Table I. Heat of Hydrolysis

	B_2O_3 (Crystalline)	B_2O_3 (Amorphous)	H_3BO_3
Mean ΔH_{298}	-3.45	-7.78	+5.45
Uncertainty	±0.03 or 1.15%	±0.05 or 0.65%	±0.01 or 0.34%
No. of runs	7	5	5

Table II. Comparison of Results with Existing Data

|		ΔH
$H_3BO_3 + 504\ H_2O \rightarrow H_3BO_3 \cdot 504\ H_2O$		
Ditte (2)	1878	+3.2
Berthelot (1)	1879	+4.8
Stackelberg (9)	1937	+5.3
Roth-Borger-Bertram (6)	1937	+5.1 ± 0.05
Katz (5)	1949	+5.3
Smisko-Mason (7)	1960	+5.27
Van Artsdalen (11)	1951	+5.17 ± 0.04
This work	1964	+5.45 ± 0.02
$B_2O_3(\text{amorphous}) + 3H_2O + 369\ H_2O \rightarrow 2(H_3BO_3 \cdot 369\ H_2O)$		
Berthelot (1)	1879	-7.3
Stackelberg (9)	1937	-8.0
Roth-Borger-Bertram (6)	1937	-7.85 ± 0.08
Southard (8)	1941	-7.839
Katz (5)	1949	-7.93
Van Artsdalen (11)	1951	-7.93 ± 0.03
This work	1964	-7.78 ± 0.05
$B_2O_3(c) + 3H_2O + 345\ H_2O \rightarrow 2(H_3BO_3 \cdot 345\ H_2O)$		
Southard (8)	1941	-3.477
Torgeson-Shomate (10)	1947	-3.3
Smisko-Mason (7)	1950	-3.48
This work	1964	-3.45 ± 0.04

No corrections were made to other data, such as standardizing to 25°, changes in atomic weights, or to final concentration.

$H_3BO_3(c)$, -261.47 kcal. per mole, the heat of formation of $H_3BO_3 \cdot 504\ H_2O$ was calculated to be -256.02 kcal. per mole. From the work of Smisko and Mason (7), the difference (interpolated) in the heats of formation of $H_3BO_3 \cdot 345$ H_2O is 0.010 kcal. per mole. This correction was considered as negligible and was not applied to the $H_3BO_3 \cdot 504\ H_2O$ value.

From the results of Equations 1 and 2, and using the value of -256.02 kcal. per mole for the heat of formation of $H_3BO_3 \cdot (345\text{-}504\ H_2O)$, the heats of formation of $B_2O_3(c)$ and $B_2O_3(\text{amorphous})$ were calculated. $\Delta Hf\ H_2O$ (1) was taken as -68.32 kcal. per mole as taken from the Handbook of Chemistry and Physics (4).

	ΔHf_{298}, Kcal./Mole
Compound	
$B_2O_3(c)$	-303.63 ± 0.42
$B_2O_3(\text{amorphous})$	-299.30 ± 0.43

The energy of transformation from crystalline to amorphous is therefore as follows:

$$B_2O_3(c) \rightarrow B_2O_3(\text{amorphous}) + 4.33\ \text{kcal./mole} \pm 0.06$$
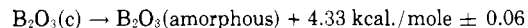
The experimental results are shown in Table I. A comparison of existing data is given in Table II.

