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Measurement and Prediction of Thermochemical Properties. Improved Benson-Type Increments for the Estimation of Enthalpies of Vaporization and Standard Enthalpies of Formation of Aliphatic Alcohols

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This work has been undertaken to revise the group-additivity values necessary for predicting standard enthalpies of formation and vaporization enthalpies of aliphatic alcohols by means of Benson's group-additivity scheme at the reference temperature $T = 298.15$ K. The database on the molar enthalpies of vaporization has been extended with measurements on some linear alcohols (1-hexanol, 1-heptanol, and 1-nonanol) and branched alkanols (2-hexanol, 5-methyl-3-hexanol, 2-methyl-2-hexanol, 3-ethyl-3-pentanol, 2-ethyl-1-hexanol, 2-methyl-2-heptanol, 3,5,5-trimethyl-1-hexanol, and 2,6-dimethyl-4-heptanol) using the transpiration method. The data were obtained from the temperature dependence of the vapor pressure measured by the transpiration method. A simultaneous compilation and evaluation of data for enthalpies in the liquid and in the gaseous phase together with vaporization enthalpies have been performed, thereby giving a basis for the validation of experimental results. The group-additivity parameters useful in the application of the Benson correlation are presented in tabular form, together with a description of their evaluation.

Introduction

Industry needs to use new or modified chemical processes that have high yields and, hence, generate only small quantities of hazardous waste streams. An integral part of such changes is a better understanding of the thermochemical behavior of the species involved. At this time, reliable quantitative information on the thermochemical properties of the organic compounds, especially on branched species, is quite limited. Ab initio calculations are currently being performed to obtain thermodynamic values, but it will be a considerable time before reliable results are available for many relevant compounds. Meanwhile, it is necessary to develop empirical procedures that will give approximate yet reasonable values for their thermochemical properties such as enthalpies of vaporization, $\Delta_l^g H_m$, and enthalpies of formation, $\Delta_f H_m^\circ$. The most successful empirical method for estimating these properties is based on the group-additivity methodology (76-Bens, 76-Kab/Rog). The use of group additivity is straightforward and easy. It does not require the computing resource that ab initio calculations do. Another advantage of using GA is the convenience of predicting thermodynamic properties for large molecules. This method serves as a valuable tool for many scientists and engineers whose work involves the thermodynamic characterization of elementary and overall reaction processes.

Experimental enthalpies of vaporization and of formation of aliphatic alcohols can be found in the literature (86-Ped/Nay). However, the available results on these properties are not always consistent, as they should be when used for comparison with predictive calculations. Accurate and reliable experimental data with small uncertainties are needed to establish or to refine empirical estimation schemes. It is recognized that there is a lack of thermochemical information for branched molecules in each class of organic compounds. Because of the paucity of experimental data, the number of additive parameters, such as a tertiary $C-(G)(C)_2(H)$ or a quaternary $C-(G)(C)_3$ carbon atom attached to a functional group (G), have been evaluated as a rule only from the data for one or two branched compounds. These parameters have to be checked for their validity. In this context, systematic investigations on branched esters (96-Ver/Bec, 95a-Rak/Ver), amines (97a-Ver), nitro compounds (97b-Ver), nitriles (94-Rak/Ver), alcohols (98-Ver, 01a-Kul/Ver, and 01b-Kul/Ver), ketones (95-Nol/Ver), imines (97-Ver/Mor), fluoroalkanes (97-Sch/Ver), carboxylic acids (00-Ver), and alkyl ethers, acetals, ketals, and ortho esters (95b-Rak/Ver, 02-Ver) have been performed in the last decade. This paper extends our previous studies on the systematic evaluation of the group-additivity contributions for the broad range of aliphatic alcohols with emphasis on branched species. Although various group-additivity methods (80-Duc/Gru, 99-Rog/Bar) give excellent correlations between observed and calculated $\Delta_l^g H_m$(298.15 K) values for linear homologues, deviation may arise, especially for the branched members of the series. Because the distribution of the bulky molecules in the liquid and their intermolecular interactions seem to be unique for branched molecules, for the reliable predictions of the vaporization enthalpies of such species a more detailed study is required. A few systematic investigations of vaporization enthalpies of the long-chained branched

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aliphatic alcohols have been reported in the literature (99-NGu/Ber, 98-Ver, 01a-Kul/Ver). We report here a systematic experimental determination of the vaporization enthalpies of a series of C_6 to C_9 branched alcohols: 2-hexanol, 5-methyl-3-hexanol, 2-methyl-2-hexanol, 3-ethyl-3-pentanol, 2-ethyl-1-hexanol, 2-methyl-2-heptanol, 3,5,5-trimethyl-1-hexanol, and 2,6-dimethyl-4-heptanol. We tested our experimental and calculation procedures with measurements on 1-hexanol, for which the temperature dependence of vapor pressure is reliable (85-Gie/Rog). Two linear alcohols—1-heptanol and 1-nonanol—were additionally investigated in the temperature range close to the reference temperature of 298.15 K. The derived new values of $\Delta_l^g H_m$ (298.15 K) together with the values already available from the literature were used to develop a group-additivity scheme for the prediction of the enthalpies of vaporization of the aliphatic alcohols.

The thermochemistry of aliphatic alcohols in the condensed state is well established. Reliable values of $\Delta_f H_m^\circ$ (l) are mostly available from Pedley (86-Ped/Nay). Additionally, we have reviewed literature data on enthalpies of vaporization and enthalpies of formation of alcohols and especially experimental results published in the hardly available sources from the former USSR. To obtain $\Delta_f H_m^\circ$ (g), we have used selected values of $\Delta_l^g H_m$ in this study and known values for the enthalpies of formation in the liquid state $\Delta_f H_m^\circ$ (l) to derive $\Delta_f H_m^\circ$ (g). Then the group-contribution method was developed to predict values of the enthalpies of formation of alcohols in both the gaseous and liquid phases as well as the enthalpies of vaporization.

Experimental Section

Materials. Pure samples of alcohols were of commercial origin. Specimens for the measurements were purified by repeated distillation under reduced pressure. To avoid traces of water, the purified liquid samples were dried over molecular sieves and distilled once more before the experiments. The degree of purity was determined by GC. No impurities (greater than mass fraction 10^{-4}) could be detected. We used the following equipment: GC (Carlo Erba Fraktometer Vega Series GC 6000), Hewlett-Packard Integrator 3390A, nitrogen flow of 0.333 $cm^3 \cdot s^{-1}$, and an SE-30 capillary column of length 25 m. The standard temperature program of the GC was $T = 303$ K for 5 min followed by a heating rate of 0.167 $K \cdot s^{-1}$ to $T = 523$ K.

