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Thermodynamic functions of hydration of hydrocarbons at 298.15 K and 0.1 MPa

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Abstract—An extensive compilation of experimental data yielding the infinite dilution partial molar Gibbs energy of hydration $\Delta_h G^O$, enthalpy of hydration $\Delta_h H^O$, heat capacity of hydration $\Delta_h Cp^O$, and volume V_2^O , at the reference temperature and pressure, 298.15 K and 0.1 MPa, is presented for hydrocarbons (excluding polyaromatic compounds) and monohydric alcohols. These results are used in a least-squares procedure to determine the numerical values of the corresponding properties of the selected functional groups. The simple first order group contribution method, which in general ignores nearest-neighbors and steric hindrance effects, was chosen to represent the compiled data. Following the precedent established by Cabani et al. (1981), the following groups are considered: CH₃, CH₂, CH, C for saturated hydrocarbons; c-CH₂, c-CH, c-C for cyclic saturated hydrocarbons; CH_{ar}, C_{ar} for aromatic hydrocarbons (containing the benzene ring); C=C, C≡C for double and triple bonds in linear hydrocarbons, respectively; c-C=C for the double bond in cyclic hydrocarbons; H for a hydrogen atom attached to the double bond (both in linear and cyclic hydrocarbons) or triple bond; and OH for the hydroxyl functional group. In addition it was found necessary to include the “pseudo”-group I(C-C) to account for the specific interactions of the neighboring hydrocarbon groups attached to the benzene or cyclic ring (in the latter case only for cis-isomers). Results of this study, the numerical values of the group contributions, will allow in most cases reasonably accurate estimations of $\Delta_h G^O$, $\Delta_h H^O$, $\Delta_h Cp^O$, and V_2^O at 298.15 K, 0.1 MPa for many hydrocarbons involved in geochemical and environmental processes. Copyright © 2000 Elsevier Science Ltd

I. INTRODUCTION

There is abundant evidence of the close association of water and hydrocarbons in the Earth's crust. The most familiar association is in oil fields where aqueous brines are pumped together with petroleum. The documented temperature range of the coexistence of hydrocarbons and water extends from ambient conditions (environmentally dangerous oil spills at sea, in rivers and into groundwater) through 320–430 K (temperatures of petroleum reservoirs) to at least 600–650 K, present-day bottom-hole temperatures from Gulf of Mexico (Price, 1982; 1993). Mechanisms of transport and transformation of hydrocarbons within Earth's crust can be explored in quantitative models given reliable values of the thermodynamic properties of these compounds in aqueous solutions over wide ranges of temperature and pressure.

As a step in this direction we present values of the standard state partial molar thermodynamic properties of many hydrocarbons in aqueous solution based on both experimental and estimation methods. During the course of this study it was found necessary to evaluate reliable values of thermodynamic functions of aqueous hydrocarbons (alkanes, alkenes, alkynes, alkylbenzenes, cyclic hydrocarbons, and aromatic hydrocarbons derived from benzene) at the reference temperature, 298.15 K, and pressure, 0.1 MPa. Indeed, despite (or probably because of) the very large number of experimental determinations at ambient conditions, no recent up-to-date compilation of the thermodynamic properties of these compounds in aqueous

solution is available (see below a short review of such sources). On the other hand, only a few tens of the thousands of possible hydrocarbons have ever been studied even at ambient conditions. Therefore, incorporating thousands of aqueous hydrocarbons in comprehensive thermodynamic models of geochemical and environmental processes requires reliable estimates of thermodynamic properties not investigated experimentally. These considerations determine the main goals of this work:

1. To make a comprehensive assessment of literature data yielding the standard state partial molar thermodynamic functions of hydration of aqueous hydrocarbons at 298.15 K and 0.1 MPa;
2. To use the selected values of the thermodynamic functions of hydration of hydrocarbons to estimate values of functional group contributions at 298.15 K and 0.1 MPa, which will allow reasonably accurate predictions of the corresponding properties for thousands of hydrocarbons for which experimental results are uncertain or absent.

It was decided to work with the standard state partial molar thermodynamic functions of hydration (for brevity referred below as “the thermodynamic functions of hydration”) rather than with the standard state partial molar properties of compounds in aqueous solution. There are two main reasons for such a decision. First, for many compounds the experimental values of the Gibbs energy of hydration and enthalpy of hydration typically have lower uncertainties (often <0.3–0.5 kJ·mol⁻¹, see Tables 1 and 2) than the values of the partial molar Gibbs energy of formation and enthalpy of formation, which include the uncertainties in enthalpy of combustion measurements (often >0.7–1.5 kJ·mol⁻¹). Using data of

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Table 1. The data base of experimental values of the Gibbs energy of vaporization and hydration of hydrocarbons and monohydric alcohols. See text for discussion of data sources. Values in italics are from aqueous solubility measurements and those in parentheses were considered to be unreliable in this study. The fifth column gives values used in the least-squares procedure. The values calculated using the resulting group contribution values, and the difference between accepted and calculated values are in sixth and seventh columns, respectively.

Compound	Formula	$\Delta_{\text{vap}}G^\circ$, $\text{kJ} \cdot \text{mol}^{-1}$	Values of $\Delta_{\text{h}}G^\circ$ from literature, $\text{kJ} \cdot \text{mol}^{-1}$	Value used in the fit	Group contribution value	Δ , $\text{kJ} \cdot \text{mol}^{-1}$
n-Alkanes						
Methane	CH ₄		16.33 ¹ , 16.26 ² , 16.30 ³	16.29(5)		
Ethane	C ₂ H ₆		15.60 ¹ , 15.55 ² , 15.59 ³	15.57(5)	15.23	0.35
Propane	C ₃ H ₈		16.09 ⁴	16.09(10)	15.95	0.14
n-Butane	C ₄ H ₁₀		16.58 ⁴	16.58(15)	16.67	-0.09
n-Pentane	C ₅ H ₁₂	0.87 ^a	17.11 ⁵ , 17.43 ⁶ , 17.43 ⁷ , 17.43 ⁸ , 17.66 ⁹ , 17.75 ¹⁰ , 17.28 ¹¹ , (15.15 ¹²), 17.69 ¹³ , 17.17 ¹⁴ , 17.81 ¹⁵ , (16.86 ¹⁶), (15.49 ¹⁷)	17.48(24)	17.40	0.08
n-Hexane	C ₆ H ₁₄	3.95 ^a	17.88 ¹⁸ , 18.22 ⁶ , (16.47 ¹⁹), 18.38 ⁷ , (19.07 ²⁰), (16.18 ²¹), 18.39 ²² , 18.00 ⁹ , 18.00 ²³ , (11.64 ²⁴), 17.57 ²⁵ , 18.65 ¹⁰ , 17.72 ²⁶ , 18.00 ²⁷ , 17.97 ¹¹ , (17.00 ¹³), 17.29 ¹⁴ , 18.65 ¹⁵ , (12.36 ²⁸), (9.62 ²⁹), (12.01 ³⁰)	18.06(39)	18.12	-0.06
n-Heptane	C ₇ H ₁₆	6.94 ^a	18.61 ¹⁸ , (16.51 ³¹), 18.96 ⁵ , 19.28 ⁷ , 18.90 ⁸ , 18.44 ⁹ , 18.36 ³² , 19.60 ¹⁰ , 19.05 ²⁶ , 18.60 ¹¹ , 19.18 ¹³ , 18.94 ¹⁵ , (15.89 ²⁹), (11.90 ³⁰)	18.90(38)	18.85	0.05
n-Octane	C ₈ H ₁₈	9.87 ^a	19.83 ¹⁸ , (13.17 ³¹), 19.59 ⁶ , 20.16 ⁷ , 19.30 ³³ , 19.13 ³³ , (11.51 ³⁴), 19.30 ³⁵ , 18.74 ⁹ , 18.43 ²⁵ , (21.09 ¹⁰), 19.90 ²⁶ , 19.40 ¹¹ , 19.29 ¹³ , 20.02 ¹⁵ , (24.93 ³⁶), (11.51 ³⁰)	19.42(51)	19.57	-0.15
n-Nonane	C ₉ H ₂₀	12.81 ^a	21.24 ¹⁵ , (14.94 ¹⁹), 20.89 ⁷ , 21.77 ¹⁰ , (22.88 ²⁶), 20.09 ¹⁵	21.0(8)	20.30	0.70
n-Decane	C ₁₀ H ₂₂	15.58 ^a	21.3 ³⁷ , (25.6 ²⁶), 21.2 ³⁸ , 23.5 ³⁹ , 24.1 ⁴⁰ , 23.6 ⁴¹	22.7(14)	21.02	1.68
n-Undecane	C ₁₁ H ₂₄	18.52 ^a	25.1 ²⁶ , 24.6 ³⁸	24.8(20)	21.75	3.05
n-Dodecane	C ₁₂ H ₂₆	21.37 ^b	22.5 ⁴² , 24.1 ⁴³ , 22.3 ⁴⁴ , 20.4 ³⁹	22.3(15)	22.47	-0.17
n-Tetradecane	C ₁₄ H ₃₀	27.08 ^b	23.04 ⁴²	23.0(15)	23.92	-0.92
Branched alkanes						
2-Methylpropane	C ₄ H ₁₀		17.32 ⁴	17.32(20)	17.07	0.25
2-Methylbutane	C ₅ H ₁₂	0.12 ^a	17.40 ⁵ , 17.68 ⁶ , 18.01 ¹⁰ , 17.94 ¹¹ , 18.02 ¹⁵ , 17.93 ⁴⁵	17.76(26)	17.79	-0.03
2,2-Dimethylpropane	C ₅ H ₁₂		18.40 ³ , 18.50 ⁴⁶ , 18.32 ⁴⁷ , 18.99 ¹⁵	18.40(20)	17.99	0.41
2-Methylpentane	C ₆ H ₁₄	3.10 ^a	(16.65 ¹⁹), 18.71 ¹⁰ , 18.49 ²⁷ , 18.25 ¹¹ , 18.57 ¹⁵	18.52(20)	18.51	0.01
3-Methylpentane	C ₆ H ₁₄	3.38 ^a	18.39 ⁸ , 18.41 ¹⁰ , (17.64 ¹¹), 18.46 ¹⁵	18.42(20)	18.51	-0.09
2,2-Dimethylbutane	C ₆ H ₁₄	2.07 ^a	18.53 ¹⁰ , 18.25 ¹¹ , 18.88 ¹⁵	18.57(32)	18.71	-0.14
2,3-Dimethylbutane	C ₆ H ₁₄	2.84 ^a	18.02 ¹⁰ , 17.61 ¹¹	17.82(40)	18.91	-1.09
2-Methylhexane	C ₇ H ₁₆	6.02 ^a	(15.98 ³¹), 20.22 ¹⁰	20.2(6)	19.24	0.96
3-Methylhexane	C ₇ H ₁₆	6.19 ^a	19.95 ¹⁰ , 18.39 ¹¹	19.1(8)	19.24	-0.14
2,2-Dimethylpentane	C ₇ H ₁₆	4.84 ^a	20.03 ¹⁰	20.0(6)	19.44	0.56
2,3-Dimethylpentane	C ₇ H ₁₆	5.90 ^a	18.53 ¹⁰	18.5(6)	19.63	-1.13
2,4-Dimethylpentane	C ₇ H ₁₆	5.00 ^a	19.87 ¹⁰ , 19.32 ¹¹ , 20.07 ¹⁵	19.84(36)	19.63	0.21
3,3-Dimethylpentane	C ₇ H ₁₆	5.43 ^a	18.70 ¹⁰	18.7(6)	19.44	-0.74
3-Methylheptane	C ₈ H ₁₈	9.04 ^a	20.41 ¹⁰	20.4(6)	19.96	0.44
2,2,4-Trimethylpentane	C ₈ H ₁₈	6.72 ^a	19.98 ⁵ , 20.55 ²⁵ , (21.82 ¹⁰), 20.38 ¹¹ , 19.93 ¹⁵ , (22.40 ³⁶)	20.13(27)	20.55	-0.42
2,3,4-Trimethylpentane	C ₈ H ₁₈	8.22 ^a	19.89 ¹⁰ , 18.59 ¹¹	19.2(7)	20.75	-1.55
4-Methyloctane	C ₉ H ₂₀	11.65 ^c	22.89 ¹⁰	22.9(10)	20.69	2.21
2,2,5-Trimethylhexane	C ₉ H ₂₀	9.44 ^c	21.25 ¹¹ , 19.36 ¹⁵	20.3(11)	21.28	-0.98
Alkenes and Dienes						
Ethene	C ₂ H ₄		13.25 ³	13.25(10)	13.35	-0.10
Propene	C ₃ H ₆		12.87 ⁴⁸	12.87(15)	13.08	-0.21
1-Butene	C ₄ H ₈		13.68 ¹⁵ , 13.59 ⁴⁹⁺⁵⁰ , 13.53 ⁵¹⁺⁵⁰ , 13.47 ⁵²⁺⁵⁰	13.57(20)	13.80	-0.23
2-Methyl-1-propene	C ₄ H ₈		12.80 ³	12.80(20)	12.81	-0.01
1-Pentene	C ₅ H ₁₀	0.31 ^d	14.96 ¹⁵	14.96(30)	14.53	0.43
2-Pentene	C ₅ H ₁₀	0.87 ^d	13.62 ¹⁵	13.62(30)	13.53	0.09
2-Methyl-2-butene	C ₅ H ₁₀	1.11 ^d	12.39 ⁵³	12.4(10)	12.53	-0.13
3-Methyl-1-butene	C ₅ H ₁₀		15.54 ¹⁵	15.54(40)	14.92	0.62
1-Hexene	C ₆ H ₁₂	3.41 ^d	14.18 ⁹ , 15.15 ²⁵ , 14.74 ²⁷ , 15.39 ⁵³ , 15.01 ¹⁵	15.07(28)	15.25	-0.18
2-Methyl-1-pentene	C ₆ H ₁₂	3.11 ^d	14.20 ¹⁵	14.20(30)	14.26	-0.06
4-Methyl-1-pentene	C ₆ H ₁₂	2.47 ^d	16.05 ¹⁵	16.05(40)	15.65	0.41
1-Heptene	C ₇ H ₁₄	6.39 ^d	14.90 ⁹	14.9(6)	15.98	-1.08
2-Heptene	C ₇ H ₁₄	6.75 ^c	15.03 ⁵⁴ , 15.03 ¹⁵	15.03(30)	14.98	0.05
1-Octene	C ₈ H ₁₆	9.32 ^c	17.41 ⁵⁵ , 16.00 ⁹ , 17.05 ¹⁵	16.9(6)	16.70	0.20
1-Nonene	C ₉ H ₁₈	12.23 ^c	16.60 ⁹	16.6(10)	17.42	-0.83
1,3-Butadiene	C ₄ H ₆		10.62 ¹⁵ , 10.56 ⁵⁶	10.61(20)	10.93	-0.32
1,4-Pentadiene	C ₅ H ₈	-0.05 ^a	11.96 ¹⁵	11.96(40)	11.66	0.30
2-Methyl-1,3-butadiene	C ₅ H ₈	0.69 ^a	10.87 ¹⁵ , 10.53 ⁴⁵	10.76(30)	10.66	0.10
1,5-Hexadiene	C ₆ H ₁₀	2.97 ^a	12.36 ¹⁵	12.36(40)	12.39	-0.03
1,6-Heptadiene	C ₇ H ₁₂	6.2 ^e	12.86 ¹⁵	12.86(50)	13.11	-0.25

(Continued)

Table 1. (Continued)

Compound	Formula	$\Delta_{\text{vap}}G^\circ$, kJ · mol ⁻¹	Values of $\Delta_{\text{h}}G^\circ$ from literature, kJ · mol ⁻¹	Value used in the fit	Group contribution value	Δ , kJ · mol ⁻¹
Alkynes and Diynes						
Ethyne	C ₂ H ₂		7.89 ³	7.89(15)	7.41	0.49
Propyne	C ₃ H ₄		(5.94 ¹⁵), 6.39 ⁵⁷ , 6.56 ⁵⁸	6.43(30)	7.13	-0.70
1-Butyne	C ₄ H ₆		7.28 ¹⁵ , 6.50 ⁵⁷	6.9(4)	7.86	-0.96
1-Pentyne	C ₅ H ₈	1.31 ^a	9.04 ⁹ , 8.04 ¹⁵	8.5(5)	8.58	-0.08
1-Hexyne	C ₆ H ₁₀	4.26 ^a	7.61 ⁹ , 9.17 ¹⁵	8.7(9)	9.31	-0.61
3-Hexyne	C ₆ H ₁₀	5.21 ^c	7.2 ⁵⁹	7.2(8)	8.31	-1.11
1-Heptyne	C ₇ H ₁₂	7.14 ^c	10.03 ¹⁵	10.0(5)	10.03	-0.03
2-Heptyne	C ₇ H ₁₂	8.3 ^e	7.5 ⁵⁹	7.5(8)	9.03	-1.53
2-Methyl-3-hexyne	C ₇ H ₁₂	6.2 ^e	9.5 ⁵⁹	9.5(8)	9.43	0.07
1-Octyne	C ₈ H ₁₄	10.02 ^c	10.9 ¹⁵	10.9(5)	10.76	0.14
2,2-Dimethyl-3-hexyne	C ₈ H ₁₄	7.4 ^e	10.5 ⁵⁹	10.5(8)	10.35	0.15
1-Nonyne	C ₉ H ₁₆	12.7 ^e	11.46 ¹⁵	11.5(6)	11.48	0.02
2,2,5-Trimethyl-3-hexyne	C ₉ H ₁₆	7.8 ^a	12.9 ⁵⁹	12.9(10)	11.46	1.44
2,2,5,5-Tetramethyl-3-hexyne	C ₁₀ H ₁₈	7.8 ^a	14.1 ⁵⁹	14.1(10)	12.38	1.72
1,6-Heptadiyne	C ₇ H ₈	8.1 ^a	1.9 ¹⁵	1.9(5)	1.22	0.68
1,8-Nonadiyne	C ₉ H ₁₂	14.0 ^e	3.0 ¹⁵	3.0(6)	2.67	0.34
Cycloalkanes						
Cyclopropane	C ₃ H ₆		11.01 ⁶⁰ , 11.19 ¹⁴ , 10.96 ⁶¹ , 10.96 ⁶²	10.98(10)	10.46	0.52
Cyclopentane	C ₅ H ₁₀	2.10 ^a	12.71 ⁵ , 12.91 ⁶ , 12.84 ³¹ , 12.92 ⁶³ , 12.98 ¹⁰ , (11.12 ¹²), 13.05 ¹⁵	12.90(12)	12.12	0.78
Cyclohexane	C ₆ H ₁₂	5.04 ^a	12.90 ⁶⁴ , 13.12 ⁵ , 13.06 ⁶ , 12.83 ¹⁹ , 12.95 ⁶⁵ , 13.06 ⁸ , 13.07 ⁶⁶ , 12.99 ⁶³ , 13.23 ⁶⁷ , 13.28 ⁵⁴ , (11.20 ²⁴), 12.55 ²⁵ , 12.67 ¹⁰ , 13.00 ⁶⁸ , 13.05 ²⁷ , (11.83 ¹²), 13.14 ¹⁵ , (12.21 ²⁸), (12.80 ²⁹)	12.99(20)	12.95	0.04
Methylcyclopentane	C ₆ H ₁₂	4.19 ^a	14.43 ⁸ , 14.67 ¹⁰ , 14.66 ¹⁵	14.59(20)	13.89	0.70
Cycloheptane	C ₇ H ₁₄	8.78 ^a	11.54 ⁶³ , 11.28 ¹⁵	11.4(6)	13.79	-2.39
Methylcyclohexane	C ₇ H ₁₄	6.90 ^a	(11.43 ¹), 14.81 ⁸ , 15.15 ³⁷ , 14.60 ⁶³ , 15.13 ³³ , 14.63 ³⁵ , 14.72 ¹⁰ , 15.05 ¹⁵	14.97(23)	14.72	0.25
Cyclooctane	C ₈ H ₁₆	12.1 ^c	11.62 ¹⁵	11.6(10)	14.62	-3.02
<i>trans</i> -1,4-Dimethylcyclohexane	C ₈ H ₁₆	8.66 ^c	16.83 ¹⁰	16.8(5)	16.50	0.30
Propylcyclopentane	C ₈ H ₁₆	10.19 ^c	16.88 ¹⁰	16.9(6)	15.34	1.56
<i>cis</i> -1,2-Dimethylcyclohexane	C ₈ H ₁₆	9.78 ^c	14.60 ¹⁵	14.6(5)	15.49	-0.89
1,1,3-Trimethylcyclopentane	C ₈ H ₁₆	7.27 ^a	18.28 ¹⁰	18.3(6)	17.60	0.70
1,1,3-Trimethylcyclohexane	C ₉ H ₁₈	10.42 ^f	17.29 ¹⁰	17.3(6)	18.44	-1.14
Pentylcyclopentane	C ₁₀ H ₂₀	16.0 ^e	18.74 ¹⁰	18.7(8)	16.79	1.91
Cycloalkenes						
Cyclopentene	C ₅ H ₈	1.63 ^a	10.1 ⁵³ , (7.61 ¹²), 10.39 ¹⁵	10.3(5)	8.80	1.50
Cyclohexene	C ₆ H ₁₀	5.27 ^e	9.03 ⁶⁹ , 8.81 ⁵⁴ , 9.32 ²⁵ , 8.94 ⁵³ , (8.65 ¹²), 9.49 ¹⁵ , 10.21 ⁷⁰ , 10.51 ⁷¹ , (10.69 ²⁸)	9.5(7)	9.63	-0.13
Cycloheptene	C ₇ H ₁₂	8.41 ^c	9.65 ¹⁵	9.65(40)	10.46	-0.81
1-Methylcyclohexene	C ₇ H ₁₂	8.0 ^f	10.65 ¹⁵	10.65(50)	9.36	1.29
1,3-Cyclopentadiene	C ₅ H ₆	1.29 ^c	10.05 ⁷²	10.0(20)	5.48	4.52
1,4-Cyclohexadiene	C ₉ H ₁₈	6.03 ^c	(5.0 ¹²), 5.72 ¹⁵	5.7(5)	6.31	-0.61
1,3,5-Cycloheptatriene	C ₉ H ₁₈	8.7 ^b	(3.50 ¹²), 3.70 ¹⁵	3.7(3)	3.82	-0.12
Alkylbenzenes						
Benzene	C ₆ H ₆	5.10 ^a	4.28 ⁷³ , 4.54 ¹⁸ , 4.16 ⁷⁴ , 4.24 ⁷⁵ , 4.60 ⁷⁶ , 3.90 ⁷⁷ , 4.41 ⁷⁸ , 4.42 ⁷⁹ , 4.12 ⁸⁰ , 4.27 ⁶ , 4.12 ¹⁸ , 4.26 ⁶⁵ , 4.20 ⁸¹ , 4.23 ⁸² , 3.88 ⁸³ , 4.31 ⁸⁴ , 4.34 ⁸⁵ , 4.34 ⁸⁶ , 4.38 ⁸⁷ , 4.10 ⁸⁸ , 4.02 ⁸⁹ , 4.32 ⁹⁰ , 4.33 ⁹¹ , 4.38 ⁹² , 4.50 ⁹⁷ , 4.62 ⁹³ , 4.50 ⁹⁴ , 4.25 ²⁰ , 4.27 ⁹⁵ , 4.33 ⁹⁶ , 4.50 ⁹⁷ , 4.52 ⁹⁸ , 4.25 ⁹⁹ , 4.50 ¹⁰⁰ , 4.52 ¹⁰¹ , 4.25 ³² , 4.26 ¹⁰² , (6.13 ²⁴), 4.26 ¹⁰³ , 4.33 ¹⁰ , (5.70 ¹⁰⁴), 4.27 ⁶⁸ , (4.23 ¹⁰⁵), 4.10 ¹⁰⁶ , 4.20 ¹⁰⁷ , 4.31 ¹¹ , 4.28 ²⁷ , (3.88 ¹²), 4.38 ¹⁰⁸ , (3.77 ¹⁰⁹), 4.35 ¹⁰⁰ , 4.27 ¹⁵ , 4.36 ¹¹¹ , 4.24 ¹¹² , (3.76 ¹¹³), 4.24 ¹¹⁴ , 4.33 ¹¹⁵ , 4.24 ¹¹⁶ , 4.27 ¹⁷ , 4.36 ¹¹⁸ , 4.26 ¹¹⁹ , (4.69 ²⁸), 4.15 ¹²⁰ , 4.33 ¹²¹ , 4.17 ³⁰ , 4.18 ¹²²	4.29(14)	4.09	0.20