ACKNOWLEDGMENT

NOMENCLATURE

ΔH_{298}	=	heat of solution or reaction at constant pressure and at 298° K., kcal./mole
ΔHf_{298}	=	heat of formation at 298° K., kcal./mole
q	=	electrical energy supplied to the calorimeter, calories
E_s	=	voltage drop across standard resistor, volts
R_s	=	0.500 ohm standard wire-wound resistor
R_h	=	heater resistance = 23.96 ohms
t_{sec}	=	heating time, seconds
ΔR	=	change in the resistance of the thermistor
ϵ	=	energy equivalent, calories/ohm

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Heats of Combustion, Formation, and Isomerization of Nineteen Alkanols

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VERY few thermochemical investigations involving modern apparatus and techniques have been carried out on the simple alkanols in spite of their importance in science and industry. The present investigation reports experi-

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mental results of the heats of combustion, in the liquid state at 25° C., of 19 alkanols in the range C_1 to C_{10}: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 2-methyl-2-butanol, 3-methyl-2-butanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol. The values of the standard heats

Measurements were made of the heats of combustion of 19 alkanols in the liquid state at 15° C. From these and other appropriate data were calculated the values of the standard heats of formation and isomerization for the liquid state at 25° C.

of formation and isomerization for the liquid state at 25° C. were calculated from these and other appropriate data. These data are important for investigating the relation between energy and molecular structure for these compounds.

EXPERIMENTAL METHOD, APPARATUS, AND PROCEDURES

The thermochemical method of the present investigation consists of two parts, a calorimetric and a chemical part (11). The chemical part involves measurement of the amount of the given combustion reaction that takes place in the calorimeter, while the calorimetric part involves measurement of the amount of the energy evolved in the given combustion reaction in the calorimeter. The final result is the quantity of energy associated with the unit amount of a given reaction.

The experimental values of this investigation are based on the absolute joule as the unit of energy. Conversion to the defined thermochemical calorie is made by using the relation 1 cal. = 4.184 (exactly) joules.

The amount of reaction in a given calorimetric alcohol combustion experiment was determined from the mass of carbon dioxide collected in the given experiment. For internal consistency with other investigations from this laboratory, the molecular weight of carbon dioxide was taken as 44.010 grams per mole. The small amount of nitric acid formed during the combustion experiment was determined, after the removal of the gaseous products of combustion from the bomb, by carefully washing the inside

of the bomb with water and titrating the aqueous solution with standard $0.01N$ aqueous sodium hydroxide using phenolphthalein as the indicator.

The apparatus and procedures used in this investigation were essentially the same as those described in earlier reports from this laboratory (4, 7), except that the electronic equipment for controlling the temperature of the jacket of the calorimeter was replaced with equipment requiring less personal attention. Details of the procedures of the present investigation were the same as those described earlier (4, 7), unless otherwise indicated.

MATERIALS

Samples of the 19 alkanols measured came from the following sources: Fifteen of the compounds were commercial samples further purified by distillation in columns of high (100 to 200 theoretical plates) separating power (15), to produce samples of the following estimated purities, in mole %: methanol, 99.9; ethanol, 99.9; 1-propanol, 99.8; 2-propanol, 99.8; 1-butanol, 99.7; 2-butanol, 99.7; 1-pentanol, 99.5; 2-pentanol, 99.5; 3-pentanol, 99.5; 2-methyl-1-butanol, 99.5; 3-methyl-1-butanol, 99.5; 2-methyl-2-butanol, 99.5; 1-hexanol, 99.3; 1-octanol, 99; and 1-decanol, 99. The remaining four compounds were purified at the Pennsylvania State University, and had the following estimated purities, in mole %: 2-methyl-1-propanol, 99.0; 3-methyl-2-butanol, 99.0; 1-heptanol, 99.3; and 1-nonanol, 98.6. It is believed that, for the compounds above C_2, the impurities in each case were isomeric and that their effect on the heat

Table I. Results of the Calibration Combustion Experiments with Benzoic Acid at 30° C.