Measurements of the Enthalpies of Vaporization by the Transpiration Method. Vapor pressures and enthalpies of vaporization of alkanols were determined by using the method of transpiration in a saturated N_2 stream (00-Ver, 01b-Ver/Kul) and by applying the Clausius−Clapeyron equation. About 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with diameter of 1 mm provide a surface that is sufficient enough for vapor−liquid equilibration. At constant temperature (±0.1 K), a nitrogen stream was passed through the U-tube, and the transported amount of gaseous material was collected in a cooling trap. The flow rate of the nitrogen stream was measured using a soap bubble flow meter and optimized to reach the saturation equilibrium of the transporting gas at each temperature under study. On one hand, the flow rate of the nitrogen stream in the saturation tube should be not too slow in order to avoid the transport of material from the U-tube due to diffusion. On the other hand, the flow rate should be not too fast in order to reach the saturation of the nitrogen stream with a compound. We tested our apparatus at different flow rates of the carrier gas in order to check the lower boundary of the flow below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired contribution. In our apparatus, the contribution due to diffusion was negligible at a flow rate of up to 0.45 $dm^3 \cdot h^{-1}$. The upper limit for our apparatus where the speed of nitrogen could already disturb the equilibration was at a flow rate of 9.0 $dm^3 \cdot h^{-1}$. Thus, we carried out the experiments in the flow rate interval of (2.5 to 4.8) $dm^3 \cdot h^{-1}$, which has ensured that the transporting gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. The amount of condensed substance was determined by GC analysis using an external standard (hydrocarbon n-C_nH_{2n+2}). The saturation vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of product collected within a definite period of time. Assuming that Dalton law of partial pressures applied to the nitrogen stream saturated with substance i of interest is valid, values of p_i^{sat} were calculated

$$p_i^{sat} = \frac{m_i R T_a}{V M_i} \qquad V = V_{N_2} + V_i \qquad (V_{N_2} \gg V_i) \quad (1)$$

where $R = 8.31451$ $J \cdot K^{-1} \cdot mol^{-1}$, m_i is the mass of transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N_2} is the volume of transporting gas, and T_a is the temperature of the soap bubble meter. The volume of transporting gas V_{N_2} was determined from the flow rate and time measurements. Data of p_i^{sat} have been obtained as a function of temperature and were fitted using following equation (01b-Ver/Kul)

$$R \ln p_i^{sat} = a + \frac{b}{T} + \Delta_l^g C_p \ln\left(\frac{T}{T_0}\right) \quad (2)$$

where a and b are adjustable parameters and $\Delta_l^g C_p$ is the difference in the molar heat capacities of the gaseous and liquid phases, respectively. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from eq 2 the expression for the vaporization enthalpy at temperature T is derived:

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p T \quad (3)$$

Values of $\Delta_l^g C_p = C_p^g - C_p^l$ have been derived from the experimental isobaric molar heat capacities of liquids, C_p^l, alcohols, and from values of the isobaric molar heat capacities C_p^g of gaseous alcohols calculated according to a procedure developed by Domalski and Hearing (93-Dom/Hea). Experimental vapor pressures of alkanols together with their enthalpies of vaporization $\Delta_l^g H_m$ are presented in Table 1.

Results and Discussion

Database of Aliphatic Alcohols. The experimental data for the evaluation of the group-additivity values (GAVs) was assembled from several sources. A critical survey of the thermodynamic properties of alcohols up to 1973 was reported by Wilhoit and Zwolinski (73-Wil/Zwo). Majer and Svoboda (85a-Maj/Svo) reviewed their data and literature data on enthalpies of vaporization available until 1984. Recently, Roganov and Baranov (99-Rog/Bar) gathered literature data on the thermodynamic properties of alcohols and especially experimental results published in

Table 1. Vapor Pressures p and $\Delta_l^g\Delta_f H_m^\circ$ (l) Obtained by the Transpiration Method

T	m	$V(N_2)$	p	$p_{exptl} - p_{calcd}$	$\Delta_l^g H_m$	T	m	$V(N_2)$	p	$p_{exptl} - p_{calcd}$	$\Delta_l^g H_m$
K[a]	mg[b]	dm^3 [c]	Pa[d]	Pa	kJ·mol^{-1}	K[a]	mg[b]	dm^3 [c]	Pa[d]	Pa	kJ·mol^{-1}
1-Hexanol; $\Delta_l^g H_m$(298.15 K) = (61.71 ± 0.26) kJ·mol^{-1} $\ln(p/Pa) = (331.2/R) - (87\,052.0/R(T/K)) - (85.0/R)\ln((T/K)/298.15)$											