(Continued)

Table 1. (Continued)

Compound	Formula	$\Delta_{\text{vap}}G^\circ$, kJ · mol ⁻¹	Values of $\Delta_{\text{H}}G^\circ$ from literature, kJ · mol ⁻¹	Value used in the fit	Group contribution value	Δ , kJ · mol ⁻¹
Alkylbenzenes (continued)						
Toluene	C ₇ H ₈	8.11 ^a	4.69 ⁶⁴ , 4.65 ⁷³ , 4.97 ¹⁸ , 4.66 ¹²³ , 4.74 ⁷⁶ , 5.10 ⁷⁸ , 4.56 ⁸⁴ , 4.54 ⁸⁵ , 4.45 ⁷⁴ , 4.25 ⁷⁷ , 4.56 ⁶⁹ , 4.64 ⁷⁹ , 4.61 ⁸⁰ , 4.59 ⁶ , 4.61 ¹⁹ , 4.12 ⁸² , 3.98 ⁸³ , 4.72 ⁶⁶ , 5.08 ¹²³ , 4.13 ¹²⁴ , 4.45 ⁹² , 4.71 ⁶⁷ , 4.53 ⁹² , 4.27 ⁸³ , 4.27 ⁹³ , 4.37 ³⁴ , 4.70 ¹²⁵ , 4.71 ⁹⁴ , 4.32 ²⁰ , 4.45 ²¹ , 4.61 ⁹⁸ , 4.79 ¹²⁶ , 4.54 ⁹⁸ , (2.02 ¹⁰⁰), 4.30 ¹⁰¹ , 4.74 ¹⁰² , (4.16 ²⁴), 4.56 ¹⁰ , (6.85 ¹⁰⁴), 4.72 ⁶⁸ , (4.88 ¹⁰⁵), 4.66 ¹²⁷ , 4.26 ¹⁰⁶ , 4.58 ¹⁰⁷ , 4.48 ¹¹ , (4.25 ¹²), 4.42 ¹²⁸ , 4.75 ¹⁵ , 4.65 ¹¹⁸ , 4.28 ¹¹⁹ , 4.81 ¹²⁰ , 4.68 ¹²¹ , (4.83 ³⁰)	4.56(23)	4.52	0.04
Ethylbenzene	C ₈ H ₁₀	10.80 ⁱ	5.13 ⁷³ , 5.43 ⁷⁶ , 5.11 ⁸⁴ , 5.06 ⁸⁵ , 5.10 ⁷⁹ , 5.08 ⁸⁰ , 5.12 ¹⁹ , 4.56 ⁸³ , 5.35 ¹²⁹ , 5.07 ¹³⁰ , 4.52 ¹²⁵ , 5.54 ⁶⁷ , 5.04 ³³ , 4.84 ¹³¹ , 5.01 ³⁵ , 5.12 ⁹³ , 4.91 ⁹ , 5.17 ⁹⁷ , 4.99 ⁹⁸ , 4.61 ¹⁰¹ , 5.42 ¹⁰² , 5.01 ²⁴ , 5.81 ¹⁰ , (7.35 ¹⁰⁴), 5.29 ¹²⁷ , 5.01 ¹³² , 5.05 ¹¹ , 5.35 ¹⁵ , 5.24 ¹¹⁸ , 4.66 ¹¹⁹ , 5.19 ¹³³ , 5.09 ¹²⁰ , 5.49 ³⁰	5.09(29)	5.24	-0.15
1,2-Dimethylbenzene (<i>o</i> -xylene)	C ₈ H ₁₀	11.70 ⁱ	4.93 ⁷⁶ , 3.94 ⁸⁴ , 4.09 ⁸⁵ , 3.61 ⁷⁷ , 3.98 ⁸⁰ , 3.92 ¹⁹ , 3.60 ¹³⁰ , 4.13 ⁶⁷ , 3.61 ⁹ , 4.12 ⁹⁷ , 4.31 ¹⁵ , 4.24 ¹²⁷ , 3.69 ¹¹ , 4.17 ¹³⁴ , 4.18 ¹⁰ , 3.81 ¹²¹	4.02(32)	3.94	0.08
1,3-Dimethylbenzene (<i>m</i> -xylene)	C ₈ H ₁₀	11.14 ⁱ	4.71 ⁸⁴ , 5.11 ⁸⁵ , 4.51 ⁷⁷ , 4.92 ⁸⁰ , 4.97 ¹⁹ , 4.85 ¹²⁹ , 5.27 ⁶⁷ , 4.96 ⁹ , 4.95 ⁹⁷ , 4.74 ¹³⁵ , 5.41 ¹⁰ , 5.19 ¹²⁷ , 4.34 ¹⁰⁶ , 4.93 ¹¹ , 5.01 ¹³⁴ , 4.46 ¹¹⁹ , 4.77 ¹²¹	4.89(28)	4.94	-0.05
1,4-Dimethylbenzene (<i>p</i> -xylene)	C ₈ H ₁₀	11.01 ⁱ	5.57 ¹⁸ , 4.84 ⁸⁴ , 5.16 ⁸⁵ , 4.34 ⁷⁷ , 5.14 ³¹ , 4.94 ¹⁹ , 4.93 ¹³⁶ , 5.11 ¹²⁹ , 4.90 ¹³⁰ , 5.09 ⁶⁷ , 4.36 ⁹ , 5.06 ⁹⁷ , 5.14 ¹⁰ , 5.16 ¹²⁷ , 4.73 ¹¹ , 5.04 ¹³⁴ , 4.58 ¹¹⁹ , 4.56 ¹²¹	4.93(30)	4.94	-0.01
Propylbenzene	C ₉ H ₁₂	13.32 ^c	6.02 ⁸⁴ , 5.97 ⁷⁷ , 5.90 ¹⁹ , 6.08 ⁷⁹ , (4.68 ⁸⁷), 5.98 ⁶⁷ , 5.81 ¹³¹ , 6.22 ⁹⁴ , 5.87 ⁹ , 6.12 ²¹ , 5.93 ⁹⁷ , 5.88 ¹³⁷ , 5.52 ¹³⁴ , 5.74 ¹³³ , (3.80 ¹²⁰), (4.27 ³⁰)	5.93(18)	5.96	-0.03
1,2,3-Trimethylbenzene	C ₉ H ₁₂	15.21 ^c	3.41 ⁹ , 3.52 ⁹⁷ , 3.07 ¹²⁷	3.34(24)	3.36	-0.02
1,2,4-Trimethylbenzene	C ₉ H ₁₂	14.51 ^c	4.57 ³¹ , 4.49 ⁹⁷ , 4.69 ¹⁰ , 4.38 ¹²⁷	4.53(30)	4.37	0.16
1,3,5-Trimethylbenzene (mesitylene)	C ₉ H ₁₂	14.11 ^c	4.86 ⁸⁴ , 5.08 ⁸⁵ , 4.73 ¹⁹ , 4.59 ¹²⁹ , 5.19 ⁹⁷ , 5.21 ⁹⁸ , 5.28 ¹²⁷ , 5.78 ¹⁰⁶ , (3.55 ¹³³)	5.09(37)	5.37	-0.28
1-Methylethylbenzene (<i>iso</i> -propylbenzene, cumene)	C ₉ H ₁₂	12.65 ^c	5.98 ⁸⁴ , 5.91 ⁸⁵ , 6.11 ³¹ , (4.26 ¹⁹), 6.13 ⁹⁷ , 6.73 ¹⁰ , 5.99 ¹²⁷ , 6.64 ¹³⁴ , 6.65 ¹⁵ , 5.47 ¹³⁸ , 5.71 ¹³³ , (3.62 ³⁰)	6.13(45)	6.36	-0.23
1-Ethyl-2-methylbenzene	C ₉ H ₁₂	14.10 ^c	4.20 ⁹	4.2(6)	4.66	-0.46
<i>n</i> -Butylbenzene	C ₁₀ H ₁₄	16.20 ^j	6.68 ⁸⁴ , 6.53 ⁸⁵ , 6.98 ⁷⁹ , 6.18 ¹²⁹ , (4.77 ¹²⁶), 6.56 ³¹⁸ , 6.66 ³⁵ , 6.56 ⁹ , 6.95 ¹²⁷ , 5.94 ¹³⁹ , (12.49 ¹³³), (3.38 ¹²⁰), (3.39 ³⁰)	6.56(33)	6.69	-0.13
2-Methylpropylbenzene (<i>iso</i> -butylbenzene)	C ₁₀ H ₁₄	14.75 ^j	8.79 ¹⁰	8.8(6)	7.08	1.72
1,1-Dimethylethylbenzene (<i>tert</i> -butylbenzene)	C ₁₀ H ₁₄	14.40 ^j	6.48 ¹²⁷ , 6.12 ¹³³	6.3(4)	7.28	-0.98
1-Methylpropylbenzene (<i>sec</i> -butylbenzene)	C ₁₀ H ₁₄	14.84 ^j	7.32 ¹²⁷ , (5.93 ¹³³)	7.3(4)	7.08	0.22
1,2,4,5-Tetramethyl- benzene	C ₁₀ H ₁₄	21.10 ^j	5.01 ¹⁰	5.0(8)	3.79	1.21
1-Methyl-2-(1-methyl- ethyl)-benzene (<i>o</i> -cymene)	C ₁₀ H ₁₄	15.18 ^c	4.48 ¹⁴⁰	4.5(10)	5.78	-1.28
1-Methyl-3-(1-methyl- ethyl)-benzene (<i>m</i> -cymene)	C ₁₀ H ₁₄	15.04 ^c	4.93 ¹⁴⁰	4.9(10)	6.78	-1.88
1-Methyl-4-(1-methyl- ethyl)-benzene (<i>p</i> -cymene)	C ₁₀ H ₁₄	15.41 ^c	4.13 ¹⁴⁰ , 7.15 ¹⁷⁴ , 6.05 ¹⁰⁰	5.8(15)	6.78	-0.98
<i>n</i> -Pentylbenzene	C ₁₁ H ₁₆	18.95 ^j	7.55 ¹³¹ , 7.22 ⁹	7.4(4)	7.41	-0.01
<i>n</i> -Hexylbenzene	C ₁₂ H ₁₈	21.83 ^j	8.16 ¹³¹ , 7.92 ⁹⁵ , 7.86 ⁹ , (6.08 ¹⁰⁴)	8.0(3)	8.14	-0.14
1,3,5-Triethylbenzene	C ₁₂ H ₁₈	20.90 ^k	5.7 ³⁵	5.7(10)	7.55	-1.85
<i>n</i> -Decylbenzene	C ₁₆ H ₂₆	33.54 ^l	11.8 ¹⁴¹	11.8(8)	11.04	0.76
1-Alcohols						
Methanol	CH ₄ O	4.36 ^a	-13.38 ⁸⁵ , -13.19 ¹⁴² , -12.98 ¹⁴³ , -12.95 ¹⁴⁴ , -13.09 ¹⁴⁵ , -13.08 ¹⁴⁶ , -13.11 ¹⁴⁷ , -13.31 ¹⁴⁸ , -13.47 ¹⁴⁹ , -13.12 ⁸⁸ , -13.40 ¹⁵⁰ , -12.97 ¹⁵¹ , -13.50 ¹⁵² , -13.44 ¹⁵³	-13.21(20)	-13.81	0.60
Ethanol	C ₂ H ₆ O	6.28 ^a	-12.93 ⁸⁵ , -12.97 ¹⁴² , (-12.30 ¹⁴³), -12.72 ¹⁴⁴ , -12.96 ¹⁵⁴ , -13.10 ¹⁴⁵ , -13.30 ¹⁴⁶ , -12.86 ¹⁵⁵ , -12.87 ⁸⁸ , -12.90 ¹⁵⁶ , -12.82 ¹⁵⁷ , (-12.38 ¹⁵⁸), -12.96 ¹⁵⁹ , -13.06 ¹⁶⁰ , -13.03 ¹⁴⁸ , -13.05 ¹⁴⁹ , -13.00 ¹⁵⁰ , -13.36 ¹⁵² , -13.02 ¹⁵³	-13.00(17)	-13.08	0.08

(Continued)

Table 1. (Continued)

Compound	Formula	$\Delta_{\text{vap}}G^\circ$, kJ · mol ⁻¹	Values of $\Delta_f G^\circ$ from literature, kJ · mol ⁻¹	Value used in the fit	Group contribution value	Δ , kJ · mol ⁻¹
1-Alcohols (continued)						
1-Propanol	C ₃ H ₈ O	8.85 ^a	-12.24 ⁸⁵ , -12.38 ¹⁴² , -12.09 ¹⁴⁴ , (-6.68 ¹⁶¹), -12.82 ¹⁴⁵ , -12.89 ¹⁴⁶ , -11.76 ¹⁵⁸ , -12.50 ¹⁵⁹ , -12.38 ¹⁴⁸ , -12.15 ¹⁴⁹ , -12.37 ¹⁵⁰ , -12.63 ¹⁵² , -12.30 ¹⁵³	-12.38(32)	-12.36	-0.02
1-Butanol	C ₄ H ₁₀ O	11.65 ^a	-11.75 ⁸⁵ , -11.90 ¹⁴² , -11.94 ¹⁴⁴ , (-9.48 ¹⁶¹), -12.38 ¹⁶² , -12.17 ¹⁴⁶ , -11.55 ¹⁴⁸ , -11.98 ¹⁴⁹ , -11.89 ⁸⁸ , -11.79 ¹⁵⁰ , -11.71 ¹⁶³ , -12.21 ¹⁵² , -11.78 ¹⁵³ , -11.82 ¹⁶⁴	-11.88(24)	-11.63	-0.25
1-Pentanol	C ₅ H ₁₂ O	14.52 ^m	-11.05 ⁸⁵ , -11.37 ¹⁴² , (-10.04 ¹⁶¹), -11.45 ¹⁴⁶ , -10.78 ¹⁴⁸ , -11.37 ⁸⁸ , -11.16 ¹⁵⁰ , -10.81 ¹⁵³ , -11.35 ¹⁶⁴ , -11.32 ¹⁶⁵	-11.13(26)	-10.91	-0.22
1-Hexanol	C ₆ H ₁₄ O	17.32 ^m	-10.31 ⁸⁵ , -10.29 ¹⁴² , (-9.71 ¹⁶¹), (-11.24 ¹⁴⁶), -10.09 ¹⁴⁸ , -10.76 ⁸⁸ , -10.51 ¹⁵⁰ , -10.06 ¹⁶³ , -10.32 ¹⁵³ , -10.65 ¹⁶⁴ , -10.69 ¹⁶⁵	-10.37(26)	-10.19	-0.18
1-Heptanol	C ₇ H ₁₆ O	20.16 ^m	-9.18 ¹⁶¹ , -10.06 ⁸⁸ , (-7.14 ¹⁶⁶), -9.80 ¹⁵³ , -10.22 ¹⁶⁴ , -10.27 ¹⁶⁵	-9.91(45)	-9.46	-0.45
1-Octanol	C ₈ H ₁₈ O	22.95 ^m	-9.17 ¹⁶³ , -9.20 ¹⁵³ , -9.36 ¹⁶⁷ , (-9.89 ¹⁶⁴), (-9.77 ¹⁶⁵)	-9.23(50)	-8.74	-0.49
Branched alcohols						
2-Propanol (<i>iso</i> -propanol)	C ₃ H ₈ O	7.04 ^a	-12.02 ¹⁴² , -11.79 ¹⁴⁴ , -12.00 ¹⁴⁸ , -12.01 ¹⁴⁹ , -11.87 ¹⁵⁵ , -11.83 ¹⁸⁸ , -11.96 ¹⁵⁰ , -11.93 ¹⁵³	-11.93(10)	-11.97	0.04
2-Butanol (<i>sec</i> -butanol)	C ₄ H ₁₀ O	9.33 ^a	-11.58 ¹⁴⁴ , -11.77 ¹⁶² , -11.18 ⁸⁸ , -11.21 ¹⁶⁸ , -10.96 ¹⁴⁸ , -11.65 ¹⁴⁹ , -11.37 ¹⁵⁰ , -11.33 ¹⁵³ , (-10.34 ¹⁶⁴)	-11.38(27)	-11.24	-0.14
2-Methyl-1-propanol (<i>iso</i> -butanol)	C ₄ H ₁₀ O	10.60 ^a	-10.91 ¹⁴² , -11.16 ¹⁶² , -10.82 ¹⁴⁸ , (-8.92 ¹⁶⁶), -11.45 ¹⁴⁹ , -10.78 ⁸⁸ , -10.88 ¹⁵⁰ , -10.97 ¹⁵³ , -11.11 ¹⁶⁴	-11.01(23)	-11.24	0.23
2-Methyl-2-propanol (<i>tert</i> -butanol)	C ₄ H ₁₀ O	7.13 ^a	-10.95 ¹⁴² , -11.06 ¹⁶² , -10.93 ¹⁴⁸ , -10.80 ¹⁶⁹ , -10.73 ¹⁷⁰ , -10.53 ¹⁴⁹ , -10.87 ⁸⁸ , -10.74 ¹⁵⁰ , -10.94 ¹⁵³	-10.83(17)	-11.05	0.22
2-Pentanol	C ₅ H ₁₂ O	11.84 ^f	-10.44 ⁸⁸ , -10.40 ¹⁴⁸ , -10.42 ¹⁵³ , -10.30 ¹⁶⁴ , -10.12 ¹⁶⁵	-10.33(20)	-10.52	0.19
3-Pentanol	C ₅ H ₁₂ O	11.15 ^f	-10.27 ¹⁶⁸ , -9.89 ¹⁶⁴ , -9.69 ¹⁶⁵	-9.95(40)	-10.52	0.57
2-Methyl-1-butanol	C ₅ H ₁₂ O	13.20 ^f	-10.72 ¹⁶⁴ , -10.40 ¹⁶⁵	-10.56(40)	-10.52	-0.04
2-Methyl-2-butanol	C ₅ H ₁₂ O	9.43 ^a	-10.54 ¹⁴⁸ , -10.59 ¹⁵³ , (-9.18 ¹⁶⁴), (-8.88 ¹⁶⁵)	-10.56(30)	-10.32	-0.24
3-Methyl-1-butanol	C ₅ H ₁₂ O	13.50 ^f	-10.23 ¹⁴² , -10.54 ¹⁵³ , -10.82 ¹⁶⁴ , -10.59 ¹⁶⁵	-10.54(30)	-10.52	-0.02
2-Hexanol	C ₆ H ₁₄ O	14.48 ^a	-10.12 ⁸⁸ , -9.59 ¹⁴⁸ , -9.88 ¹⁶⁴ , -9.62 ¹⁶⁵	-9.80(30)	-9.80	0.00
3-Hexanol	C ₆ H ₁₄ O	13.89 ^f	-9.08 ¹⁶⁸ , -9.41 ¹⁶⁴ , -9.28 ¹⁶⁵	-9.26(40)	-9.80	0.54
2-Methyl-1-pentanol	C ₆ H ₁₄ O	15.44 ^f	-9.43 ¹⁶⁴ , -9.55 ¹⁶⁵	-9.49(40)	-9.80	0.31
3-Methyl-2-pentanol	C ₆ H ₁₄ O	13.66 ^f	-9.72 ¹⁶⁴	-9.7(4)	-9.40	-0.30
3-Methyl-3-pentanol	C ₆ H ₁₄ O	11.93 ⁿ	-9.60 ¹⁴⁸ , -9.66 ¹⁶⁴ , -9.34 ¹⁶⁵	-9.53(23)	-9.60	0.07
4-Methyl-2-pentanol	C ₆ H ₁₄ O	13.23 ^f	-8.75 ¹⁶⁴ , -8.78 ¹⁶⁵	-8.8(4)	-9.40	0.60
2-Ethyl-1-butanol	C ₆ H ₁₄ O	15.57 ^f	-10.13 ¹⁶⁴ , -9.78 ¹⁷¹	-9.9(4)	-9.80	-0.10
2,3-Dimethyl-2-butanol	C ₆ H ₁₄ O	11.28 ⁿ	-9.01 ¹⁶⁴	-9.0(4)	-9.21	0.21
2-Heptanol	C ₇ H ₁₆ O	17.3 ^o	-9.23 ¹⁶⁴	-9.2(5)	-9.07	-0.13
3-Heptanol	C ₇ H ₁₆ O	16.37 ^f	-8.45 ¹⁶⁴ , -8.64 ¹⁷¹	-8.55(40)	-9.07	0.52
4-Heptanol	C ₇ H ₁₆ O	16.61 ^f	-8.75 ¹⁶⁴ , -8.72 ¹⁷¹ , -8.77 ¹⁶⁸	-8.75(40)	-9.07	0.32
3-Ethyl-3-pentanol	C ₇ H ₁₆ O	13.07 ^f	-8.44 ¹⁶⁴	-8.4(5)	-8.87	0.47
2-Octanol	C ₈ H ₁₈ O	20.19 ^p	-8.79 ¹⁶⁵	-8.8(6)	-8.35	-0.45
3-Octanol	C ₈ H ₁₈ O	19.66 ^f	-8.60 ¹⁷¹	-8.6(6)	-8.35	-0.25
2-Ethyl-1-Hexanol	C ₈ H ₁₈ O	21.04 ^p	-9.49 ¹⁶⁴	-9.5(6)	-8.35	-1.15
Cyclic alcohols						
Cyclopentanol	C ₅ H ₁₀ O	14.55 ^q	-15.10 ¹⁶⁸ , -14.88 ¹⁷¹	-15.0(3)	-15.14	0.15
Cyclohexanol	C ₆ H ₁₂ O	17.36 ^f	-14.79 ¹⁴² , -15.06 ¹⁶⁸ , -15.19 ¹⁶⁴ , -15.32 ¹⁷¹	-15.09(25)	-14.31	-0.78
Cycloheptanol	C ₇ H ₁₄ O	20.25 ^s	-15.68 ¹⁷¹ , -14.88 ¹⁶⁸	-15.2(5)	-13.48	-1.72
Monoterpenes						
Terpinolene (cyclohexene, 1-methyl-4-(1-methyl- ethylidene-))	C ₁₀ H ₁₆	17.39 ^h	6.40 ¹⁷⁷ , 6.30 ¹⁸⁰	6.3(15)	5.56	0.74
Sabinene (bicyclo[3.1.0] hexane, 4-methylene-1- (1-methylethyl-))	C ₁₀ H ₁₆	14.03 ^e	>9.6 ¹⁷⁴ , 10.38 ¹⁷⁷	10.4(15)	9.76	0.64
α -Phellandrene (1,3-cyclo- hexadiene, 2-methyl-5- (1-methylethyl-))	C ₁₆ H ₁₆	15.47 ^h	9.90 ¹⁷⁷	9.9(15)	9.65	0.25
α -Terpinene (1,3-cyclo- hexadiene, 1-methyl-4- (1-methylethyl-))	C ₁₀ H ₁₆	15.38 ^c	7.38 ¹⁷⁴	7.4(15)	7.60	-0.20
γ -Terpinene (1,4-cyclo- hexadiene, 1-methyl-4- (1-methylethyl-))	C ₁₀ H ₁₆	16.80 ^w	7.08 ¹⁸⁰	7.1(15)	7.60	-0.50

