5-Methyl-2,4(1H,3H)-pyrimidinedione (Thymine)	100.7	220	174	84.5	5.2
262.	1,3-Dimethyl-2,4(1H,3H)-pyrimidinedione	105.8	295.0	174	82.2	2.9
263.	1,3,5-Trimethyl-2,4(1H,3H)-pyrimidinedione	131.4	373.0	174	72.3	-7.0
264.	1,3,6-Trimethyl-2,4(1H,3H)-pyrimidinedione	131.4	357.2	174	56.5	-22.8
265.	5-Ethyl-1,3-Dimethyl-2,4(1H,3H)-pyrimidinedione	152.8	473.4	174	85.3	6.0
266.	1,3-Diethyl-5-methyl-2,4(1H,3H)-pyrimidinedione	175.4	565.1	174	89.6	10.3
267.	2,5-Piperazinedione	123.2	149	45	68.9	23.1
268.	3,6-Dimethyl-2,5-piperazinedione	167.1	335	45	18.4	-27.4
269.	1,4-Dimethyl-2,5-piperazinedione	158.1	296	45	50.1	4.3
270.	4-Amino-2(1H)pyrimidinone (Cytosine)	91.3	208.5	110	105.9	—
271.	Theophylline	160.3	586	170	452.8	—
272.	Caffeine	184	669	170	443.6	—

(a) All quantities are given in J mol^{-1} K^{-1}

(b) Calculated from group contributions according to Benson (Refs. 14,15) unless otherwise indicated.

(c) Sources of experimental data. Sources of data not utilized in this work are enclosed in parentheses.

(d) $\Delta = \bar{C}^{\circ}_{P,2}(\mathrm{exp}) - \bar{C}^{\circ}_{P,2}(\mathrm{calc})$. Calculated values were obtained from Eq.2 using parameters reported in Table I.

(e) Experimental value from Stull (Ref.172).

(f) Evaluated by us as $\Delta C^{\circ}_{P,h} + C^{\circ}_{P,gas}$, where the hydration heat capacity is the experimental value.

(g) The whole molecule may be considered as a unique single group.

(h) Compound not used to determine any parameter of Tables I to III.

(i) Evaluated by us as $\Delta C^{\circ}_{P,s} + C^{\circ}_{P,\ell}$. The heat capacity of solution, $\Delta C^{\circ}_{P,s}$, and the molar heat capacity of the pure liquid, $C^{\circ}_{P,\ell}$, were taken from the first and second quoted reference, respectively.

(j) Single compound used to calculate one parameter of Table I or II.

(k) Experimental value from Benson (Ref.14).

(l) Calculated according to Rihani (Ref.153).

(m) $\Delta = \bar{C}^{\circ}_{P,2}(\mathrm{exp}) - \bar{C}^{\circ}_{P,2}(\mathrm{calc})$. Calculated values were obtained from Eq.1 using parameters reported in Tables I to III.

(n) Calculated using the correction parameter of polyols (Table III).

(o) This compound contains one or more groups not included in Table I.

TABLE VI. van der Waals Volumes (V_w) and Partial Molar Volumes ($\bar{V}_2^{\circ}$) in Water at 25°C [a]

	MONOFUNCTIONAL COMPOUND	V_w[b]	$\bar{V}_2^{\circ}$(exp)	Ref.[c]	Δ[d]
1.	Methane	17.1	37.3	130 (176)	e
2.	Ethane	27.3	51.2	130 (176)	-0.32
3.	Propane	37.6	67.0	130	-0.32
4.	Benzene	48.4	83.1	130	0.95
5.	Methylbenzene	59.5	97.71	59	-0.31
6.	Methanol	21.7	38.25	105 (2,76,92, 128,134,175)	-0.95
7.	Ethanol	31.9	55.12	105 (2,76,92, 128,134,175)	0.12
8.	1-Propanol	42.2	70.63	105 (2,76,92, 98,128,134, 175)	-0.17
9.	2-Propanol	42.2	71.93	98 (76,92)	1.34
10.	1-Butanol	52.4	86.48	105 (72,76,92, 98,128,134, 175)	-0.12
11.	2-Methyl-1-propanol	52.4	86.75	105 (72,76)	0.36
12.	2-Butanol	52.4	86.65	98 (36,72,76, 92,105)	0.26
13.	2-Methyl-2-propanol	52.4	87.73	105 (61,72,92, 136)	0.88
14.	1-Pentanol	62.6	102.88	105 (76,98,128, 134,175)	0.48
15.	2,2-Dimethyl-1-propanol	62.6	101.87	105	-0.78
16.	2-Pentanol	62.6	102.55	98	0.36
17.	3-Pentanol	62.6	101.28	36 (98,105)	-0.91
18.	2-Methyl-2-butanol	62.6	102.5[f]	136	-0.15
19.	1-Hexanol	72.9	117.56	128 (98)	-0.64
20.	2-Hexanol	72.9	118.49	98	0.50
21.	3-Hexanol	72.9	117.14	36	-0.85
22.	1-Heptanol	83.1	133.43	128	-0.56
23.	2-Heptanol	83.1	134.39	98	0.60
24.	3-Heptanol	83.1	133.3	98	-0.49
25.	4-Heptanol	83.1	133.2	36	-0.59
26.	2-Propen-1-ol	38.7	64.3	175	-0.50
27.	Cyclobutanol	44.3	75.6	69	1.42
28.	Cyclopentanol	53.6	89.06	36 (69)	0.79
29.	Cyclohexanol	63.5	103.54	36 (69)	1.18
30.	Cycloheptanol	73.3	116.88	36 (69)	-0.45
31.	Cyclooctanol	83.1	129.7	69	-0.85
32.	Cyclopropanemethanol	45.5	76.0	69	0.11
33.	α-Methylcyclopropanemethanol	55.7	92.4	69	0.92
34.	Cyclopentanemethanol	63.9	103.6	69	-0.47
35.	α-Methylcyclopentanemethanol	74.1	118.2	69	-1.46
36.	Cyclohexanemethanol	73.7	118.1	69	-0.06
37.	Phenol	53.9	86.17	88 (60,87,101)	0.00[g]
38.	Benzenemethanol	64.1	100.82[h]	76	-0.69
39.	1,1'-Oxybisethane (Ethyl ether)	51.5	90.4	69	0.00[g]
40.	2,2'-Oxybispropane	72.0	115.0	69	-6.58[i]
41.	Oxirane	23.5	45.5[j]	18	-3.32[i]
42.	Oxetane	32.5	61.35	119 (69)	-1.56
43.	Tetrahydrofuran	41.9	76.85	34 (69,74)	-0.15
44.	Tetrahydro-2H-pyran	51.7	91.73	34 (69,74,112)	0.64
45.	2-Methyltetrahydrofuran	52.1	94.00	34 (69)	0.27
46.	Oxepane	61.5	105.46	119 (69)	0.27
47.	2,5-Dimethyltetrahydrofuran	62.3	111.00	34 (69)	0.54
48.	Ammonia	13.8	24.86	36 (87,171)	e
49.	Methanamine	24.2	41.68	36 (87,107,178)	-0.67
50.	Ethanamine	34.4	58.37	36 (107)	0.22
51.	1-Propanamine	44.7	74.12	36 (107)	0.17
52.	2-Propanamine	44.7	75.5[h]	108	1.76
53.	1-Butanamine	54.9	89.8	36 (107)	0.05
54.	2-Methyl-1-propanamine	54.9	89.5[h]	108	-0.04
55.	2-Butanamine	54.9	89.1[h]	108	-0.44
56.	2-Methyl-2-propanamine	54.9	93.0[h]	108	3.00[i]
57.	1-Pentanamine	65.1	105.7	36	0.16
58.	1-Hexanamine	75.4	121.6	36	0.26
59.	1-Heptanamine	85.6	137.6	36	0.46
60.	Cyclopentanamine	56.1	90.98	163	-0.44
61.	Cyclohexanamine	66.0	105.35	163	-0.16
62.	Cycloheptanamine	75.8	118.50	163	-1.10
63.	Cyclooctanamine	85.6	133.4	163	-0.29
64.	Tricyclo[3,3,1,1^{3,7}]decan-1-amine (1-Adamantanamine)	92.0	138.9	163	-0.79[k]
65.	Benzenamine (Aniline)	56.4	89.30	171 (87)	0.00[g]
66.	Benzenemethanamine	66.6	104.7[h]	107	0.05
67.	N-Methylmethanamine	34.8	59.80	36 (87,107,178)	-0.29
68.	N-Ethylethanamine	55.3	91.68	36 (107)	-0.01
69.	N-Propyl-1-propanamine	75.8	123.06	36	-0.22
70.	N-Butyl-1-butanamine	96.2	155.4	36	0.52
71.	Aziridine	27.3	48.87	34	-0.48
72.	Azetidine	36.3	63.71	34	0.27
73.	Pyrrolidine	45.6	77.77	34 (108)	0.24
74.	Piperidine	55.5	92.13	41 (87,108, 112,117)	0.51
75.	Hexahydro-1H-azepine	65.3	105.55	34	-0.16
76.	Octahydroazocine	75.1	120.09	34	0.29
77.	2,6-Dimethylpiperidine	76.0	124.4	133	-0.67
78.	N,N-Dimethylmethanamine	45.3	78.8	36 (87,178)	4.45[i]
79.	N-Ethyl-N-methylethanamine	65.8	106.77	36	0.84
80.	N,N-Diethylethanamine	76.0	120.9	36 (178)	-0.84
81.	1-Methylpyrrolidine	56.2	97.29	34	0.42
82.	1-Methylpiperidine	66.0	110.54	34 (117)	-0.42
83.	Pyridine	45.5	77.3	133 (51,70,71, 87,108)	-0.59
84.	2-Methylpyridine	56.6	94.1	133 (51,70)	0.34
85.	3-Methylpyridine	56.6	93.7	133 (70)	-0.06
86.	4-Methylpyridine	56.6	93.7	133 (70)	-0.06
87.	2,6-Dimethylpyridine	67.8	110.0	133 (51,70)	0.37
88.	Quinoline	71.1	115.53	71	0.00[g]
89.	2-Propanone	39.0	66.8	69 (17,113)	0.10
90.	2-Butanone	49.3	82.9	69 (17,155)	0.40
91.	2-Pentanone	59.5	98.0	69	-0.29
92.	3-Pentanone	59.5	98.08	155	-0.21
93.	3-Methyl-2-butanone	59.5	95.0	69	-3.08[i]
94.	Cyclobutanone	41.2	70.9	69	-0.36
95.	Cyclopentanone	50.5	84.5	69	-0.85
96.	Cyclohexanone	60.4	99.7	69	0.26
97.	Cycloheptanone	70.1	113.8	69	0.27
98.	Cyclooctanone	79.9	128.0	69	0.38
99.	Cyclononanone	89.8	142.0	69	0.29
100.	Benzaldehyde	60.9	96.08	59	0.00[g]
101.	Formic acid	23.0	34.7	143 (55,87,111)	-1.83[i]
102.	Acetic acid	33.2	51.9	143 (55,87,111)	-0.90
103.	Propanoic acid	43.4	67.9	143 (55,87)	-0.70
104.	Butanoic acid	53.7	84.6	143 (55,87,111)	0.20
105.	Pentanoic acid	63.9	100.5	143 (95)	0.31
106.	2-Methylbutanoic acid	63.9	100.5	143	0.51
107.	3-Methylbutanoic acid	63.9	100.5	143	0.51
108.	2,2-Dimethylpropanoic acid	63.9	100.5	143	0.05
109.	Hexanoic acid	74.1	116.0	95	0.01
110.	Benzoic acid	65.6	98.77	59	0.00[g]
111.	Formic acid ethyl ester	42.5	72.8	69	0.36
112.	Acetic acid methyl ester	42.5	72.46	155	-0.45
113.	Acetic acid ethyl ester	52.7	88.8	69 (155)	0.09
114.	Dihydro-2(3H)-furanone (γ-Butyrolactone)	43.1	73.3	69	-0.99
115.	Dihydro-5-methyl-2(3H)-furanone	53.3	92.0	69	0.99
116.	Formamide	25.5	38.523	79 (17,55,64, 92,124)	-0.78
117.	Acetamide	35.7	55.824	79 (55,92,113, 124,125)	0.25
118.	Propanamide	45.9	71.540	79 (55,92,124, 155)	0.17
119.	Butanamide	56.1	87.1	92 (55)	-0.07
120.	Hexanamide	76.6	119.2	55	0.43
121.	N-Methylformamide	36.1	56.784	79 (63)	-0.77
122.	N-Ethylformamide	46.3	74.019	79	0.67
123.	N-Methylacetamide	46.3	74.039	79 (13,17)	0.21
124.	N-Propylformamide	56.5	87.891	79	-1.26
125.	N-Ethylacetamide	56.6	90.718	79 (13)	1.09
126.	N-Methylpropanamide	56.6	89.752	79	0.13
127.	N-Propylacetamide	66.8	105.090	79	-0.33
128.	N-Ethylpropanamide	66.8	105.390	79	-0.03
129.	N-Propylpropanamide	77.0	121.526	79	0.30
130.	2-Piperidinone	56.8	90.3	163	-0.31
131.	Hexahydro-2H-azepin-2-one	66.5	105.0	163	0.31
132.	N,N-Dimethylformamide	46.6	74.50	62 (79,92)	0.36
133.	N,N-Dimethylacetamide	56.8	90.510	79 (13,17,64, 92)	0.10
134.	N,N-Diethylformamide	67.0	107.146	79 (13)	1.41
135.	N,N-Dimethylpropanamide	67.1	105.364	79	-0.85
136.	N,N-Diethylacetamide	77.3	121.681	79 (13)	-0.33
137.	N,N-Diethylpropanamide	87.5	137.667	79 (13)	-0.13
138.	N,N-Dipropylacetamide	97.7	154.216	79 (13)	0.62
139.	N,N-Bis(1-methylethyl)acetamide	97.7	152.0	13	-1.19
140.	1-Methyl-2-pyrrolidinone	57.4	90.4	13	0.00[g]
141.	Fluoromethane	19.4	35.9	100	0.00[g]
142.	Chloromethane	25.3	46.2	100	0.00[g]
143.	Bromomethane	28.1	53.0	100	1.50
144.	Iodomethane	32.9	63.7	100	0.00[g]
145.	Bromoethane	38.3	66.7	175	-0.60
146.	1-Bromopropane	48.5	82.2	175	-0.90
147.	3-Bromo-1-propene	46.0	77.6	175	0.50
148.	1,1'-Thiobisethane (Diethyl sulfide)	58.6	99.5	175	0.00[g]
149.	Sulfinylbismethane (Dimethyl sulfoxide)	42.9	68.92	113 (64)	0.00[g]
150.	Benzenethiol	60.7	94.10	123	0.00[g]
151.	Acetonitrile	28.4	47.40	64	0.00[g]
152.	Ethanethioamide (Thioacetamide)	41.0	66.42	125 (163)	0.00[g]
153.	Carbonic acid dimethyl ester	46.0	77.6	69	-1.95
154.	Carbonic acid diethyl ester	66.5	113.1	69	1.95