265.0	1.81	10.070	4.68	0.1	64.53	313.2	4.52	0.295	370.07	7.8	60.43
268.2	2.22	8.499	6.64	0.2	64.26	318.2	4.84	0.221	526.95	5.9	60.01
273.4	1.70	3.899	10.85	−0.3	63.82	318.2	5.58	0.255	527.77	6.7	60.01
278.2	1.39	1.957	17.48	−0.6	63.41	323.2	3.99	0.129	748.08	8.8	59.58
283.2	1.14	0.986	28.16	−1.2	62.98	323.2	8.50	0.287	714.41	−24.9	59.58
288.1	1.54	0.821	45.36	−0.9	62.57	328.1	7.33	0.171	1029.71	1.3	59.17
293.2	1.99	0.653	74.04	1.4	62.13	328.2	7.70	0.183	1012.21	−23.0	59.16
293.3	1.84	0.614	72.46	−0.9	62.13	333.1	8.92	0.150	1432.75	10.1	58.74
298.2	2.79	0.582	115.97	4.7	61.71	333.2	11.57	0.191	1457.84	26.1	58.73
298.3	2.28	0.493	111.93	−0.3	61.70	338.2	13.08	0.159	1976.41	19.6	58.31
303.2	1.88	0.271	167.00	−0.6	61.28	343.2	16.59	0.151	2639.31	−5.0	57.88
303.2	3.23	0.470	166.13	−1.4	61.28	348.2	20.70	0.143	3475.38	−59.6	57.46
303.3	2.77	0.398	167.79	−1.1	61.28	353.2	26.09	0.135	4639.36	−37.9	57.03
308.2	4.33	0.414	252.40	4.1	60.86	357.2	22.97	0.096	5785.11	−25.0	56.69
308.3	3.59	0.343	252.75	2.6	60.85	358.2	28.40	0.112	6131.47	3.4	56.61
310.4	4.57	0.366	300.55	6.8	60.67	363.2	26.06	0.080	7874.65	−79.0	56.18
313.1	2.89	0.193	360.88	1.3	60.44						
1-Heptanol; $\Delta_l^g H_m$(298.15 K) = (66.94 ± 0.38) kJ·mol^{-1} $\ln(p/Pa) = (348.8/R) - (95\,348.9/R(T/K)) - (95.3/R)\ln((T/K)/298.15)$											
283.4	0.720	2.010	7.68	−0.21	68.35	301.2	0.935	0.469	42.45	−0.50	66.65
286.2	0.690	1.407	10.49	0.01	68.08	303.2	1.179	0.492	50.96	−0.23	66.46
289.2	0.683	1.039	14.05	−0.04	67.79	304.2	0.963	0.369	55.61	−0.20	66.36
292.2	0.784	0.871	19.19	0.38	67.51	307.2	0.951	0.268	75.51	3.42	66.08
292.2	1.040	1.173	18.92	0.10	67.51	308.2	1.453	0.410	75.39	−3.00	65.98
293.2	0.657	0.655	21.31	0.63	67.41	310.2	0.882	0.201	93.30	0.77	65.79
293.7	0.703	0.670	22.38	0.69	67.36	313.2	1.722	0.302	121.41	3.32	65.51
295.2	1.215	1.005	25.75	0.81	67.22	313.2	1.769	0.328	114.71	−3.38	65.51
295.2	1.158	1.005	24.55	−0.39	67.22	316.2	1.688	0.235	153.05	3.20	65.22
296.7	0.679	0.503	28.80	0.15	67.08	318.2	1.978	0.246	171.04	−4.07	65.03
298.2	0.852	0.573	31.57	−1.27	66.94	319.2	1.776	0.201	187.81	−1.31	64.93
298.3	1.005	0.670	31.94	−1.19	66.93	323.2	1.995	0.164	258.80	3.00	64.55
1-Nonanol; $\Delta_l^g H_m$(298.15 K) = (74.67 ± 0.30) kJ·mol^{-1} $\ln(p/Pa) = (371.9/R) - (107\,469.0/R(T/K)) - (110.0/R)\ln((T/K)/298.15)$											
284.3	0.81	16.200	0.86	−0.04	76.20	323.3	2.63	1.145	39.15	−0.48	71.91
288.2	1.02	12.833	1.36	−0.03	75.77	326.2	2.09	0.702	50.93	0.69	71.59
292.2	1.08	8.455	2.20	0.06	75.33	326.3	2.90	1.018	48.58	−2.07	71.58
296.2	1.16	5.874	3.38	0.13	74.89	329.2	1.37	0.364	64.46	0.59	71.26
300.2	1.32	4.450	5.09	0.22	74.45	329.3	3.51	0.933	64.23	−0.15	71.25
304.2	1.24	3.010	7.05	−0.15	74.01	332.2	1.63	0.340	82.36	1.59	70.93
308.2	1.20	1.909	10.73	0.22	73.57	332.3	2.16	0.465	79.23	−2.17	70.92
308.2	1.18	1.957	10.36	−0.16	73.57	335.4	2.46	0.413	101.70	−1.43	70.58
311.3	1.43	1.697	14.34	0.36	73.23	338.3	2.62	0.362	123.68	−4.39	70.26
313.3	1.39	1.405	16.98	0.23	73.01	341.2	2.89	0.310	159.19	0.90	69.94
314.3	1.75	1.612	18.50	0.19	72.90	344.3	3.00	0.258	198.11	0.56	69.60
317.2	1.85	1.357	23.25	−0.38	72.58	347.3	3.64	0.258	240.57	−3.03	69.27
318.2	1.50	1.003	25.66	−0.21	72.47	350.3	4.66	0.258	307.62	8.59	68.94
320.3	2.18	1.230	30.27	−0.56	72.24	353.4	5.68	0.258	375.05	7.17	68.60
323.2	1.63	0.702	39.87	0.57	71.92						
2-Hexanol; $\Delta_l^g H_m$(298.15 K) = (57.04 ± 0.22) kJ·mol^{-1} $\ln(p/Pa) = (338.9/R) - (86\,976.1/R(T/K)) - (100.4/R)\ln((T/K)/298.15)$											
274.5	3.332	2.142	38.84	0.6	59.42	293.2	9.791	1.237	191.97	−4.3	57.54
276.3	4.055	2.213	45.52	0.2	59.24	290.5	7.522	1.176	155.38	−2.1	57.81
275.5	4.117	2.400	42.69	0.7	59.32	293.4	8.110	0.960	204.78	5.3	57.52
276.5	3.077	1.629	46.85	0.7	59.22	294.4	3.662	0.422	210.12	−5.9	57.42
278.3	4.767	2.136	55.12	0.6	59.04	296.2	9.471	0.935	245.22	−3.9	57.24
279.5	3.489	1.448	59.39	−1.4	58.92	297.4	3.329	0.302	267.08	−6.5	57.12
281.3	3.900	1.320	72.53	1.0	58.74	296.5	6.321	0.600	255.02	0.0	57.21
282.2	3.962	1.229	79.00	1.5	58.65	300.4	4.269	0.302	342.10	−2.3	56.82
282.5	3.700	1.146	79.09	−0.5	58.62	299.5	6.485	0.480	326.66	5.0	56.91
284.3	3.931	1.008	95.29	2.1	58.44	302.5	6.469	0.384	407.00	3.8	56.61
285.4	6.284	1.475	103.96	1.5	58.33	303.4	4.196	0.241	419.95	−11.1	56.52
285.5	3.822	0.935	99.77	−3.6	58.32	305.5	5.389	0.252	516.26	13.5	56.31
288.4	3.965	0.754	127.97	−4.3	58.03	306.4	4.004	0.181	533.95	−2.6	56.22
287.5	4.272	0.864	120.42	−2.2	58.12	307.6	5.968	0.240	600.07	15.3	56.10
292.1	3.807	0.516	178.95	−0.6	57.65	309.4	5.155	0.181	687.06	22.8	55.92
291.4	3.770	0.543	168.56	−1.0	57.72						