(Continued)

Table 1. (Continued)

Compound	Formula	$\Delta_{\text{vap}}G^\circ$, kJ · mol ⁻¹	Values of $\Delta_f G^\circ$ from literature, kJ · mol ⁻¹	Value used in the fit	Group contribution value	Δ , kJ · mol ⁻¹
Monoterpenes (continued)						
Limonene (cyclohexene, 1-methyl-4-(1-methyl- ethenyl-))	C ₁₀ H ₁₆	15.49 ^t	6.57 ¹⁷⁸ , 6.34 ¹⁷⁸ , 6.39 ¹⁷⁹ , 7.46 ¹⁷⁴ , 9.32 ¹⁷⁷ , 7.37 ¹³⁹ , 9.50 ¹⁸⁰	7.6(13)	8.71	-1.41
β -Myrcene (1,6-octadiene, 7-methyl-3-methylene-)	C ₁₀ H ₁₆	14.84 ^u	6.03 ¹⁷⁸ , 6.04 ¹⁷⁸ , >8.76 ¹⁷⁴ , 10.08 ¹⁷⁷	8.0(20)	9.42	-1.42
α -Pinene (bicyclo[3.1.1]- hept-2-ene, 2,6,6-tri- methyl-)	C ₁₀ H ₁₆	12.67 ^t	12.30 ¹⁷⁸ , 12.63 ¹⁸ , 14.36 ¹⁸⁰ , 8.97 ¹⁷⁴ , 13.50 ¹⁷⁷	12.3(20)	10.18	2.12
β -Pinene (bicyclo[3.1.1]- heptane, 6,6-dimethyl-2- methylene-)	C ₁₀ H ₁₆	13.71 ^t	9.64 ¹⁷⁸ , 7.01 ¹⁷⁴ , 10.89 ¹⁷³	9.6(16)	10.52	-0.92
Camphene (bicyclo[2.2.1]- heptane, 2,2-dimethyl-3- methylene-)	C ₁₀ H ₁₆	15.17 ^v	(6.36 ¹⁷⁴), 9.27 ¹⁷⁷	9.3(20)	10.52	-1.22
Tricyclene (tricyclo[2.2.1.0.2,6]heptane, 1,7,7-trimethyl-)	C ₁₀ H ₁₆	15.15 ^v	13.20 ¹⁷⁷	13.2(15)	11.99	1.21
Miscellaneous compounds						
1-Buten-3-yne (vinylacetylene)	C ₄ H ₄		7.94 ⁵⁷	7.9(10)	4.99	2.91
4-Ethenylcyclohexene	C ₈ H ₁₂	9.59 ^c	9.45 ¹⁵	9.5(5)	9.26	0.24
Ethynylbenzene (styrene)	C ₈ H ₈	11.91 ^a	4.14 ¹⁰⁰ , 2.59 ¹³³ , 3.36 ¹⁷¹ , 2.33 ¹⁷³	3.1(8)	2.37	0.73
Indane	C ₉ H ₁₀	15.34 ^c	1.96 ¹⁷⁵ , 1.99 ¹⁷⁶ , 2.49 ¹⁰	2.1(6)	0.18	1.92
Tetralin (naphthalene, 1,2,3,4-tetrahydro-)	C ₁₀ H ₁₂	18.86 ^c	1.55 ¹⁹ , 0.84 ³³ , 0.94 ³⁵	1.1(4)	1.01	0.09

^a Reid et al. (1987); ^b Ruzicka and Majer (1994); ^c Daubert and Danner (1996); ^d Steele and Chirico (1993); ^e estimated using the Lee-Kessler method (see Reid et al. (1987)); ^f Smith and Srivastava (1986); ^g Steele et al. (1996); ^h Stephenson and Malanovsky (1987); ⁱ Chirico et al. (1997a,b,c,d); ^k Steele et al. (1997a); ^l Sherblom et al. (1992); ^m Ambrose and Walton (1989); ⁿ Wiberg and Hao (1991); ^o assuming the constant CH₂ increment between 2-pentanol, 2-hexanol, 2-hexanol, and 2-octanol; ^p Ambrose and Ghiassie (1990); ^q Ambrose and Ghiassie (1987); ^r Steele et al. (1997b); ^s Cabani et al. (1975); ^t Rodrigues and Bernardo-Gil (1995); ^u Fichan et al. (1999); ^v estimated using the Lee-Kessler method with a correction to the entropy of fusion to estimated the vapor pressure of a solid compound; ^w Li et al. (1998).

¹ Cosgrove and Walkley (1981); ² Rettich et al. (1981); ³ Wilhelm et al. (1977); ⁴ Haydyk (1986); ⁵ Lutsyk et al. (1996); ⁶ Lutsyk et al. (1992); ⁷ Jonsson et al. (1982); ⁸ Rudakov and Lutsyk (1979); ⁹ Tewari et al. (1982a); ¹⁰ Price (1976); ¹¹ Polak and Lu (1973); ¹² Pierotti and Liabastre (1972); ¹³ Nelson and De Ligny (1968); ¹⁴ Barone et al. (1966); ¹⁵ McAuliffe (1966); ¹⁶ Wishnia (1963); ¹⁷ Namiot and Beider (1960); ¹⁸ Park et al. (1997); ¹⁹ Ashworth et al. (1988); ²⁰ Bittrich et al. (1983); ²¹ Tewari et al. (1982b); ²¹ Vejrosta et al. (1982); ²³ Aquan-Yuenet al. (1979); ²⁴ Korenman and Arefeva (1978); ²⁵ Budantseva et al. (1976); ²⁶ Krasnoshchekova and Gubergits (1973); ²⁷ Leinonen and Mackay (1973); ²⁸ McBain and Lissant (1951); ²⁹ Durand (1948); ³⁰ Stearns et al. (1947); ³¹ Hansen et al. (1993); ³² Bittrich et al. (1979); ³³ Burris and MacIntyre (1986); ³⁴ Ho (1985); ³⁵ Burris and Macintyre (1984); ³⁶ Baker (1960); ³⁷ Hellinger and Sandler (1995); ³⁸ McAuliffe (1969); ³⁹ Franks (1966); ⁴⁰ Baker (1959); ⁴¹ Becke and Quitzsch (1977); ⁴² Coates et al. (1985); ⁴³ Button (1976); ⁴⁴ Sutton and Calder (1974); ⁴⁵ Pavlova et al. (1966); ⁴⁶ Shoor et al. (1969); ⁴⁷ Wetlaufer et al. (1964); ⁴⁸ Serra et al. (1998); ⁴⁹ Wehe and McKetta (1961); ⁵⁰ Dec and Gill (1985b); ⁵¹ Brooks and McKetta (1955a); ⁵² Leland et al. (1955); ⁵³ Natarajan and Venkatachalam (1972); ⁵⁴ Schwarz (1980); ⁵⁵ Economou et al. (1997); ⁵⁶ Ross and Hudson (1957); ⁵⁷ Simpson and Lovell (1962); ⁵⁸ Inga and McKetta (1961a); ⁵⁹ Helmkamp et al. (1957); ⁶⁰ Hafemann and Miller (1969); ⁶¹ Thomsen and Gjaldbak (1963); ⁶² Imai (1961); ⁶³ Groves (1988); ⁶⁴ Dewulf et al. (1999); ⁶⁵ Tucker et al. (1981); ⁶⁶ McAllife (1971); ⁶⁷ Sanemasa et al. (1987); ⁶⁸ Mackay and Shiu (1975); ⁶⁹ Nielsen et al. (1994); ⁷⁰ Farkas (1965); ⁷¹ Duque-Estrada et al. (1964); ⁷² Streitwieser and Nebenzahl (1976); ⁷³ Allen et al. (1998); ⁷⁴ Peng and Wan (1997); ⁷⁵ Alaei et al. (1996); ⁷⁶ Turner et al. (1996); ⁷⁷ Dewulf et al. (1995); ⁷⁸ Hoff et al. (1993); ⁷⁹ Perlinger et al. (1993); ⁸⁰ Robbins et al. (1993); ⁸¹ Green and Frank (1979); ⁸² Vitenberg et al. (1975); ⁸³ Hartkopf and Karger (1973); ⁸⁴ Li et al. (1993); ⁸⁵ Li and Carr (1993); ⁸⁶ Cooling et al. (1992); ⁸⁷ Sanemasa et al. (1989); ⁸⁸ Mash and Pemberton (1980); ⁸⁹ Duhem and Vidal (1978); ⁹⁰ Sun et al. (1997); ⁹¹ Zou et al. (1997); ⁹² Keeley et al. (1988); ⁹³ Keeley et al. (1986); ⁹⁴ Sanemasa et al. (1984); ⁹⁵ May et al. (1983); ⁹⁶ Dutta-Choudhury et al. (1982); ⁹⁷ Sanemasa et al. (1982); ⁹⁸ Sanemasa et al. (1981); ⁹⁹ Lara et al. (1981); ¹⁰⁰ Banerjee et al. (1980); ¹⁰¹ Ben-Naim and Wilf (1980); ¹⁰² Mackay et al. (1979); ¹⁰³ May et al. (1978); ¹⁰⁴ Krasnoshchekova and Gubergits (1975); ¹⁰⁵ Sada et al. (1975); ¹⁰⁶ Vesala (1974); ¹⁰⁷ Bradley et al. (1973); ¹⁰⁸ Corby and Elworthy (1971); ¹⁰⁹ Worley (1967); ¹¹⁰ Franks et al. (1963); ¹¹¹ Taha et al. (1966); ¹¹² Desnoyers et al. (1965); ¹¹³ Udovenko and Aleksandrova (1963); ¹¹⁴ Alexander (1959c); ¹¹⁵ Arnold et al. (1958); ¹¹⁶ Hayashi and Sasaki (1956); ¹¹⁷ McDevit and Long (1952); ¹¹⁸ Morrison and Billett (1952); ¹¹⁹ Bohon and Claussen (1951); ¹²⁰ Klevens (1950); ¹²¹ Andrews and Keefer (1950); ¹²² Gross and Saylor (1931); ¹²³ Ramachandran et al. (1996); ¹²⁴ Smith et al. (1993); ¹²⁵ Banerjee (1984); ¹²⁶ Rossi and Thomas (1981); ¹²⁷ Sutton and Calder (1975); ¹²⁸ Desnoyers and Ichhaporia (1969); ¹²⁹ Chen and Wagner (1994c); ¹³⁰ Keeley et al. (1991); ¹³¹ Owens et al. (1986); ¹³² Brown and Wasik (1974); ¹³³ Andrews and Keefer (1950); ¹³⁴ Hermann (1972); ¹³⁵ Chernoglazova and Simulin (1976); ¹³⁶ Knauss and Copenhaver (1995); ¹³⁷ DeVoe et al. (1981); ¹³⁸ Glew and Robertson (1956); ¹³⁹ Massaldi and King (1973); ¹⁴⁰ Lun et al. (1997); ¹⁴¹ Sherblom et al. (1992); ¹⁴² Dallas (1992); ¹⁴³ Pividal et al. (1992); ¹⁴⁴ Landau et al. (1991); ¹⁴⁵ Richon et al. (1985); ¹⁴⁶ Lebert and Richon (1984); ¹⁴⁷ Christian et al. (1981); ¹⁴⁸ Merk and Riederer (1997); ¹⁴⁹ Snider and Dawson (1985); ¹⁵⁰ Rytting et al. (1978); ¹⁵¹ Cox et al. (1973); ¹⁵² Burnett (1963); ¹⁵³ Butler et al. (1935); ¹⁵⁴ Park et al. (1987); ¹⁵⁵ Nord et al. (1984); ¹⁵⁶ Pemberton and Mash (1978); ¹⁵⁷ d'Avila and Silva (1970); ¹⁵⁸ Shaffer and Daubert (1969); ¹⁵⁹ Hansen and Miller (1954); ¹⁶⁰ Burnett and Swoboda (1962); ¹⁶¹ Djerki and Laub (1988); ¹⁶² Sagert and Lau (1986); ¹⁶³ Buttery et al. (1969); ¹⁶⁴ Barton (1984); ¹⁶⁵ Stephenson et al. (1984); ¹⁶⁶ Shiu and Mackay (1997); ¹⁶⁷ Dallos and Liszi (1995); ¹⁶⁸ Cabani et al. (1975b); ¹⁶⁹ Koga (1995); ¹⁷⁰ Koga et al. (1990); ¹⁷¹ Stephenson and Stuart (1986); ¹⁷² Frilette and Hohenstein (1948); ¹⁷³ Lane (1946); ¹⁷⁴ Weidenhamer et al. (1993); ¹⁷⁵ Yalkowsky and Valvani (1980); ¹⁷⁶ Mackay and Shiu (1977); ¹⁷⁷ Schmid et al. (1992); ¹⁷⁸ Fichan et al. (1999); ¹⁷⁹ Gironi et al. (1995); ¹⁸⁰ Li et al. (1998).

Table 2. The data base of experimental values of the enthalpies of vaporization and hydration of hydrocarbons and monohydric alcohols. See text for discussion of data sources; values in italics are calculated from the temperature dependence of the Gibbs energy of hydration and those in parentheses were considered to be unreliable in this study. Also listed are the corresponding values calculated with the proposed group contribution method and the difference between the calculated values and the experimental data.

Compound	Formula	$\Delta_{vap}H^{\circ}$, kJ · mol ⁻¹	Values of $\Delta_h H^{\circ}$ from literature, kJ · mol ⁻¹	Value used in the fit	Group contribution value	Δ , kJ · mol ⁻¹
n-Alkanes						
Methane	CH ₄		-13.18 ¹ , -13.06 ²	-13.1(1)		
Ethane	C ₂ H ₆		-19.52 ¹ , -19.30 ²	-19.4(2)	-17.37	-2.03
Propane	C ₃ H ₈		-23.27 ¹ , -22.90 ² , -22.61 ³	-22.9(3)	-21.13	-1.77
<i>n</i> -Butane	C ₄ H ₁₀		-25.92 ¹ , -25.93 ²	-25.9(3)	-24.89	-1.01
<i>n</i> -Pentane	C ₅ H ₁₂	26.75 ^a	-28.75 ⁴	-28.8(3)	-28.65	-0.15
<i>n</i> -Hexane	C ₆ H ₁₄	31.73 ^a	-31.7 ⁴ , -31.3 ⁵	-31.6(4)	-32.41	0.81
<i>n</i> -Heptane	C ₇ H ₁₆	36.66 ^a	-35.1 ⁶⁺⁷⁺⁸	-35.1(30)	-36.17	1.07
<i>n</i> -Octane	C ₈ H ₁₈	41.53 ^a	-38.4 ⁶⁺⁷	-38.4(40)	-39.92	1.52
Branched alkanes						
2-Methylpropane	C ₄ H ₁₀		-24.19 ¹	-24.2(4)	-25.76	1.56
2-Methylbutane	C ₅ H ₁₂	25.22 ^a	-25.1 ⁹⁺¹⁰	-25.1(50)	-29.52	4.42
2,2-Dimethylpropane	C ₅ H ₁₂		-25.1 ¹	-25.1(3)	-29.81	4.71
2-Methylpentane	C ₆ H ₁₄	30.10 ^a	-32.6 ⁷⁺⁹	-32.6(60)	-33.28	0.68
2,3-Dimethylbutane	C ₆ H ₁₄	29.33 ^a	-29.2 ⁷⁺⁹	-29.2(60)	-34.15	4.95
Alkenes and Dienes						
Ethene	C ₂ H ₄		-16.46 ¹	-16.5(3)	-16.62	0.12
Propene	C ₃ H ₆		-21.64 ¹	-21.6(3)	-20.43	-1.17
1-Butene	C ₄ H ₈		-24.88 ¹	-24.9(4)	-24.19	-0.71
2-Methyl-1-propene	C ₄ H ₈		-24.7 ¹¹	-24.7(20)	-24.24	-0.46
2-Methyl-2-butene	C ₅ H ₁₀	27.34 ^a	-29.6 ¹²⁺¹⁰	-29.6(20)	-28.04	-1.56
1-Hexene	C ₆ H ₁₂	30.6 ^b	-32.2 ¹³	-32.2(30)	-31.71	-0.49
1-Octene	C ₈ H ₁₆	40.44 ^a	-36.9 ¹³	-36.9(30)	-39.23	2.33
1,3-Butadiene	C ₄ H ₆		-27.0 ¹⁴⁺¹⁵⁺¹⁶	-27.0(30)	-23.49	-3.51
2-Methyl-1,3-butadiene	C ₅ H ₈	26.8 ^c	-22.7 ¹⁷⁺¹⁰	-22.7(60)	-27.30	4.60
Alkynes and Diynes						
Ethyne	C ₂ H ₂		-14.62 ¹	-14.6(3)	-14.82	0.22
Propyne	C ₃ H ₄		-20.2 ¹⁶⁺¹⁸	-20.2(20)	-18.63	-1.57
1-Butyne	C ₄ H ₆		-16.0 ¹⁶⁺¹⁷	-16.0(60)	-22.39	6.39
Cycloalkanes						
Cyclopropane	C ₃ H ₆		-23.26 ⁷	-23.3(4)	-18.36	-4.94
Cyclopentane	C ₅ H ₁₀	28.72 ^a	-25.4 ⁷⁺¹⁹ ; -28.5 ²⁰	-27.0(20)	-29.08	2.08
Cyclohexane	C ₆ H ₁₂	33.12 ^a	-33.2 ⁴ , -32.9 ⁵	-33.1(3)	-34.44	1.34
Methylcyclohexane	C ₇ H ₁₄	35.44 ^a	-45.7 ²¹⁺⁷⁺²²	-45.7(30)	-39.06	-6.64
Cycloalkenes						
Cyclopentene	C ₅ H ₈	28.1 ^c	-25.7 ²⁰	-25.7(30)	-26.54	0.84
Cyclohexene	C ₆ H ₁₀	33.57 ^a	-32.0 ²⁰	-32.0(30)	-31.90	-0.10
1,4-Cyclohexadiene	C ₉ H ₁₈	34.8 ^d	-31.8 ²⁰	-31.8(30)	-29.36	-2.44
1,3,5-Cycloheptatriene	C ₉ H ₁₈	38.5 ^c	-32.5 ²⁰	-32.5(40)	-32.18	-0.32
Alkylbenzenes						
Benzene	C ₆ H ₆	33.92 ^a	-31.71 ³ , -31.70 ²³ , -31.58 ²⁴ , -31.84 ²⁵ , (-33.46 ²⁶), (-33.12 ⁵)	-31.7(2)	-32.28	0.58
Toluene	C ₇ H ₈	38.06 ^a	-36.26 ²⁴ , -36.33 ⁴ , (-37.22 ²⁶)	-36.3(3)	-35.50	-0.80
Ethylbenzene	C ₈ H ₁₀	42.26 ^a	-40.24 ⁴	-40.2(4)	-39.26	-0.94
1,2-Dimethylbenzene (<i>o</i> -xylene)	C ₈ H ₁₀	43.45 ^c	-36.6 ⁹⁺²⁷⁺²⁸⁺²⁹⁺³⁰	-36.6(20)	-36.71	0.11
1,3-Dimethylbenzene (<i>m</i> -xylene)	C ₈ H ₁₀	42.72 ^c	-38.5 ⁹⁺²⁷⁺²⁸⁺²⁹⁺³⁰⁺³¹	-38.5(20)	-38.71	0.21
1,4-Dimethylbenzene (<i>p</i> -xylene)	C ₈ H ₁₀	42.36 ^c	-38.6 ⁹⁺²⁷⁺²⁸⁺²⁹⁺³⁰⁺³²⁺³³	-38.6(20)	-38.71	0.11
Propylbenzene	C ₉ H ₁₂	46.24 ^a	-43.94 ⁴	-43.9(4)	-43.02	-0.88
1,2,3-Trimethylbenzene	C ₉ H ₁₂	49.06 ^a	-37.5 ³⁰	-37.5(20)	-37.93	0.43
1,2,4-Trimethylbenzene	C ₉ H ₁₂	47.94 ^a	-39.9 ³⁰	-39.9(20)	-39.93	0.03
1,3,5-Trimethylbenzene (mesitylene)	C ₉ H ₁₂	47.51 ^a	-39.3 ³⁰ , -43.0 ³²	-41.0(30)	-41.93	0.93
1-Methylethylbenzene (<i>iso</i> -propylbenzene, cumene)	C ₉ H ₁₂	45.15 ^a	-39.6 ³⁰	-39.6(20)	-43.89	4.29
<i>n</i> -Butylbenzene	C ₁₀ H ₁₄	51.37 ^f	-46.1 ³⁴⁺³⁵⁺³⁶	-46.1(30)	-46.77	0.67
<i>n</i> -Pentylbenzene	C ₁₁ H ₁₆	55.33 ^f	-48.8 ³⁶	-48.8(30)	-50.53	1.73
<i>n</i> -Hexylbenzene	C ₁₂ H ₁₈	60.24 ^f	-52.2 ³⁶ , -52.6 ³⁷	-52.4(40)	-54.29	1.89