No. of Experiments	Range of Mass of CO_2, G.	Range of k, Min.$^{-1}$	Range of K, Ohm	Range of U, Ohm	Range of ΔR_c, Ohm	Range of q_i, J	Range of q_n, J	Range of E_i, J/Ohm	E_i, Mean and Standard Deviation from the Mean, J/Ohm
7	1.53524 to 1.54395	0.001612 to 0.001676	0.000942 to 0.000979	0.000171 to 0.000363	0.196398 to 0.197498	70.80 to 75.45	5.54 to 6.35	206,995 to 207,047	207,015 ±15

Table II. Summary of the Results of the Calorimetric Combustion Experiments on Nineteen Aliphatic Alkanols in the Liquid State at 30°

Compound	No. of Experiments	Range of B, Ohm/G. CO_2	Mean Value of B, Ohm/G. CO_2	Standard Deviation of the Mean, Ohm/G. CO_2
Methanol	5	0.0794979 to 0.0795318	0.0795085	±0.0000062
Ethanol	4	0.0748962 to 0.0749267	0.0749143	±0.0000065
1-Propanol	4	0.0737312 to 0.0737527	0.0737441	±0.0000047
2-Propanol	4	0.0732869 to 0.0733004	0.0732950	±0.0000030
1-Butanol	4	0.0733120 to 0.0733463	0.0733352	±0.0000079
2-Butanol	4	0.0728597 to 0.0728887	0.0728767	±0.0000069
2-Methyl-1-propanol	4	0.0731010 to 0.0731336	0.0731215	±0.0000075
1-Pentanol	5	0.0728412 to 0.0728568	0.0728487	±0.0000030
2-Pentanol	4	0.0726375 to 0.0726630	0.0726504	±0.0000070
3-Pentanol	5	0.0725643 to 0.0725889	0.0725818	±0.0000045
2-Methyl-1-butanol	4	0.0728696 to 0.0728918	0.0728794	±0.0000054
3-Methyl-1-butanol	5	0.0728701 to 0.0728962	0.0728831	±0.0000048
2-Methyl-2-butanol	4	0.0723721 to 0.0723894	0.0723806	±0.0000042
3-Methyl-2-butanol	4	0.0726460 to 0.0726733	0.0726611	±0.0000064
1-Hexanol	4	0.0726988 to 0.0727374	0.0727202	±0.0000080
1-Heptanol	4	0.0726488 to 0.0726697	0.0726604	±0.0000047
1-Octanol	4	0.0725059 to 0.0725342	0.0725186	±0.0000063
1-Nonanol	4	0.0723036 to 0.0723287	0.0723163	±0.0000059
1-Decanol	5	0.0722943 to 0.0723075	0.0723020	±0.0000031

No. of Experiments	Mass of CO_2, G.	k, Min.$^{-1}$	K, Ohm	U, Ohm	ΔR_c, Ohm	Δr_i, Ohm	Δr_n, Ohm
81	2.30867 to 2.82149	0.001553 to 0.001893	0.000741 to 0.001430	−0.000069 to 0.001099	0.182218 to 0.207512	0.000301 to 0.000391	0.000018 to 0.000039

Table IV. Values[a] of the Heat of Combustion in the Liquid State at 30° and 25° C.