MONOFUNCTIONAL COMPOUND	V_w^b	$\overline{V}_2^\circ$(exp)	Ref.^{c}	Δ^d
155. 1,3-Dioxolan-2-one	35.7	62.3	69	0.00^g
156. 2,5-Pyrrolidinedione	48.2	72.3	163	0.00^g
157. Nitrobenzene	62.6	97.71	59	0.00^g
158. Urea	32.6	44.238	89 (17,55,92, 103,124,125, 133)	•
159. Thiourea	37.9	54.793	103 (124,125, 163)	•
160. Carbamic acid ethyl ester (Urethane)	49.6	78.884	103	0.00^g
161. Methylurea	43.2	62.2	92 (124)	-1.10
162. Ethylurea	53.4	80.2	92	1.10
163 Propylurea	63.7	94.9	92	0.00
164. (1-Methylethyl)urea	63.7	99.0	92	4.31^i
165. Butylurea	73.9	116.1	92	5.40^i
166. N,N-Dimethylurea	53.7	78.88	148	0.00^g
167. N,N-Diethylurea	74.2	114.9	92	4.42^i
168. N,N'-Dimethylurea	53.8	80.04	148 (92,124, 125)	0.00^g
169. N,N'-Diethylurea	74.3	116.1	92	4.46^i
170. Tetramethylurea	74.8	115.30	148 (92,125)	0.00^g

POLYFUNCTIONAL COMPOUND	V_w^b	$\overline{V}_2^\circ$(exp)	Ref.^{c}	Δ^d	Δ^e
171. 1,2-Ethanediol	36.5	54.60	120 (65,69,90, 92,105,124, 129,134,136, 150,175)	-3.89	-0.06
172. 1,2-Propanediol	46.8	71.22	98 (65,136)	-2.86	0.97
173. 1,3-Propanediol	46.8	71.89	134 (65,69,129, 136,175)	-2.39	0.59
174. 2,3-Butanediol	57.0	86.56	98	-3.10	0.73
175. 1,3-Butanediol	57.0	88.32	98 (136)	-1.55	1.43^i
176. 1,4-Butanediol	57.0	88.35	98 (69,105,129, 134,136,175)	-1.73	0.59
177. 2,2-Dimethyl-1,3-propanediol	67.2	102.34	105	-3.79	-0.81
178. 2,4-Pentanediol	67.2	104.64	98	-0.82	2.16^i
179. 1,5-Pentanediol	67.2	104.35	98 (69,129, 134,175)	-1.53	0.28
180. 2,5-Hexanediol	77.5	120.5	40	-0.76	1.56^i
181. 1,6-Hexanediol	77.5	120.49	105 (69,134)	-1.19	0.22
182. 1,7-Heptanediol	87.7	136.40	98	-1.08	0.02
183. 1,8-Octanediol	97.9	152.6	69	-0.68	0.17
184. 1,10-Decanediol	118.4	184.4	69	-0.47	0.05
185. *cis*-1,2-Cyclohexanediol	68.1	101.3	69	-5.48	-1.65
186. *trans*-1,2-Cyclohexanediol	68.1	103.0	69	-3.78	0.05
187. 1,4-Cyclohexanediol (*cis*, *trans* mixture)	68.1	105.3	40	-1.48	0.84
188. 1-Methyl-*trans*-1,2-cyclohexanediol	78.3	116.6	69	-7.01	-3.18^i
189. *trans*-1,2-Cycloheptanediol	77.8	117.0	69	-3.87	-0.04
190. *cis*-1,5-Cyclooctanediol	87.7	132.5	69	-2.46	-0.65
191. Tricyclo[3,3,1,1^{3,7}]decane-1,3-diol (1,3-Adamantanediol)	94.1	138.2	69	-2.86^k	0.12
192. Tricyclo[3,3,1,1^{3,7}]decane-1,4-diol	94.1	139.3	69	-1.64^k	0.68
193. 1,2-Benzenediol	59.4	87.065	103	-3.14	-1.16
194. 1,3-Benzenediol	59.4	88.919	103	-1.29	0.69
195. 1,4-Benzenediol	59.4	88.696	103	-1.51	0.47
196. 1,2,3-Propanetriol	51.4	70.95^m	65 (92,124)	-6.61	0.95
197. 2-(Hydroxymethyl)-2-methyl-1,3-propanediol	71.8	102.30	105	-7.32	0.24^n
198. (R^*,S^*)-1,2,3,4-Butanetetrol (Mesoerythritol)	66.2	87.70^m	65 (124)	-9.53	0.55
199. 2,2-Bis(hydroxymethyl)-1,3-propanediol (Pentaerythritol)	76.4	101.81	105	-11.29	-0.21^n
200. D-Arabinitol	81.0	103.31^m	65	-12.39	0.21
201. L-Arabinitol	81.0	103.0	99 (65)	-12.70	-0.30
202. Ribitol	81.0	103.2	99 (65)	-12.50	0.10
203. D-Xylitol	81.0	102.4	99 (162)	-13.30	-0.70
204. Galactitol	95.8	119.3	99	-15.48	-0.36
205. D-Mannitol	95.8	119.33	98 (65,69,99)	-15.45	-0.33
206. Glucitol (Sorbitol)	96.8	119.9	99 (65,69)	-14.88	0.24
207. *myo*-Inositol	86.5	121	137	-3.42	—
208. Poly(vinyl alcohol) monomer unit	25.1	33.3^f	135	-1.57	0.95^n
209. Dimethoxymethane	45.0	80.42	119 (69)	-1.46	0.98^i
210. Diethoxymethane	65.4	113.88	119	0.40	2.84^i
211. 1,2-Dimethoxyethane	55.2	95.88	119 (69,90, 175)	-1.80	0.10
212. 1,2-Diethoxyethane	75.7	127.29	119	-2.00	-0.10
213. 1,3-Dioxolane	34.7	65.37	34 (69)	-4.78	-1.26
214. 1,3-Dioxane	44.5	80.82	119	-3.42	0.10
215. 1,4-Dioxane	44.5	80.96	34 (69,74, 112)	-3.28	—
216. 1,3-Dioxepane	54.3	95.98	119 (69)	-2.35	1.17
217. 1,1'-Oxybis(2-methoxyethane)	79.4	132.69	120 (69,90, 175)	-3.87	-0.19
218. 1,1'-Oxybis(2-ethoxyethane)	99.6	165.0	69 (156)	-3.16	0.52
219. 1,3,5-Trioxane	37.3	69.51	119 (69)	-7.87	—
220. 2,4,6-Trimethyl-1,3,5-trioxane	68.0	123.71	119	-3.85	—