(Continued)

Table 2. (Continued)

Compound	Formula	$\Delta_{vap}H^{\circ}$, kJ · mol ⁻¹	Values of $\Delta_f H^{\circ}$ from literature, kJ · mol ⁻¹	Value used in the fit	Group contribution value	Δ , kJ · mol ⁻¹
1-Alcohols						
Methanol	CH ₄ O	37.83 ^a	-45.12 ³⁸ , (-44.87 ³⁹), (-44.83 ⁴⁰), -45.12 ⁴¹ , (-44.88 ⁴²), -45.12 ²³ , -45.16 ⁴³ , -45.17 ⁴⁴ , -44.93 ⁵ , -45.07 ²⁶ , -45.08 ⁴⁵ , -45.11 ⁴⁶ , -45.18 ⁴⁷ , -45.16 ⁴⁸	-45.13(20)	-49.62	4.49
Ethanol	C ₂ H ₆ O	42.46 ^a	-52.66 ³⁸ , -52.63 ³⁹ , -52.48 ⁴⁰ , -52.61 ⁴¹ , (-52.21 ⁴²), -52.61 ²³ , -52.65 ⁴³ , -52.43 ⁴⁹ , (-52.96 ⁵⁰), -52.63 ⁵¹ , -52.63 ⁴⁶ , -52.64 ⁴⁴ , -52.59 ⁵ , -52.59 ²⁶ , -52.56 ⁴⁵ , -52.59 ⁵² , -52.71 ⁵³ , -52.42 ⁴⁷ , -52.46 ⁵⁴ , -52.46 ⁴⁸	-52.59(15)	-53.38	0.79
1-Propanol	C ₃ H ₈ O	47.50 ^a	(-57.96 ³⁸), (-52.71 ³⁹), (-57.40 ⁴⁰), -57.55 ⁴¹ , (-57.31 ⁴²), -57.72 ²³ , -57.62 ⁴³ , -57.60 ⁵⁵ , -57.67 ²⁶ , -57.62 ⁴⁴ , -57.63 ⁴⁵ , (-56.70 ⁵²), (-56.70 ⁴⁸)	-57.65(20)	-57.14	-0.51
1-Butanol	C ₄ H ₁₀ O	52.42 ^a	-61.79 ³⁸ , (-61.16 ⁴⁰), -61.69 ⁵⁶ , -61.74 ⁴¹ , -61.74 ²³ , -61.66 ⁴³ , -61.67 ⁵⁷ , -61.50 ⁴⁶ , (-61.42 ⁵²), -61.70 ⁴⁵ , -61.83 ⁴⁴ , -61.62 ²⁶ , (-60.58 ⁴⁸)	-61.72(20)	-60.90	-0.82
1-Pentanol	C ₅ H ₁₂ O	57.04 ^a	-65.11 ³⁸ , -65.03 ⁵⁶ , -65.03 ⁴¹ , -64.76 ⁴³ , -64.86 ⁴⁴ , -64.70 ²⁶ , -65.14 ⁵² , (-63.39 ⁴⁸)	-65.0(3)	-64.66	-0.34
1-Hexanol	C ₆ H ₁₄ O	61.61 ^a	-68.02 ⁴¹ , -68.17 ⁵⁸ , (-67.4 ⁵²), (-66.25 ⁴⁸)	-68.1(4)	-68.42	0.32
1-Heptanol	C ₇ H ₁₆ O	66.81 ^a	-71.69 ⁴¹ , -72.18 ⁵⁸	-71.7(4)	-72.18	0.38
1-Octanol	C ₈ H ₁₈ O	70.98 ^a	-74.38 ⁵⁹ , -74.35 ⁴¹	-74.4(7)	-75.94	1.54
Branched alcohols						
2-Propanol	C ₃ H ₈ O	45.48 ^a	-58.5 ⁶⁰ , -58.24 ³⁸ , -58.57 ³⁹ , (-58.17 ⁴²), -58.58 ⁴³ , -58.37 ²⁶ , -58.55 ⁴⁴ , -58.46 ⁴⁵	-58.5(2)	-58.01	-0.49
2-Butanol	C ₄ H ₁₀ O	49.81 ^a	-62.80 ⁶¹ , -62.83 ⁴³ , 62.70 ⁶² , -62.89 ⁴⁴	-62.8(2)	-61.77	-1.03
2-Methyl-2-propanol	C ₄ H ₁₀ O	50.8 ^a	-60.11 ⁴³ , -60.20 ⁴⁴	-60.2(2)	-61.77	1.57
2-Methyl-2-propanol	C ₄ H ₁₀ O	46.74 ^a	-64.05 ⁴³ , -64.18 ⁶³ , -64.20 ⁴⁴ , (-64.69 ⁴⁶), -63.94 ²⁶ , -64.05 ⁴⁵	-64.1(3)	-62.06	-2.04
3-Pentanol	C ₅ H ₁₂ O	54.03 ^a	-66.8 ⁶²	-66.8(7)	-65.53	-1.27
2-Methyl-2-butanol	C ₅ H ₁₂ O	50.17 ^a	-68.46 ⁴³ , -68.72 ⁴⁴ , -68.12 ²⁶	-68.5(5)	-65.82	-2.68
3-Hexanol	C ₆ H ₁₄ O	57.0 ^g	-69.6 ⁶²	-69.6(7)	-69.29	-0.31
4-Heptanol	C ₇ H ₁₆ O	62.6 ^g	-75.3 ⁶²	-75.3(11)	-73.05	-2.25
Unsaturated linear alcohols						
2-Propen-1-ol	C ₃ H ₆ O	47.3 ^c	-54.4 ⁴⁴	-54.4(15)	-56.44	2.04
2-Buten-1-ol	C ₄ H ₈ O	49.2 ^h	-57.3 ⁴⁴	-57.3(30)	-60.25	2.95
3-Buten-1-ol	C ₄ H ₈ O	49.8 ^h	-58.2 ⁴⁴	-58.2(30)	-60.20	2.00
4-Penten-1-ol	C ₅ H ₁₀ O	54.9 ^h	-60.8 ⁴⁴	-60.8(30)	-63.96	3.76
3-Pentyn-1-ol	C ₅ H ₈ O	58.8 ^h	-64.5 ⁴⁴	-64.5(40)	-62.21	-2.29
Cyclic alcohols						
Cyclopentanol	C ₅ H ₁₀ O	57.63 ^a	-67.76 ⁶² , -67.97 ⁴⁴	-67.8(3)	-65.96	-1.84
Cyclohexanol	C ₆ H ₁₂ O	62.02 ^a	-69.92 ⁶² , -71.03 ⁴⁴ , -70.7 ⁶⁸	-70.7(7)	-71.32	0.62
Cycloheptanol	C ₇ H ₁₄ O	67.57 ^g	-74.60 ⁶² , -74.83 ⁴⁴	-74.7(7)	-76.67	1.97
Monoterpenes						
Terpinolene	C ₁₀ H ₁₆	54.2 ^d	-45.5 ⁶⁷	-45.5(60)	-44.83	-0.67
γ -Terpinene	C ₁₀ H ₁₆	50.5 ^d	-35.5 ⁶⁷	-35.5(60)	-45.36	9.86
Limonene	C ₁₀ H ₁₆	48.92 ⁱ	-39.7 ⁶⁶⁺ , -38.2 ⁶⁷	-39.0(60)	-47.20	8.20
α -Pinene	C ₁₀ H ₁₆	43.3 ^d	-39.4 ⁶⁷	-39.4(60)	-39.35	-0.05
Miscellaneous compounds						
1-Buten-3-yne (vinylacetylene)	C ₄ H ₄		-14.4 ³	-14.4(60)	-21.69	7.29
Ethylbenzene (styrene)	C ₈ H ₈	44.81 ^d	-35.0 ⁶⁴	-35.0(40)	-38.56	3.56
Tetralin	C ₁₀ H ₁₂	54.1 ^d	-44.4 ⁶⁵	-44.0(50)	-45.07	1.07
2-Cyclohexen-1-ol	C ₆ H ₁₀ O	63.1 ^h	-70.9 ⁴⁴	-70.9(30)	-68.77	-2.13

^a Majer and Svoboda (1985); ^b Steele and Chirico (1993); ^c Cox and Pilcher (1970); ^d Daubert and Danner (1996); ^e Chirico et al. (1997a,b,c,d); ^f Ruzicka et al. (1994); ^g Cabani et al. (1975); ^h calculated using the group contribution values in Domalski and Hearing (1993); ⁱ Atik et al. (1987).
¹ Dec and Gill (1984); ² Olofsson et al. (1984); ³ Hallén and Wadsö (1989); ⁴ Gill et al. (1976); ⁵ Reid et al. (1969); ⁶ Jonsson et al. (1982); ⁷ Price (1976);
⁸ Nelson and De Ligny (1968); ⁹ Polak and Lu (1973); ¹⁰ Pavlova et al. (1966); ¹¹ Wilhelm et al. (1977); ¹² Taft et al. (1955); ¹³ Economou et al. (1997);
¹⁴ Ross and Hudson (1957); ¹⁵ Reed and McKetta (1959); ¹⁶ Simpson and Lovell (1962); ¹⁷ McAuliffe (1966); ¹⁸ Inga and McKetta (1961a); ¹⁹ Hansen et al. (1993);
²⁰ Pierotti and Liabastre (1972); ²¹ Rudakov and Lutsyk (1979); ²² Burris and MacIntyre (1984); ²³ Nilsson and Wadsö (1984); ²⁴ Lisi et al. (1980);
²⁵ Gill et al. (1975); ²⁶ Krishnan and Friedman (1969); ²⁷ Ashworth et al. (1988); ²⁸ Dewulf et al. (1995); ²⁹ Robbins et al. (1993); ³⁰ Sanemasa et al. (1982);
³¹ Chernoglavova and Simulin (1976); ³² Chen and Wagner (1994c); ³³ Knauss and Copenhaver (1995); ³⁴ Perlinger et al. (1993); ³⁵ Rossi and Thomas (1981);
³⁶ Owens et al. (1985); ³⁷ May et al. (1983); ³⁸ Pfeiffer et al. (1995); ³⁹ Dohnal et al. (1994); ⁴⁰ Trampe and Eckert (1991); ⁴¹ Hallén et al. (1986);
⁴² Korolev et al. (1985); ⁴³ Row and Somsen (1981); ⁴⁴ Arnett et al. (1969); ⁴⁵ Alexander and Hill (1969); ⁴⁶ Arnett and McKelvey (1969); ⁴⁷ Bertrand et al. (1966);
⁴⁸ Aveyard and Lawrence (1964); ⁴⁹ Landgren et al. (1978); ⁵⁰ Pannell (1973); ⁵¹ Arnett et al. (1972); ⁵² Aveyard and Mitchell (1968); ⁵³ Franks and Watson (1968);
⁵⁴ Arnett et al. (1965); ⁵⁵ Franks et al. (1973); ⁵⁶ De Lisi et al. (1987); ⁵⁷ Nwankwo and Wadsö (1980); ⁵⁸ Hill and White (1974);
⁵⁹ Hallén et al. (1989); ⁶⁰ Davis et al. (1995); ⁶¹ Anderson and Olofsson (1988); ⁶² Cabani et al. (1975); ⁶³ Sköld et al. (1976); ⁶⁴ Lane (1946); ⁶⁵ Ashworth et al. (1988);
⁶⁶ Massaldi and King (1973); ⁶⁷ Li et al. (1998); ⁶⁸ Costa et al. (1999).

higher precision allows more reliable determination of the numerical values of the properties of functional groups. Second, almost all group contribution methods dealing with aqueous species presuppose the existence of the universal contribution to the thermodynamic functions, independent of the nature of a compound (see the corresponding discussion in Pierotti et al., 1959 and Cabani et al., 1981). The interpretation of this term is particularly simple for the functions of hydration, because this contribution arises naturally in the theoretical models developed for the thermodynamics of transfer of a solute from the ideal gas state to the state of solution as the functions of hydration of a material point (see, for example, Pierotti, 1976). Importantly, this contribution can be calculated independently of experimental data for solutes using only thermophysical properties of pure water (see Section 4.2). This circumstance allows fixing one term in the fitting procedure, thus notably decreasing the uncertainties in the numerical values of the thermodynamic functions of hydration for selected groups.

The functions under consideration are the Gibbs energy, $\Delta_h G^O$, the enthalpy $\Delta_h H^O$, the heat capacity $\Delta_h Cp^O$, and volume $\Delta_h V^O \equiv V_2^O$ (V_2^O stands for the infinite dilution partial molar volume of a solute)¹. Here and further in the text the subscript 2 refers to a solute species. Any thermodynamic function of hydration of a species, $\Delta_h Y^O$, is defined as the difference between the corresponding function of the species in the standard aqueous solution, Y_2^O , and one in the ideal gas state, Y° .

$$\Delta_h Y^O = Y_2^O - Y^\circ. \quad (1)$$

The standard state adopted for gaseous species is unit fugacity of ideal gas at any temperature and pressure of 0.1 MPa; that for aqueous species calls for unit activity of a hypothetical one molal solution referenced to infinite dilution at any temperature and pressure; and the standard state for liquids and solids is the pure compound at any temperature and $P = P_s$, where P_s stands for saturation vapor pressure over a liquid or solid compound. Many hydrocarbons exist as condensed phases at 298.15 K and 0.1 MPa, and thermodynamic functions of hydration must be calculated from vaporization and solubility data as described below. Having the thermodynamic functions of hydration for a compound, one can calculate the standard state partial molar properties of the compound in aqueous solution, provided that the thermodynamic properties of the compound in the ideal gas state are known. There are a number of reliable compilations of properties for many organic substances in the ideal gas state, including Domalski and Hearing (1993), Frenkel et al. (1994), and Helgeson et al. (1998).

We were able to locate many experimental results for the Gibbs energy of hydration of hydrocarbons (see below) but only a few for enthalpy, and a very few for heat capacity and volume. To get more robust estimates of the group contributions for thermodynamic functions of hydration besides the Gibbs energy, we included the monohydric alcohols, for which there are many highly accurate calorimetric and volumetric data.

There are a number of compilations of experimental data that can be used to evaluate the standard partial molar thermodynamic functions of hydration of hydrocarbons and alcohols (Irmann, 1965; Hine and Mookerjee, 1975; Wilhelm et al., 1977; Cabani et al., 1981; Abraham, 1984; Barton, 1984; Høiland, 1986; Shaw, 1989(a,b); Shock and Helgeson, 1990; Amend and Helgeson, 1997; and others). However, most of these are concerned with either particular classes of species, like gases (Wilhelm et al., 1977), liquids and solids (Barton, 1984; Shaw, 1989 a,b); or with particular properties, like V_2^O (Høiland, 1986), aqueous solubility (Irmann, 1965), the Gibbs energy of hydration (Hine and Mookerjee, 1975; Mackay and Shiu, 1979); or the standard partial molar properties in aqueous solution (Shock and Helgeson, 1990; Amend and Helgeson, 1997). The most comprehensive set of thermodynamic functions of hydration, which are of primary interest for our study, was compiled by Cabani and coworkers (1981). These authors considered all the functions of hydration, $\Delta_h G^O$, $\Delta_h H^O$, $\Delta_h Cp^O$, V_2^O , for many different classes of organic compounds, including hydrocarbons and alcohols, and covered all of the literature through the end of 1979. Since then, a large number of accurate experimental measurements have been published, allowing an update of data for thermodynamic functions of hydration and functional group contributions.

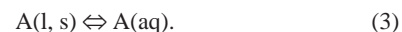
2. SOURCES OF DATA LEADING TO THE STANDARD THERMODYNAMIC FUNCTIONS OF HYDRATION OF NONELECTROLYTES

2.1. The Standard Partial Molar Gibbs Energy of Hydration

The Gibbs energy of hydration can be evaluated from the following two main groups of experimental data: (1) aqueous solubility of solids or liquids combined with the Gibbs energy of vaporization of the corresponding compounds; and (2) gas/water distribution equilibria, given as Henry's law constants, or gas/water partition coefficients, or activity coefficients of a solute in aqueous solution at infinite dilution. Data of the latter type call for the symmetrical normalization of activities, where activity coefficients are equal to one for pure compounds. This standard state normalization is often taken to be "based on Raoult's law."

2.1.1. Thermodynamics of solubility, vaporization and hydration of a liquid or solid nonelectrolyte

The following thermodynamic cycle is employed to evaluate the Gibbs energy of hydration from aqueous solubility data:



A combination of Eqns. 2 and 3 gives:



Equation 2 refers to an equilibrium process of transfer of a pure compound A from a gaseous (g) state to a state of a pure liquid (l) or solid (s). Equation 3 refers to the equilibrium process of transfer of the compound A from the state of liquid/or solid to

¹ Note below in the text that the accepted standard state for a pure gas is defined at constant pressure, therefore, there is no pressure dependence of the thermodynamic properties of an ideal gas. This definition requires the molar volume of an ideal gas and all its temperature derivatives to be equal to zero.

an aqueous solution (aq). Equation 4 defines the process of hydration of the compound A.

As mentioned above, a variety of types of experimental data can be used to obtain thermodynamic properties of hydration. We have converted all data to the standard states and other conventions used in this study, which can be illustrated by comparison of several statements for the chemical potential of a compound in different states, as discussed in this section. For the pure compound in the gaseous state in equilibrium with liquid or solid

$$\mu_g(T, P) = \mu_g^o(T, P^\ominus) + RT \ln a = \mu_g^o(T, P^\ominus) + RT \ln \frac{\psi P_s}{P^\ominus}, \quad (5)$$

where μ and μ^o stand for the chemical potential and for the standard state chemical potential of a compound; the subscript g defines the state of the compound; R represents the gas constant; T designates temperature (in K); P , P_s , P^\ominus stand for total pressure (0.1 MPa for the purposes of the present work), saturated vapor pressure over the liquid/or solid compound, and the standard state pressure of the ideal gas (0.1 MPa), respectively; a represents the activity of the compound; and ψ denotes the fugacity coefficient of the gas.

For the pure compound in the solid/or liquid state:

$$\mu_{l,s}(T, P) = \mu_{l,s}^o(T, P_s) + \int_{P_s}^P V_{l,s}(T, P) dP \approx \mu_{l,s}^o(T, P_s), \quad (6)$$

where the subscripts l and s define the state of the compound, and $V_{l,s}(T, P)$ represents the molar volume of the liquid/or solid compound. Note that for the total pressure $P = 0.1$ MPa the

contribution of the integral $\int_{P_s}^P V_{l,s}(T, P) dP$ is less than 0.05–0.10 $\text{kJ} \cdot \text{mol}^{-1}$ even if the molar volume of pure phase is 500–1000 $\text{cm}^3 \cdot \text{mol}^{-1}$, and is generally negligible for practical purposes.

For the case in which the liquid or solid compound forms an “organic-rich” phase in equilibrium with a coexisting “water-rich” solution

$$\begin{aligned} \mu_{l,s}(T, P) &= \mu_{l,s}^o(T, P_s) + \int_{P_s}^P V_{l,s}(T, P) dP + RT \ln a \\ &\approx \mu_{l,s}^o(T, P_s) + RT \ln X \gamma_o, \quad (7) \end{aligned}$$

where X and γ_o stand for the saturation mole fraction and the saturation activity coefficient (for symmetrical normalization) of the compound in the “organic-rich” phase. If the compound is a solid, then $X = 1$ and $\gamma_o = 1$.

For the compound in an aqueous solution coexisting with the “organic-rich” phase

$$\mu_2(T, P) = \mu_2^o(T, P) + RT \ln a = \mu_2^o(T, P) + RT \ln m \gamma_w, \quad (8)$$

where m and γ_w stand for the saturation molality and the saturation activity coefficient (for unsymmetrical normalization) of the compound in the aqueous solution coexisting with the “organic-rich” phase.

Now, for the process represented by Eqn. 2 one obtains

$$\begin{aligned} \Delta_r G(2) \equiv 0 &= \mu_{l,s}(T, P) - \mu_g(T, P) = \mu_{l,s}^o(T, P) - \mu_g^o(T, P^\ominus) \\ &\quad - RT \ln \frac{\psi P_s}{P^\ominus} = -\Delta_{\text{vap}} G^o - RT \ln \frac{\psi P_s}{P^\ominus} \\ &\quad \text{or } \Delta_{\text{vap}} G^o = -RT \ln \frac{\psi P_s}{P^\ominus}, \quad (9) \end{aligned}$$

where the subscript *vap* defines “vaporization” as the phase transition process. The term $\Delta_{\text{vap}} G^o$ stands for the difference between the standard Gibbs energy of a compound in the ideal gas state and in the state of a pure liquid or solid.

For the process indicated by Eqn. 3

$$\begin{aligned} \Delta_r G(3) \equiv 0 &= \mu_2(T, P) - \mu_{l,s}(T, P) = \mu_2^o(T, P) - \mu_{l,s}^o(T, P) \\ &\quad + RT \ln \frac{m \gamma_w}{X \gamma_o} = \Delta_{\text{sol}} G^o + RT \ln \frac{m \gamma_w}{X \gamma_o} \\ &\quad \text{or } \Delta_{\text{sol}} G^o = -RT \ln \frac{m \gamma_w}{X \gamma_o}, \quad (10) \end{aligned}$$

where the subscript *sol* defines “solution” as the phase transition process. As a result, the corresponding expression for the process represented by Eqn. 4 is given by

$$\begin{aligned} \Delta_r G(4) \equiv 0 &= \mu_2^o(T, P) - \mu_g^o(T, P) - RT \ln \frac{\psi P_s}{P^\ominus} \\ &\quad + RT \ln \frac{m \gamma_w}{X \gamma_o} = \Delta_h G^o + \Delta_{\text{vap}} G^o - \Delta_{\text{sol}} G^o \\ &\quad \text{or } \Delta_h G^o = \Delta_{\text{sol}} G^o - \Delta_{\text{vap}} G^o. \quad (11) \end{aligned}$$

Therefore, the standard state partial molar Gibbs energy of hydration is the difference between the standard partial molar Gibbs energy of solution, evaluated from aqueous solubility data, and the standard Gibbs energy of vaporization, evaluated from vapor-liquid equilibria for pure compounds.

All hydrocarbons considered in this study have equilibrium saturation molalities at 298.15 K and 0.1 MPa less than 0.03 $\text{mol} \cdot \text{kg}^{-1}$, and the equilibrium mole fraction of water in the saturated “organic-rich” phase is less than 0.005. Therefore, for this class of compounds the simplified approximation for the standard Gibbs energy of solution, $\Delta_{\text{sol}} G^o = -RT \ln m$, is quite accurate.