Compound	B at 30° C., Ohm/G. CO_2	$-\Delta E_B$ at 30° C., Kj./Mole	$-\Delta E_B^0$ at 30° C., Kj./Mole	$-\Delta Hc^0$ at 30° C. Kj./Mole	$-\Delta Hc^0$ at 30° C. Kcal./Mole	$-\Delta Hc^0$ at 25° C. Kj./Mole	$-\Delta Hc^0$ at 25° C. Kcal./Mole
Methanol	0.0795085 ±0.0000124	724.31 ±0.13	724.11 ±0.13	725.37 ±0.13	173.37 ±0.03	725.69 ±0.13	173.45 ±0.03
Ethanol	0.0749143 ±0.0000130	1,364.92 ±0.26	1,364.56 ±0.26	1,367.08 ±0.26	326.74 ±0.06	1,367.57 ±0.26	326.86 ±0.06
1-Propanol	0.0737441 ±0.0000094	2,015.41 ±0.30	2,014.85 ±0.30	2,018.63 ±0.30	482.46 ±0.07	2,019.40 ±0.30	482.64 ±0.07
2-Propanol	0.0732950 ±0.0000060	2,003.13 ±0.22	2,002.57 ±0.22	2,006.35 ±0.22	479.53 ±0.05	2,006.91 ±0.22	479.66 ±0.05
1-Butanol	0.0733352 ±0.0000158	2,672.30 ±0.61	2,671.56 ±0.61	2,676.60 ±0.61	639.72 ±0.15	2,677.46 ±0.61	639.92 ±0.15
2-Butanol	0.0728767 ±0.0000138	2,655.60 ±0.54	2,654.86 ±0.54	2,659.90 ±0.54	635.73 ±0.13	2,660.57 ±0.54	635.89 ±0.13
2-Methyl-1-propanol	0.0731215 ±0.0000150	2,664.52 ±0.59	2,663.78 ±0.59	2,668.82 ±0.59	637.86 ±0.14	2,669.65 ±0.59	638.06 ±0.14
1-Pentanol	0.0728487 ±0.0000060	3,318.22 ±0.37	3,317.29 ±0.37	3,323.59 ±0.37	794.36 ±0.09	3,324.64 ±0.37	794.61 ±0.09
2-Pentanol	0.0726504 ±0.0000140	3,309.19 ±0.68	3,308.26 ±0.68	3,314.56 ±0.68	792.20 ±0.16	3,315.44 ±0.68	792.41 ±0.16
3-Pentanol	0.0725818 ±0.0000090	3,306.06 ±0.48	3,305.13 ±0.48	3,311.43 ±0.48	791.45 ±0.11	3,312.26 ±0.48	791.65 ±0.11
2-Methyl-1-butanol	0.0728794 ±0.0000108	3,319.62 ±0.55	3,318.69 ±0.55	3,324.99 ±0.55	794.69 ±0.13	3,325.97 ±0.55	794.92 ±0.13
3-Methyl-1-butanol	0.0728831 ±0.0000096	3,319.79 ±0.50	3,318.86 ±0.50	3,325.16 ±0.50	794.73 ±0.12	3,326.21 ±0.50	794.98 ±0.12
2-Methyl-2-butanol	0.0723806 ±0.0000084	3,296.90 ±0.45	3,295.97 ±0.45	3,302.27 ±0.45	789.26 ±0.11	3,303.08 ±0.45	789.45 ±0.11
3-Methyl-2-butanol	0.0726611 ±0.0000128	3,309.68 ±0.63	3,308.75 ±0.63	3,315.05 ±0.63	792.32 ±0.15	3,315.93 ±0.63	792.53 ±0.15
1-Hexanol	0.0727202 ±0.0000160	3,974.84 ±0.92	3.973.73 ±0.92	3,981.29 ±0.92	951.55 ±0.22	3,982.60 ±0.92	951.86 ±0.22
1-Heptanol	0.0726604 ±0.0000094	4,633.50 ±0.69	4,632.21 ±0.69	4,641.03 ±0.69	1,109.23 ±0.17	4,642.52 ±0.69	1,109.59 ±0.17
1-Octanol	0.0725186 ±0.0000126	5,285.09 ±1.00	5,283.71 ±1.00	5,293.79 ±1.00	1,265.25 ±0.24	5,295.46 ±1.00	1,265.65 ±0.24
1-Nonanol	0.0723163 ±0.0000118	5,929.14 ±1.06	5,927.51 ±1.06	5,938.85 ±1.06	1,419.42 ±0.25	5,940.80 ±1.06	1,419.89 ±0.25
1-Decanol	0.0723020 ±0.0000062	6,586.63 ±0.75	6,584.78 ±0.75	6,597.38 ±0.75	1,576.81 ±0.18	6,599.65 ±0.75	1.577.35 ±0.18

[a] The uncertainties reported here are twice the standard deviation.

of combustion per mole of carbon dioxide produced in the combustion would be negligible. These estimates of purity were conservatively based on the method of purification and the simple physical properties of the materials.

