QUARTERLY REVIEWS

THERMODYNAMIC PROPERTIES OF ORGANIC OXYGEN COMPOUNDS

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The measurement of accurate thermodynamic data is of rapidly increasing importance from two aspects: first, the data are a basic requirement of modern chemical technology and secondly, they contribute to theories of molecular structure. In recent years systematic investigations of certain groups of compounds have resulted in comprehensive compilations of their thermodynamic properties; an outstanding example is the American Petroleum Institute Research Project 44 on hydrocarbons.[1] Other important classes of compounds have received much less attention, however, and the aim of this article is to review the existing state of knowledge of the thermodynamic properties of organic compounds containing only carbon, hydrogen, and oxygen. Attention is restricted to data on heats, entropies, and free energies of formation, heat capacities, and related properties of single substances; properties of binary and other mixtures, thermodynamic dissociation constants, and critical data are excluded. After a brief survey of experimental and computational sources, the available measurements on the various classes of these compounds are considered in detail and an attempt is made to select the most reliable values. Regularities in the data are then discussed and related to recent methods for the estimation of thermodynamic properties where measurements are lacking. Finally, some applications of the data to the determination of bond-energy terms and to barrier heights to free rotation are reviewed.

Experimental Sources

The measurements of heats of combustion by bomb calorimetry, as a source of heats of formation, is a familiar technique, the experimental details of which have been reviewed.[2] The accuracy of the method has increased considerably during the last sixty years and in the best experi-

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[1] Rossini, Pitzer, Arnett, Braun, and Pimental, "Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.

[2] (*a*) Rossini (Ed.), "Experimental Thermochemistry," Interscience Publishers Inc., New York, 1956; (*b*) Skinner, "Modern Aspects of Thermochemistry," Royal Institute of Chemistry, London, 1958; (*c*) Coops, VanNes, Kentie, and Dienske, *Rec. Trav. chim.*, 1947, **66**, 113, 131.

ments is now about ±0·02%. Cottrell[3] has distinguished three classes of combustion results: modern work of high precision, modern work of relatively low precision, and older work, for the greater part now over sixty years old. Most of the work on organic oxygen compounds falls in the second and the third category. Rossini[4] pointed out in 1937 that most of the old data were subject to uncertainties often as large as several kcal./mole; for many compounds these are still the only values available. In fact, recent developments[2a] of combustion techniques for organic sulphur, nitrogen, and halogen compounds have yielded values far superior in accuracy to those available for even simple oxygen compounds.

The flame calorimeter[2a] has been used much less than the bomb calorimeter but the few results obtained are of great importance. The heats of formation of some organic oxygen compounds have also been derived from measurements of heats of hydrogenation and of hydrolysis.[2b]

To obtain free energies, heats of formation must be combined with entropy values, and for organic compounds in general the most accurate results are obtained from low-temperature heat-capacity measurements. If the entropy of a substance is zero at absolute zero then the entropy S at T''' is given, for example, by:

$$S = \int_0^{T'} (C_p/T)\mathrm{d}T + (\Delta H'/T') + \int_{T'}^{T''} (C_p/T)\mathrm{d}T + (\Delta H''/T'') + \int_{T''}^{T'''} (C_p/T)\mathrm{d}T$$

where C_p is the heat capacity at temperature T and at constant pressure, and $\Delta H'$, $\Delta H''$ are the enthalpy changes accompanying an isothermal change of state, whether of transition, fusion, or vaporisation. If the terms in this expression were available from 0°K, then an absolute value of the entropy could be obtained, but in practice some extrapolation is needed from the lowest temperature at which the measurements are made, down to 0°K. If the former is low enough, say about 10°K, then a Debye function can be used, its parameters being evaluated from the measurements at the lowest temperatures. However, in much of the earlier work, especially that of Parks and his co-workers the measurements did not go below 90°K and an extrapolation procedure[5] was used which may give rise to an error in the entropy at 25°C of about one cal./deg./mole.

To complete the evaluation of the entropy of a compound in the gas state, measurements of vapour heat capacities and of the heat of vaporisation are required. The latter can be obtained by direct measurement and by the use of vapour-pressure data combined with the Clapeyron equation. Variation of vapour pressure with temperature has been expressed by

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[3] Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 2nd. Ed., 1958.

[4] Rossini, *Ind. Eng. Chem.*, 1937, **29**, 1424.