POLYFUNCTIONAL COMPOUND	V_w^b	$\overline{V}_2^\circ$(exp)	Ref.^{c}	Δ^d	Δ^e
221. 2,5-Dimethoxytetrahydrofuran	69.7	122.34	119 (69)	-2.69	—
222. Tetramethoxymethane	72.8	126.2	69	-2.10	—
223. 2,5,8,11-Tetraoxadodecane	103.5	169.63	120 (90,180)	-5.81	-0.29
224. 2,5,8,11,14-Pentaoxapentadecane	127.7	206.66	120 (90)	-7.66	-0.30
225. 2,5-Dimethoxy-2-(dimethoxymethyl)-tetrahydrofuran	107.8	177.1	69	-10.71	—
226. 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6)	145.0	223.4	120	-2.50	—
227. Hydrazine	21.1	30.13	164	-3.06	0.39
228. 1,2-Ethanediamine	41.5	62.88	42 (107,118, 163)	-1.90	0.19
229. 1,2-Propanediamine	51.8	78.1^h	108	-2.27	-0.19
230. 1,3-Propanediamine	51.8	78.83	42 (163)	-1.75	-0.32
231. 1,4-Butanediamine	62.0	93.6	163 (108)	-2.77	-1.50^i
232. 1,5-Pentanediamine	72.2	109.40	163	-2.77	-1.78^i
233. 1,6-Hexanediamine	82.5	124.8	163	-3.17	-2.40^i
234. 1,7-Heptanediamine	92.7	141.52	163	-2.25	-1.65^i
235. 1,8-Octanediamine	102.9	157.3	163	-2.27	-1.80^i
236. 1,9-Nonanediamine	113.2	172.85	163	-2.52	-2.16^i
237. 1,10-Decanediamine	123.4	188.3	163	-2.86	-2.58^i
238. *trans*-1,4-Cyclohexanediamine	73.1	108.9	163	-4.17	-2.90^i
239. Piperazine	52.1	83.53	41 (112,163)	-1.76	0.00^g
240. 1-Methylpiperazine	62.6	102.30	41	-2.32	0.00^g
241. 1,4-Dimethylpiperazine	73.1	121.00	41	-2.96	0.00^g
242. 1,4-Diazabicyclo[2,2,2]octane	65.1	105.93	41 (163,182)	-8.10	—
243. 1,3,5,7-Tetraazatricyclo[3,3,1,1^{3,7}]-decane (HMT)	72.5	111.4	163	-5.73^k	—
244. Diethylenetriamine	69.5	101.2	118	-3.74	0.94
245. Triethylenetetramine	97.5	137.6	118	-7.51	-0.49
246. Tetraethylenepentamine	125.4	175.9	118	-9.38	-0.02
247. Poly(ethyleneimine) 600^o	28.1	38.61	118	-2.16	0.11^i
248. Poly(ethyleneimine) 1200^o	28.1	38.08	118	-2.41	-0.10^i
249. Poly(ethyleneimine) 1800^o	28.0	37.85	118	-2.52	-0.30^i
250. Poly(ethyleneimine) 50000^o	28.0	37.16	118	-3.02	-0.68^i
251. Poly(ethyleneimine) 75000^o	28.0	37.42	118	-2.75	-0.41^i
252. Poly(ethyleneimine) monomeric unit	28.0	37.5	118	-2.67	-0.33
253. 2-Pyridinamine	53.5	83.0	133	-2.06	0.40
254. 3-Pyridinamine	53.5	82.1	45	-2.96	-0.50
255. 4-Pyridinamine	53.5	82.7	45	-2.36	0.10
256. Pyrazole	36.2	62.26	71	-0.47	—
257. Imidazole	36.2	59.95	71	-2.78	—
258. Pyridazine	42.6	70.42	71	-3.20	-0.40
259. Pyrimidine	42.6	70.33	71	-3.29	-0.49
260. Pyrazine	42.6	70.82	71	-2.80	0.00
261. 4-Phenylpyrimidine	85.9	134.09	71	-1.91	0.89
262. 2,2'-Bipyridine	85.9	134.29	71	-1.71	—
263. 4,4'-Bipyridine	85.9	133.21	71	-2.79	—
264. 1H-Benzimidazole	61.8	98.53	71	-3.67	—
265. Quinazoline	68.2	108.48	77	-4.61	-1.81^i
266. Quinoxaline	68.2	109.16	71	-3.93	-1.13^i
267. 1,10-Phenanthroline	93.8	142.42	71	-10.13	—
268. 1,3,5-Triazine	39.7	54.79	71	-14.57	—
269. 1H-Benzotriazole	58.9	94.49	71	-3.44	—
270. Ethanedioic acid	39.2	49.12	97	-4.96	-0.44
271. Propanedioic acid	49.3	67.22	97	-2.66	0.86^i
272. Butanedioic acid	59.5	82.94	97 (125)	-2.74	0.00^g
273. Pentanedioic acid	69.7	99.14	97	-2.33	-0.20
274. Hexanedioic acid	80.0	115.66	97	-1.61	0.05
275. Heptanedioic acid	90.2	131.93	97	-1.14	0.15
276. Poly(acrylic acid) monomeric unit	35.8	46.2	77	-2.26	—
277. Ethanediamide	44.2	55.0	163	-4.63	-0.62
278. Propanediamide	54.3	72.6	163	-2.82	0.29
279. Butanediamide	64.5	88.8	163	-2.43	0.00^g
280. 2-Acetamido-N-methylpropanamide	85.8	126.1	17	-1.42	—
281. N,N,N',N'-Tetramethylheptanediamide	137.5	211	57	2.71	—
282. N,N,N',N'-Tetramethyloctanediamide	147.7	224	57	-0.09	—
283. N,N,N',N'-Tetramethylnonanediamide	157.9	236	57	-3.89	—
284. N,N,N',N'-Tetramethyldecanediamide	168.1	250	57	-5.69	—
285. 2,4-Imidazolidinedione	44.8	65.0	163	-4.18	—
286. Dihydro-2,4-(1H,3H)-pyrimidinedione	54.6	76.3	163	-6.97	—
287. 2,5-Piperazinedione	55.1	76.7	45	-6.57	—
288. 3,6-Dimethyl-2,5-piperazinedione	75.5	112.4	45	-4.33	—
289. 1,4-Dimethyl-2,5-piperazinedione	76.1	113.4	45	2.37	—
290. Poly(N-methylacrylamide) monomeric unit	49.9	66.6	17	-2.89	—
291. 2-Methoxyethanol	45.9	76.11	156 (90)	-2.97	-0.21
292. 2-Ethoxyethanol	56.1	90.97	156 (90)	-2.91	-0.15
293. 2-Propoxyethanol	66.3	107.10	156 (90)	-2.58	0.18
294. 2-Butoxyethanol	76.6	122.91	156 (90)	-2.57	0.19
295. Tetrahydro-2-furanmethanol	56.7	93.8	74	-3.41	-0.10