DATA OF THE PRESENT INVESTIGATION

The results of the calorimetric combustion experiments with benzoic acid to determine the energy equivalent of the standard calorimetric system are given in Table I. NBS Standard benzoic acid, No. 39h, was used, with the value of 26,434 ± 3 joules per gram mass for the heat of combustion of this sample under the conditions of the standard bomb process at 25° C., with appropriate corrections being made for the differences between the actual and standard bomb processes.

A summary of the results of the calorimetric combustion experiments on the 19 alkanols is given in Table II. In the 81 experiments referred to in Table II, the ranges observed in the several calorimetric quantities are given in Table III.

Table IV presents the resulting values of the standard heats of combustion, for the liquid state at 25° C., for the 19 compounds. The recorded values of $-\Delta E_B^0$ and $-\Delta Hc^0$ refer to the following general reaction, with each substance in its standard state at the indicated temperature:

$$C_nH_{2n+1}OH(\text{liq.}) + 3/2n\ O_2\ (g) = n\ CO_2\ (g) + (n+1)\ H_2O\ (\text{liq.})$$
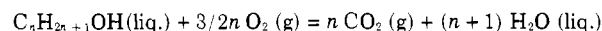
The correction applied to $-\Delta E_B$ to obtain $-\Delta E_B^0$ was calculated by the method of Washburn (12, 24). The values used for these corrections were the same for isomers, and were as follows for the C_1 to C_{10} alkanols, in kilojoules per mole: C_1, 0.20; C_2, 0.36; C_3, 0.56; C_4, 0.74; C_5, 0.93; C_6, 1.11; C_7, 1.29; C_8, 1.38; C_9, 1.63; and C_{10}, 1.85. Other details of the calculations were performed as described previously (4).

DATA OF OTHER INVESTIGATIONS

Table V gives a comparison of the values from the present investigation with those of earlier investigations. Some of the earlier investigations were reviewed by Rossini (13, 14)

Table V. Comparison of the Standard Heat of Combustion in the Liquid State from the Present Work with the Values from Previous Investigations

Compound	Investigators	Year	Reference	$-\Delta Hc^{v}$ at 25° C., Kcal./Mole
Methanol	Thomsen	1880	13, 21	173.4
	Stohmann, Kleber, and Langbein	1889	13, 19	168.3
	Richards and Davis	1920	10, 13	170.7
	Roth and Müller	1927	13, 17	171.9
	Roth and Banse	1931	13, 16	173.6
	I. G. Farbenfabrik	1931	6, 13	173.7
	Rossini	1932	13	173.64 ± 0.05[a]
	Present investigation			173.45 ± 0.03
Ethanol	Thomsen	1880	13, 21	330.3
	Berthelot and Matignon	1892	3	325.6
	Atwater and Rosa	1899	1	325.1
	Atwater and Snell	1903	2	325.8
	Emery and Benedict	1911	5	326.1
	Richards and Davis	1920	10	327.1
	Roth and Müller	1927	17	328.8
	Rossini	1932	13	326.66 ± 0.10[a]
	Present investigation			326.86 ± 0.06
1-Propanol	Zubow	1903	14, 25	480.6
	Richards and Davis	1920	10, 14	482.1
	Present investigation			482.64 ± 0.07
2-Propanol	Zubow	1903	20	474.9
	Parks and Moore	1939	8	478.9
	Parks, Mosley and Peterson	1950	9	479.2 ± ?
	Present investigation			479.66 ± 0.05
1-Butanol	Zubow	1920	14, 20	638.6
	Richards and Davis	1920	10, 14	637.7
	Verkade and Coops	1927	14, 23	638.9
	Skinner and Snelson	1960	18	639.31 ± 0.20
	Tjebbes	1960	22	638.3 ± ?
	Present investigation			639.92 ± 0.15
2-Butanol	Skinner and Snelson	1960	18	635.91 ± 0.22
	Present investigation			635.89 ± 0.13
2-Methyl-1-propanol	Zubow	1920	25	635.8
	Richards and Davis	1920	10	636.5
	Skinner and Snelson	1960	18	637.79 ± 0.20
	Present investigation			638.06 ± 0.14
1-Pentanol	Verkade and Coops	1927	14, 23	794.89 ± 0.48
	Present investigation			794.61 ± 0.09
1-Hexanol	Verkade and Coops	1927	14, 23	951.05 ± 0.57
	Present investigation			951.86 ± 0.22
1-Heptanol	Zubow	1920	14, 25	1,105.0 ± 2.8
	Verkade and Coops	1927	14, 23	1,107.51 ± 0.66
	Present investigation			1,109.59 ± 0.17
1-Octanol	Verkade and Coops	1927	14, 23	1,263.96 ± 0.76
	Present investigation			1,265.65 ± 0.24
1-Nonanol	Verkade and Coops	1927	14, 23	1,419.79 ± 0.85
	Present investigation			1,419.89 ± 0.25
1-Decanol	Verkade and Coops	1927	14, 23	1,575.60 ± 0.95
	Present investigation			1,577.35 ± 0.18