In contrast, alcohols and water demonstrate high mutual solubilities. The mole fraction of water in the “alcohol-rich” phase may exceed 0.5 and the saturation molality of alcohols in the “water-rich” phase may be as high as 1–3 $\text{mol} \cdot \text{kg}^{-1}$ (alcohols with carbon number three and less and 2-methyl-2-propanol (“*tert*-butyl alcohol”), are completely miscible with water and are not considered in this discussion). In such a situation it is necessary to evaluate the activity coefficients of alcohols in the coexisting phases. Apelblat (1990) presented Margules parameters for more than ten alcohol-water systems (including normal, branched and cyclic alcohols) at 298.15 K and 0.1 MPa, which allows us to calculate the activity coefficients at saturation (for symmetrical normalization) for alcohols in “alcohol-rich” phases, and to use these results for evaluating γ_o . As shown in Figure 1, when values of γ_o for alcohols from Apelblat (1990) are plotted against X , the mole

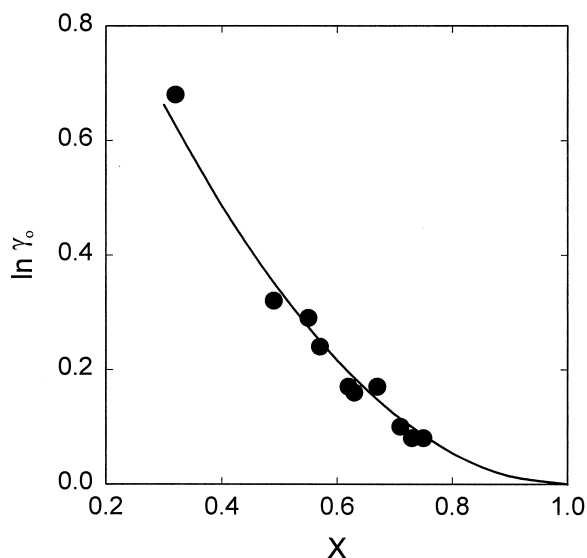


Fig. 1. Values of γ_0 , the activity coefficients of alcohols in "alcohol-rich" phases, at 298.15 K and 0.1 MPa (filled points) plotted versus the mole fraction, X , of alcohols in "alcohol-rich" phases as calculated from Apelblat (1990). The solid curve is the fitted approximation: $\ln \gamma_0 = 1.35(1 - X)^2$. Both γ_0 and X refer to saturation properties, i.e. in equilibrium with the coexisting "water-rich" phase.

fraction of the alcohols in the "alcohol-rich" phases, the points generally fall into a single curve. We used this empirical result to estimate γ_0 for many alcohol-water systems using the approximation $\ln \gamma_0 = 1.35(1 - X)^2$ with the expected accuracy within 5–10% for γ_0 .

Suri et al. (1985) summed up their own and literature data on the excess Gibbs energy of nonelectrolyte-water mixtures at 298.15 K and 0.1 MPa, and recommended binary (pairwise) interaction coefficients for many functional groups, including CH_3 , CH_2 , CH , and OH (Suri et al., 1985). For the case of a binary water-alcohol solution, the following approximation is used for the concentration dependence of the osmotic coefficient, Φ , of solution: $RT \cdot \Phi = 1 + g_{AA} \cdot m$, where g_{AA} is the alcohol-alcohol self-interaction parameter, equal to the sum of binary interaction coefficients for the groups that constitute the given alcohol. Integrating the Gibbs-Duhem relation for chemical potentials for isothermal-isobaric conditions, one obtains the following statement for the saturation activity coefficient (for unsymmetrical normalization) of alcohols in "water-rich" phases: $RT \ln \gamma_w = 2g_{AA} \cdot m$. Note that the calculated activity coefficients are so different from unity that the assumption of ideal mixing is justified only when $X > 0.8$ for the "alcohol-rich" phases and for alcohols with carbon number \geq seven for the "water-rich" phases. Sources of data on the saturation molalities of individual systems are given in Section 3.

To evaluate the fugacity coefficients, ψ , of pure compounds in the gaseous state we employed the virial equation of state truncated at the second virial coefficient, B:

$$\ln \psi = \frac{BP_s}{RT}, \quad (12)$$

with values of B estimated using both the Tsonopoulos (1974) and the Hayden and O'Connell (1975) correlations. The latter

correlation is more accurate for large hydrocarbons and especially for alcohols. Contribution of the $RT \ln \psi$ term never exceeds $0.10 \text{ kJ} \cdot \text{mol}^{-1}$, and it is practically unimportant for all alcohols and all hydrocarbons with carbon number \geq six.

2.1.2. Thermodynamics of water/gas partitioning

Numerous authors report results of experimental studies of the distribution of a solute between water and a gaseous phase. A direct measure of the equilibrium constant for reaction (4) is the Henry's law constant, K_H , in units $\text{mol} \cdot \text{kg}^{-1} \cdot \text{bar}^{-1}$, or $\text{mol} \cdot \text{kg}^{-1} \cdot (0.1 \text{ MPa})^{-1}$, defined by:

$$\Delta_r G^\circ(4) \equiv \Delta_h G^\circ = -RT \ln K_H. \quad (13)$$

Henry's law constants are obtained from measurements of the partial pressure of a solute over its aqueous solution, or solubility of gases in water, or equilibrium concentrations of the solute in coexisting phases. Literature values of K_H were recalculated where necessary in this study to the molality scale and to bar pressure units.

Many measurements of concentrations of a solute in coexisting aqueous and gaseous phases are reported (particularly in the "environmental" literature) as distribution constants, K_d , at infinite dilution given by:

$$K_d = \frac{C(g)}{C(aq)}, \quad (14)$$

where C stands for molarity, the number of moles of a solute in 1000 cm^3 of an aqueous or gaseous phase. Assuming ideal gas behavior for the gaseous phase, one obtains $C(g) = \frac{n}{V} = \frac{P}{RT}$ (units for $C(g)$ are $\text{mol} \cdot \text{l}^{-1}$, note that units for P are MPa). Converting molarity to molality for an infinitely dilute solution one has $C(aq) = \frac{m\rho_0}{1000}$ (units are $\text{mol} \cdot \text{l}^{-1}$ if the pure water density ρ_0 is given as $\text{g} \cdot \text{cm}^{-3}$). Substitution yields

$$K_d = \frac{C(g)}{C(aq)} = \frac{1000P}{RTm\rho_0}. \quad (15)$$

For the case of an ideal gas approximation for the gaseous phase, $K_H = \frac{m}{P}$, and the relation between K_d and K_H (units for K_H are $\text{mol} \cdot \text{kg}^{-1} \cdot \text{bar}^{-1}$) is as follows:

$$\ln K_H = -\ln K_d - \ln \frac{RT\rho_0}{100}. \quad (16)$$

Often, especially in the chemical engineering literature, the results of water/gas partitioning studies are given as values of the infinite dilution activity coefficients for the symmetrical normalization of activities, γ^∞ (where, for a component i , $\gamma_i \rightarrow 1$ as $X_i \rightarrow 1$), using the mole fraction concentration scale. A relation between K_H and γ^∞ can be obtained by comparing two statements for the chemical potential of a solute: one using the ideal gas as the standard state, the mole fraction concentration scale and the symmetrical normalization of activities

$$\mu(T, P) = \mu_s^\circ(T, P^\ominus) + RT \ln \frac{\psi P_s}{P^\ominus} + RT \ln X \gamma_{sym}, \quad (17)$$

where γ_{sym} stands for the activity coefficient at finite concen-

tration of a solute for a symmetrical normalization of activities; and the second one employing an ideal aqueous solution as the standard state, the unsymmetrical normalization of activities (where, for a component i , $\gamma_i \rightarrow 1$ if X_i or $m_i \rightarrow 0$) and the molality concentration scale :

$$\mu(T,P) = \mu_2^o(T,P) + RT \ln m \gamma_w. \quad (18)$$

Both statements are equally correct for the chemical potential of the solute. As the standard Gibbs energy of hydration of a solute is the difference between the standard chemical potentials of the solute in an ideal aqueous solution state and ideal gas state, one then obtains

$$\Delta_h G^o = \mu_2^o(T,P) - \mu_g^o(T,P^\ominus) = RT \ln \frac{\psi P_s}{P^\ominus} + RT \ln X \gamma_{sym} - RT \ln m \gamma_w. \quad (19)$$

At infinite dilution, m and $X \rightarrow 0$, $\gamma_w \rightarrow 1$, $\gamma_{sym} \rightarrow \gamma^\infty$, and $\frac{X}{m} \rightarrow \frac{1}{n_w}$, where $n_w = \frac{1000}{M_w}$ (the number of moles of H₂O in 1000 g of water), and M_w stands for the molar mass of water, in g. Therefore, for infinite dilution one obtains

$$\Delta_h G^o = RT \ln \frac{\psi P_s}{P^\ominus} + RT \ln \gamma^\infty - RT \ln \frac{1000}{M_w} = -\Delta_{vap} G^o + RT \ln \gamma^\infty - RT \ln \frac{1000}{M_w}. \quad (20)$$

Sources of data on K_H , K_d , and γ^∞ and given in the "Database" section.

2.2. The Standard Partial Molar Enthalpy of Hydration $\Delta_h H^o$

According to its definition the standard partial molar enthalpy of hydration is the difference between the enthalpy of a compound in the ideal gas state and that of the compound in the standard aqueous solution. For compounds that are gases at ambient conditions the enthalpies of hydration can be measured directly as enthalpies of solution of the gases in water (including small corrections due to the nonideality of the gaseous phase). For liquids or solids an analogue of Eqn. 11 is valid, namely

$$\Delta_h H^o = \Delta_{sol} H^o - \Delta_{vap} H^o, \quad (21)$$

where $\Delta_{sol} H^o$ stands for the standard enthalpy of solution of the liquid or solid in water (available from experimental determinations for many alcohols and some hydrocarbons); $\Delta_{vap} H^o$ stands for the standard enthalpy of vaporization of a compound, i.e. the difference in the enthalpy of the compound between the ideal gas state and the state of the liquid or solid. Values of $\Delta_{vap} H^o$ are available either from calorimetric measurements, or they can be evaluated from the temperature dependence of the vapor pressure of pure compounds (Majer and Svoboda, 1985; Reid et al., 1987). Another, but less accurate, source of data on $\Delta_h H^o$ is the temperature dependence of either $\Delta_h G^o$ or $\Delta_s G^o$, where one can evaluate, respectively, $\Delta_h H^o$ or $\Delta_s G^o$ by means of the Van't Hoff relation: $\Delta H^o = -T^2 \left(\frac{\partial}{\partial T} \left[\frac{\Delta G^o}{T} \right]_p \right)$.

2.3 The Standard Partial Molar Heat Capacity of Hydration $\Delta_h Cp^o$

The standard partial molar heat capacity of hydration is defined as

$$\Delta_h Cp^o = Cp_2^o - Cp(g), \quad (22)$$

where $Cp(g)$ and Cp_2^o stand for the heat capacity of a compound in the ideal gas state and the standard state heat capacity of the compound in aqueous solution, respectively. Values of $Cp(g)$ are known or can be reliably estimated for most hydrocarbons and alcohols. Values of the infinite dilution partial molar heat capacity are available from direct calorimetric measurements for quite a few organic compounds. A more practical, though less accurate, way to obtain $\Delta_h Cp^o$ (or $\Delta_{sol} Cp^o$) for sparingly soluble compounds is by means of the relation $\Delta Cp = \left(\frac{d\Delta H}{dT} \right)_p$, i.e. from the temperature dependence of the heats of hydration (or solution). Values of $\Delta_h Cp^o$ estimated through double differentiation of $\Delta_h G^o$ in temperature are, as a rule, only approximate, and were not used in this study.

2.4. The Standard Partial Molar Volume, V_2^o

The standard state partial molar volume V_2^o is defined as $V_2^o \equiv \Delta_h V^o = \left(\frac{\partial \Delta_h G^o}{\partial P} \right)_T$. We used only V_2^o values based on volumetric measurements, and discarded results available in the literature from the pressure dependence of the solubility of gases/liquids, as they are less accurate.

3. A DESCRIPTION OF THE DATA BASES

We performed an extensive literature search of solubility, water/gas distribution, enthalpy of solution and other data. In the case of a few well-studied "gases" (ethane, propane, *n*-butane and 2-methylpropane) we accepted recent recommendations of the thermodynamic functions of hydration from comprehensive critical reviews (Wilhelm et al., 1977; Haydyk, 1986).

3.1. Data Base for the Standard Partial Molar Gibbs Energy of Hydration

Data on the Gibbs energy of hydration of hydrocarbons and alcohols at 298.15 K and 0.1 MPa are given in Table 1 together with values we adopted for the standard Gibbs energy of vaporization at 298.15 K for compounds that are liquids or solids at 298.15 K. Values of $\Delta_h G^o$ calculated from aqueous solubility data are given in italics. Values that we considered to be unreliable are given in parentheses.

The literature values of $\Delta_h G^o$ are given in the fourth column of Table 1 in the following order: first we entered results based on gas/water partitioning data (Henry's law and gas-water distribution constants, γ^∞ results) in chronological order with the latest data first. Then we give in italics values of the Gibbs energy of hydration based on aqueous solubility data in chronological order starting with the latest determinations. In the fifth column of Table 1, "value used in the fit" we give, as a rule, the mean value together with its standard deviation. The standard deviation is shown in parenthesis as the number of

significant figures, i.e. 18.40(45) means 18.40 ± 0.45 , and 18.4(15) means 18.4 ± 1.5 . In cases where only a few independent determinations of $\Delta_f G^\circ$ are available (say, less than 4), the value in parentheses is our judgment of the accuracy of the result.

We used for hydrocarbons all literature values for pure, well-characterized compounds that we located. For smaller members of each homologous series (alkanes, alkenes, alkynes, cycloalkanes, alkylbenzenes, alcohols, etc.) there are, as a rule, many $\Delta_f G^\circ$ values from different sets of measurements (solubility, Henry's law and distribution constants, infinite dilution activity coefficients), which are usually consistent with each other. However, for compounds with higher carbon numbers typically only solubility data are available, and the agreement between results of different authors is often unsatisfactory.

The problems with the experimental study of the solubility of sparingly soluble organic liquids in water are well known. First, the most often discussed problem is the formation of emulsions, clusters, and aggregates of hydrocarbons when using the traditional "shake-flask" method, which might result in grossly overestimated values of the solubility of a compound. Second, when shaking and agitation are not used, the steady-state concentration of hydrocarbon in a solution may be achieved only after very long times. Coates et al. (1985) reported that up to 100 days' duration is required to obtain agreement between solubility values from oversaturation (after initial shaking) and from undersaturation (unshaken flask) for higher alkanes. Solubility values from short-term experiments may differ by 10–100 times from "true" ones. However, in the overwhelming majority of cases the duration of experiments did not exceed a few days. Because of these reasons data for compounds with carbon numbers above eight are rarely in good agreement, and in most cases must be considered to be semiquantitative. For alkanes with carbon numbers above twelve we used only the data of Coates et al. (1985) confirmed in very long experiments (up to 100 days). For alcohols in water we used the mutual solubility data recommended in the compilation by Barton (1984) together with more recent results (Stephenson et al., 1984; Stephenson and Stuart, 1986; Dallos and Liszi, 1995).

An additional problem arises from the low solubility of longer chain length organic compounds. Many results in the older studies, up to the beginning of the 1960's, were obtained using "visual" or "cloud-point" observations; they are, as a rule, unreliable for compounds with solubilities below $n \cdot 10^{-3} \text{ mol} \cdot \text{kg}^{-1}$. UV-spectroscopy based measurements are often unreliable for compounds with solubility below $10^{-5} \text{ mol} \cdot \text{kg}^{-1}$. Such suspect results are given in the Table 1 in parentheses. Results of a few studies were not considered. As an example, the study of Fühner (1924) is based on "visual" measurements and it is now mainly of historic interest. In addition, as stated in Shaw (1989a) it is not clear whether results of Krzyzanowska and Szeliga (1978) are independent of those of Price (1976), and, therefore, data of Krzyzanowska and Szeliga (1978) were discarded.

All data refer to pure water as a solvent except results reported by Helmkamp et al. (1957) who report solubility data for higher alkynes obtained in 1 M KNO_3 . We used these data because of a scarcity of data for these compounds. Rather than attempting a correction for possible "salting-out" effects, we just increased the uncertainty intervals for such compounds. A

few results for hydrocarbons refer to temperatures of 293 or 303 K. We used these data in cases where only a few data were reported for compounds, and it is expected that the temperature correction to 298.15 K is within the uncertainty of the solubility data.

A particular problem is the selection of reliable values of the vapor pressure of pure compounds at 298.15 K that are needed to evaluate $\Delta_{\text{vap}} G^\circ$. There are many vapor pressure compilations for hydrocarbons (Reid et al., 1987; Daubert and Danner, 1996; Stephenson and Malanowsky, 1987; Smith and Srivastava, 1986; and others listed in Table 1), some of which only cite the published values, and others involve smoothing procedures and even extrapolations. As a rule, we used values from Reid et al. (1987), if available, or data of later experimental determinations. Otherwise, we used values from Daubert and Danner (1996). For cases where there are no data in these sources, we used other compilations as indicated in Table 1. In a few cases, values of the vapor pressure of hydrocarbons were estimated using the Lee-Kessler method (see Reid et al., 1987). For alcohols any extrapolations toward low temperatures are questionable (see Ruzicka and Majer, 1996). Therefore, we only used values based on direct measurements from experimental studies. For 1-alcohols the vapor pressure results are taken from Reid et al. (1987) and Ambrose and Walton (1989), and for other alcohols we used compiled values based on experimental determinations given by Smith and Srivastava (1986) or more recently published results (Ambrose and Ghibasee, 1987; 1990; Wiberg and Hao, 1991).

3.2. Data Base for the Standard Partial Molar Enthalpy of Hydration

Data on the enthalpy of hydration of hydrocarbons and alcohols at 298.15 K and 0.1 MPa are given in Table 2 together with values used in this study for the standard enthalpy of vaporization at 298.15 K (for compounds which are liquids or solids at 298.15 K). Values of $\Delta_f H^\circ$ calculated from the temperature dependence of the standard Gibbs energy of hydration or solution are given in italics. The values of $\Delta_{\text{vap}} H^\circ$ at 298.15 K are taken, as a rule, from the compilation by Majer and Svoboda (1985) or from later experimental results. However, for most unsaturated alcohols there are no experimental determinations of the enthalpy of vaporization, and we estimated these quantities using group contribution values from Domalski and Hearing (1993).

It must be noted that estimates of $\Delta_f H^\circ$ for cycloalkenes are based entirely on the temperature dependence of the solubility data from Pierotti and Liabastre (1972). The solubility data from this work are themselves, as a rule, systematically higher than other reported values for practically all hydrocarbons studied. However, as pointed out in Shaw (1989a), the temperature dependencies of the solubility values from Pierotti and Liabastre (1972) are similar to other sets of data, and we decided to accept estimations of $\Delta_f H^\circ$ from this work.

3.3. Data Base for the Standard Partial Molar Heat Capacity of Hydration

Data on the heat capacity of hydration of hydrocarbons and alcohols at 298.15 K and 0.1 MPa are given in Table 3 together

Table 3. The data base of experimental values of the heat capacities in the ideal gas state and the heat capacities of hydration of hydrocarbons and monohydric alcohols used in this study. Values in italics are from the temperature dependence of the enthalpy of hydration, those in parentheses are considered to be unreliable in this study. Also listed are values calculated using the proposed group contribution method and the difference between the calculated values and the experimental data.