Table 1 (Continued)

T / K[a]	m / mg[b]	$V(N_2)$ / dm^3 [c]	p / Pa[d]	$p_{exptl} - p_{calcd}$ / Pa	$\Delta_l^g H_m$ / kJ·mol^{-1}	T / K[a]	m / mg[b]	$V(N_2)$ / dm^3 [c]	p / Pa[d]	$p_{exptl} - p_{calcd}$ / Pa	$\Delta_l^g H_m$ / kJ·mol^{-1}
5-Me-hexanol-3; $\Delta_l^g H_m$(298.15 K) = (59.82 ± 0.31) kJ·mol^{-1} ln(p/Pa) = (350.0/R) − (91 095.0/R(T/K)) − (104.9/R)ln((T/K)/298.15)											
275.2	1.98	1.593	27.15	0.4	62.23	296.2	4.13	0.478	183.86	5.9	60.03
278.2	2.23	1.328	36.44	0.6	61.92	299.2	4.61	0.425	230.70	3.6	59.71
281.2	2.35	1.062	47.62	0.0	61.60	302.2	5.38	0.398	287.03	−1.0	59.40
284.2	2.32	0.797	62.36	−0.5	61.29	305.3	4.58	0.266	365.98	0.0	59.07
287.2	2.59	0.690	80.14	−2.2	60.97	308.2	5.74	0.266	458.24	2.9	58.77
290.2	2.86	0.584	104.63	−2.6	60.66	311.2	7.11	0.266	567.51	−0.2	58.46
293.2	3.38	0.531	135.41	−3.2	60.34						
2-Me-hexanol-2; $\Delta_l^g H_m$(298.15 K) = (58.57 ± 0.35) kJ·mol^{-1} ln(p/Pa) = (374.6/R) − (97 684.6/R(T/K)) −(131.2/R)ln((T/K)/298.15)											
274.4	0.84	0.534	34.89	0.2	61.68	291.3	4.15	0.558	159.70	−2.4	59.47
276.5	2.72	1.381	43.16	0.5	61.41	294.3	5.11	0.531	206.10	−2.0	59.07
274.8	2.58	1.619	35.15	−1.0	61.63	294.4	2.64	0.265	213.40	3.6	59.06
279.5	2.84	1.062	58.15	1.4	61.01	298.3	5.01	0.372	288.60	1.4	58.55
282.4	2.91	0.85	74.10	−0.1	60.63	301.3	4.64	0.265	374.00	11.0	58.15
285.3	2.84	0.637	96.25	−0.2	60.25	304.3	5.57	0.265	448.30	−7.7	57.76
288.3	3.05	0.531	123.60	−1.9	59.86	306.2	7.14	0.292	521.70	−3.6	57.51
3-Et-pentanol-3; $\Delta_l^g H_m$(298.15 K) = (57.34 ± 0.21) kJ·mol^{-1} ln(p/Pa) = (400.4/R) − (14 625.0/R(T/K)) − (158.6/R)ln((T/K)/298.15)											
275.3	3.88	1.593	53.33	0.7	60.97	296.3	8.11	0.531	324.90	−6.2	57.64
278.4	4.33	1.328	70.85	0.1	60.48	299.3	9.11	0.478	405.49	−12.7	57.16
281.3	4.62	1.062	93.81	1.2	60.02	302.2	7.83	0.319	521.99	1.1	56.70
284.3	4.50	0.797	121.33	0.1	59.54	305.2	8.31	0.266	663.97	14.3	56.23
287.3	4.65	0.637	156.12	−1.5	59.07	308.2	10.11	0.266	808.14	2.7	55.75
290.3	5.04	0.531	202.55	−0.7	58.59	311.2	13.90	0.292	1009.03	16.5	55.28
293.3	6.43	0.531	258.03	−2.3	58.12						
2-Me-heptanol-2; $\Delta_l^g H_m$(298.15 K) = (62.87 ± 0.18)kJ·mol^{-1} ln(p/Pa) = (368.1/R) − (98 387.1/R(T/K)) − (119.1/R)ln((T/K)/298.15)											
275.4	0.98	1.619	11.78	0.3	65.58	296.2	3.37	0.797	80.71	−2.1	63.10
278.4	1.89	2.336	15.66	0.0	65.22	299.3	3.86	0.69	106.60	−1.3	62.73
281.2	2.29	2.124	20.75	0.1	64.88	302.3	3.83	0.531	137.50	−0.9	62.37
284.2	2.73	1.858	28.21	0.5	64.53	305.2	4.95	0.531	177.40	2.3	62.03
287.2	3.01	1.593	36.22	−0.6	64.17	308.2	5.04	0.425	226.00	4.0	61.67
290.2	3.29	1.328	47.45	−1.1	63.81	311.3	4.76	0.319	284.40	2.5	61.30
293.2	3.51	1.062	63.17	−0.5	63.46	314.2	4.92	0.265	353.20	2.6	60.95
2-Et-hexanol-1; $\Delta_l^g H_m$(298.15 K) = (68.51 ± 0.27) kJ·mol^{-1} ln(p/Pa) = (371.9/R) − (103 065.7/R(T/K)) − (115.9/R)ln((T/K/298.15))											
293.8	2.14	2.639	15.36	−0.1	69.02	316.3	4.32	0.743	110.05	−1.1	66.41
298.7	2.64	2.030	24.60	0.1	68.45	319.2	4.19	0.564	140.19	0.5	66.08
301.6	3.03	1.812	31.60	−0.3	68.12	322.2	3.81	0.416	173.22	−2.8	65.73
304.5	3.01	1.366	41.71	0.4	67.78	325.2	3.81	0.327	220.45	−0.2	65.38
307.4	3.38	1.188	53.71	0.5	67.44	328.2	5.25	0.356	278.19	3.1	65.03
310.3	3.76	1.040	68.41	0.4	67.11	331.2	5.36	0.297	340.97	−0.3	64.69
313.3	3.97	0.861	87.21	0.0	66.76						
3,5,5-tri-Me-hexanol-1; $\Delta_l^g H_m$(298.15 K) = (67.86 ± 0.42) kJ·mol^{-1} ln(p/Pa) = (345.4/R) − (95 856.6/R(T/K)) − (93.9/R)ln((T/K)/298.15)											
288.2	1.25	3.212	6.72	−0.1	68.79	309.4	2.22	0.815	46.80	−0.8	66.80
291.3	1.38	2.600	9.15	−0.1	68.50	312.4	2.33	0.661	60.52	−0.6	66.52
294.4	1.90	2.600	12.57	0.1	68.21	315.4	2.11	0.473	76.67	−1.2	66.24
297.4	2.25	2.268	17.08	0.5	67.93	318.4	1.88	0.332	97.20	−1.6	65.96
300.4	3.16	2.458	22.14	0.4	67.65	321.4	1.75	0.235	127.70	3.1	65.68
303.4	1.91	1.157	28.41	0.0	67.37	324.4	2.13	0.235	155.70	−0.6	65.40
306.4	2.02	0.921	37.71	0.8	67.09						
2,6-di-Me-heptanol-4; $\Delta_l^g H_m$(298.15 K) = (65.17 ± 0.29) kJ·mol^{-1} ln(p/Pa) = (364.3/R) − (100 053.3/R(T/K)) − (117.0/R)ln((T/K)/298.15)											
278.2	0.67	2.39	4.91	0.3	67.50	303.2	1.56	0.558	48.05	−1.0	64.58
283.3	0.88	1.937	7.90	0.1	66.91	306.2	1.59	0.451	60.55	−2.4	64.23
288.2	1.31	1.806	12.57	−0.1	66.33	312.2	1.58	0.265	102.40	0.4	63.53
291.2	1.52	1.593	16.52	−0.3	65.98	315.2	1.98	0.265	128.00	−0.7	63.17
294.2	1.70	1.354	21.61	−0.6	65.63	318.2	2.58	0.265	166.90	5.5	62.82
297.2	1.82	1.062	29.50	0.4	65.28	321.2	3.87	0.319	208.80	7.5	62.47
300.2	1.71	0.797	36.99	−0.9	64.93						

[a] Temperature of saturation. N_2 gas flow (2.5 to 4.8) dm^3·h^{-1}. [b] Mass of transferred sample condensed at T = 243 K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at T = 243 K.

uncommon journals in the former USSR. We have used these compilations as well as the recent original papers for a survey of enthalpies of formation and enthalpies of vaporization of aliphatic alcohols as listed in Table 2. Having revealed the lack of thermodynamic information on the branched alcohols in the literature, we have

Table 2. Experimental Results Available for Linear and Branched Aliphatic Alcohols at 298.15 K in kJ mol^{-1} [a]