[a] Converted from measurements in the gaseous state.

and the resulting values from those investigations are taken from his reports. The modern investigations may be identified as the following: methanol and ethanol, Rossini (13); 2-propanol, Parks, Mosley, and Peterson (9); 1-butanol, 2-butanol, and 2-methyl-1-propanol, Skinner and Snelson (18); and 1-butanol, Tjebbes (22). Within the respective limits of uncertainty, the values from these earlier modern investigations are in substantial accord with the values from the present investigation. Of the other earlier investigations, the following also appear to be in substantial accord with the results of the present investigation: methanol, Roth and Banse (16), I.G. Farbenfabrik (6); ethanol, Emery and Benedict (5), Richards and Davis (10); 2-propanol, Parks and Moore (18); 1-butanol, 1-pentanol, 1-hexanol, and 1-nonanol, Verkade and Coops (14, 23).

Nearly all of the older values are lower than the modern ones. One possible explanation for this is that in the older investigations, the amount of reaction was determined from the mass of sample burned. Since alcohols are hygroscopic, the small amount of water absorbed would yield too large a mass for the sample and, hence, too small a value for the heat of combustion per unit quantity. In the experiments

Table VI. Values^a of the Standard Heat of Formation in the Liquid State

	ΔHf^0 at 25° C.	
Compound	Kj./mole	Kcal./mole
Methanol	−239.49 ± 0.17	−57.24 ± 0.04
Ethanol	−276.98 ± 0.29	−66.20 ± 0.07
1-Propanol	−304.55 ± 0.38	−72.79 ± 0.09
2-Propanol	−317.02 ± 0.29	−75.77 ± 0.07
1-Butanol	−325.81 ± 0.67	−77.87 ± 0.16
2-Butanol	−342.67 ± 0.59	−81.90 ± 0.14
2-Methyl-1-propanol	−333.59 ± 0.63	−79.73 ± 0.15
1-Pentanol	−357.94 ± 0.50	−85.55 ± 0.12
2-Pentanol	−367.15 ± 0.75	−87.75 ± 0.18
3-Pentanol	−370.33 ± 0.59	−88.51 ± 0.14
2-Methyl-1-butanol	−356.64 ± 0.63	−85.24 ± 0.15
3-Methyl-1-butanol	−356.39 ± 0.59	−85.18 ± 0.14
2-Methyl-2-butanol	−379.53 ± 0.54	−90.71 ± 0.13
3-Methyl-2-butanol	−366.64 ± 0.71	−87.63 ± 0.17
1-Hexanol	−379.36 ± 1.00	−90.67 ± 0.24
1-Heptanol	−398.78 ± 0.84	−95.31 ± 0.20
1-Octanol	−425.18 ± 1.13	−101.62 ± 0.27
1-Nonanol	−459.19 ± 1.21	−109.75 ± 0.29
1-Decanol	−479.74 ± 0.96	−114.66 ± 0.23