Compound	Formula	$C_p^o(g)$, $J \cdot K^{-1} \cdot mol^{-1}$	Values of $\Delta_h C_p^o$ from literature, $J \cdot K^{-1} \cdot mol^{-1}$	Value used in the fit	Group contribution value	Δ , $J \cdot K^{-1} \cdot mol$
n-Alkanes						
Methane	CH ₄	35.7	209 ¹ , 217 ² , 242 ³	220(15)		
Ethane	C ₂ H ₆	52.6	273 ⁴ , 284 ² , 317 ⁵	280(20)	263	17
Propane	C ₃ H ₈	74.4	319 ⁴ , 332 ² , 389 ⁵	330(30)	327	3
n-Butane	C ₄ H ₁₀	97.2	383 ⁶ , 390 ²	385(20)	391	-6
n-Pentane	C ₅ H ₁₂	120.1	440 ⁷	440(50)	454	-14
n-Hexane	C ₆ H ₁₄	143.0	490 ⁷	490(50)	518	-28
Branched alkanes						
2-Methylpropane	C ₄ H ₁₀	97.3	360 ⁶ , 377 ²	370(20)	393	-23
2,2-Dimethylpropane	C ₅ H ₁₂	119.5	486 ²	490(30)	463	27
Alkenes and Dienes						
Ethene	C ₂ H ₄	42.8	237 ²	240(20)	235	5
Propene	C ₃ H ₆	65.9	278 ²	280(30)	302	-22
1-Butene	C ₄ H ₈	86.5	389 ²	390(30)	366	25
Alkynes and Diynes						
Ethyne	C ₂ H ₂	45.1	154 ²	150(20)	150	0
Cycloalkanes						
Cyclopropane	C ₃ H ₆	55.9	303 ²	310(20)	238	62
Cyclohexane	C ₆ H ₁₂	106.3	410 ⁷	410(30)	476	-66
Alkylbenzenes						
Benzene	C ₆ H ₆	81.7	290 ⁸ , 285 ⁹ , 279 ⁷ , (220 ¹⁰)	290(15)	290	0
Toluene	C ₇ H ₈	103.6	357 ⁸ , 326 ⁷	340(30)	323	17
Ethylbenzene	C ₈ H ₁₀	129.0	370 ⁷	370(30)	387	-17
Propylbenzene	C ₉ H ₁₂	152.0	450 ⁷	450(30)	450	0
1-Alcohols						
Methanol	CH ₄ O	43.9	112 ¹¹ , 114 ¹² , 113 ¹³ , 114 ¹⁴ , 114 ¹⁵ , 113 ¹⁶ , (134 ¹⁷), 112 ¹⁸	114(5)	138	-24
Ethanol	C ₂ H ₆ O	64.2	204 ¹¹ , 199 ¹⁹ , 196 ¹³ , 197 ¹⁴ , 196 ¹⁵ , 197 ¹⁶ , (211 ¹⁷), (190 ¹⁸)	199(5)	201	-2
1-Propanol	C ₃ H ₈ O	87.1	274 ¹¹ , 269 ²⁰ , 268 ¹⁹ , 265 ¹³ , 263 ¹⁴ , 266 ¹⁵ , 268 ¹⁶ , 260 ²⁰ , (292 ¹⁷), 267 ¹⁸	268(6)	265	3
1-Butanol	C ₄ H ₁₀ O	110.0	337 ¹¹ , 344 ²⁰ , 336 ¹⁹ , 334 ²² , 330 ²³ , 328 ¹³ , 327 ¹⁵ , 331 ¹⁶ , 334 ²⁴ , (369 ¹⁷), 326 ¹⁸	335(10)	328	7
1-Pentanol	C ₅ H ₁₂ O	132.9	411 ¹¹ , 445 ²⁰ , 407 ¹⁹ , 402 ²² , 391 ¹⁵ , 397 ²⁵ , 399 ¹⁶ , 426 ¹⁷	402(10)	392	10
1-Hexanol	C ₆ H ₁₄ O	155.8	482 ²⁰ , 456 ¹⁶ , 451 ²⁶	460(20)	456	4
1-Heptanol	C ₇ H ₁₆ O	178.7	514 ¹⁶ , 552 ²⁶	520(30)	519	1
1-Octanol	C ₈ H ₁₈ O	201.6	571 ¹⁶	570(30)	583	-13
Branched alcohols						
2-Propanol	C ₃ H ₈ O	89.6	272 ²⁷ , 310 ¹⁷ , 284 ¹⁸	272(15)	268	4
2-Butanol	C ₄ H ₁₀ O	112.5	336 ¹⁵ , 352 ²⁸ , 346 ²⁹ , (370 ¹⁸)	340(15)	331	9
2-Methyl-1-propanol	C ₄ H ₁₀ O	110.0	323 ¹⁵ , 350 ¹⁷	330(15)	331	-8
2-Methyl-2-propanol	C ₄ H ₁₀ O	111.1	354 ¹³ , 353 ³⁰ , 353 ¹⁵ , 352 ²⁵ , 353 ³¹ , (386 ¹⁷), (374 ¹⁸)	353(10)	338	15
3-Pentanol	C ₅ H ₁₂ O	135.4	405 ¹⁵ , 430 ²⁹	410(15)	395	15
2,2-Dimethyl-1-propanol	C ₅ H ₁₂ O	132.2	372 ¹⁵	370(20)	401	-31
2-Methyl-2-butanol	C ₅ H ₁₂ O	134.0	405 ²⁷ , 399 ¹⁷	405(15)	401	4
3-Hexanol	C ₆ H ₁₄ O	158.3	468 ²⁹	470(40)	458	12
Unsaturated linear alcohols						
2-Propen-1-ol	C ₃ H ₆ O	76.0	259 ¹⁷	260(40)	240	20
2-Buten-1-ol	C ₄ H ₈ O	98.9	321 ¹⁷	320(40)	306	14
3-Buten-1-ol	C ₄ H ₈ O	99.2	300 ¹⁷	300(40)	303	-3
4-Penten-1-ol	C ₅ H ₁₀ O	122.1	311 ¹⁷	310(40)	367	-57
3-Pentyn-1-ol	C ₅ H ₈ O	111.6	287 ¹⁷	290(40)	285	5
Cyclic alcohols						
Cyclopentanol	C ₅ H ₁₀ O	101.8	359 ²⁹ , 395 ¹⁷	370(60)	273	97
Cyclohexanol	C ₆ H ₁₂ O	129.8	333 ³² , 384 ²⁹ , 403 ¹⁷	340(15)	353	-13
Cycloheptanol	C ₇ H ₁₄ O	138.3	423 ²⁹ , 465 ¹⁷	440(40)	432	8

(Continued)

Table 3. (Continued)

Compound	Formula	$C_p^o(g)$, $J \cdot K^{-1} \cdot mol^{-1}$	Values of $\Delta_h C_p^o$ from literature, $J \cdot K^{-1} \cdot mol^{-1}$	Value used in the fit	Group contribution value	Δ_h , $J \cdot K^{-1} \cdot mol$
Miscellaneous compounds						
2-Cyclohexen-1-ol	$C_6H_{10}O$	124.8	<i>373</i> ¹⁷	370(50)	370	0

¹ Naghibi et al. (1986); ² Dec and Gill (1985b); ³ Oloffson et al. (1984); ⁴ Naghibi et al. (1987a); ⁵ Dec and Gill (1984); ⁶ Naghibi et al. (1987b); ⁷ Gill et al. (1976); ⁸ Makhatazde and Privalov (1988); ⁹ Hallén et al. (1989); ¹⁰ Gill et al. (1975); ¹¹ Makhatazde et al. (1997); ¹² Makhatazde and Privalov (1990); ¹³ Perron and Desnoyers (1981); ¹⁴ Benson et al. (1980); ¹⁵ Jolicoeur and Lacroix (1976); ¹⁶ Hallén et al. (1986); ¹⁷ Arnett et al. (1969); ¹⁸ Alexander and Hill (1969); ¹⁹ Makhatazde and Privalov (1989); ²⁰ De Lisi et al. (1991); ²¹ Franks et al. (1973); ²² De Lisi et al. (1987); ²³ Roux-Desgranges et al. (1982); ²⁴ Nwankwo and Wadsö (1980); ²⁵ Sköld et al. (1976); ²⁶ Hill and White (1974); ²⁷ Roux et al. (1980); ²⁸ Anderson and Oloffson (1988); ²⁹ Conti et al. (1976); ³⁰ de Visser et al. (1997); ³¹ Avedikian et al. (1975); ³² Tasker and Wood (1983).

with values we adopted for the heat capacity of the compounds at 298.15 K in the ideal gas state taken from Domalski and Hearing (1993). Values of $\Delta_h C_p^o$ calculated from the temperature dependence of the standard enthalpy of hydration or solution are given in italics. In all there are 7(0) results for alkanes (in parentheses is the number of determinations based on direct calorimetric measurements of the heat capacity of a compound), 4(0) for hydrocarbons with double and triple bonds, 2(0) for cyclic hydrocarbons, 4(2) for alkylbenzenes, and 17(14) for alcohols. Estimations available in the literature that are based on the second derivative of the temperature dependence of the Gibbs energy of hydration were not used because of their low accuracy.

3.4. Data Base for the Standard Partial Molar Volume

Data on V_2^o of hydrocarbons and alcohols at 298.15 K and 0.1 MPa are given in Table 4. Most values of V_2^o for hydrocarbons that are gases at 298.15 K and 0.1 MPa come from Moore et al. (1982). However, these values were obtained at a total pressure of about 0.1 MPa, where the solubility of gases is small, and therefore, these results have rather large uncertainties. The most accurate and numerous data are available for aqueous alcohols, and values listed in Table 4 are mainly values obtained during the last 20–25 years using vibrating-tube densimeters. Values of V_2^o estimated from the pressure dependence of the solubility of gases and liquids were discarded as less accurate. In all there are 5 results for alkanes, 4 for hydrocarbons with double and triple bonds, 1 for a cyclic hydrocarbon, 3 for alkylbenzenes, and 31 for alcohols.

4. GROUP CONTRIBUTION VALUES

It is well known that most thermodynamic functions of homologous series of organic compounds in gaseous, liquid and solid states, as well as in aqueous solution, show remarkably constant linear dependence on the carbon number (Abraham, 1984; Shock and Helgeson, 1990; Helgeson et al., 1998, and many others). This fact forms the basis for group additivity methods used to describe available data and predict the thermodynamic functions of many organic compounds not studied experimentally. Each substance is considered to consist of particular “building blocks,” or “groups,” characterized by values of the thermodynamic property of interest. It is necessary to mention the common deviations from linearity among the members of any homologous series with low carbon numbers.

Cyclic compounds also deviate from linearity and present a particular problem for any group contribution method, because of the differences in geometry and energetics for each cyclic ring.

It is impossible within one paper to give a complete coverage of even the most important works on the group contribution methods for organic compounds. Each year several papers are published dealing with additivity methodologies or their application to the thermodynamic and thermophysical properties of pure compounds and mixtures. A group contribution method for estimating activity coefficients in mixtures that is widely used in chemical engineering is UNIFAC (see, for example, Reid et al., 1987), however, values predicted for dilute aqueous solutions may be orders of magnitude in error (Voutsas and Tassios, 1997). Methods developed specifically for activity coefficients at infinite dilution in water are more accurate, such as the pioneering work of Pierotti et al. (1959). However, only Cabani et al. (1981) and Amend and Helgeson (1997) have presented comprehensive group contribution treatments for all properties of interest for aqueous species, not only for chemical potentials. The former work covers a much larger number of groups and compounds, but only at 298.15 K, and the latter paper gives the temperature and pressure dependence of a smaller number of group contributions that differ from those chosen in this study.

4.1. Selection of the Group Contributions Scheme

In the most comprehensive scheme for group contributions, the second-order group additivity method (see, for instance, Domalski and Hearing, 1993), the thermodynamic properties of a group are envisioned to depend on the nature of the surrounding atoms and groups. These methods include explicitly nearest-neighbor interactions. As a consequence, the properties of the methylene group, CH_2 , for example, do not have unique values, but a number of them depending on the local environment of the group. Despite the elegance of these methods, the quantity and accuracy of experimental data on the thermodynamic functions of hydration of organic compounds typically preclude the possibility of accounting quantitatively for the second-order effects, i.e. nearest-neighbor interactions (but see below for a number of exceptions).

In such a situation the only practical option is to adopt a more simple scheme of group contributions. We decided to accept the groups proposed by Cabani et al. (1981). Each group is defined as an arrangement of atoms, and (contrary to the

Table 4. The data base of the infinite dilution partial molar volumes of hydrocarbons and monohydric alcohols in water at 298.15 K, 0.1 MPa. In cases where many data are available for a compound, only the latest results obtained using a vibrating-tube densitometer are given in the Table. Also listed are values calculated using the proposed group contribution method and the difference between the calculated values and the experimental data.

Compound	Formula	Values of V_2^∞ from literature, $\text{cm}^3 \cdot \text{mol}^{-1}$	Value used in the fit	Group contribution value	Δ , $\text{cm}^3 \cdot \text{mol}^{-1}$
n-Alkanes					
Methane	CH_4	37.2 ¹ , (34.5) ² , 37.4 ³ , 36.5 ⁴	37.3(5)		
Ethane	C_2H_6	51 ² , 52.9 ⁴	52(1)	51.4	0.6
Propane	C_3H_8	70.7 ² , 67 ⁴	69(2)	67.1	1.9
<i>n</i> -Butane	C_4H_{10}	76.6 ²	77(5)	82.8	-5.8
Branched alkanes					
2-Methylpropane	C_4H_{10}	83.1 ²	83(5)	82.9	0.1
2,2-Dimethylpropane	C_5H_{12}	100.5 ²	100(6)	98.7	1.3
Alkenes and Dienes					
Ethene	C_2H_4	45.7 ⁵ , 51.3 ²	47(3)	48.4	-1.4
Propene	C_3H_6	56.7 ²	57(3)	59.9	-2.9
1-Butene	C_4H_8	62.3 ²	62(6)	75.6	-13.6
1,3-Butadiene	C_4H_6	68.3 ²	68(4)	68.4	-0.4
Alkynes and Diynes					
Ethyne	C_2H_2	42.5 ²	42.5(10)	42.5	0.0
Cycloalkanes					
Cyclopropane	C_3H_6	54.3 ²	54(2)	44.2	9.8
Alkylbenzenes					
Benzene	C_6H_6	82.6 ⁶ , 83.5 ⁷ , 82.6 ⁸ , 81.3 ⁹ , 83.2 ⁴	82.6(5)	82.6	0.0
Toluene	C_7H_8	98.6 ⁶ , 96.6 ⁷ , 97.5 ⁸ , 97.0 ⁹ , 97.7 ¹⁰	97.5(10)	98.2	-0.7
Ethylbenzene	C_8H_{10}	114.5 ⁶	114.5(1)	113.8	0.7
1-Alcohols					
Methanol	CH_3O	38.10 ¹¹ , 38.18 ¹² , 38.10 ¹³ , 38.2 ¹⁴ , 38.1 ¹⁵ , 38.25 ¹⁶	38.15(10)	39.36	-1.21
Ethanol	$\text{C}_2\text{H}_5\text{O}$	55.09 ¹¹ , 55.10 ¹² , 55.0 ¹⁷ , 55.1 ¹⁴ , 55.05 ¹⁵ , 55.1 ¹⁶	55.1(1)	55.06	0.04
1-Propanol	$\text{C}_3\text{H}_7\text{O}$	70.77 ¹¹ , 70.7 ¹⁸ , 70.71 ¹² , 70.8 ¹⁷ , 70.65 ¹⁴ , 70.7 ¹⁵ , 70.63 ¹⁶ , 70.75 ¹⁹	70.7(1)	70.75	-0.05
1-Butanol	$\text{C}_4\text{H}_9\text{O}$	86.52 ¹¹ , 86.63 ¹² , 86.5 ¹⁷ , (86.09 ¹⁴), 86.43 ²⁰ , 86.65 ²¹ , 86.6 ¹⁵ , 86.48 ¹⁶ , 86.62 ¹⁹	86.6(2)	86.5	0.1
1-Pentanol	$\text{C}_5\text{H}_{11}\text{O}$	102.47 ¹¹ , 102.62 ¹² , 102.3 ¹⁷ , (101.52 ¹⁴), 101.95 ²⁰ , 101.95 ²² , 102.62 ¹⁹ , 102.88 ¹⁶	102.4(5)	102.1	0.3
1-Hexanol	$\text{C}_6\text{H}_{13}\text{O}$	118.47 ¹² , (115.5 ¹⁴), 118.65 ¹⁹	118.5(5)	117.8	0.7
1-Heptanol	$\text{C}_7\text{H}_{15}\text{O}$	129.4 ¹⁴ , 133.4 ²³	133(2)	133.5	-0.5
Branched alcohols					
2-Propanol	$\text{C}_3\text{H}_7\text{O}$	71.82 ¹² , 71.60 ²⁴ , 71.83 ²⁵ , 71.93 ¹⁹	71.8(1)	70.9	0.9
2-Butanol	$\text{C}_4\text{H}_9\text{O}$	86.55 ¹² , 86.53 ¹⁶ , 86.64 ¹⁹	86.6(1)	86.6	0.0
2-Methyl-1-propanol	$\text{C}_4\text{H}_9\text{O}$	86.46 ¹² , 86.75 ¹⁶	86.5(2)	86.6	-0.1
2-Methyl-2-propanol	$\text{C}_4\text{H}_9\text{O}$	87.81 ¹² , 87.81 ²⁶ , 87.9 ¹⁵ , 87.76 ²⁷ , 87.73 ¹⁶ , 87.90 ²⁸	87.8(1)	86.7	1.1
2-Pentanol	$\text{C}_5\text{H}_{11}\text{O}$	102.55 ¹⁹	102.6(5)	102.2	0.4
3-Pentanol	$\text{C}_5\text{H}_{11}\text{O}$	101.14 ¹⁶ , 101.16 ¹⁹	101.2(3)	102.2	-1.0
2-Methyl-2-butanol	$\text{C}_5\text{H}_{11}\text{O}$	101.37 ¹² , 101.38 ²⁹ , 101.15 ¹⁶	101.3(2)	102.4	-1.1
2,2-Dimethyl-1-propanol	$\text{C}_5\text{H}_{11}\text{O}$	102.29 ¹² , 102.32 ³⁰ , 101.9 ¹⁶	102.3(2)	102.4	-0.1
Branched alcohols (continued)					
2-Hexanol	$\text{C}_6\text{H}_{13}\text{O}$	118.49 ¹⁹	118.5(5)	117.9	0.6
3-Hexanol	$\text{C}_6\text{H}_{13}\text{O}$	117.14 ³¹	117.1(5)	117.9	-0.8
2-Heptanol	$\text{C}_7\text{H}_{15}\text{O}$	134.39 ¹⁹	134.4(10)	133.6	0.8
3-Heptanol	$\text{C}_7\text{H}_{15}\text{O}$	133.3 ¹⁹	133.3(10)	133.6	-0.3
4-Heptanol	$\text{C}_7\text{H}_{15}\text{O}$	133.2 ¹⁹	133.2(10)	133.6	-0.4
Unsaturated linear alcohols					
2-Propen-1-ol	$\text{C}_3\text{H}_5\text{O}$	64.3 ³²	64.3(10)	63.6	0.7

(Continued)

Table 4. (Continued)

Compound	Formula	Values of V_2° from literature, $\text{cm}^3 \cdot \text{mol}^{-1}$	Value used in the fit	Group contribution value	Δ , $\text{cm}^3 \cdot \text{mol}^{-1}$
Cyclic alcohols					
Cyclobutanol	$\text{C}_4\text{H}_8\text{O}$	75.6 ³³	75.6(10)	74.2	1.4
Cyclopropanmethanol	$\text{C}_4\text{H}_8\text{O}$	76.0 ³³	76.0(10)	75.6	0.4
Cyclopentanol	$\text{C}_5\text{H}_{10}\text{O}$	89.06 ³¹ , 88.2 ³³	89.0(5)	88.6	0.4
Cyclopropanethanol	$\text{C}_5\text{H}_{10}\text{O}$	92.4 ³³	92.4(10)	91.3	1.1
Cyclohexanol	$\text{C}_6\text{H}_{12}\text{O}$	103.45 ³⁴ , 103.54 ³¹ , 102.7 ³³ , 103.0 ³⁵	103.5(5)	102.9	0.6
Cyclohexanmethanol	$\text{C}_6\text{H}_{12}\text{O}$	103.6 ³³	103.6(10)	104.3	-0.7
Cycloheptanol	$\text{C}_7\text{H}_{14}\text{O}$	116.88 ³¹ , 116.9 ³³	116.9(5)	117.3	-0.4
Cyclopentanethanol	$\text{C}_7\text{H}_{14}\text{O}$	118.2 ³³	118.2(10)	118.6	-0.4
Cyclohexanmethanol	$\text{C}_7\text{H}_{14}\text{O}$	118.1 ³³	118.1(10)	120.0	-1.9
Cyclooctanol	$\text{C}_8\text{H}_{16}\text{O}$	129.7 ³³	129.7(20)	131.7	-2.0

¹ Hnedkovsky et al. (1995); ² Moore et al. (1982); ³ Tiepel and Gubbins (1972); ⁴ Masterton (1954); ⁵ Biggerstaff and Wood (1988); ⁶ Sakurai (1990); ⁷ Makhatadze and Privalov (1988); ⁸ Dutta-Choudhury et al. (1982); ⁹ Shahidi (1981); ¹⁰ Desnoyers and Ichaporia (1969); ¹¹ Makhatadze et al. (1997); ¹² Sakurai et al. (1994); ¹³ Makhatadze et al. (1990); ¹⁴ De Lisi et al. (1986b); ¹⁵ Perron and Desnoyers (1981); ¹⁶ Jolicoeur and Lacroix (1976); ¹⁷ Makhatadze and Privalov (1989); ¹⁸ Criss and Wood (1996); ¹⁹ Høiland and Vikinstad (1976); ²⁰ De Lisi et al. (1986a); ²¹ Roux-Desgranges et al. (1980); ²² De Lisi et al. (1984); ²³ Manabe and Koda (1975); ²⁴ Wurzbürger et al. (1990); ²⁵ Sakurai (1988); ²⁶ Sakurai (1987); ²⁷ de Visser et al. (1977); ²⁸ Avedikian et al. (1975); ²⁹ Sakurai (1989); ³⁰ Roux et al. (1980); ³¹ Cabani et al. (1974); ³² Terasawa et al. (1975); ³³ Edward et al. (1973); ³⁴ Tasker and Wood (1983); ³⁵ Neal and Goring (1970).

second-order group additivity method) is characterized only by its constituent atoms, i.e. the thermodynamic properties of the methylene group CH_2 , for example, are taken to be the same in all types of organic compounds. Following the recommendations of Cabani et al. (1981) we use the following groups: CH_3 , CH_2 , CH , and C for saturated hydrocarbons; c-CH_2 , c-CH , and c-C for cyclic saturated hydrocarbons; CH_{ar} and C_{ar} for aromatic hydrocarbons (containing the benzene ring); $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ for double bond and triple bonds in linear hydrocarbons, respectively; $\text{c-C}=\text{C}$ for the double bond in cyclic hydrocarbons; H for a hydrogen atom attached to the double (both in linear and cyclic hydrocarbons) or triple bond; and OH for the hydroxyl functional group. This first-order scheme of group contributions does not take into account possible nearest-neighbor interactions and steric hindrance effects. However, we found a few examples where nearest-neighbor interactions contribute significantly to the total values of the thermodynamic functions of hydration, and had to be included explicitly.

An examination of Table 1 reveals that among different isomers of dimethylbenzenes (xylenes) and trimethylbenzenes, the isomers with two methyl groups in neighboring (ortho) positions, have less positive values of the Gibbs energy of hydration than those in the meta and para positions (compare 1,2 with 1,3 and 1,4-dimethylbenzenes). Another example, which is less convincing because only one determination for each compound comes from different laboratories, is the difference between the Gibbs energy of hydration of trans-1,4-dimethylcyclohexane and cis-1,2-dimethylcyclohexane. In the latter compound both methyl groups are in neighboring positions upward from the general plane of the ring, and for this isomer $\Delta_h G^\circ$ is less positive than it is for trans-1,4-dimethylcyclohexane. Based on these bits of evidence, it was decided to introduce the "pseudo-group" $\text{I}(\text{C-C})$, which represents the nearest-neighbor interactions of two methyl (CH_3) or methylene (CH_2) groups attached either to the benzene ring or to the cyclic ring for the case of cis-isomers.