		$\Delta_f H^\circ_m$ (l) exptl	$\Delta_f H^\circ_m$ calcd	Δ	$\Delta_l^g H_m$ exptl	$\Delta_l^g H_m$ calcd	Δ	$\Delta_f H^\circ_m$ (g)^a exptl	$\Delta_f H^\circ_m$ (g) calcd	Δ
1	2	3	4	5	6	7	8	9	10	11
1	1-butanol	−325.8 ± 0.7 65-Cha/Ros −327.6 ± 1.1 78-Sac/Pes **−327.2** ± 0.3 69-Mos/Dec	−324.7	2.5	**52.3** ± 0.1 66-Wadso	52.7	0.4	−274.9 ± 0.4	−273.9	1.0
2	2-butanol	−342.6 ± 0.6 65-Cha/Ros **−342.8** ± 1.0 78- Sac/Pes	−339.5	3.3	**49.7** ± 0.1 66-Wadso	49.5	−0.2	−293.01 ± 1.0	−291.2	1.9
3	2-Me-propanol-1	−333.6 ± 0.6 65-Cha/Ros **−333.2** ± 0.7 78- Sac/Pes	−333.7	−0.5	**50.8** ± 0.1 66-Wadso	49.3	−1.5	−282.4 ± 0.8	−284.1	−1.7
4	2-Me-propanol-2	**−359.2** ± 0.8 75-Mos/Dec	−359.3	−0.1	**46.6** ± 0.1 66-Wadso	47.0	0.4	−312.6 ± 0.8	−313.1	−0.5
5	1-pentanol	**−351.6** ± 0.4 75-Mos/Dec −357.9 ± 0.5 65-Cha/Ros −352.6 ± 0.8 69-Gun/Har	−350.5 −357.9 ± 0.5 65-Cha/Ros −352.6 ± 0.8 69-Gun/Har	1.1 −357.9 ± 0.5 65-Cha/Ros −352.6 ± 0.8 69-Gun/Har	57.7 ± 1.1 60-Green 56.9 ± 0.2 69-Gan/Har **56.9** ± 0.2 66-Wadso	57.5	0.6	−294.7 ± 0.5	−294.6	0.1
6	2-pentanol	−367.1 ± 0.7 65-Cha/Ros −366.4 ± 1.7 70-Con **−365.2** ± 1.1 74-Sac/Pes	−365.4	−0.2	55.15 79-Tho/Mea 52.6 ± 1.3 65-Cha/Ros 53.0 ± 0.4 63-McC/Lei **54.2** ± 0.3 85a-Maj/Svo	54.3	0.1	−311.0 ± 1.2	−312.0	−1.0
7	3-pentanol	−370.3 ± 0.6 65-Cha/Ros **−368.9** ± 0.8 74-Sac/Pes	−366.4	2.5	53.2 ± 0.1 88-Pes/Shv 55.1 79-Tho/Mea **52.9** ± 0.3 63-McC/Lei	52.7	−0.2	−316.0 ± 0.9	−313.3	2.7
8	2-Me-butanol-1	**−356.6** ± 0.6 65-Cha/Ros	−356.4	0.2	55.5 79-Tho/Mea **54.1** ± 0.3 63+McC/Lei	54.4	0.3	−302.5 ± 0.7	−302.3	0.2
9	3-Me-butanol-1	**−355.9** ± 1.6 85-Mar/Shv −356.4 ± 0.6 65-Cha/Ros	−355.3	0.6	54.3 ± 0.1 63-McC/Lei **55.0** ± 1.3 65-Cha/Ros	56.0	1.7	−301.6 ± 1.6	−301.0	0.6
10	2-Me-butanol-2	−379.4 ± 0.9 91-Wib/Hao −379.5 ± 0.5 65-Cha/Ros **−383.3** ± 1.2 87-Shvaro	−383.0	0.3	49.2 ± 0.4 63-McC/Lei 50.1 85b-Maj/Svo 50.2 ± 0.3 88-Pes/Shv **51.5** ± 0.3 01b-Kul/Ver	50.4	−1.1	−331.8 ± 1.2	−332.4	−0.6
11	3-Me-butanol-2	**−369.9** ± 1.4 70-Conn −366.6 ± 0.7 65-Cha/Ros	−371.3	−1.4	53.5 ± 0.4 70-Conn 51.7 ± 0.6 63-McC/Lei **51.6** ± 0.3 01b-Kul/Ver	51.2	−0.4	−318.3 ± 1.4	−319.7	−1.4
12	2,2-di-Me-propanol-1		−371.7		**51.8** ± 0.3 01b-Kul/Ver	50.1	−1.7		−320.6	
13	1-hexanol	−379.4 ± 1.0 65-Cha/Ros −383.9 ± 2.0 60-Green **−377.5** ± 0.5 75-Mos/Dec	−376.3	1.2	61.6 ± 0.2 66-Wadso 61.8 ± 0.2 77-Man/Sel 62.8 ± 1.3 60-Green 61.1 ± 0.4 92-NGu/Kas **61.7** ± 0.3 this work	62.3	0.6	−315.8 ± 0.6	−315.6	0.2
14	2-hexanol	−394.1 ± 0.9 81-Wib/Was **−392.0** ± 0.9 84-Wib/Was −392.3 ± 1.2 80-Sac	−391.2	0.8	57.9 ± 0.2 75-Bra/And 56.5 ± 0.3 92-NGu/Kas **57.0** ± 0.2 this work	59.1	2.1	−335.0 ± 0.9	−333.0	2.0
15	3-hexanol	**−390.3** ± 0.9 84-Wib/Was −393.9 ± 0.9 80-Sac	−392.2	−1.9	58.3 ± 0.4 79-Tho/Mea 57.0 ± 0.2 75-Cab/Con **58.6 ± 0.4** 01b-Kul/Ver	57.4	−1.2	−331.7 ± 1.0	−334.1	−2.4

Table 2 (Continued)

		$\Delta_f H^\circ_m$ (l) exptl	$\Delta_f H^\circ_m$ calcd	Δ	$\Delta_l^g H_m$ exptl	$\Delta_l^g H_m$ calcd	Δ	$\Delta_f H^\circ_m$ (g)[a] exptl	$\Delta_f H^\circ_m$ (g) calcd	Δ
1	2	3	4	5	6	7	8	9	10	11
16	2-Me-pentanol-1		−382.2		63.4 79-Tho/Mea **59.4** ± 0.3 01b-Kul/Ver	59.2	−0.2		−323.2	
17	3-Me-pentanol-1		−378.0		**61.7** ± 0.3 01b-Kul/Ver	61.1	0.6		−319.0	
18	4-Me-pentanol-1		−381.1		**60.5** ± 0.3 85b-Maj/Svo	60.8	0.3		−321.9	
19	2-Me-pentanol-2	**−408.6** ± 1.3 87-Shvaro	−408.8	−0.2	54.8 ± 0.3 85b-Maj/Svo **54.8** ± 0.1 87-Shvaro	55.2	0.4	−353.8 ± 1.3	−353.2	0.6
20	3-Me-pentanol-2		−394.0		58.4 79-Tho/Mea **58.2** ± 0.3 01b-Kul/Ver	56.2	−2.0		−337.7	
21	4-Me-pentanol-2	**−394.7** ± 0.8 74-Sac/Pes	−396.0	−1.3	58.0 79-Tho/Mea **57.3** ± 0.3 01b-Kul/Ver	57.6	−0.3	−337.4 ± 0.9	−339.4	−2.0
22	2-Me-pentanol-3	**−396.4** ± 1.0 74-Sac/Pes	−398.1	−1.7	56.7 ± 0.1 75-Bra/And **56.0** ± 0.5 01b-Kul/Ver	54.3	−1.7	−340.4 ± 1.2	−341.8	−1.4
23	3-Me-pentanol-3	−404.9 ± 0.9 91-Wib/Hao **−406.3** ± 1.7 73-Sac/Pes	−406.8	−0.5	56.7 ± 0.8 91-Wib/Hao 54.0 ± 1.0 91-73-Sac/Pes **55.7** ± 0.3 01b-Kul/Ver	53.9	−1.8	−350.6 ± 1.7	−351.6	−1.0
24	2,2-di-Me-butanol-1	-	−391.3		**56.1** 73/Wil/Zwo	55.4	0.7		−335.6	
25	3,3-di-Me-butanol-1		−389.2		61.0 96-Ulb/Klu **58.0** ± 0.2 01b-Kul/Ver	58.7	−0.7		−333.2	
26	2,3-di-Me-butanol-2	**−411.0** ± 1.5 91-Wib/Hao	−411.6	−0.6	**54.0** ± 0.8 91-Wib/Hao	52.4	−1.6	−357.0 ± 1.7	−357.9	−0.9
27	3,3-di-Me-butanol-2		−406.2		**53.8** ± 0.3 01b-Kul/Ver	52.2	−1.6		−353.0	
28	2-Et-butanol-1		−379.1		63.5 79-Tho/Mea **60.3** ± 0.3 01b-Kul/Ver	59.4	−0.9		−320.2	
29	1-heptanol	−409.4 ± 2.3 60-Green −398.8 ± 0.8 65-Cha/Ros **−403.4** ± 0.5 75-Mos/Dec	−402.1	1.3	67.8 ± 1.5 60-Green 66.8 ± 0.2 77-Man/Sel 66.8 ± 0.4 92-NGu/Kas **66.9** ± 0.4 this work	67.0	0.1	−336.5 ± 0.6	−336.4	0.1
30	2-heptanol	**−416.9** ± 0.7 84-Wib/Was −416.7 ± 3.2 80-Sac	−417.0	−0.1	61.5 ± 0.2 75-Bra/And 59.9 ± 0.6 63-Tho/Mea 61.5 ± 0.5 99-NGu/Ber 62.7 ± 0.9 80-Sac **62.1** ± 0.4 04-Ver/Hei	63.9	1.8	−354.8 ± 0.8	−353.9	0.9
31	3-heptanol	−416.8 ± 0.7 84-Wib/Was **−418.1** ± 1.3 80-Sac	−418.0	0.1	61.5 ± 0.9 63-Tho/Mea 62.4 ± 0.7 79-Tho/Mea 63.6 ± 1.0 80-Sac **60.3** ± 0.2 99-NGu/Ber	62.2	1.9	−357.8 ± 1.3	−355.1	2.7
32	4-heptanol	**−416.3** ± 0.7 84-Wib/Was −409.9 ± 1.5 80-Sac	−418.0	−1.7	60.3 ± 0.5 63-Tho/Mea 62.6 ± 0.6 75-Cab/Con 62.3 ± 0.9 80-Sac **62.4** ± 0.3 04-Ver/Hei	62.2	−0.2	−353.9 ± 0.8	−355.1	−1.2