^{a}The uncertainties reported here are twice the standard deviation.

of the present investigation, the amount of reaction was determined from the mass of carbon dioxide formed, so that any small amount of water absorbed in the sample would affect the results only by the heat of solution of that small amount of water in the sample. This effect is believed to be negligible relative to the heat of combustion.

HEATS OF FORMATION AND ISOMERIZATION FROM THE PRESENT WORK

Table VI gives the values of the standard heats of formation for the 19 alkanols in the liquid state at 25° C., calculated in the same manner as described earlier (4).

From the values of the ratios of the quantity B given in Table II, values of heats of isomerization may readily be obtained for the C_3, C_4, and C_5 isomers (4). These are given in Table VII.

NOMENCLATURE AND DEFINITIONS OF SYMBOLS

ΔR_c = the corrected increase in temperature of the calorimeter system, expressed as the increase in resistance in ohms of the given platinum resistance thermometer at a mean temperature of 29° C., as measured with the given resistance bridge

q_i = the heat evolved, in absolute joules, by the ignition process of heating and burning the iron wire

q_n = the heat evolved, in absolute joules, by the formation of the small amount of nitric acid in the combustion

E_i = the energy equivalent, over the temperature interval 28° to 30° C., of the initial calorimeter system used in the calibration experiments, obtained as the ratio $(-\Delta E + q_i + q_n)/\Delta R_c$, where $-\Delta E$ is the heat evolved by combustion of the given mass of benzoic acid under the conditions of the experiment

Δr_i = the increase in temperature of the calorimeter system, expressed as the increase in resistance in ohms of the platinum thermometer, produced by the ignition process of heating and burning the iron wire

Δr_n = the increase in temperature of the calorimeter system, expressed as the increase in resistance of the platinum thermometer, produced by the formation of the small amount of nitric acid in the combustion

B = $[(\Delta R_c - \Delta r_i - \Delta r_n)/m_{CO_2}][1 + (C + \delta)/E_{si}]$

m_{CO_2} = the mass of carbon dioxide formed in the combustion of the alcohol

C = the heat capacity of the amount of alcohol placed in the bomb, expressed as joules per ohm increase in resistance of the given platinum resistance thermometer

Table VII. Values^a of the Heat of Isomerization in the Liquid State at 25° C.

No. of carbon atoms	Compound	B at 30° C., Ohm/G. CO_2	Ratio of the Heat of Combustion in the Bomb Process, B_i/B_n at 30° C.	Heat of Isomerization, ΔH^0 (Isomerization) at 25° C., Kcal./Mole
3	1-Propanol	0.0737441 ±0.0000094	1.000000 ±0.000180	0.00
	2-Propanol	0.0732950 ±0.0000060	0.993910 ±0.000150	−2.98 ± 0.11
4	1-Butanol	0.0733352 ±0.0000158	1.000000 ±0.000305	0.00
	2-Butanol	0.0728767 ±0.0000138	0.993748 ±0.000285	−4.03 ± 0.21
	2-Methyl-1-propanol	0.0731215 ±0.0000150	0.997086 ±0.000296	−1.86 ± 0.22
5	1-Pentanol	0.0728487 ±0.0000060	1.000000 ±0.000116	0.00
	2-Pentanol	0.0726504 ±0.0000140	0.997278 ±0.000209	−2.20 ± 0.22
	3-Pentanol	0.0725818 ±0.0000090	0.996336 ±0.000148	−2.96 ± 0.19
	2-Methyl-1-butanol	0.0728794 ±0.0000108	1.000421 ±0.000169	+0.31 ± 0.19
	3-Methyl-1-butanol	0.0728831 ±0.0000096	1.000472 ±0.000155	+0.37 ± 0.19
	2-Methyl-2-butanol	0.0723806 ±0.0000084	0.993574 ±0.000141	−5.16 ± 0.18
	3-Methyl-2-butanol	0.0726611 ±0.0000128	0.997425 ±0.000193	−2.08 ± 0.21

^{a}The uncertainties reported here are twice the standard deviation.