[5] Kelley, Parks, and Huffman, *J. Phys. Chem.*, 1929, **33**, 1802.

many empirical equations,[6] of which the Antoine equation is currently the most favoured. It has the disadvantage that it causes calculated heats of vaporisation to vary approximately as T^{-2} and to increase to unreasonably large values at temperatures much below the observed range. Equations of the Kirchoff–Nernst form imply a more reasonable dependence of heat of vaporisation upon temperature and are more satisfactory; alternatively the equation due to Cox[7] has been used to represent recent accurate work.

However, the most accurate values for heats of vaporisation are those obtained by vapour flow calorimetry, a method which simultaneously yields accurate values for the heat capacity of the vapour.[8] In recent years the technique has become of great importance in obtaining complete thermodynamic functions for organic molecules in the vapour state, though it has not yet come to be widely used. These accurate measurements of vapour heat capacity and heat of vaporisation can be used[9] to obtain values for the second virial coefficient; the results can of course be supplemented by those derived from P–V–T measurements.

Additional to these thermodynamic quantities derived from heat measurements are those calculated by statistical mechanics from spectroscopic and molecular-structure data.[10] From the molecular dimensions are obtained the moments of inertia required for the calculations of the rotational contribution to the thermodynamic functions. The vibrational contributions can be computed by the standard methods of the harmonic-oscillator, rigid-rotator treatment if the complete vibrational assignment of the molecule is available from the interpretation of the infrared and Raman spectra. If the molecule has a group capable of internal rotation then the magnitude of the energy barrier to this rotation can be obtained from the difference between the calculated and the observed specific heat and entropy of the vapour, corrected to the ideal gas state. The contribution of this barrier to the thermodynamic functions can then be evaluated. A further difference between observed and calculated specific heats can be attributed, in the most accurate work, to the effect of anharmonicity,[9] which for polyatomic molecules must be treated empirically.[11] In some instances therefore, such as acetone[12] where an unobserved frequency has

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[6] Partington, "An Advanced Treatise on Physical Chemistry," Longmans Green and Co., London, 1951, Vol. II, pp. 265—274.

[7] Cox, *Ind. Eng. Chem.*, 1936, **28**, 613.

[8] Sturtevant, in Weissberger (Ed.), "Physical Methods of Organic Chemistry," Interscience Publishers Inc., New York, 1959, Vol. I, Part I, 3rd. Ed.

[9] Scott, Waddington, Smith and Huffman, *J. Chem. Phys.*, 1947, **15**, 565.

[10] (*a*) Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand Co. Inc., New York, 1945; (*b*) Janz, "Estimation of Thermodynamic Properties of Organic Compounds," Academic Press Inc., New York, 1958; (*c*) Godnev, "Calculations of Thermodynamic Functions from Molecular Data," State Publishing House, Moscow, 1956.

[11] McCullough, Finke, Hubbard, Good, Pennington, Merserley, and Waddington, *J. Amer. Chem. Soc.*, 1954, **76**, 2661; Pennington and Kobe, *J. Chem. Phys.*, 1954, **22**, 1442.

[12] Pennington and Kobe, *J. Amer. Chem. Soc.*, 1957, **79**, 300.

also to be selected, the choice of suitable values for barrier height, anharmonicity, and missing frequency to fit the measured properties may be somewhat arbitrary but no large errors are likely if the measurements cover a wide range of temperature. The complete calculations then provide the following thermodynamic functions over a range of temperatures: the free energy function $(G^\circ - H_0^\circ)/T$, heat content function $(H^\circ - H_0^\circ)/T$ as well as specific heat C_p° and entropy S°. From the measured heat of formation at one temperature and the appropriate values for the elements,[1] ΔH_0° can be found and thence the standard heat ΔH_f°, free energy ΔG_f°, and logarithm of the equilibrium constant of formation, $\log_{10} K_f$, over the same temperature range.

Relatively few organic oxygen compounds have been the subject of a comprehensive study; for those substances where they are available space does not permit the complete tabulation of all the functions, and in the following survey only the values of ΔH_f°, S°, and ΔG_f° at 25°C are given.

Thermodynamic Properties

No systematic review of the thermodynamic properties of organic oxygen compounds has been made since the pioneer work of Parks and Huffman[13] nearly thirty years ago. The heats of formation used by these authors were based essentially on the measurements of heats of combustion recorded in the International Critical Tables; about the same time appeared the extensive compilation by Kharasch[14] summarising the combustion data on organic oxygen and other compounds. The Landolt–Börnstein tables and their supplements[15] give more recent work as does Timmerman's book,[16] whilst the National Bureau of Standards Circular 500[17] gives selected values for compounds containing not more than two carbon atoms. Various authors have listed some heats of combustion and formation in discussing the thermochemistry[18] and resonance energies[19] of oxygen compounds.