Table 2 (Continued)

		$\Delta_f H^\circ_m$ (l) exptl	ΔH°_m calcd	Δ	$\Delta_l^g H_m$ exptl	$\Delta_l^g H_m$ calcd	Δ	$\Delta_f H^\circ_m$ (g)[a] exptl	$\Delta_f H^\circ_m$ (g) calcd	Δ
1	2	3	4	5	6	7	8	9	10	11
33	2-Me-hexanol-2	−**435.2** ± 1.3 87-Shvaro	−434.7	0.5	58.0 ± 0.5 63-Tho/Mea 61.2 ± 0.5 88-Pes/Shv **58.6** ± 0.4 this work	60.0	1.4	−376.6 ± 1.4	−374.2	2.4
34	5-Me-hexanol-3		−422.9		**59.8** ± 0.3 this work	60.8	1.0		−361.5	
35	2,2-di-Me-pentanol-3		−433.1		**54.8** 96-Ulb/Klu	55.4	0.6		−375.1	
36	3-Et-pentanol-3		−430.5		**57.3** ± 0.2 this work	57.3	0.0		−370.7	
37	2,4-di-Me-pentanol-3		−429.8		53.9 ± 0.7 63-Tho/Mea	56.0	2.1		−370.3	
38	1-octanol	−435.0 ± 2.7 60-Green −425.2 ± 1.1 65-Cha/Ros −**426.6** ± 0.6 75-Mos/Dec −428.0 ± 1.1 69-Gun/Har	−427.9	−1.3	72.8 ± 1.7 60-Green 71.1 ± 0.4 69-Gan/Har 71.0 ± 0.4 77-Man/Sel 71.2 ± 0.6 92-NGu/Kas **70.1** ± 0.3 01a-Kul/Ver	71.8	1.7	−356.5 ± 0.7	−357.3	−0.8
39	2-octanol	−**441.5** ± 1.0 80-Sac	−442.8	−1.3	67.2 ± 0.4 66-Gei/Fru 66.4 ± 0.4 90-Amb/Ghi 66.9 ± 0.7 99-NGu/Ber **67.9** ± 0.3 04-Ver/Hei	68.6	0.7	−373.6 ± 1.0	−374.8	−1.2
40	3-octanol	−**443.3** ± 1.0 80-Sac	−443.9	−0.6	69.3 ± 0.8 66-Gei/Fru 66.2 ± 0.8 99-NGu/Ber **67.9** ± 0.4 04-Ver/Hei	67.0	−0.9	−375.4 ± 1.1	−376.0	−0.6
41	4-octanol	−**436.0** ± 2.5 80-Sac	−443.9	−7.9	66.5 ± 0.7 66-Gei/Fru **67.2** ± 0.5 04-Ver/Hei	67.0	−0.2	−368.8 ± 2.5	−376.0	−7.2
42	2-Me-heptanol-2		−460.5		**62.9** ± 0.2 this work	64.8	1.9		−395.0	
43	2-Et-1-hexanol	−**432.9** ± 0.8 60-Tje	−430.7	2.2	66.5 ± 0.5 90-Amb/Ghi 66.6 61-Dyk/Sep 63.7 ± 1.3 73-Lyn/Wic **68.1** ± 0.3 this work	69.0	0.9	−364.8 ± 2.5	−362.1	2.7
44	2,4,4-tri-Me-1-pentanol		−437.4	-	**63.2** 96-Ulb/Klu	64.7	1.5		−371.9	
45	2-Et-4-Me-1-pentanol		−435.6	-	62.4 61-Dyk/Sep	67.5	5.1		−368.4	
46	1-nonanol	−460.5 ± 3.0 60-Green −459.2 ± 1.2 65-Cha/Ros −**453.6** ± 0.6 75-Mos/Dec	−453.8	−0.2	77.8 ± 1.9 60-Green 76.9 ± 0.8 77-Man/Sel 75.1 ± 0.6 92-Ngu/Kas **74.7** ± 0.3 this work	76.6	1.9	−378.9 ± 0.7	−378.3	0.6
47	2-nonanol		−468.6		72.0 ± 0.6 99-Ngu/Ber **72.9** ± 0.6 04-Ver/Hei	73.4	0.5		−395.6	
48	3-nonanol		−469.7		**71.0** ± 0.8 99-Ngu/Ber **70.9** ± 0.3 04-Ver/Hei	71.8	0.8 0.9		−396.9	
49	4-nonanol		−469.7		**71.5** ± 0.3 04-Ver/Hei	71.8	0.3		−396.9	
50	5-nonanol		−469.7		**71.4** ± 0.4 04-Ver/Hei	71.8	0.4		−396.9	
51	2,6-di-Me-4-heptanol		−479.4		**65.2** ± 0.3 this work	68.6	3.4		−409.6	
52	3,5,5-tri-Me-1-hexanol	−**456.9** ± 2.9 60-Nich	−459.0	−2.1	**67.9** ± 0.4 this work	71.4	3.5	−389.0 ± 2.9	−388.6	0.4

Table 2 (Continued)