	POLYFUNCTIONAL COMPOUND	V_w^b	$\bar{V}_2^o$(exp)	Ref.[c]	Δ^d	Δ^ℓ
296.	Tetrahydro-2h-pyran-2-methanol	66.5	108.1	74	-3.21	0.10
297.	Diethylene glycol	60.7	92.17	120 (90,158)	-5.20	-1.52
298.	Triethylene glycol	84.9	129.27	120 (90,158)	-6.98	-1.46
299.	Tetraethylene glycol	109.0	166.25	120 (90,158)	-8.88	-1.52
300.	Pentaethylene glycol	133.2	203.85	158	-10.16	-0.96
301.	Hexaethylene glycol monododecyl ether	279.2	435.6	91	-10.67	0.37
302.	Heptaethylene glycol monododecyl ether	303.4	472.7	91	-12.45	0.43
303.	Octaethylene glycol monododecyl ether	327.5	509.7	91	-14.33	0.39
304.	Poly(ethylene glycol) 284 [o]	24.5	37.41	158	-2.05	-0.33^i
305.	Poly(ethylene glycol) 600 [o]	24.3	37.14	120 (158)	-2.02	-0.23^i
306.	Poly(ethylene glycol) 1000 [o]	24.3	37.03	120 (158)	-2.02	-0.21^i
307.	Poly(ethylene glycol) 2000 [o]	24.2	36.96	120	-2.00	-0.18^i
308.	Poly(ethylene glycol) 15000 [o]	24.2	36.87	120	-2.02	-0.18^i
309.	Poly(ethylene glycol) 20000 [o]	24.2	36.9	18	-2.09	-0.25^i
310.	Poly(ethylene glycol) monomeric unit	24.2	36.9	120 (90,158)	-1.98	-0.14
311.	Dipropylene glycol	81.1	124.64	158	-3.90	-0.22
312.	Tripropylene glycol	115.5	177.61	158	-5.40	0.12
313.	Tetrapropylene glycol	149.9	231.36	158	-6.12	1.24
314.	Pentapropylene glycol	184.3	283.75	158	-8.20	1.00
315.	Poly(propylene glycol) 313 [o]	34.7	53.35	158	-3.00	-1.27^i
316.	Poly(propylene glycol) 410 [o]	34.6	53.17	158	-1.67	-0.09^i
317.	Poly(propylene glycol) 940 [o]	34.5	53.13	158	-1.50	-0.30^i
318.	Poly(propylene glycol) monomeric unit	34.4	53.09	158	-1.38	0.46
319.	2-Aminoethanol	39.0	59.25	42 (106,108)	-2.38	0.00^g
320.	3-Amino-1-propanol	49.3	75.21	42 (106)	-2.22	-0.37
321.	4-Amino-1-butanol	59.5	91.17	106	-2.07	-0.63
322.	5-Amino-1-pentanol	69.7	107.07	106	-1.97	-0.85
323.	6-Amino-1-hexanol	80.0	123.36	106	-1.48	-0.60
324.	2-(Methylamino)ethanol	49.7	77.07	42	-2.30	-0.02
325.	2-(Ethylamino)ethanol	59.9	92.91	42	-2.26	0.02
326.	2-(Dimethylamino)ethanol	60.2	94.17	42	0.54	2.72^i
327.	2-(Diethylamino)ethanol	80.6	123.04	42 (106)	-2.18	0.00^g
328.	3-Pyridinol	51.0	75.4	133	-6.51	—
329.	2,2'-Iminobisethanol (Diethanolamine)	64.5	94.35	106	-4.31	—
330.	2,2'-(Ethylimino)bisethanol	85.2	125.01	106	-3.71	—
331.	2,2',2"-Nitrilotrisethanol (Triethanolamine)	89.8	127.76	106	-4.44	—
332.	2-Hydroxyacetic acid	37.8	51.75	96	-4.53	-1.95
333.	2-Hydroxypropanoic acid	48.0	69.38	96	-2.49	0.09
334.	2-Hydroxybutanoic acid	58.3	85.45	96	-2.22	0.36
335.	2-Hydroxy-2-methylpropanoic acid	58.3	86.78	96	-1.35	1.23
336.	2-Hydroxypentanoic acid	68.5	100.47	96	-3.00	-0.42
337.	2-Hydroxy-3-methylbutanoic acid	68.5	100.83	96	-2.43	0.15
338.	2-Hydroxyhexanoic acid	78.7	117.26	96	-2.01	0.57
339.	L-Tartaric acid	68.7	83.45	131	-8.77	—
340.	*meso*-Tartaric acid	68.7	82.90	131	-9.32	—
341.	2-Hydroxyacetamide	40.3	56.2	164 (84,124)	-2.86	-0.16
342.	2-Hydroxypropanamide	50.5	73.12	164 (85)	-1.53	1.17^i
343.	4-Hydroxybutanamide	60.7	88.90	164	-1.75	-0.11
344.	4-Hydroxypentanamide	71.0	105.1	164	-1.14	0.50
345.	5-Hydroxypentanamide	71.0	105.4	164	-1.05	0.23
346.	6-Hydroxyhexanamide	81.2	121.1	164	-1.15	-0.16
347.	4-Hydroxyoctanamide	101.7	151.9	164	-1.74	-0.10
348.	4-Hydroxydecanamide	122.1	183.3	164	-1.94	-0.30
349.	2-Methoxyethanamine	48.4	79.59	42	-1.64	0.00^g
350.	3-Methoxy-1-propanamine	58.6	95.55	42	-1.48	-0.20
351.	Morpholine	48.3	82.56	41 (108,112)	-2.20	0.00^g
352.	4-Methylmorpholine	58.8	101.28	41	-2.82	0.00^g
353.	Dichloromethane	34.7	58.06	2	1.38	—
354.	Trichloromethane	43.5	72.3	137	5.35	—
355.	L-Arabinose	70.1	93.2	99 (162)	-15.54	-0.70
356.	D-Ribose	70.1	95.2	99 (75,125)	-13.54	1.30
357.	2-Deoxy-D-ribose	65.5	93.8	162	-10.53	0.60
358.	D-Xylose	70.1	95.4	99 (162)	-13.34	1.50
359.	D-Fructose	84.9	110.4	162	-18.66	-0.11
360.	D-Galactose	84.9	110.2	99 (75,162)	-18.75	-0.20
361.	D-Glucose	84.9	112.04	125 (75,99, 124,162)	-16.91	1.64
362.	2-Deoxy-D-glucose	80.3	110.4	162	-14.14	0.70
363.	D-Mannose	84.9	111.7	162 (99)	-17.25	1.30
364.	L-Sorbose	84.9	110.6	162	-18.46	0.09
365.	Cellobiose	157.4	213.6	162	-24.70	4.98^i
366.	Lactose	157.4	209.1	99 (162)	-29.20	0.48
367.	Maltose	157.4	208.8	162 (99)	-29.50	0.18
368.	Melibiose	157.4	204.0	162	-34.30	-4.62^i
369.	Sucrose	157.8	211.6	99 (65,78, 125,159,162)	-28.51	1.17
370.	Trehalose	157.4	206.9	162	-31.40	-1.72
371.	Cellotriose	229.9	309.2	162	-38.45	2.36
372.	4-O-β-Laminaribiosyl-D-glucose	229.9	312.2	162	-35.45	5.36^i
373.	Maltotriose	229.9	304.8	162	-42.85	-2.04
374.	Melezitose	230.3	310.0	99 (162)	-39.46	1.35
375.	D-Raffinose	230.3	307.0	99 (162)	-42.46	-1.65
376.	2-O-β-Cellotriosylglycerol	268.9	359.5	162	-46.10	-1.58
377.	Cellotetraose	302.5	409.0	162	-48.00	3.94
378.	3-O-β-Cellotriosyl-D-glucose	302.5	410.5	162	-46.50	5.44^i
379.	4-O-β-Laminaribiosylcellobiose	302.5	410.5	162	-46.50	5.44^i
380.	Stachyose	302.9	401.0	162	-57.81	-5.87^i
381.	Cellopentaose	375.0	499.6	162	-66.74	-3.67
382.	Cellohexaose	447.5	601.7	162	-73.99	0.21
383.	Soluble starch monomeric unit	72.5	97.5	162	-11.85	-0.72
384.	Amylose monomeric unit	72.5	99.0	162	-10.35	0.78
385.	α-Cyclodextrin	435.5	602.0	162	-67.50	-0.72
386.	β-Cyclodextrin	507.6	710.8	162	-68.04	9.87^i
387.	Methyl-α-D-galactopyranoside	94.2	132.6	162	-15.95	-1.11
388.	Methyl-β-D-galactopyranoside	94.2	132.9	162	-15.65	-0.81
389.	Methyl-α-D-glucopyranoside	94.2	132.6	162 (24,75)	-15.95	-1.11
390.	Methyl-β-D-glucopyranoside	94.2	133.6	162 (75)	-14.95	-0.11
391.	3-O-Methyl-D-glucose	94.2	134.0	162	-14.55	0.29
392.	Methyl-α-D-mannopyranoside	94.2	132.9	162	-15.65	-0.81
393.	Ethyl-α-D-glucopyranoside	104.5	149.45	24	-14.95	-0.11
394.	Hexyl-α-D-glucopyranoside	145.4	215.6	24	-11.94	2.90
395.	Octyl-α-D-glucopyranoside	165.8	246.8	24	-12.34	2.50
396.	Cyclohexyl-α-D-glucopyranoside	136.0	197.4	24	-14.31	0.53
397.	Cyclohexyl-α-D-mannopyranoside	136.0	197.7	24	-14.01	0.83
398.	Phenyl-β-D-glucopyranoside	126.4	177.5	162	-17.56	-2.72
399.	Methyl-β-cellobioside	166.7	231.0	162	-26.90	-0.93
400.	Phenyl-β-cellobioside	198.9	283.6	162	-20.80	5.17^i
401.	Phenyl-β-lactoside	198.9	283.3	162	-21.10	4.87^i
402.	Permethylated β-cyclodextrin	703.6	1077	162	-113.42	—
403.	Galacturonic acid	86.2	107.6	99	-19.15	—
404.	Glucuronic acid	86.2	110.2	99	-16.55	—
405.	2-(Hexylsulfinyl)ethanol	108.9	166.5	52	-0.69	0.00
406.	3-(Hexylsulfinyl)-1-propanol	119.1	182.3	52	-0.69	-0.15
407.	4-(Hexylsulfinyl)-1-butanol	129.3	198.3	52	-0.49	-0.06
408.	2-(Octylsulfinyl)ethanol	129.3	198.1	52	-0.69	0.00
409.	3-(Octylsulfinyl)-1-propanol	139.6	213.9	52	-0.69	-0.15
410.	4-(Octylsulfinyl)-1-butanol	149.8	229.9	52	-0.49	-0.06
411.	2,5-Hexanedione	71.2	111.6	69	-1.87	0.00^g
412.	1,4-Cyclohexanedione	61.9	92.8	69	-8.12	—
413.	Ethanedioic acid dimethyl ester	57.9	91.4	69	-2.90	—
414.	Methoxyacetic acid methyl ester	56.4	93.3	69	-2.69	—
415.	Acetic acid methoxymethyl ester	56.4	94.4	69	-1.59	—
416.	5-Hydroxytricyclo$[3,3,1,1^{3,7}]$-decanone (2-Adamantanone)	91.0	137.2	69	-0.83^k	—
417.	Hydrazinecarbothioamide	45.4	64.0	163	e	—
418.	2-Thioxo-4-imidazolidinone	50.1	76.5	163	p	—
419.	3-Hydroxybenzaldehyde	66.5	97.87	121	-2.25	—
420.	4-Hydroxybenzaldehyde	66.5	96.94	121	-3.18	—
421.	3-Nitrophenol	68.2	99.71	121	-2.04	—
422.	4-Nitrophenol	68.2	98.23	121	-3.52	—
423.	3-Hydroxybenzonitrile	66.1	97.5	101	p	—
424.	4-Hydroxybenzonitrile	66.1	98.3	101	p	—
425.	Caffeine	97.3	144.2	46	-7.16	—

(a) All quantities are given in $cm^3 mol^{-1}$

(b) Van der Waals volumes were evaluated using group contribution reported by Bondi (Refs. 19,20), except for H(C), O(ether), COO, NH, and CS groups, whose values were taken from Edward (Ref.68). Ring corrections were applied following Edward (Ref.69) and Shahidi (Ref.163).

(c) Sources of experimental data. Sources of data not utilized in this work are enclosed in parentheses.

(d) $\Delta = \bar{V}_2^o(exp) - \bar{V}_2^o(calc)$. Calculated values were obtained from Eq.2 using parameters reported in Table I.

(e) The whole molecule may be considered as a unique single group.

(f) At 30°C.

(g) Single compound used to calculate one parameter of Table I or II.

(h) At 20°C.

(i) Compound not used to determine any parameter of Tables I to III.

(j) At 10°C.

(k) Calculated using the correction parameter for the adamantane ring system (Table III).

(l) $\Delta = \bar{V}_2^o(exp) - \bar{V}_2^o(calc)$. Calculated values were obtained from Eq.1 using parameters reported in Tables I to III.

(m) At 24°C.

(n) Calculated using the correction parameter of polyols (Table III).