Each of the compounds in Tables 1–4 except methane, CH_4 , can be represented by the selected groups. As examples, *n*-hexane is the sum $2 \cdot \text{CH}_3 + 4 \cdot \text{CH}_2$, 2,2,4-trimethylpentane $5 \cdot \text{CH}_3 + 1 \cdot \text{CH}_2 + 1 \cdot \text{CH} + 1 \cdot \text{C}$, propene $1 \cdot \text{C}=\text{C} + 3 \cdot \text{H} + \text{CH}_3$, 2-methyl-2-butene $1 \cdot \text{C}=\text{C} + 1 \cdot \text{H} + 3 \cdot \text{CH}_3$, 1-butyne $1 \cdot \text{C}\equiv\text{C} + 1 \cdot \text{H} + 1 \cdot \text{CH}_2 + 1 \cdot \text{CH}_3$, 1,6-heptadiyne $2 \cdot \text{C}\equiv\text{C} + 2 \cdot \text{H} + 3 \cdot \text{CH}_2$, cis-1,2-dimethylcyclohexane $2 \cdot \text{CH}_3 + 4 \cdot \text{c-CH}_2 + 2 \cdot \text{c-CH} + 1 \cdot \text{I}(\text{C-C})$, trans-1,2-dimethylcyclohexane $2 \cdot \text{CH}_3 + 4 \cdot \text{c-CH}_2 + 2 \cdot \text{c-CH}$, 1-methylcyclohexene $1 \cdot \text{CH}_3 + 1 \cdot \text{c-C}=\text{C} + 1 \cdot \text{H} + 4 \cdot \text{c-CH}_3$, 1,3,5-cycloheptatriene $3 \cdot \text{c-C}=\text{C} + 6 \cdot \text{H} + 1 \cdot \text{c-CH}_2$, benzene $6 \cdot \text{CH}_{\text{ar}}$, 1-methyl-4-(1-methylethyl)-benzene, or *p*-cymene, $3 \cdot \text{CH}_3 + 1 \cdot \text{CH} + 4 \cdot \text{CH}_{\text{ar}} + 2 \cdot \text{C}_{\text{ar}}$, 1,2,4,5-tetramethylbenzene $4 \cdot \text{CH}_3 + 2 \cdot \text{CH}_{\text{ar}} + 4 \cdot \text{C}_{\text{ar}} + 2 \cdot \text{I}(\text{C-C})$, 2-methyl-2-butanol $3 \cdot \text{CH}_3 + 1 \cdot \text{CH}_2 + 1 \cdot \text{C} + 1 \cdot \text{OH}$, etc. In Table 5 we give the statistics for the number of compounds containing each group for each of the thermodynamic properties considered in this study.²

4.2. Determinations of the Group Contribution Values for the Different Thermodynamic Functions of Hydration

Assuming group additivity any thermodynamic property Y of an organic compound can be written as

$$Y = Y_o + \sum_i n_i Y_i, \quad (23)$$

where n_i stands for the number of times the i -th group is present in the compound, and Y_i is the contribution to the Y property of the i -th group. Cabani et al. (1981) mentioned that the term Y_o arises from theoretical considerations; however, these authors treated it as an adjustable parameter. In our initial attempts we

² Structural formulae can be checked in the organic chemistry handbooks. A convenient on-line handbook is the "NIST Chemistry WebBook, NIST Standard Reference Database Number 69, November 1998, Eds. W. G. Mallard and P. P. J. Linstrom," <http://webbook.nist.gov>.

Table 5. The number of compounds containing the selected groups for each of the thermodynamic properties.

Group	$\Delta_h G^o$	$\Delta_h H^o$	$\Delta_h C_p^o$	V_2^o
CH ₃	133	57	30	29
CH ₂	91	35	24	27
CH	48	12	6	11
C	15	3	4	4
C=C	29	17	7	5
C≡C	16	5	2	1
H	50	27	9	6
c-CH ₂	36	17	6	11
c-CH	22	7	4	10
c-C	7	1	0	0
c-C=C	14	9	1	0
CH _{ar}	26	16	4	3
C _{ar}	24	15	3	2
I(C-C)	7	3	0	0
OH	35	25	25	31

found that Y_o for any property, determined as an adjustable parameter by the fit, has a rather large uncertainty (for example, $\pm 1.3 \text{ kJ} \cdot \text{mol}^{-1}$ for $\Delta_h G^o$, $\pm 5.2 \text{ kJ} \cdot \text{mol}^{-1}$ for $\Delta_h H^o$ and $\pm 5.5 \text{ cm}^3 \cdot \text{mol}^{-1}$ for V_2^o at the 0.95 confidence level). We presume these uncertainties arise from the strong covariance between values of Y_o and those of other groups, first of all CH₃. Therefore, it was decided to use fixed values of Y_o , equal to their theoretical values, see below.

The statistical quality of the data description is somewhat worse when Y_o is fixed. For instance, in the case of the Gibbs energy of hydration, the averaged $\frac{\Delta}{\delta}$ values (Δ stands for the difference between the experimental and calculated value, δ represents the uncertainty of the data point) are equal to 1.05 and 1.15 for the unconstrained and constrained (Y_o is fixed) fit, respectively. However, this difference in the goodness of the fit is not large, and the unconstrained fit represents improvement mainly for cyclic compounds, which are expected to demonstrate larger deviations from group additivity compared with linear compounds.

From Eqn. 23 it is clear that Y_o is equal to Y for an imaginable compound without any groups at all, i.e. for a material point. It follows from theoretical models (see, for example, Pierotti, 1976), that the transfer of the material point from an ideal gas to the standard aqueous solution is accompanied by a non-zero change of the Gibbs energy. Namely, the Gibbs energy of hydration of the material point $\Delta_h G_{mp}^o$ is equal to

$$\Delta_h G_{mp}^o = RT \ln \frac{RT}{V_1^o} - RT \ln \frac{1000}{M_w} \approx 7.96 \text{ kJ} \cdot \text{mol}^{-1}, \quad (24)$$

where V_1^o stands for the molar volume of pure water at the specified T and P (298.15 K and 0.1 MPa in our case); the first term is the so-called "standard-state conversion" term; the second term is needed for the hypothetical $1 \text{ mol} \cdot \text{kg}^{-1}$ standard state for the aqueous solution. The numerical value at the right side of Eqn. 24 is valid at 298.15 K and 0.1 MPa.

Proper thermodynamic manipulations of Eqn. 24 result in the other thermodynamic functions of hydration of the material point:

Table 6. Numerical values of the group contributions to each thermodynamic functions of hydration at 298.15 K, 0.1 MPa together with their uncertainties at the 0.95 confidence level. The values used as fixed parameters or determined by using other constraints are shown in square brackets, and values based on the only one compound are marked by an asterisk.

Group	$\Delta_h G^o$, kJ · mol ⁻¹	$\Delta_h H^o$, kJ · mol ⁻¹	$\Delta_h C_p^o$, J · K ⁻¹ · mol ⁻¹	V_2^o , cm ³ · mol ⁻¹
CH ₃	3.63(13)	-7.54(43)	132(5)	25.14(52)
CH ₂	0.72(06)	-3.76(22)	64(3)	15.70(13)
CH	-1.79(29)	-0.9(12)	-2(13)	6.35(64)
C	-4.50(49)	2.6(19)	-63(18)	-3.0(12)
C=C	-10.23(85)	0.6(34)	[-25]	[-7.3]
C≡C	-8.36(44)	[-5.19]	[20]	14.1*
H	3.91(30)	-3.7(11)	65(11)	13.6(10)
c-CH ₂	0.83(07)	-5.36(26)	79(4)	14.36(26)
c-CH	-1.03(39)	-2.4(18)	-50(24)	16.9(13)
c-C	-2.72(98)	5.6*		
c-C=C	-9.47(61)	-0.7(25)	46*	
CH _{ar}	-0.65(08)	-5.00(23)	48(3)	13.58(24)
C _{ar}	-3.85(27)	-0.67(89)	-50(22)	4.0(16)
I(C-C)	-1.01(44)	[2.0(20)]		
OH	-25.40(22)	-39.79(81)	6(9)	13.10(66)
Y _o	[7.96]	[-2.29]	[0]	[1.12]

$$\Delta_h H_{mp}^o = -T^2 \left(\frac{\partial}{\partial T} \left[\frac{\Delta_h G_{mp}^o}{T} \right] \right)_p = RT(\alpha T - 1) \approx -2.29 \text{ kJ} \cdot \text{mol}^{-1}, \quad (25)$$

$$\Delta_h V_{mp}^o \equiv V_{mp}^o = \left(\frac{\partial}{\partial P} [\Delta_h G_{mp}^o] \right)_T = RT \kappa_T \approx 1.12 \text{ cm}^3 \cdot \text{mol}^{-1}, \quad (26)$$

$$\Delta_h C_{p,mp}^o = \left(\frac{\partial}{\partial T} [\Delta_h H_{mp}^o] \right)_p = R \left(T^2 \left(\frac{\partial \alpha}{\partial T} \right)_p + 2\alpha T - 1 \right) \approx 0.06 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \approx 0, \quad (27)$$

where

$$\alpha = \left(\frac{\partial \ln V_1^o}{\partial T} \right)_p \text{ and } \kappa_T = - \left(\frac{\partial \ln V_1^o}{\partial P} \right)_T$$

stand for the thermal expansion and the isothermal compressibility coefficients of pure water, respectively. All numerical values in the right sides of Eqns. 24–27 are valid at 298.15 K and 0.1 MPa, and were calculated using the equation of state for pure water proposed by Hill (1990). Consequently, in our treatment the values of Y_o were fixed and taken equal to the thermodynamic functions of hydration of the material point.

To derive the numerical values of Y_i for each of the chosen groups we used the weighted least-squares procedure (methane can not be represented by the selected groups and was excluded from the fit). The selection of weights is plagued by two main problems. First, the most accurate results are obtained for the lowest members of any homologous series, which are of limited use for the estimation of group contribution values because compounds with carbon numbers below 4–5 show the greatest deviation from additivity. Second, the first-order group contribution method is only an approximation, often incapable in

principle of highly-accurate representation of thermodynamic properties of organic compounds due to the intrinsic limitations discussed above. Therefore, the minimum uncertainties of data used to estimate statistical weights were taken to be $\pm 0.3 \text{ kJ} \cdot \text{mol}^{-1}$ for $\Delta_h G^\circ$; $\pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ for $\Delta_h H^\circ$; $\pm 20 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $\Delta_h C_p^\circ$; and $\pm 0.5 \text{ cm}^3 \cdot \text{mol}^{-1}$ for V_2° .

For functions other than the Gibbs energy of hydration we attempted to reduce the dimension of the regression task because of the limited numbers of experimental data points. For the enthalpy of hydration the value of I(C-C) was fixed to $2.0(\pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$ as determined from $\Delta_h H^\circ$ for different isomers of di- and trimethylbenzenes. Another constraint was placed on the value of $\Delta_h H^\circ(\text{C}\equiv\text{C})$, the enthalpy of hydration of the group containing the triple bond, namely $\Delta_h H^\circ(\text{C}\equiv\text{C}) = \Delta_h H^\circ(\text{C}=\text{C}) + 2\Delta_h H^\circ(\text{H}) + 1.8 \text{ kJ} \cdot \text{mol}^{-1}$, where $1.8(\pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$ is the difference between the enthalpy of hydration of ethene and ethyne which is accurately known from calorimetric determinations. Analogous constraints were used for $\Delta_h C_p^\circ$ (by comparing values of the heat capacity of hydration for alkane-alkene, alkane-alkyne, aliphatic alcohol-unsaturated alcohol pairs), namely: $\Delta_h C_p^\circ(\text{C}=\text{C}) = \Delta_h C_p^\circ(\text{CH}_3) + \Delta_h C_p^\circ(\text{CH}_2) - 3\Delta_h C_p^\circ(\text{H}) - 25 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $\Delta_h C_p^\circ(\text{C}\equiv\text{C}) = \Delta_h C_p^\circ(\text{CH}_3) + \Delta_h C_p^\circ(\text{CH}_2) - \Delta_h C_p^\circ(\text{H}) - 110 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and $V_2^\circ(V_2^\circ(\text{C}=\text{C})) = 2V_2^\circ(\text{CH}_3) - 4V_2^\circ(\text{H}) - 3.0 \text{ cm}^3 \cdot \text{mol}^{-1}$. The values of $\Delta_h H^\circ(\text{c}-\text{C})$, $\Delta_h C_p^\circ(\text{c}-\text{C}=\text{C})$ and $V_2^\circ(\text{C}\equiv\text{C})$ were each estimated from only one compound, α -pinene, 2-cyclohexen-1-ol and ethyne, respectively.

The resulting numerical values of the group contributions to the thermodynamic functions of hydration are shown in Table 6. Calculated values of $\Delta_h G^\circ$, $\Delta_h H^\circ$, $\Delta_h C_p^\circ$, and V_2° are given in Tables 1–4 for each compound under consideration, as well as values of Δ , the difference between the “experimental” and calculated values. A comparison of “experimental” and calculated values are shown in Figure 2, which provides the framework for the following section.

5. DISCUSSION

An examination of Δ values taken from Tables 1–4 and plotted in Figure 2 reveals that, in most cases, the simple first-order group contribution method gives a representation of the thermodynamic functions of hydration of hydrocarbons and monohydric alcohols well within the expected uncertainties. As mentioned above, it is not expected that this method will work for the lowest members of a homologous series, and indeed, for most compounds with carbon numbers of three or less, Δ can exceed the experimental uncertainty by several fold. Cyclic compounds are another class of substances where deviations might considerably exceed experimental uncertainty because of the intrinsically poor performance of the group contribution scheme to represent the energetics of C-C bonds that strongly depend on the geometry of the compound. Considering the other 117 organic compounds for which $\Delta_h G^\circ$ is available, 83 exhibit values of $\Delta < 0.58 \text{ kJ} \cdot \text{mol}^{-1}$ (corresponding to a difference in $\log K < 0.1$). There are only 5 compounds where Δ exceeds $1.74 \text{ kJ} \cdot \text{mol}^{-1}$ (corresponding to a difference in $\log K > 0.3$). Gross deviations are more common for larger compounds, where experimental measurements are difficult and may bear considerable uncertainties. In a few cases one can

speculate that large differences arise because we are not accounting for specific interactions between neighboring double and triple bonds (see 1-buten-3-yne) or between closely packed neighboring groups in “overcrowded” compounds (see systematic deviations for different isomers of cymene). However, more convincing evidence is needed to draw definite conclusions.

In general, the representation of $\Delta_h H^\circ$ is more uncertain than that of $\Delta_h G^\circ$. Nevertheless, for 78 compounds where values of $\Delta_h H^\circ$ are available, values of Δ are $< 2.0 \text{ kJ} \cdot \text{mol}^{-1}$ for 48, and only for 6 compounds does Δ exceed $5.0 \text{ kJ} \cdot \text{mol}^{-1}$. For 30 of the 42 compounds with experimental $\Delta_h C_p^\circ$ data Δ is $< 20 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and in most cases large discrepancies between “experimental” and calculated values are for cyclic compounds. The representation of the $44V_2^\circ$ values is quite accurate for most of the hydrocarbons and alcohols, except for some “gaseous” hydrocarbons (n-butane, 1-butene and cyclopropane) where experimental data were obtained at atmospheric pressure (Moore et al., 1982). At these conditions the concentrations of the solutes are very low and, therefore, might bear large uncertainties.

A direct comparison of the numerical values of the group contributions obtained in this work with earlier investigations is meaningful only for the methylene group (CH_2) because of the different scheme for group selection and the different values of Y_0 selected here and elsewhere. Our value of $\Delta_h G^\circ(\text{CH}_2) = 0.72 \pm 0.06 \text{ kJ} \cdot \text{mol}^{-1}$ compares well with 0.74 reported by Cabani et al. (1981), and falls within the range 0.61–1.03 as obtained by Abraham (1984) for different homologous series of hydrocarbons and alcohols. Analogous comparisons are possible for $\Delta_h H^\circ(\text{CH}_2)$: $-3.76 \pm 0.22 \text{ kJ} \cdot \text{mol}^{-1}$ in this work and -3.24 from Cabani et al. (1981), -2.82 to -3.83 with an average -3.56 from Abraham (1984); and for $\Delta_h C_p^\circ(\text{CH}_2)$: $64 \pm 3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ as compared with 64.5 from Cabani et al. (1981) and 69.8 from Makhatadze and Privalov (1989). Our value of $V_2^\circ(\text{CH}_2) = 15.70 \pm 0.13 \text{ cm}^3 \cdot \text{mol}^{-1}$ is close to a large number of literature estimates, falling typically in a range from 15.8 to $16.0 \text{ cm}^3 \cdot \text{mol}^{-1}$ (Amend and Helgeson, 1997; Shock and Helgeson, 1990; Wurzbürger et al., 1990; Høiland, 1986; Cabani et al., 1981; and others).

It is expected that the numerical values of group contributions obtained here will allow a reasonably accurate estimation of the thermodynamic functions of hydration for many hydrocarbons and monohydric alcohols at 298.15 K and 0.1 MPa. The present values should not be used to construct estimates for polyols because of exceptionally strong OH-OH interactions (see Cabani et al., 1981). As no phenols were considered here, we do not recommend the use of our group contribution values to evaluate the thermodynamic functions of hydration for this class of compounds. The optimistic estimates of uncertainties given here are based on the examples discussed above: ± 0.5 – 1.0 and 2 – $4 \text{ kJ} \cdot \text{mol}^{-1}$ for the Gibbs energy and enthalpy of hydration, respectively; ± 20 – $40 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for the heat capacity of hydration; and ± 0.5 – $1.5 \text{ cm}^3 \cdot \text{mol}^{-1}$ for the partial molar volume. For cyclic compounds, and perhaps for compounds with many closely-packed neighboring groups, the uncertainties might be larger. The current group contribution method can be easily extended to include other organic compounds of geochemical and environmental significance.

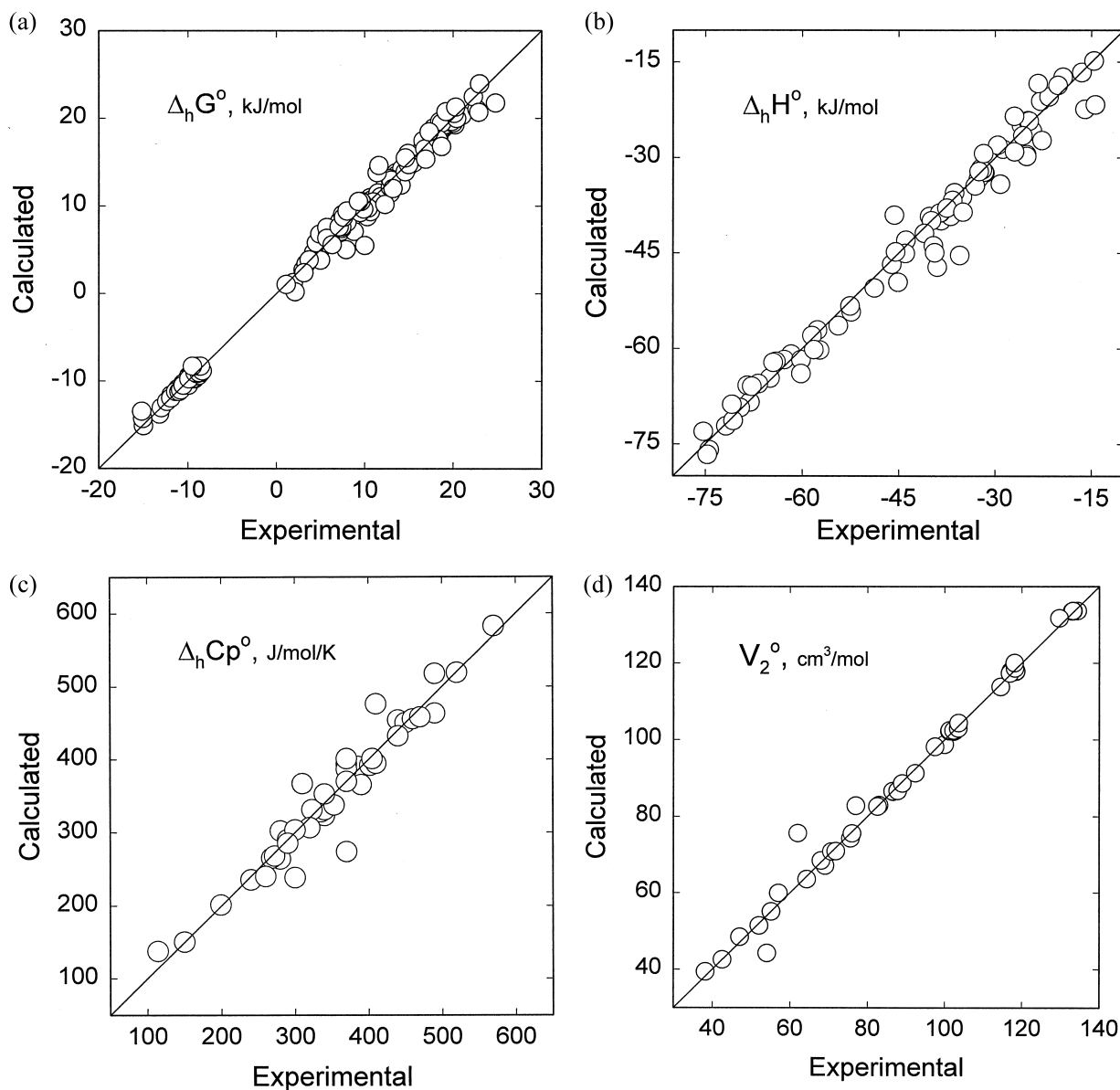


Fig. 2. A comparison of experimental and calculated values of (a) the Gibbs energy of hydration, $\text{kJ} \cdot \text{mol}^{-1}$, (b) the enthalpy of hydration, $\text{kJ} \cdot \text{mol}^{-1}$, (c) the heat capacity of hydration, $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and (d) the partial molar volumes, $\text{cm}^3 \cdot \text{mol}^{-1}$ for hydrocarbons and monohydric alcohols considered in this study.

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APPENDIX 1. PARTIAL MOLAR THERMODYNAMIC PROPERTIES OF HYDROCARBONS AND MONOHYDRIC ALCOHOLS IN THE STANDARD AQUEOUS SOLUTION AT 298.15 K AND 0.1 MPAS

Most computer codes used for geochemical modeling require values of the standard state partial molar thermodynamic properties of components in aqueous solution. Therefore it was decided to tabulate the standard state partial molar Gibbs energy of formation, $\Delta_f G^\circ$, enthalpy of formation, $\Delta_f H^\circ$, entropy, S° , heat capacity, C_p° , volume, V° , all at 298.15 K, 0.1 MPa, for some aqueous hydrocarbons and alcohols. The requirement for tabulation is that the values be internally consistent with the values of the thermodynamic functions of hydration obtained in this study, the functions of vaporization for pure compounds selected here, and the thermochemical data for pure compounds calculated using the algorithms and group contribution values recommended by Domalski and Hearing (1993). We should mention that the results of Domalski and Hearing (1993) were adopted by Helgeson et al. (1998) for the reference temperature 298.15 K, and by such a choice we provide the consistency between the partial properties in Table A1 and the properties of hydrocarbons and alcohols in liquid and crystalline state given by Helgeson et al. (1998).