		$\Delta_f H^\circ_m$ (l) exptl	$\Delta_f H^\circ_m$ calcd	Δ	$\Delta_l^g H_m$ exptl	$\Delta_l^g H_m$ calcd	Δ	$\Delta_f H^\circ_m$ (g)[a] exptl	$\Delta_f H^\circ_m$ (g) calcd	Δ
1	2	3	4	5	6	7	8	9	10	11
53	2,2,4,4-tetra-Me-pentanol-3	−**450.8** ± 0.9 98-Ver	−481.0	−30.5	53.8 ± 0.9 98-Ver	57.2	3.4	−397.0 ± 1.3	−415.6	−18.6
54	1-decanol	−486.1 ± 3.3 60-Green −479.7 ± 1.0 65-Cha/Ros −**478.1** ± 1.1 75-Mos/Dec	−479.6	−1.5	77.8 ± 0.8 65-Dav/Kyb 82.9 ± 2.1 60-Green 81.5 ± 0.8 77-Man/Sel 81.5 ± 0.8 79-Svens 81.4 ± 0.8 92-NGu/Kas **80.9** ± 0.3 01a-Kul/Ver	81.4	−0.5	−397.2 ± 1.0	−399.0	−1.8
55	2-decanol		−494.5		**77.4** ± 0.9 99-NGu/Ber	78.2	0.8		−416.5	
56	3,7-di-Me-1-octanol		−486.2		82.0 47-Stull	78.7	−3.3		−408.9	
57	1-undecanol	−**504.9** ± 0.8 75-Mos/Dec	−505.4	0.5	86.7 ± 0.9 91-Khas 85.1 ± 0.9 92-NGu/Kas **84.7** ± 0.3 01a-Kul/Ver	86.2	1.5	−420.2 ± 0.9	−419.9	0.3
58	2-undecanol		−520.3		76.3 47-Stull **80.8** ± 1.0 99-NGu/Ber	83.0	2.2		−437.4	
59	1-dodecanol	−**528.5** ± 0.8 75-Mos/Dec	−531.2	−2.7	96.6 ± 1.7 65-Davies 92.0 ± 0.6 77-Man/Sel 91.8 ± 0.6 79-Svens 88.7 ± 0.8 92-NGu/Kas **90.0** ± 0.3 01a-Kul/Ver	90.9	0.9	−438.5 ± 0.9	−440.9	−2.4
60	2-dodecanol		546.1		**86.7** ± 1.1 99-NGu/Ber	87.8	1.1		−458.3	
61	2,2,4,4-tetra-Me-3 -iPr-pentanol-3	−**476.6** ± 2.1 98-Ver	−542.5	−65.9	**58.5** ± 0.8 98-Ver	63.9	5.4	−418.1 ± 2.2	−465.6	−47.5
62	1-tridecanol	−**573.8** ± 0.9 75-Mos/Dec	−557.0	16.8	95.0 ± 0.9 92-Ngu/Kas **95.8** ± 0.6 01a-Kul/Ver	95.7	−0.1	−478.0 ± 1.1	−461.7	16.3
63	1-tetradecanol	−**581.4** ± 0.7 75-Mos/Dec −579.7 ± 1.8 91-Ste/Chi	−582.9	−1.5	96.9 ± 0.8 92-NGu/Kas **98.7** ± 0.6 01a-Kul/Ver	100.5	1.8	−482.7 ± 0.9	−482.5	0.2
64	2-tetradecanol		−597.7		95.4 ± 1.3 99-NGu/Ber	97.3	1.9		−500.0	
65	1-pentadecanol	−**634.7** ± 0.6 75-Mos/Dec	608.7	26.0	104.5 ± 1.1 92-NGu/Kas **102.5** ± 0.6 01a-Kul/Ver	105.3	2.8	−532.2 ± 0.8	−503.5	28.7
66	1-hexadecanol		−634.5		110.6 ± 1.4 92-NGu/Kas **108.8** ± 0.6 01a-Kul/Ver	110.1	1.3		−524.4	
67	2-hexadecanol		−649.3		103.9 ± 1.3 99-NGu/Ber	106.9	3.00		−541.8	

[a] Values taken in the group-additivity calculations are in bold.

performed a series of experimental studies on these species (98-Ver, 01a-Kul/Ver), and in this work we report some additional vapor-pressure measurements on eight branched and three linear aliphatic alcohols (Table 1).

There were several reports of the temperature dependence of the vapor pressure of the aliphatic alcohols in the literature. However, most authors did not calculate enthalpies of vaporization from their results. Hence, original experimental results published in the literature have been systematically treated using eqs 2 and 3, and $\Delta_l^g H_m$(298.15 K) have been calculated and added to the database. The collection of the available experimental results on aliphatic alcohols is presented in Table 2.

Improvement of the Benson Group-Additivity Scheme. A group is defined by Benson (76-Ben) as "a polyvalent atom (ligancy ≥ 2) in a molecule together with all of its ligands." In this work, we endorse and follow Benson. A group is written as $X{-}(A)_i(B)_j(C)_k(D)_l$, where X is the central atom attached to i A atoms, j B atoms, and so forth. In the present discussion, only C, H, and O atoms are considered, so X is necessarily a carbon or oxygen atom. In addition, there are several corrections for nonbonded interactions that are required because of spatial interactions that are not defined in terms of a series of chemical bonds. The most common and relevant to this work are the 1,4 interaction (or gauche interaction) and the 1,5 interaction of two methyl groups. The presence or absence of these corrections depends on interactions of parts of a molecule whose proximity is not implicit in bonding alone. These considerations pose problems for any algorithmic approach to additivity schemes, without which the codification of computer-executable procedures for calculating thermochemical properties would be almost trivial.

The first correction, as defined by Benson (76-Ben), is for gauche interactions (or 1,4 interactions) of large groups, that is, anything larger than H atoms. A rapid method for identifying gauche interactions along single bonds is to draw a line skeleton formula of a molecule and count the number of hydrogen-containing groups bound to the atoms at each end of the bond. If there is only one at each end, as in *n*-butane, then they can be trans or gauche to each other. If there are two at one end and one at the other end, then there must be one gauche interaction (most stable form), and there may be two (least stable form), as can be seen for 2-methylbutane. With three groups at one end and one at the other, there will always be two gauche interactions in all conformations (e.g., 2,2-dimethylbutane).

The second correction, as defined by Benson (76-Ben), is due to the repulsions between H atoms on 1,5-C atoms of the alkane chain. Thus, in 2,2,4,4-tetra-methylpentane, we would calculate four gauche interactions. However, the proximity of the H atoms on these adjacent on 1,5-C atoms of CH_3 groups is much closer than in gauche *n*-butane, and one finds correspondingly larger repulsion energies.

In contrast to Benson's definition of the gauche correction, we have suggested in this work that the 1,4-interaction should be applied systematically. In this case, this correction becomes a general one and not the occasional contribution, as defined by Benson. For instance, in *n*-pentane there are no gauche interactions, but at the same time, there are two 1,4 interactions $(C{-}C)_{1-4}$ of the first and fourth C atoms as well as the second and fifth C atoms. Similarly for 2-methylpentane, there is one gauche interaction, but there are three 1,4 interactions. To set a general example, let us consider the incrementation of 2,2,5-trimethylhexene:

$$CH_3{-}C(CH_3)_2{-}CH_2{-}CH_2{-}CH(CH_3){-}CH_3$$

$$5C{-}(C)(H)_3 + 2C{-}(C)_2(H)_2 + C{-}(C)_3(H) + C{-}(C)_4 + 6(C{-}C)_{1-4}$$

In our opinion, there are at least two advantages to introducing into the Benson scheme the 1,4 correction as the systematic contribution instead of the gauche interaction. First, this suggestion simplifies the codification of computer-executable procedures for calculating thermochemical properties. Second, the accuracy of the predictions is expected to be even better. Indeed, we have checked this suggestion using the same data set on thermochemical properties of alkanes, as used by Cohen (96-Coh), and have calculated the gaseous and the liquid standard enthalpies of formation of 68 alkanes using the new 1,4 correction $(C{-}C)_{1-4}$ and, for comparison, using the gauche corrections, as assumed by Benson. We have revealed that the average standard deviation from the experimental data for the given data set of alkanes using the new 1,4 correction has been more then twice as accurate as those using the gauche correction! So far, for the set of gaseous enthalpies of formation the average standard deviation was ±1.7 kJ mol^{-1} when using the 1,4 correction and ±3.7 kJ mol^{-1} when using Benson's gauche correction. The deviations for the set of liquid enthalpies of formation were appropriately ±1.6 kJ mol^{-1} and ±3.8 kJ mol^{-1}. Thus, our simple redefinition (in comparison to Benson's) of the 1,4 interactions, which has been performed in this work, has substantially enhanced the accuracy of the predictive scheme without changing the number of parameters.