(o) The number next to the name is the molecular weight given by the authors. Reported quantities refer to one mole of monomer unit.

(p) This compound contains one or more groups not included in Table I.

TABLE VII. Free Energies of Hydration (ΔG_h°) at 25°C [a]

	MONOFUNCTIONAL COMPOUND	ΔG_h°(exp)	Ref.[b]	Δ^c
1.	Methane	8.37	183 (4,27,29,94, 139,181)	d
2.	Ethane	7.66	183 (4,27,29,94, 139,181)	0.26
3.	Propane	8.18	183 (4,94,139,181)	0.04
4.	Butane	8.70	183 (4,27,29,94, 139,181)	-0.18
5.	2-Methylpropane	9.70	183 (94)	0.19
6.	Pentane	9.76	94 (138)	0.14
7.	2-Methylbutane	9.97^{e}	22,132	-0.28
8.	2,2-Dimethylpropane	10.46	183 (94)	0.59
9.	Hexane	10.40^{e}	66,127 (94,138)	0.03
10.	2-Methylpentane	10.56	94	-0.43
11.	3-Methylpentane	10.50	94	-0.49
12.	2,2-Dimethylbutane	10.85	94	0.24
13.	Heptane	10.96	94 (138)	-0.15
14.	2,4-Dimethylpentane	12.04	94	-0.32
15.	Octane	12.10	94 (138)	0.25
16.	2,2,4-Trimethylpentane	11.93	94	-0.79
17.	2,2,5-Trimethylhexane	11.39^{e}	22,132	-2.07^{f}
18.	Cyclopropane	3.13	183	-0.18
19.	Cyclopentane	5.02	94	0.20
20.	Cyclohexane	5.14	94	-0.43
21.	Methylcyclopentane	6.68	94	1.02
22.	Cycloheptane	3.33^{e}	22,132	-2.99^{f}
23.	Methylcyclohexane	7.14	94	0.73
24.	Cyclooctane	3.58^{e}	22,132	-3.49^{f}
25.	*cis*-1,2-Dimethylcyclohexane	6.62	94	-0.63
26.	Ethene	5.32	183 (4,94,181)	-0.31
27.	1-Propene	5.31	94 (183)	0.10
28.	1-Butene	5.77	94	-0.18
29.	2-Methyl-1-propene	4.87	183 (94)	0.09
30.	1-Pentene	6.96	94	0.27
31.	*trans*-2-Pentene	5.59	94	0.06
32.	2-Methyl-2-butene	5.48	94	1.12
33.	3-Methyl-1-butene	7.65	94	0.33
34.	1-Hexene	7.02	94	-0.41
35.	2-Methyl-1-pentene	6.15^{e}	66,132	-0.12
36.	4-Methyl-1-pentene	7.99	94	-0.07
37.	*trans*-2-Heptene	6.96	94	-0.05
38.	1-Octene	9.08	94	0.16
39.	Cyclopentene	2.34	94	0.47
40.	Cyclohexene	1.54	94	-1.08
41.	1-Methylcyclohexene	2.80	94	0.61
42.	1,3-Butadiene	2.57	183 (94)	-0.45
43.	1,4-Pentadiene	3.94	94	0.38
44.	2-Methyl-1,3-butadiene	2.85	94	0.26
45.	1,5-Hexadiene	4.22	94	-0.28
46.	2,3-Dimethyl-1,3-butadiene	1.66	94	-0.51
47.	1,3,5-Cycloheptatriene	-4.14^{e}	22,132	-1.61^{f}
48.	Ethyne	-0.05	183 (94)	0.38
49.	1-Propyne	-1.28	183 (94)	-0.42
50.	1-Butyne	-0.68	94 (183)	-0.56
51.	1-Pentyne	0.06	94	-0.56
52.	1-Hexyne	1.20	94	-0.17
53.	1-Heptyne	2.51	94	0.40
54.	1-Octyne	2.97	94	0.12
55.	1-Nonyne	4.40	94	0.81
56.	1-Buten-3-yne	0.17	183	3.22^{f}
57.	Benzene	-3.62	181 (4,6,94)	0.30
58.	Methylbenzene	-3.71	181 (6,94)	0.13
59.	Ethylbenzene	-3.33	181 (6,94)	-0.23
60.	1,2-Dimethylbenzene	-3.77	94	-0.01
61.	1,3-Dimethylbenzene	-3.50	181 (6,94)	0.26
62.	1,4-Dimethylbenzene	-3.37	181 (6,94)	0.39
63.	Propylbenzene	-2.23	94	0.13
64.	(1-Methylethyl)benzene	-1.26	94 (181)	0.47
65.	1,2,4-Trimethylbenzene	-3.60	94	0.08
66.	Butylbenzene	-1.66	94	-0.05
67.	(1-Methylpropyl)benzene	-1.88	94	-0.89
68.	(1,1-Dimethylethyl)benzene	-1.83	94	-0.46
69.	(1,1-Dimethylpropyl)benzene	-0.74	94	-0.11
70.	1,1'-Biphenyl	-11.06^{e}	23,127	4.02^{f}
71.	1,1'-Methylenebisbenzene	-11.78^{e}	1,58	2.56^{f}
72.	9H-Fluorene	-14.41^{e}	23,127 (181)	6.10^{f}
73.	Naphthalene	-10.01^{e}	23,127 (94,181)	0.75
74.	1-Methylnaphthalene	-9.91^{e}	66,127	0.77
75.	1-Ethylnaphthalene	-10.02^{e}	66,127	-0.08
76.	1,3-Dimethylnaphthalene	-10.35^{e}	66,127	0.25
77.	1,4-Dimethylnaphthalene	-11.79^{e}	66,127	-1.19
78.	2,3-Dimethylnaphthalene	-11.64^{e}	1,127	-1.04
79.	2,6-Dimethylnaphthalene	-11.00^{e}	1,127	-0.40
80.	Acenaphthene	-13.17^{e}	1,127 (94,181)	2.27^{f}
81.	Anthracene	-17.70^{e}	23,127 (94,181)	-0.10
82.	Phenanthrene	-16.53^{e}	23,127 (94,181)	1.07
83.	Pyrene	-18.68^{e}	23,127 (181)	4.10^{f}
84.	Methanol	-21.40	26 (94)	0.32
85.	Ethanol	-20.98	26 (94)	0.00
86.	1-Propanol	-20.19	26	0.05
87.	2-Propanol	-19.90	26	-0.28
88.	1-Butanol	-19.73	26 (30)	-0.23
89.	2-Methyl-1-propanol	-18.93	26	-0.06
90.	2-Butanol	-19.15	38 (26)	-0.28
91.	2-Methyl-2-propanol	-18.89	26	0.36
92.	1-Pentanol	-18.72	26	0.04
93.	3-Methyl-1-butanol	-18.50	26	-0.37
94.	2-Pentanol	-18.38	26	-0.25
95.	3-Pentanol	-18.22	38	-0.09
96.	2-Methyl-2-butanol	-18.54	26	-0.03
97.	1-Hexanol	-18.26	26 (30)	-0.25
98.	2,3-Dimethyl-2-butanol	-16.38	94	0.76
99.	3-Hexanol	-17.05	38 (94)	0.34
100.	4-Methyl-2-pentanol	-15.64	94	1.12
101.	2-Methyl-3-pentanol	-16.26	94	0.50
102.	2-Methyl-2-pentanol	-16.44	94	1.33
103.	1-Heptanol	-17.76	26	-0.49
104.	4-Heptanol	-16.76	38	-0.12
105.	1-Octanol	-17.13	26 (30)	-0.60
106.	2-Propen-1-ol	-21.06	94	2.11^{f}
107.	Cyclopentanol	-22.99	38	0.47
108.	Cyclohexanol	-22.91	38 (94)	-0.20
109.	Cycloheptanol	-22.95	38	-0.99
110.	Phenol	-27.68	145	-1.32
111.	2-Methylphenol	-24.58	146	1.70
112.	4-Methylphenol	-25.67	146	0.61
113.	4-(1,1-Dimethylethyl)phenol	-24.79	146	-0.92
114.	Oxybismethane (Methyl ether)	-7.93	94	0.45
115.	1,1'-Oxybisethane	-6.84	166(27)	0.05
116.	1-Methoxypropane	-6.96	94	-0.07
117.	2-Methoxypropane	-8.39	94	-2.13^{f}
118.	1-Ethoxypropane	-7.59	27	-1.44
119.	2-Methoxy-2-methylpropane	-9.25	94	-3.35^{f}
120.	1,1'-Oxybispropane (Propyl ether)	-4.83	27	0.58
121.	2,2'-Oxybispropane	-2.23	94	1.92^{f}
122.	1,1'-Oxybisbutane	-3.48	94	0.44
123.	Tetrahydrofuran	-14.52	33 (166)	-0.29
124.	Tetrahydro-2H-pyran	-13.07	33	0.40
125.	2-Methyltetrahydrofuran	-13.82	33	-0.43
126.	2,5-Dimethyltetrahydrofuran	-12.22^{i}	33	0.33
127.	Methoxybenzene	-4.34	94	0.00^{g}
128.	Methanamine	-19.09	48	0.81
129.	Ethanamine	-18.84	48 (27)	0.32
130.	1-Propanamine	-18.37	48 (27)	0.05
131.	1-Butanamine	-17.97	48 (27)	-0.29
132.	1-Pentanamine	-17.14	48	-0.20
133.	1-Hexanamine	-16.87	48	-0.68
134.	N-Methylmethanamine	-17.93	48	0.34
135.	N-Ethylethanamine	-17.02	48 (73)	-0.24
136.	N-Propyl-1-propanamine	-15.31	48 (73)	0.00
137.	N-Butyl-1-butanamine	-13.92	48 (73)	-0.10
138.	Aziridine	-22.66	38	0.75
139.	Azetidine	-23.25	38	-0.58
140.	Pyrrolidine	-22.94	32	-1.03
141.	Piperidine	-21.38	32	-0.22
142.	Hexahydro-2H-azepine	-20.54	32	-0.14
143.	Octahydroazocine	-18.43	38	1.22
144.	N,N-Dimethylmethanamine	-13.55	48	0.67
145.	N,N-Diethylethanamine	-12.65	48	-0.67
146.	1-Methylpyrrolidine	-16.65	32	0.19
147.	1-Methylpiperidine	-16.29	32	-0.19
148.	Pyridine	-19.66	6 (12,32)	0.45
149.	2-Methylpyridine	-19.38	6	0.65
150.	3-Methylpyridine	-19.97	6	0.06
151.	4-Methylpyridine	-20.65	6	-0.62
152.	2-Ethylpyridine	-18.13	6	1.16
153.	3-Ethylpiridine	-19.26	6	0.03
154.	4-Ethylpiridine	-19.82	6	-0.53
155.	2,3-Dimethylpyridine	-20.19	6	-0.24
156.	2,4-Dimethylpyridine	-20.35	6	-0.40
157.	2,5-Dimethylpyridine	-19.74	6	0.21
158.	2,6-Dimethylpyridine	-19.25	6	0.70
159.	3,4-Dimethylpyridine	-21.84	6	-1.90^{f}
160.	3,5-Dimethylpyridine	-20.26	6	-0.31
161.	4-(1,1-Dimethylethyl)pyridine	-18.68	12	-1.13
162.	2,6-Bis(1,1-dimethylethyl)-pyridine	-1.70	12	13.31^{f}