δ = a very small correction term, expressed as joules per ohm increase in resistance of the given platinum resistance thermometer, to take account of the variations in mass of the glass ampoule from the standard value, and variations in the mean temperature of an experiment from the standard value of 29° C.

The mean value of the energy equivalent, E_i, is for an initial system containing a benzoic acid pellet having a mass equal to the mean of the masses of the pellets used in the experiments. However, the desired energy equivalent for the alcohol experiments is that for a system containing no pellet, but containing instead a mass of soft glass equal to the mean mass of the glass ampoules used in the alcohol experiments. The following expressions were used in calculating the desired energy equivalent, E_{si}:

$$E_{si} = E_i - D(1.21\ m_s - 0.711\ m_g)$$

Here,

D = number of degrees Celsius (centigrade) equivalent to one unit of the temperature scale used

m_s = the mean mass, in grams, of the pellets of benzoic acid used in the calibration experiments

m_g = the mean mass in grams, of the soft glass ampoules used in the experiments

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Boiling Points and Boiling Point Numbers of Some Substituted Perfluoroalkanes

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Application of the Kinney equation:

b.p. in ° C. = 230.14(total boiling point number)$^{1/3}$ − 543

furnishes adequate results (root mean square error, 2.6°; simple average error, 2.0°) in calculations of normal boiling points of 83 substituted perfluoroalkanes. These include straight chain perfluoromonocarboxylic acids, perfluoro(β-alkoxypropionyl) fluorides, and perfluoroalkyl compounds containing isocyanate, nitroso, perfluoro-oxacyclobutyl, lone hydrogen, sulfonyl fluoride, the SF$_4$ group, and the SF$_5$ group. Calculations involve use of 10 new values of the boiling point number (b.p.n.) and the previous b.p.n.s. of −1.83 for carbon and 2.04 for fluorine in perfluoroalkanes.

ACCEPTABLE results occur in application of the Kinney equation (*17-19*):

$$\text{b.p. in ° C.} = 230.14(\text{total boiling point number})^{1/3} - 543 \quad (1)$$

in calculations of the normal boiling points of hydrocarbons (*17-19*), silanes and organosilicon compounds (*21*), germanes and alkylgermanium compounds (*3*), boranes and alkylboron compounds (*3*), alkyl derivatives of bivalent sulfur, selenium, and tellurium (*3*), alkyl derivatives of trivalent organophosphorus compounds (*3*), alkyl derivatives of trivalent organoarsenic compounds (*3*), and perfluoroalkanes, perfluorocycloalkanes and perfluoroalkenes (*3*).

Postelnek (*24*) and Haszeldine and Smith (*14*) offer other methods of calculation on boiling points of saturated linear perfluoroalkanes and a few cycloperfluoroalkanes.

Satisfactory calculations of b.p.n.s through the Kinney equation (*17*) (Equation 1) are practical in 10 homologous series of substituted perfluoroalkanes in which the average increment in b.p.n. per CF$_2$ group varies only between 2.22 and 2.29. Calculations in each series involve all possible mathematical combinations. Published (*3*) atomic b.p.n.s of −1.83 for carbon and 2.04 for fluorine furnish the b.p.n. 2.25 for CF$_2$ and fit these 10 series adequately (while there is omission of 12 series with increments in b.p.n. per CF$_2$ group in the ranges 1.85 to 2.14 and 2.34 to 2.50). Further