Table 3. Group-Additivity Values for Calculation of Enthalpies of Formation and Enthalpies of Vaporization of Aliphatic Alcohols at 298.15 K in kJ mol^{-1}

increment	$\Delta_f H^\circ_m$ (l)	no. in database[a]	$\Delta_l^g H_m$	no. in database[a]	$\Delta_f H^\circ_m$ (g)	no. in database[a]
$C{-}(C)(H)_3$	−46.20	68	6.33	68	−40.28	49
$C{-}(C)_2(H)_2$	−28.93	60	4.52	52	−23.80	44
$C{-}(C)_3(H)$	−16.51	39	1.24	33	−13.68	26
$C{-}(C)_4$	−7.32	32	−2.69	25	−8.45	18
$(C{-}C)_{1-4}$	3.11	65	0.26	57	2.92	48
$(C{-}C)_{1-5}$	9.38	11	−0.42	8	10.66	8
$C{-}(C)(H)_2(O)$	−32.25	26	6.90	26	−29.03	26
$C{-}(C)_2(H)(O)$	−29.86	27	1.90	27	−29.97	27
$C{-}(C)_3(O)$	−30.25	8	−3.76	8	−33.74	8
$O{-}(C)(H)$	−190.40	63	31.80	58	−158.60	63
$(C{-}OH)_{1-4}$	−1.05	62	−1.63	57	−1.22	62

[a] Total number of compounds in the experimental database used for the calculation of an increment.

Evaluation of the GAVs. Our approach for the reevaluation of the GAVs was similar to that of others (96-Coh) in that we began by deriving GAVs for the alkane groups using as a database the same set of thermodynamic properties for 68 compounds as had been used by Cohen (96-Coh). The method of polyfunctional least squares was used to evaluate the parameters. The alkane groups, together with the derived increments for the liquid phase, vaporization enthalpy, and gaseous phase, are shown in Table 3. With these values fixed, we then turned to aliphatic alcohols to derive GAVs necessary for those compounds: $C{-}(C)(H)_2(O)$, $C{-}(C)_2(H)(O)$, $C{-}(C)_3(O)$, and $O{-}(C)(H)$ and a new parameter $(C{-}OH)_{1-4}$. These groups and their derived GAVs are listed in Table 3. GAVs for the liquid and gaseous phase enthalpies of formation, as well as GAVs for vaporization enthalpy, were derived in separate but parallel exercises. The GAVs evaluated in this work are based solely on experimental data, not on calculated values. It is worth mentioning that for the branched alkanes such as 2,2,4-trimethylpentane and 2,2,4,4-tetramethylpentane the additional (but the same as in the original Benson scheme) 1,5 correction $(C{-}C)_{1-5}$ has been applied. It is also quite obvious that by calculation of the branched alcohols (entries 43, 51, and 52 listed in Table 2) the parameter $(C{-}C)_{1-5}$ for the branching of the alkane chain has been also taken into account. However, some highly branched species (e.g., 2,2,4,4-tetramethyl-3-isopropyl-3-pentanol) were deliberately omitted by evaluation of the GAVs because of their complexity. The values of the reevaluated Benson increments and nonbonded 1,4 and 1,5 interactions for the calculation of thermodynamic properties of alkanes and alcohols are presented in Table 3.

Extension of Benson's Methodology for the Prediction of Enthalpies of Vaporization. Original works by Benson (76-Ben) and updated compilations (96-Coh) do not provide group-additivity values for the calculation of vaporization enthalpies at 298.15 K. This is not the fault of the empirical and half-empirical methods for the estimation of the enthalpies of vaporization of organic compounds (89-Maj/Svo, 81-Chi/Hym, 1981, 80-Duc/Gru). However, it seems to be logical to follow Benson's methodology for this thermodynamic property as well. In this work, for the prediction of vaporization enthalpies of alcohols we have applied the same definition of groups and the same evaluation procedure as those for enthalpies of formation.

The summary of the vaporization enthalpies of aliphatic alcohols involved in the calculation is presented in column 6 of Table 2. GAVs are listed in column 3 of Table 3.

Validation of the Experimental Results Available for Aliphatic Alcohols. The compilation of the available experimental data on aliphatic alcohols is listed in Table 2. It is conspicuous that very often the spread in an enthalpy measured by several groups (even very experienced groups) is dramatically larger than its experimental uncertainty (entries 1−16, 19−23, 25, 28−33, 38−41, 43, 46−48, 54, 57−59, 62, 63, 65, and 67 in Table 2). Such scatter in the data forces one to set preferences, but one needs a criterion to assess the reliability of the experimental results. It has been possible in this work to evaluate independently the reliability of individual experimental data. One of the best flags of possible experimental errors is a large discrepancy between experimental and calculated values, especially if other, closely related compounds show no such discrepancy. In the frame of this work, we have evaluated GAVs for the three thermodynamic properties simultaneously. Taking into account that all three of these properties are not independent and that they are connected by the general equation

$$\Delta_f H^\circ_m\,(g) = \Delta_f H^\circ_m\,(l) + \Delta_l^g H_m$$

it has been possible to check experimental data sets for each individual compound from Table 2 for internal consistency by fitting them into the correlation and by minimizing the deviation of predicted and experimental properties. Using simultaneous optimization of the GAVs for enthalpies of formation (in the gaseous and in liquid states) and enthalpy of vaporization, we have been able to select a set of reliable experimental values for each individual compound involved in the data treatment. These values are given in bold in Table 2 and could be recommended as an internally consistent data set. An analysis of the results presented in Table 2 shows that the average standard deviation of the selected experimental data taken into correlation and the average standard deviation between experimental and predicted values are at the same level of 0.6 to 1.5 kJ mol^{-1}. However, for several alcohols (entries 41, 45, 51, 53, 56, 61, 62, and 65 in Table 2) large deviations between experimental and calculated values have been observed. We suggest that for the highly branched alcohol (entries 53 and 61 in Table 2) these large deviations could be possibly reduced by the introduction of some additional parameters into the calculating scheme. Deviations for entries 41, 62, and 65 in Table 2 are experimental outliers rather than due to an imperfection of the group-additive procedure.

Some special comments require the data published in reference [65-Cha/Ros]. The $\Delta_f H^\circ_m$ (l) in this work were derived from bomb combustion measurements in one of the most reputable laboratories. However, large deviations of 3 to 6 kJ $mol^{-1}$of $\Delta_f H^\circ_m$ (l) for entries 5, 10, 11, 13, 29, 46 (Table 2) are apparent in comparison to other available data and to the calculated values (column 4 of Table 2). A reviewer of this paper, Dr. E. Domalski, has pointed this fact out and has provided some additional information in this context. In the 1980s, he had a conversation about this variation with Dr. Daniel Stull of Dow Chemical Company at a calorimetry conference. He told him that the *n*-alkanol samples that Dr. Chao used in the bomb combustion studies were not tested for water content but were used as received and assumed to be water-free. Thus, the large deviations of the experimental $\Delta_f H^\circ_m$ (l) from the reference [65-Cha/Ros] might be affected by water traces and for this reason have not been taken into account by the calculation of increments.

The structural-additive methods, based on the classical theory of structure, make it possible to solve a number of vital practical problems: to understand the interrelations of structure and energetics of organic molecules, to detect and explain anomalies in the structures and properties of certain substances, to check the experimental data with mutual consistency, and to predict the values of the substance properties, which have not been investigated experimentally. Benson's group-additivity method seems to have the most widespread acceptance at present and the overall best record for reliability among estimation techniques. We follow this method, and the distinctive features of the present work are

- an extended experimental study of the thermochemical properties of alcohols;

- systematic gathering and uniform treatment of the available experimental data from the literature;

- an extension and revision of Benson's group-additivity method;

- a strict reliance on experimental values as a basis for evaluating GAVs; and

- a simultaneous compilation and evaluation of data for enthalpies in the liquid and in the gaseous phase together with vaporization enthalpies, thereby giving an additional basis for the validation of experimental results.

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