	MONOFUNCTIONAL COMPOUND	ΔG°_h(exp)	Ref.[b]	Δ[c]
163.	2-Propanone	-16.12	45 (27,28,30)	-0.46
164.	2-Butanone	-15.22	45 (30)	-0.30
165.	2-Pentanone	-14.76	30 (81)	-0.58
166.	3-Pentanone	-14.28	45 (81)	-0.10
167.	3-Methyl-2-butanone	-13.56[e]	5,81 (81)	-0.01
168.	2-Hexanone	-13.76[e]	5,81 (81)	-0.33
169.	4-Methyl-2-pentanone	-12.81[e]	5,81 (81)	0.00
170.	2-Heptanone	-12.72	30 (160)	-0.03
171.	4-Heptanone	-12.24[e]	5,81 (81,160)	0.45
172.	2,4-Dimethyl-3-pentanone	-11.46[e]	25,160 (160)	-0.02
173.	2-Octanone	-12.06	30	-0.11
174.	2-Nonanone	-10.41	30	0.80
175.	5-Nonanone	-11.18[e]	5,81 (81)	0.03
176.	2-Undecanone	-9.05	30	0.68
177.	Tricyclo[3,3,1,1^{3,7}]decanone (2-Adamantanone)	-18.66[e]	25,25	[h]
178.	1-Phenylethanone (Acetophenone)	-19.18	94	0.00[g]
179.	Acetaldehyde	-14.66	30	-0.06
180.	Propanal	-14.40	30	-0.54
181.	Butanal	-13.29	30	-0.17
182.	Pentanal	-12.68	30	-0.30
183.	Hexanal	-11.76	30	-0.12
184.	Heptanal	-11.18	30	-0.28
185.	Octanal	-9.58	30	0.57
186.	Nonanal	-8.69	30	0.72
187.	*trans*-2-Butenal	-17.68	31	-0.46
188.	*trans*-2-Hexenal	-15.40	31	0.34
189.	*trans*-Z-Octenal	-14.40	31	-0.15
190.	*trans*,*trans*-2,4-Hexadienal	-19.39	31	0.44
191.	Benzaldehyde	-16.84	94	0.00[g]
192.	Acetic acid	-28.05	27 (94,184)	-0.06
193.	Propanoic acid	-27.09	27 (94)	0.16
194.	Butanoic acid	-26.59	27 (94)	-0.09
195.	Formic acid methyl ester	-11.64	94	0.88
196.	Formic acid ethyl ester	-11.07	94	0.71
197.	Acetic acid methyl ester	-13.87	27	-0.93
198.	Formic acid propyl ester	-10.39	94	0.65
199.	Formic acid 1-methylethyl ester	-8.45	94	1.96[f]
200.	Acetic acid ethyl ester	-12.95	27 (30)	-0.75
201.	Propanoic acid methyl ester	-12.27	30	-0.07
202.	Formic acid 2-methylpropyl ester	-9.30	94	0.37
203.	Acetic acid propyl ester	-11.95	27	-0.48
204.	Acetic acid 1-methylethyl ester	-11.07	94	-0.24
205.	Propanoic acid ethyl ester	-11.70	94	-0.24
206.	Butanoic acid methyl ester	-11.85	30	-0.39
207.	Formic acid 3-methylbutyl ester	-8.90	94	0.02
208.	Acetic acid butyl ester	-10.67	94	0.05
209.	Acetic acid 2-methylpropyl ester	-9.87	94	0.22
210.	Propanoic acid propyl ester	-10.27	94	0.45
211.	Propanoic acid 1-methylethyl ester	-9.30	94	0.79
212.	Butanoic acid ethyl ester	-10.44	94	0.28
213.	Pentanoic acid methyl ester	-10.77	30	-0.05
214.	Acetic acid pentyl ester	-10.27	94	-0.29
215.	Acetic acid 3-methylbutyl ester	-9.25	94	0.10
216.	Butanoic acid propyl ester	-9.53	94	0.45
217.	Pentanoic acid ethyl ester	-10.56	94	-0.58
218.	Hexanoic acid methyl ester	-10.41	30	-0.43
219.	Acetic acid hexyl ester	-9.47	94	-0.23
220.	Propanoic acid pentyl ester	-8.33	94	0.91
221.	Heptanoic acid ethyl ester	-9.64	94	-1.15
222.	Octanoic acid methyl ester	-8.53	30	-0.04
223.	Benzoic acid methyl ester	-17.92	94	0.00[g]
224.	Acetamide	-40.63	184	0.00[g]
225.	Fluoromethane	-0.92	183 (4,94)	0.00[g]
226.	Chloromethane	-2.33	183 (4,94)	0.70
227.	Chloroethane	-2.63	94	-0.34
228.	1-Chloropropane	-1.14	94	0.41
229.	2-Chloropropane	-1.03	94	-0.11
230.	1-Chlorobutane	-0.57	94	0.24
231.	1-Chloropentane	-0.29	94	-0.23
232.	2-Chloropentane	0.29	94	-0.27
233.	3-Chloropentane	0.17	94	-0.39
234.	Chloroethene	-2.48	183 (94)	2.74[f]
235.	3-Chloro-1-propene	-2.40	94	2.08[f]
236.	Chlorobenzene	-4.69[e]	66,127 (94)	0.00[g]
237.	Bromomethane	-3.43	183 (4,94)	0.09
238.	Bromoethane	-2.91	94	-0.13
239.	1-Bromopropane	-2.34	94	-0.30
240.	2-Bromopropane	-2.00	94	-0.59
241.	1-Bromobutane	-1.71	94	-0.41
242.	1-Bromo-2-methylpropane	-0.11	94	0.56
243.	1-Bromo-3-methylbutane	0.86	94	0.79
244.	Bromobenzene	-6.11	94	-0.23
245.	1-Bromo-4-methylbenzene	-5.82	94	-0.02
246.	1-Bromo-2-ethylbenzene	-4.97	94	0.09
247.	1-Bromo-2-(1-methylethyl)benzene	-3.54	94	0.15
248.	Iodomethane	-3.71	94 (4)	0.04
249.	Iodoethane	-3.03	94	-0.02
250.	1-Iodopropane	-2.45	94	-0.19
251.	2-Iodopropane	-1.94	94	-0.30
252.	1-Iodobutane	-1.08	94	0.45
253.	Methanethiol	-5.19	94	0.49
254.	Ethanethiol	-5.42	94	-0.49
255.	Benzenethiol	-10.67	94	0.00[g]
256.	Thiobismethane (Dimethylsulfide)	-6.45	94	0.51
257.	1,1'-Thiobisethane	-5.99	94	-0.51
258.	Methylthiobenzene	-11.42	94	0.00[g]
259.	Acetonitrile	-16.26	94	0.35
260.	Propanenitrile	-16.09	27	-0.22
261.	Butanenitrile	-15.25	27	-0.13
262.	Nitroethane	-15.52	94	-0.61
263.	1-Nitropropane	-13.98	94	0.19
264.	2-Nitropropane	-13.13	94	0.41
265.	Nitrobenzene	-17.23	94	-1.62
266.	1-Methyl-2-nitrobenzene	-15.01	94	0.52
267.	1-Methyl-3-nitrobenzene	-14.44	94	1.09

	POLYFUNCTIONAL COMPOUND	ΔG°_h(exp)	Ref.[b]	Δ[c]	Δ[i]
268.	1,2-Ethanediol	-32.03	27	17.33	0.00[g]
269.	1,2,3-Propanetriol	-38.56	28 (27)	37.81	—
270.	Dimethoxymethane	-12.27	94	11.14	4.28[f]
271.	1,2-Dimethoxyethane	-20.23	43	2.43	-1.99
272.	1,1-Diethoxyethane	-13.70	94	6.85	-0.01
273.	1,2-Dietoxyethane	-14.78	94	6.40	1.99
274.	1,3-Dioxolane	-17.14	33	16.13	—
275.	1,4-Dioxane	-21.15	33	11.36	0.00[g]
276.	1,2-Ethanediamine	-31.78	43 (94)	13.94	0.00[g]
277.	Piperazine	-30.86	37	17.02	0.00[g]
278.	1-Methylpiperazine	-32.53	37	10.29	0.00[g]
279.	1,4-Dimethylpiperazine	-31.70	37	6.05	0.00[g]
280.	2-Methylpyrazine	-23.09	31	13.12	0.45
281.	2-Ethylpyrazine	-22.83	31	12.64	-0.03
282.	2-(2-Methylpropyl)pyrazine	-21.11	31	12.25	-0.42
283.	2-Ethyl-3-methoxypyrazine	-18.39	31	12.50	—
284.	2-(2-Methylpropyl)-3-methoxypyrazine	-15.41	31	18.37	—
285.	2-Methoxyethanol	-28.31	43	7.70	0.05
286.	2-Ethoxyethanol	-27.64	43	7.63	-0.02
287.	2-Propoxyethanol	-26.84	43	7.69	0.04
288.	2-Butoxyethanol	-26.22	43	7.57	-0.07
289.	2-Methoxyethanamine	-27.39	43	6.80	0.00[g]
290.	3-Methoxy-1-propanamine	-28.98	43	4.47	0.09
291.	Morpholine	-30.02	37	10.18	0.00[g]
292.	4-Methylmorpholine	-26.51	37	8.62	0.00[g]
293.	1,1-Difluoroethane	-0.46	94	6.66	-0.19
294.	Dichloromethane	-5.88	94	6.84	-0.01
295.	1,1-Dichloroethane	-3.54	94	7.81	0.96
296.	1,1-Dichlorobutane	-2.91	94	6.96	0.11
297.	Dibromomethane	-8.82	94	5.48	-1.37
298.	Chlorofluoromethane	-3.24	183 (94)	7.37	0.52
299.	1,2-Dichloroethane	-7.25	94	4.73	0.32
300.	1,2-Dichloropropane	-5.25	94	5.36	0.95
301.	1,2-Dibromoethane	-8.79	94	4.17	-0.24
302.	1,2-Dibromopropane	-8.10	94	3.49	-0.92
303.	1-Bromo-2-Chloroethane	-8.16	94	4.31	-0.10
304.	1,3-Dichloropropane	-7.93	94	3.31	0.47
305.	1,3-Dibromopropane	-8.22	94	4.00	1.16
306.	*cis*-1,2-Dichloroethene	-4.91	94	11.17	—
307.	*trans*-1,2-Dichloroethene	-3.20	94	12.88	—
308.	1,2-Dichlorobenzene	-5.71	94	-0.25	—
309.	1,3-Dichlorobenzene	-4.11	94	1.35	—
310.	1,4-Dichlorobenzene	-4.22	94	1.24	—
311.	1,4-Dibromobenzene	-9.64	94	-1.80	—
312.	Trifluoromethane	3.37	94	18.80	1.53
313.	Trichloromethane	-4.46	28 (94)	17.32	0.05
314.	1,1,1-Trichloroethane	-1.03	94	20.39	3.12
315.	Tribromomethane	-8.90	94	14.35	-2.92
316.	Chlorodifluoromethane	-2.08	183 (94)	15.47	-1.80
317.	1,1,2-Trichloroethane	-8.16	94	12.88	—
318.	Trichloroethene	-1.83	94	25.10	—
319.	Tetrafluoromethane	13.03	183 (94)	36.42	1.84