Using the familiar relations

$$\Delta_h Y^\circ = Y_2^\circ(aq) - Y^\circ(g) \quad (A1)$$

$$\Delta_{vap} Y^\circ = Y^\circ(g) - Y^\circ(l,s), \quad (A2)$$

where Y stands for any thermodynamic function, and all other abbreviations are defined in the text, one obtains for the partial property of the standard aqueous solution

$$Y_2^\circ(aq) = \Delta_h Y^\circ + \Delta_{vap} Y^\circ + Y^\circ(l,s). \quad (A3)$$

For practical use the following relations hold:

$$\Delta_f H^\circ(aq) = \Delta_f H^\circ + \Delta_{vap} H^\circ + \Delta_f H^\circ(l,s), \quad (A4)$$

$$S_2^\circ(aq) = \Delta_h S^\circ + \Delta_{vap} S^\circ + S^\circ(l,s) = \frac{\Delta_h H^\circ - \Delta_h G^\circ}{T} + \frac{\Delta_{vap} H^\circ - \Delta_{vap} G^\circ}{T} + S^\circ(l,s), \quad (A5)$$

where temperature $T = 298.15$ K. To calculate the Gibbs energy of formation consistently with the values of $\Delta_f H^\circ$ and S_2° , requires:

$$\Delta_f G^\circ(aq) = \Delta_f H^\circ(aq) - T \cdot \left\{ S_2^\circ(aq) - p \cdot S^\circ(C(c)) - \frac{q}{2} \cdot S^\circ(H_2(g)) - \frac{r}{2} \cdot S^\circ(O_2(g)) \right\}, \quad (A6)$$

where p , q , r are the stoichiometric coefficients for C, H, and O in the compound of the composition $C_p H_q O_r$; $S^\circ(C(c)) = 5.74(10) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $S^\circ(H_2(g)) = 130.680(3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and $S^\circ(O_2(g)) = 205.152(5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ stand for the standard state entropies of the elements carbon, hydrogen, and oxygen in their reference states, as adopted by CODATA (Cox et al., 1989), all at 298.15 K, 0.1 MPa.

The standard state partial molar heat capacity is obtained by means of

$$C_p^\circ = \Delta_h C_p^\circ + C_p^\circ(g), \quad (A7)$$

where the values of the heat capacity of pure compounds in the ideal gas state are calculated using the algorithm outlined in Domalski and Hearing (1993).

In Table A1 we give the values of the standard state partial molar thermodynamic functions of some hydrocarbons and alcohols in aqueous solution at 298.15 K, 0.1 MPa. Properties of thousands of other aqueous compounds can be computed if necessary. As a rule, the values of thermodynamic functions of hydration needed in Eqns. (A4)–(A7) were calculated using the group contribution results of this study. However, for linear hydrocarbons with carbon number ≤ 3 and cyclic hydrocarbons, the experimental results given in Tables 1–4 were used, if available. Sources of data for the Gibbs energy and enthalpy of vaporization of pure compounds are given in Tables 1–4. The tabulation is performed for compounds with the number of carbon atoms up to twelve. The estimates for higher members of homologous series can be done in a simple way by observing a regular trend in the change of the numerical values of the thermodynamic functions with carbon number. This trend is consistent with the following values of the standard molar partial properties of the CH_2 group at 298.15 K, 0.1 MPa: 8.8–9.0 $\text{kJ} \cdot \text{mol}^{-1}$ for the Gibbs energy of formation, -24.2 to $-24.6 \text{ kJ} \cdot \text{mol}^{-1}$ for the enthalpy of formation, 24.2 – $25.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for the entropy, 86 – $87 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for the heat capacity. Corresponding estimates given by Shock and Helgeson (1990) are $8.58 \text{ kJ} \cdot \text{mol}^{-1}$, $-23.72 \text{ kJ} \cdot \text{mol}^{-1}$, $28.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $88.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, respectively, and those given by Amend and Helgeson (1997), $9.38 \text{ kJ} \cdot \text{mol}^{-1}$, $-23.72 \text{ kJ} \cdot \text{mol}^{-1}$, $25.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $86.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, respectively.

For a few compounds other sources of auxiliary thermochemical information have been used. In the case of toluene the entropy of the liquid phase calculated using the algorithm of Domalski and Hearing (1993) differs by more than $12 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ from experimental determinations. Therefore, for toluene we used a thermochemical cycle based on $S^\circ(C_7H_8(g)) = 320.99 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ as recommended by Frenkel et al. (1994). For ethanol the difference between the experimental and calculated values of the enthalpy of formation of the liquid exceeds $2.5 \text{ kJ} \cdot \text{mol}^{-1}$ using the algorithm of Domalski and Hearing (1993). Thus we accepted the value of $\Delta_f H^\circ(aq) = -288.2(4) \text{ kJ} \cdot \text{mol}^{-1}$ for ethanol as recommended in Pedley et al. (1986), and for $S^\circ(C_2H_6O(g)) = 280.64 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ from (Frenkel et al., 1994).

The representative uncertainties of the Gibbs energy and enthalpy of hydration of hydrocarbons and alcohols are expected to be $\pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ and ± 2 – $4 \text{ kJ} \cdot \text{mol}^{-1}$, respectively, except for the cyclic compounds. The partial molar thermodynamic properties of hydrocarbons and alcohols bear larger uncertainties than the corresponding functions of hydration due to uncertainties of the enthalpy of formation and the entropy of pure compounds. According to Helgeson et al. (1998) the representative uncertainties associated with $\Delta_f H^\circ$ for a solid/liquid/gaseous

Table A1. Standard state partial molar thermodynamic functions of some hydrocarbons and monohydric alcohols in aqueous solution at 298.15 K, 0.1 MPa.

Compound	Formula	$\Delta_f G^\circ$, kJ · mol ⁻¹	$\Delta_f H^\circ$, kJ · mol ⁻¹	S_{298}° , J · mol ⁻¹ · K ⁻¹	C_p° , J · mol ⁻¹ · K ⁻¹	V_2° , cm ³ · mol ⁻¹
Normal alkanes						
Methane	CH ₄	-34.12	-87.58	87.79	256	37.3
Ethane	C ₂ H ₆	-17.43	-103.92	113.4	315	51.5
Propane	C ₃ H ₈	-8.54	-128.05	139.1	401	67.2
<i>n</i> -Butane	C ₄ H ₁₀	0.42	-151.68	166.2	489	82.9
<i>n</i> -Pentane	C ₅ H ₁₂	9.55	-174.46	195.6	574	98.6
<i>n</i> -Hexane	C ₆ H ₁₄	18.66	-198.01	222.5	660	114
<i>n</i> -Heptane	C ₇ H ₁₆	27.66	-223.29	243.9	746	130
<i>n</i> -Octane	C ₈ H ₁₈	36.61	-247.90	267.8	833	146
<i>n</i> -Nonane	C ₉ H ₂₀	45.56	-272.48	291.8	918	161
<i>n</i> -Decane	C ₁₀ H ₂₂	54.34	-296.97	316.6	1005	177
<i>n</i> -Undecane	C ₁₁ H ₂₄	63.29	-321.30	341.4	1091	193
<i>n</i> -Dodecane	C ₁₂ H ₂₆	72.16	-345.84	365.8	1177	208
2-Methylalkanes						
2-Methylpropane	C ₄ H ₁₀	-2.79	-158.93	152.7	467	83.0
2-Methylbutane	C ₅ H ₁₂	5.48	-181.95	184.1	577	98.7
2-Methylpentane	C ₆ H ₁₄	14.47	-206.55	207.9	663	114
2-Methylhexane	C ₇ H ₁₆	23.42	-231.15	231.8	749	130
2-Methylheptane	C ₈ H ₁₈	32.33	-255.94	255.2	835	146
2-Methyloctane	C ₉ H ₂₀	41.19	-280.44	279.7	921	161
2-Methylnonane	C ₁₀ H ₂₂	50.05	-304.94	304.2	1008	177
2-Methyldecane	C ₁₁ H ₂₄	58.98	-329.77	327.4	1093	193
2-Methylundecane	C ₁₂ H ₂₆	67.87	-353.24	353.3	1180	209
3-Methylalkanes						
3-Methylpentane	C ₆ H ₁₄	16.95	-204.00	208.1	662	114
3-Methylhexane	C ₇ H ₁₆	25.78	-228.79	231.8	747	130
3-Methylheptane	C ₈ H ₁₈	34.64	-253.55	255.5	834	146
3-Methyloctane	C ₉ H ₂₀	43.46	-278.12	279.9	920	161
3-Methylnonane	C ₁₀ H ₂₂	52.50	-302.68	303.6	1006	177
3-Methyldecane	C ₁₁ H ₂₄	61.43	-326.58	329.9	1092	193
3-Methylundecane	C ₁₂ H ₂₆	70.35	-350.96	354.7	1178	209
2,2-Dimethylalkanes						
2,2-Dimethylpropane	C ₅ H ₁₂	2.43	-193.18	156.7	610	98.7
2,2-Dimethylbutane	C ₆ H ₁₄	12.85	-217.00	178.6	669	114
2,2-Dimethylpentane	C ₇ H ₁₆	21.64	-241.86	202.2	756	130
2,2-Dimethylhexane	C ₈ H ₁₈	30.50	-264.22	234.0	842	146
2,2-Dimethylheptane	C ₉ H ₂₀	39.34	-290.90	251.3	929	161
2,2-Dimethyloctane	C ₁₀ H ₂₂	48.03	-316.80	271.7	1015	177
2,2-Dimethylnonane	C ₁₁ H ₂₄	57.00	-340.39	299.0	1102	193
2,2-Dimethyldecane	C ₁₂ H ₂₆	65.92	-364.88	323.4	1188	209
Cycloalkanes						
Cyclopropane	C ₃ H ₆	115.47	29.96	122.5	356	54
Cyclobutane	C ₄ H ₈	123.18	4.63	148.1	390	59
Cyclopentane	C ₅ H ₁₀	51.69	-106.20	152.5	480	73
Cyclohexane	C ₆ H ₁₂	44.99	-156.13	143.9	516	87
Methylcyclopentane	C ₆ H ₁₂	55.71	-135.78	176.3	509	101
Cycloheptane	C ₇ H ₁₄	75.97	-157.84	170.7	679	102
Methylcyclohexane	C ₇ H ₁₄	47.85	-188.86	161.0	616	115
Cyclooctane	C ₈ H ₁₆	103.23	-169.63	176.2	775	116
1-Alkenes						
Ethene	C ₂ H ₄	81.79	36.14	119.7	283	48.4
1-Propene	C ₃ H ₆	75.74	-1.22	151.2	344	59.9
1-Butene	C ₄ H ₈	85.08	-25.40	175.1	476	75.6
1-Pentene	C ₅ H ₁₀	93.79	-48.74	204.1	539	91.3
1-Hexene	C ₆ H ₁₂	102.91	-73.11	228.2	625	107
1-Heptene	C ₇ H ₁₄	111.90	-97.71	251.9	712	123
1-Octene	C ₈ H ₁₆	120.85	-122.34	275.7	798	138
1-Nonene	C ₉ H ₁₈	129.77	-146.75	300.3	885	154
1-Decene	C ₁₀ H ₂₀	138.75	-171.23	324.5	972	170
1-Undecene	C ₁₁ H ₂₂	147.61	-195.70	349.1	1058	186
1-Dodecene	C ₁₂ H ₂₄	156.56	-219.87	374.5	1145	201

(Continued)

Table A1. (Continued)

Compound	Formula	$\Delta_f G^\circ$, kJ · mol ⁻¹	$\Delta_f H^\circ$, kJ · mol ⁻¹	S_2° , J · mol ⁻¹ · K ⁻¹	Cp_2° , J · mol ⁻¹ · K ⁻¹	V_2° , cm ³ · mol ⁻¹
<i>cis</i> -2-Alkenes						
<i>cis</i> -2-Butene	C ₄ H ₈	77.53	-29.27	187.5	450	71.4
<i>cis</i> -2-Pentene	C ₅ H ₁₀	87.02	-52.72	213.4	535	87.1
<i>cis</i> -2-Hexene	C ₆ H ₁₂	96.14	-76.87	238.2	622	103
<i>cis</i> -2-Alkenes (continued)						
<i>cis</i> -2-Heptene	C ₇ H ₁₄	105.08	-102.29	259.4	707	119
<i>cis</i> -2-Octene	C ₈ H ₁₆	114.00	-126.74	283.9	794	134
<i>cis</i> -2-Nonene	C ₉ H ₁₈	122.89	-151.23	308.4	880	150
<i>cis</i> -2-Decene	C ₁₀ H ₂₀	131.97	-175.69	332.3	967	166
<i>cis</i> -2-Undecene	C ₁₁ H ₂₂	140.80	-200.25	356.7	1053	181
<i>cis</i> -2-Dodecene	C ₁₂ H ₂₄	149.75	-224.71	381.1	1140	197
<i>trans</i> -2-Alkenes						
<i>trans</i> -2-Butene	C ₄ H ₈	75.16	-36.12	172.4	457	71.4
<i>trans</i> -2-Pentene	C ₅ H ₁₀	82.79	-60.09	202.9	543	87.1
<i>trans</i> -2-Hexene	C ₆ H ₁₂	91.77	-84.74	226.5	628	103
<i>trans</i> -2-Heptene	C ₇ H ₁₄	100.77	-109.55	249.5	715	119
<i>trans</i> -2-Octene	C ₈ H ₁₆	109.71	-134.01	273.9	802	134
<i>trans</i> -2-Nonene	C ₉ H ₁₈	117.60	-159.53	298.3	888	150
<i>trans</i> -2-Decene	C ₁₀ H ₂₀	127.58	-182.99	322.6	975	166
<i>trans</i> -2-Undecene	C ₁₁ H ₂₂	136.51	-207.45	347.0	1061	181
<i>trans</i> -2-Dodecene	C ₁₂ H ₂₄	145.46	-232.01	371.0	1147	197
Dienes						
1,3-Butadiene	C ₄ H ₆	159.83	85.71	166.4	420	68.4
2-Methyl-1,3-butadiene (isoprene)	C ₅ H ₈	154.37	45.21	185.3	512	79.9
1,4-Pentadiene	C ₅ H ₈	183.00	78.42	200.7	508	84.1
1,5-Hexadiene	C ₆ H ₁₀	192.03	53.83	224.3	595	99.8
1,6-Heptadiene	C ₇ H ₁₂	201.07	29.33	248.3	681	115
1,7-Octadiene	C ₈ H ₁₄	209.99	4.84	272.6	768	131
Cycloalkenes						
Cyclopentene	C ₅ H ₈	122.69	7.92	165.5	489	71.5
Cyclohexene	C ₆ H ₁₀	117.09	-37.11	170.7	598	85.8
1-Alkynes						
Ethyne	C ₂ H ₂	218.19	212.40	122.7	195	42.5
1-Propyne	C ₃ H ₄	202.34	167.72	162.5	279	54.0
1-Butyne	C ₄ H ₆	211.03	144.27	191.1	363	69.7
1-Pentyne	C ₅ H ₈	221.91	117.33	200.7	449	85.4
1-Hexyne	C ₆ H ₁₀	230.87	92.84	224.9	535	101
1-Heptyne	C ₇ H ₁₂	239.77	68.36	249.3	622	117
1-Octyne	C ₈ H ₁₄	248.66	43.92	274.0	709	133
1-Nonyne	C ₉ H ₁₆	257.36	19.40	299.0	795	148
1-Decyne	C ₁₀ H ₁₈	266.27	-5.08	323.4	882	164
1-Undecyne	C ₁₁ H ₂₀	275.19	-29.57	347.8	968	180
1-Dodecyne	C ₁₂ H ₂₂	285.10	-54.05	372.2	1055	195
Alkylbenzenes						
Benzene	C ₆ H ₆	133.86	51.18	149.2	372	82.6
Methylbenzene (toluene)	C ₇ H ₈	127.05	14.11	184.1	427	98.2
Ethylbenzene	C ₈ H ₁₀	135.89	-10.40	208.7	516	114
<i>n</i> -Propylbenzene	C ₉ H ₁₂	144.44	-35.85	231.1	602	130
<i>n</i> -Butylbenzene	C ₁₀ H ₁₄	153.32	-59.33	258.9	689	145
<i>n</i> -Pentylbenzene	C ₁₁ H ₁₆	162.06	-84.86	280.4	775	161
<i>n</i> -Hexylbenzene	C ₁₂ H ₁₈	170.98	-109.44	304.5	862	177
Methylated benzenes						
1,2-Dimethylbenzene	C ₈ H ₁₀	130.70	-14.26	213.1	488	114
1,3-Dimethylbenzene	C ₈ H ₁₀	127.90	-20.29	202.3	482	114
1,4-Dimethylbenzene	C ₈ H ₁₀	127.80	-20.55	201.9	481	114
1,2,3-Trimethylbenzene	C ₉ H ₁₂	130.61	-42.41	255.4	550	129
1,2,4-Trimethylbenzene	C ₉ H ₁₂	127.62	-49.54	241.6	543	129
1,3,5-Trimethylbenzene	C ₉ H ₁₂	124.90	-55.21	231.7	538	129
1,2,3,4-Tetramethylbenzene	C ₁₀ H ₁₄	130.40	-72.88	290.3	612	145
1,2,3,5-Tetramethylbenzene	C ₁₀ H ₁₄	127.40	-78.85	280.3	605	145
1,2,4,5-Tetramethylbenzene	C ₁₀ H ₁₄	135.80	-72.23	274.3	605	145
Pentamethylbenzene	C ₁₁ H ₁₆	143.46	-99.42	294.0	675	160
Hexamethylbenzene	C ₁₂ H ₁₈	156.13	-112.83	342.9	744	176

(Continued)

Table A1. (Continued)

Compound	Formula	$\Delta_f G^\circ$, kJ · mol ⁻¹	$\Delta_f H^\circ$, kJ · mol ⁻¹	S_2° , J · mol ⁻¹ · K ⁻¹	C_p° , J · mol ⁻¹ · K ⁻¹	V_2° , cm ³ · mol ⁻¹
1-Alcohols						
Methanol	CH ₄ O	-175.66	-246.41	132.4	158	38.2
Ethanol	C ₂ H ₆ O	-181.03	-288.20	146.6	263	55.1
1-Propanol	C ₃ H ₈ O	-169.38	-310.79	169.8	355	70.7
1-Butanol	C ₄ H ₁₀ O	-161.05	-335.67	193.3	445	86.6
1-Pentanol	C ₅ H ₁₂ O	-152.16	-360.06	218.1	535	102.4
1-Hexanol	C ₆ H ₁₄ O	-143.34	-384.32	243.5	612	117.8
1-Heptanol	C ₇ H ₁₆ O	-134.49	-408.55	269.0	698	133.5
1-Octanol	C ₈ H ₁₈ O	-125.69	-432.71	294.9	785	149
1-Nonanol	C ₉ H ₂₀ O	-117.47	-458.59	316.9	867	165
1-Decanol	C ₁₀ H ₂₂ O	-108.37	-482.97	341.0	953	181
1-Undecanol	C ₁₁ H ₂₄ O	-99.29	-507.35	365.2	1039	196
1-Dodecanol	C ₁₂ H ₂₆ O	-90.17	-531.74	389.3	1125	212
2-Alcohols						
2-Propanol	C ₃ H ₈ O	-185.89	-331.70	153.5	357	71.8
2-Butanol	C ₄ H ₁₀ O	-175.40	-355.22	175.8	444	86.6
2-Pentanol	C ₅ H ₁₂ O	-166.88	-379.33	202.8	530	102
2-Hexanol	C ₆ H ₁₄ O	-158.22	-404.52	225.7	616	118
2-Heptanol	C ₇ H ₁₆ O	-149.39	-429.02	250.3	703	134
2-Octanol	C ₈ H ₁₈ O	-140.48	-453.45	274.9	789	149
2-Nonanol	C ₉ H ₂₀ O	-131.55	-477.98	299.1	876	165
2-Decanol	C ₁₀ H ₂₂ O	-122.64	-502.51	323.4	962	181
2-Undecanol	C ₁₁ H ₂₄ O	-113.63	-526.94	347.6	1049	196
2-Dodecanol	C ₁₂ H ₂₆ O	-104.71	-551.47	371.9	1136	212
2-Methyl-1-Alcohols						
2-Methyl-1-propanol	C ₄ H ₁₀ O	-165.17	-340.96	189.3	441	86.5
2-Methyl-1-butanol	C ₅ H ₁₂ O	-154.57	-365.62	207.5	528	102
2-Methyl-1-pentanol	C ₆ H ₁₄ O	-145.67	-390.03	232.2	614	118
2-Methyl-1-hexanol	C ₇ H ₁₆ O	-136.76	-414.56	256.5	701	134
2-Methyl-1-heptanol	C ₈ H ₁₈ O	-127.74	-438.99	280.7	787	149
2-Methyl-1-octanol	C ₉ H ₂₀ O	-118.83	-463.52	305.0	874	165
2-Methyl-1-nonanol	C ₁₀ H ₂₂ O	-109.91	-488.05	329.2	959	181
2-Methyl-1-decanol	C ₁₁ H ₂₄ O	-101.01	-512.48	353.8	1046	196
2-Methyl-1-undecanol	C ₁₂ H ₂₆ O	-91.99	-537.01	377.7	1133	212
2-Methyl-2-alcohols						
2-Methyl-2-propanol	C ₄ H ₁₀ O	-181.15	-375.99	125.4	464	87.8
2-Methyl-2-butanol	C ₅ H ₁₂ O	-168.66	-398.30	145.1	536	101
2-Methyl-2-pentanol	C ₆ H ₁₄ O	-159.81	-420.48	177.5	622	118
2-Methyl-2-hexanol	C ₇ H ₁₆ O	-150.86	-445.03	201.5	709	134
2-Methyl-2-heptanol	C ₈ H ₁₈ O	-141.94	-469.46	226.1	795	149
2-Methyl-2-octanol	C ₉ H ₂₀ O	-133.03	-493.99	250.4	882	165
2-Methyl-2-nonanol	C ₁₀ H ₂₂ O	-124.11	-518.42	274.9	969	181
2-Methyl-2-decanol	C ₁₁ H ₂₄ O	-115.10	-542.95	298.9	1054	196
2-Methyl-2-undecanol	C ₁₂ H ₂₆ O	-106.18	-567.38	323.4	1141	212

phase are ± 2.1 kJ · mol⁻¹ and those associated with S° are ± 2.1 J · mol⁻¹ · K⁻¹, which mean that the representative uncertainties associated with the Gibbs energy of formation for a solid/liquid/gaseous phase are ± 2.2 kJ · mol⁻¹. So, the expected uncertainties of the partial molar Gibbs energy of formation of most aqueous compounds are within ± 2.5 kJ · mol⁻¹ and those for the enthalpy of formation are within ± 4 kJ · mol⁻¹. In most cases the results tabulated in Table A1 agree within these brackets with values of the partial molar properties of aqueous hydrocarbons and alcohols given in Shock and Helgeson (1990) and Amend and Helgeson (1997).

A more accurate tabulation of the partial molar properties of aqueous hydrocarbons and alcohols presupposes a consideration of a large variety of the original thermochemical information available and a careful selection of the most reliable values of the enthalpy of formation and entropy of solid/liquid/gaseous phases.

We used our best efforts to deliver high quality values in the data bases presented. However, it is impossible to guarantee the absence of misprints and mismatches in the Tables given, and we will be grateful for any report of errors found.