	POLYFUNCTIONAL COMPOUND	ΔG°_h(exp)	Ref.[b]	Δ[c]	Δ[i]
320.	Tetrachloromethane	0.40	94	32.25	-2.33
321.	Chlorotrifluoromethane	10.56	94	36.06	1.48
322.	Dichlorodifluoromethane	7.08	94	34.70	0.12
323.	Bromotrifluoromethane	7.48	94	33.47	-1.11
324.	1,1,2,2-Tetrachloroethane	-9.87	94	20.23	—
325.	2-Chloro-1,1,1-trifluoroethane	0.23	94	24.99	—
326.	Tetrafluoroethene	5.76	183	35.09	—
327.	Tetrachloroethene	0.23	94	38.02	—
328.	Pentachloroethane	-5.71	94	34.46	—
329.	Hexachloroethane	-5.88	94	44.36	—
330.	1,1,2,2-Tetrachloro-1,2-difluoroethane	3.42	94	49.43	-1.80
331.	1,1,2-Trichloro-1,2,2-trifluoroethane	7.42	94	51.31	0.08
332.	1,1-Dichlorotetrafluoroethane	10.50	94	52.28	1.05
333.	1,2-Dichloro-1,1,2,2-tetrafluoroethane	9.70	94	51.48	0.25
334.	Chloropentafluoroethane	11.99	94	51.65	0.42
335.	1,1,2,3,3,3-Hexafluoro-1-propene	9.67	183	53.15	—
336.	4-Bromophenol	-29.85	145	-1.53	—
337.	3-Nitrophenol	-40.31	122	-2.26	—
338.	4-Nitrophenol	-44.58	145 (122)	-6.53	—
339.	3-Hydroxybenzaldehyde	-39.81	122	-0.53	—
340.	4-Hydroxybenzaldehyde	-43.83	145 (122)	-4.55	—
341.	3-Hydroxybenzonitrile	-40.44	122	h	—
342.	4-Hydroxybenzonitrile	-42.57	122	h	—
343.	2-Chloropyridine	-18.39	12	2.49	—
344.	3-Chloropyridine	-16.80	12	4.08	—
345.	1,1'-Thiobis(2-Chloroethane)	-16.40	94	8.45	—
346.	2,2,2-Trifluoroethanol	-18.02	154	25.44	—
347.	1,1,1-Trifluoropropan-2-ol	-17.40	154	24.68	—
348.	2,2,3,3-Tetrafluoropropan-1-ol	-20.41	154	29.18	—
349.	2,2,3,3,3-Pentafluoro-propan-1-ol	-17.38	154	40.22	—
350.	1,1,1,3,3,3-Hexafluoro-propan-2-ol	-15.77	154	48.78	—

(a) All quantities are given in kJ mol^{-1}. ΔG°_h refers to the isothermal transfer of the molecule from the ideal 1M gas state to the hypothetical ideal aqueous solution at the same concentration.

(b) Sources of experimental data. Sources of data not utilized in this work are enclosed in parentheses.

(c) $\Delta = \Delta G^\circ_h(\text{exp}) - \Delta G^\circ_h(\text{calc})$. Calculated values were obtained from Eq.2 using parameters reported in Table I.

(d) The whole molecule may be considered as a unique single group.

(e) Evaluated by us as $\Delta G^\circ_h(\text{exp}) = RT\ln P/X - 17.88$ (kJ mol^{-1}). The vapor pressure P(atm) of the pure compound and the solute mole fraction X in saturated aqueous solution were taken from the first and second quoted reference, respectively.

(f) Compound not used to determine any parameter of Tables I to III.

(g) Single compound used to calculate one parameter of Table I or II.

(h) This compound contains one or more groups not included in Table I.

(i) $\Delta = \Delta G^\circ_h(\text{exp}) - \Delta G^\circ_h(\text{calc})$. Calculated values were obtained from Eq.1 using parameters reported in Tables I to III.

TABLE VIII. Enthalpies of Hydration (ΔH°_h) at 25°C [a]

	MONOFUNCTIONAL COMPOUND	$-\Delta H^\circ_h$(exp)	Ref.[b]	Δ[c]
1.	Methane	13.79	183 (4,29,139,181)	d
2.	Ethane	19.76	183 (4,29,139,181)	-1.11
3.	Propane	22.50	183 (4,139,181)	-0.61
4.	Butane	25.97	183 (4,139,181)	-0.83
5.	2-Methylpropane	22.49	183	1.61
6.	Pentane	24.70	80 (138)	3.67
7.	2,2-Dimethylpropane	27.84	183	0.14
8.	Hexane	31.60	80 (138)	0.02
9.	Heptane	33.89	138	0.97
10.	Octane	39.75	138	-1.64
11.	Cyclopropane	13.72	183	9.37[e]
12.	Cyclohexane	33.20	80	-0.91
13.	Ethene	15.33	183 (4,181)	0.46
14.	1-Propene	28.21	183	-8.85[e]
15.	2-Methyl-1-propene	24.68	183	-1.76
16.	1,3-Butadiene	37.68	183	-17.61[e]
17.	Ethyne	14.79	183	-3.37
18.	1-Propyne	15.62	183	-0.64
19.	1-Butyne	15.51	183	2.71
20.	1-Buten-3-yne	14.40	183	1.29
21.	Benzene	31.77	80 (4,6,181)	-0.41
22.	Methylbenzene	36.26	80 (6,181)	0.27
23.	Ethylbenzene	40.24	80 (6,181)	-0.46
24.	1,3-Dimethylbenzene	41.51	6 (181)	0.20
25.	1,4-Dimethylbenzene	40.96	6 (181)	0.75
26.	Propylbenzene	43.90	80	-0.88
27.	(1-Methylethyl)benzene	41.46	181	0.63
28.	Naphthalene	46.86	181	-2.53
29.	9H-Fluorene	53.14	181	9.93[e]
30.	Acenaphthene	49.62	181	6.43[e]
31.	Anthracene	58.58	181	-1.27
32.	Phenanthrene	54.39	181	2.92
33.	Pyrene	63.60	181	0.86
34.	Methanol	44.52	71 (3,28)	8.12[e]
35.	Ethanol	52.40	71 (3,28)	3.48
36.	1-Propanol	57.45	71 (3,28)	1.68
37.	2-Propanol	58.21	71 (3,28)	-0.11
38.	1-Butanol	61.58	71 (3,29)	0.79
39.	2-Methyl-1-propanol	60.15	71 (28)	1.19
40.	2-Butanol	62.72	38 (29,71)	-1.38
41.	2-Methyl-2-propanol	63.92	71 (3,28)	-1.94
42.	1-Pentanol	64.75	71 (29)	0.86
43.	3-Pentanol	65.98	38	-1.40
44.	2-Methyl-2-butanol	65.65	29	-0.43
45.	1-Hexanol	66.20	71	2.66
46.	3-Hexanol	69.58	38	-1.75
47.	4-Heptanol	75.31	38	-4.24
48.	Cyclopentanol	66.86	38	0.91
49.	Cyclohexanol	70.50	38	0.34
50.	Cycloheptanol	74.56	38	-0.65
51.	Phenol	56.94	145	-0.85
52.	2-Methylphenol	62.68[f]	10,54 (146)	-1.41
53.	3-Methylphenol	58.66[f]	10,54	2.61
54.	4-Methylphenol	61.63[f]	10,54 (146)	-0.36
55.	4-(1,1-Dimethylethyl)phenol	63.81	146	6.80[e]
56.	1,1'-Oxybisethane (Ethyl ether)	47.01[f]	9,116 (29,166)	0.00[g]
57.	Tetrahydrofuran	47.26	33 (74)	-0.49
58.	Tetrahydro-2H-pyran	48.88	33 (74)	0.97
59.	2-Methyltetrahydrofuran	51.38	33	-0.05
60	2,5-Dimethyltetrahydrofuran	56.30	33	-0.43

	MONOFUNCTIONAL COMPOUND	$-\Delta H_h^\circ$(exp)	Ref.^{b}	Δ^{c}
51.	Ethanamine	54.02	28	-1.31
62.	1-Propanamine	55.75	71	0.20
63.	2-Propanamine	55.05	71	-0.13
64.	1-Butanamine	59.04	71	0.15
65.	2-Methyl-1-propanamine	57.13	71	1.03
66.	2-Methyl-2-propanamine	58.98	71	-0.18
67.	1-Pentanamine	62.12	71	0.32
68.	1-Hexanamine	65.76	71	-0.08
69.	N-Ethylethanamine	65.12	73	-0.52
70.	N-Propyl-1-propanamine	72.30^{f}	16,179 (73)	-1.22
71.	N-(1-Methylethyl)-2-propanamine	69.58	73	-0.56
72.	N-Butyl-1-butanamine	75.99	73	1.57
73.	2-Methyl-N-(2-methylpropyl)-1-propanamine	65.12	73	10.38^{e}
74.	N-(1-Methylpropyl)-2-butanamine	74.77	73	0.73
75.	Aziridine	49.97	32	6.58^{e}
76.	Azetidine	59.66	32	-0.04
77.	Pyrrolidine	63.57	32	-0.88
78.	Piperidine	65.41	32	0.35
79.	Hexahydro-1H-azepine	68.26	32	0.57
80.	Octahydroazocine	66.93	32	4.97^{e}
81.	N,N-Diethylethanamine	69.68^{f}	16,179	0.00^{g}
82.	1-Methylpyrrolidine	63.42	32	-0.36
83.	1-Methylpiperidine	65.77	32	0.36
84.	Pyridine	49.84	32 (6,11)	-0.83
85.	2-Methylpyridine	55.10	11 (6)	-0.92
86.	3-Methylpyridine	54.60	11 (6)	-0.42
87.	4-Methylpyridine	55.52	11 (6)	-1.34
88.	2-Ethylpyridine	55.69	6	1.74
89.	3-Ethylpyridine	53.47	6	3.96
90.	4-Ethylpyridine	52.22	6	5.21^{e}
91.	2,3-Dimethylpyridine	57.70	6	1.66
92.	2,4-Dimethylpyridine	60.71	11 (6)	-1.35
93.	2,5-Dimethylpyridine	60.84	11 (6)	-1.47
94.	2,6-Dimethylpyridine	61.97	11 (6)	-2.60
95.	3,4-Dimethylpyridine	56.65	6	2.71
96.	3,5-Dimethylpyridine	60.50	11 (6)	-1.14
97.	4-(1,1-Dimethylethyl)pyridine	57.86	12	5.66^{e}
98.	2,6-Bis(1,1-dimethylethyl)pyridine	57.03	12	21.00^{e}
99.	2-Propanone	40.89^{f}	45,54 (28)	0.94
100.	2-Butanone	45.71^{f}	45,54 (56)	-0.64
101.	2-Pentanone	48.70	56 (25,81)	-0.39
102.	3-Pentanone	49.45^{f}	45,54 (25,56,81)	-1.14
103.	3-Methyl-2-butanone	47.40	56 (81)	-0.12
104.	2-Hexanone	51.80	56 (81)	-0.24
105.	3,3-Dimethyl-2-butanone	49.90	56	1.26
106.	4-Methyl-2-pentanone	47.70	81	2.83
107.	2-Heptanone	56.90	25 (160)	-2.10
108.	4-Heptanone	60.25	25 (81,160)	-5.45^{e}
109.	2,4-Dimethyl-2-pentanone	53.00	56 (25,160)	-0.26
110.	2-Nonanone	62.34	25	-1.05
111.	5-Nonanone	67.11	25 (81)	-5.82^{e}
112.	1-Cyclopropylethanone	49.30	56	1.51
113.	Dicyclopropylmethanone	60.40	56	-0.60
114.	Cyclopentanone	51.71^{f}	45,161	-0.48
115.	Cyclohexanone	53.82^{f}	45,161	0.48
116.	Tricyclo[3,3,1,1^{3,7}]decanone (2-Adamantanone)	57.32	25	17.91^{e}
117.	Formic acid	47.0	71	1.15
118.	Acetic acid	52.8	71	-1.08
119.	Propanoic acid	56.5	71	-1.54
120.	Butanoic acid	59.5	71	-1.30
121.	2-Methylpropanoic acid	54.4	71	2.77
122.	Acetic acid methyl ester	42.50	152	-1.08
123.	Acetic acid ethyl ester	45.60	152 (28)	-0.94
124.	Acetic acid butyl ester	49.00	152	2.15
125.	Butanoic acid methyl ester	48.10	56	-0.20
126.	2-Methylpropanoic acid methyl ester	47.50	56	0.63
127.	Pentanoic acid methyl ester	51.60	56	-0.45
128.	2,2-Dimethylpropanoic acid methyl ester	49.60	56	1.15
129.	N,N-Dimethylformamide	62.89^{f}	126,54	0.00^{g}
130.	N-Butylacetamide	88.30	71	0.00^{g}
131.	Fluoromethane	18.13	183 (4)	0.00^{g}
132.	Chloromethane	23.15	183 (4)	0.00^{g}
133.	Chloroethene	26.51	183	-2.64^{e}
134.	Bromomethane	25.53	183 (4)	0.00^{g}
135.	Iodomethane	25.90	4	0.00^{g}
136.	Sulfinilbismethane (Dimethylsulfoxide)	71.91^{f}	53,54	0.00^{g}
137.	Acetonitrile	34.69^{f}	45,102	0.88
138.	Propanenitrile	39.68^{f}	45,102	-0.88
139.	Nitromethane	35.73^{f}	169,54	0.00^{g}
140.	Urea	72.24^{f}	173,54	d

	POLYFUNCTIONAL COMPOUND	$-\Delta H_h^\circ$(exp)	Ref.^{b}	Δ^{c}	Δ^{h}
141.	1,2-Ethanediol	72.30^{f}	53,172	20.82	0.00^{g}
142.	1,2,3-Propanetriol	103.47	28	29.11	—
143.	1,2-Dimethoxyethane	59.34	115	9.65	3.45
144.	1-Ethoxy-2-methoxyethane	66.04	115	6.09	-0.01
145.	1-(2-Methoxyethoxy)propane	69.09	115	6.29	0.19
146.	1,2-Diethoxyethane	71.92	115	3.46	-2.64
147.	1-(2-Methoxyethoxy)butane	72.48	115	6.14	0.04
148.	1-(2-Propoxyethoxy)propane	76.79	115	5.07	-1.03
149.	1,3-Dioxolane	39.92	33	24.41	—
150.	1,4-Dioxane	47.97	33 (74)	19.43	0.00^{g}
151.	Hydrazine	61.09^{f}	49,172	19.19	-26.74^{e}
152.	Methylhydrazine	66.36^{f}	49,54	22.57	—
153.	1,1-Dimethylhydrazine	68.37^{f}	49,54	22.40	—
154.	1,2-Dimethylhydrazine	74.06^{f}	49,54	23.51	—
155.	1,2-Ethanediamine	76.10^{f}	144,179 (144)	10.67	0.00^{g}
156.	1,3-Propanediamine	85.65^{f}	144,179 (144)	4.36	-0.78
157.	1,4-Butanediamine	91.59	144	1.67	-0.81
158.	1,5-Pentanediamine	95.06	144	1.44	0.25
159.	Piperazine	90.37	37	8.85	0.00^{g}
160.	1-Methylpiperazine	90.42	37	9.18	0.00^{g}
161.	1,4-Dimethylpiperazine	9.71	37	9.26	0.00^{g}
162.	2-Methoxyethanol	60.44	115	20.57	2.76
163.	2-Ethoxyethanol	66.36	115	17.89	0.08
164.	2-Propoxyethanol	69.95	115	17.54	-0.27
165.	2-(1-Methylethoxy)ethanol	70.53	115	15.93	-1.88
166.	2-Butoxyethanol	73.64	115	17.10	-0.71
167.	Tetrahydro-2-furanmethanol	67.32	74	21.24	0.52
168.	Tetrahydro-2H-pyran-2-methanol	71.43	74	20.20	-0.52
169.	2-Methoxyethanamine	63.51	43	14.32	0.00^{g}
170.	3-Methoxypropanamine	72.30	43	8.77	1.87
171.	Morpholine	69.45	37	13.86	0.00^{g}
172.	4-Methylmorpholine	68.66	37	15.02	0.00^{g}
173.	4-Methoxypyridine	59.12	11	16.94	—
174.	Tetrafluoromethane	15.06	183	10.86	—
175.	Trichloromethane	41.17	28	-3.54	—
176.	Chlorofluoromethane	21.70	183	4.18	—
177.	Chlorodifluoromethane	33.59	183	-6.01	—
178.	Tetrafluoroethene	21.69	183	6.29	—
179.	1,1,2,3,3,3-Hexafluoro-1-propene	21.08	183	15.21	—
180.	3-Hydroxybenzaldehyde	66.94	122	i	—
181.	4-Hydroxybenzaldehyde	68.20	122 (145)	i	—
182.	3-Nitrophenol	67.68	122	i	—
183.	4-Nitrophenol	68.62	122 (145)	i	—
184.	3-Hydroxybenzonitrile	70.71	122	i	—
185.	4-Hydroxybenzonitrile	70.29	122	i	—
186.	3-Chlorophenol	50.33^{f}	10,54	i	—
187.	4-Chlorophenol	35.90^{f}	10,54	i	—
188.	4-Bromophenol	68.07	145	i	—
189.	4-Pyridinecarbonitrile	41.97	11	i	—
190.	2-Chloropyridine	49.45	12	i	—
191.	3-Chloropyridine	46.23	12 (11)	i	—
192.	4-(Trifluoromethyl)pyridine	48.79	11	13.19	—
193.	2,2,2-Trifluoroethanol	50.07	154	13.60	—
194.	1,1,1,-Trifluoropropan-2-ol	53.54	154	12.35	—
195.	2,2,3,3-Tetrafluoropropan-1-ol	57.93	154	10.68	—
196.	2,2,3,3,3-Pentafluoropropan-1-ol	51.87	154	20.11	—
197.	1,1,1,3,3,3-Hexafluoropropan-2-ol	57.10	154	16.57	—

(a) All quantities are given in kJ mol^{-1}. ΔH_h° refers to the isothermal transfer of the molecule from the ideal gas state to ideal aqueous solution.

(b) Sources of experimental data. Sources of data not utilized in this work are enclosed in parentheses.

(c) $\Delta = \Delta H_h^\circ(\text{exp}) - \Delta H_h^\circ(\text{calc})$. Calculated values were obtained from Eq.2 using parameters reported in Table 1.

(d) The whole molecule may be considered as a unique single group.

(e) Compound not used to determine any parameter of Tables I to III.

(f) The experimental value was calculated by us as $\Delta H_h^\circ = \Delta H_s^\circ - \Delta H_v^\circ$. The enthalpy of solution, ΔH_s°, and vaporization (or sublimation), ΔH_v°, both at 25°C, were taken from the first and second quoted reference, respectively.

(g) Single compound used to calculate one parameter of Table I or II.

(h) $\Delta = \Delta H_h^\circ(\text{exp}) - \Delta H_h^\circ(\text{calc})$. Calculated values were obtained from Eq.1 using parameters reported in Tables I and II.

(i) This compound contains one or more groups not included in Table I.

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