To maintain consistency all values given below have been converted on the basis of the atomic weights C = 12·010, H = 1·008, O = 16·000 and revised to the fundamental constants employed in the tabulations for hydrocarbons.[1] Heats of combustion have wherever possible been con-

[13] Parks and Huffman, "The Free Energies of Some Organic Compounds," A.C.S. Monograph No. 60, The Chemical Catalogue Co., Inc., New York, 1932.

[14] Kharasch, *Bur. Stand. J. Res.*, 1929, **2**, 359.

[15] Roth and Scheele (Eds.) Landolt–Börnstein, "Physikalisch-Chemische Tabellen," Julius Springer, Berlin, 5th Edn., Hauptwerk., 1923, p. 1586; I Eng. Bd., 1927, p.866; II Eng. Bd., 1931, p. 1633; III Eng. Bd., 1936, p. 2896.

[16] Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, 1950.

[17] Rossini, Wagman, Evans, Levine, and Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, Washington, 1952.

[18] (*a*) Gray, *Trans. Faraday Soc.*, 1956, **52**, 444; (*b*) Gray and Williams, *ibid.*, 1959, **55**, 760; (*c*) Gray and Williams, *Chem. Rev.*, 1959, **59**, 239.

[19] Klages, *Chem. Ber.*, 1949, **82**, 358; Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, 1955.

verted to the basis of the modern thermochemical caloric (= 4·1840 abs. joules) and 298·16°K (25°C); the heats of formation quoted are based on the values[17] ΔH_f CO_2 (g, 25°C) = − 94·0518 and ΔH_f H_2O (l, 25°C) = − 68·3174 kcal./mole. Free energies of formation are derived from the entropy values at 25°C by using the values[17] $S°$ C (graphite) = 1·361, $S°$ H_2 (g) = 31·211, $S°$ O_2 (g) = 49·003 cal./deg./mole.

Limits of error for heats of formation are given in the Tables only when they have been given by the authors, but it is not possible to bring them to a uniform basis. In many cases they are not available, and it has been preferred not to assign estimated limits of error; for some compounds a comment on accuracy is given in the text.

(*a*) *Alcohols, Phenols and Polyhydric Alcohols.*—The available data for alcohols at 25°C are summarised in Table 1.

Although measurements of the low-temperature specific heats[20] and of the heat of vaporisation[21] of methyl alcohol were made several years ago, accurate determination of the complete thermodynamic functions is dependent upon the value of the barrier height to internal rotation. This has been the subject of several investigations.[22] Further difficulties arose as to the actual treatment of the internal rotation since at low temperatures the molecule fell outside the range of validity of the method usually used, and also from the anomalous behaviour of the vapour specific heat which showed an increase with decrease of temperature near the saturation curve. It was shown by Weltner and Pitzer,[23] using heat-capacity measurements obtained by flow calorimetry, that this behaviour was due to association by hydrogen bonding and they determined the rather large corrections for gas imperfections arising from this. With structural information available from microwave spectroscopy, a revised vibrational assignment, and a new theoretical treatment of the barrier-height problem, Ivash, Li, and Pitzer[24] calculated the complete thermodynamic functions and tabulated them for the range 100—1000°K.

Similar difficulties arise with ethyl alcohol, studied by Aston and his co-workers.[25] The values for the barriers to free rotation necessary to give agreement between calculated and observed[26,21] entropies were found[25a] to be very high, especially for the hydroxyl group (10,000 cal./mole). More reasonable values were required by use of a method[25c,d] in which the unsymmetrical barrier for this rotation was treated by the use of a potential-energy function with unequal minima, that is, a *trans*-form of lower energy than the skew forms, and thermodynamic functions cal-

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[20] Kelley, *J. Amer. Chem. Soc.*, 1929, **51**, 181.

[21] Fiock, Ginnings, and Holton, *J. Res. Nat. Bur. Stand.*, 1931, **6**, 881.

[22] Halford, *J. Chem. Phys.*, 1949, **17**, 111; 1950, **18**, 361, 1051, and references herein.

[23] Weltner and Pitzer, *J. Amer. Chem. Soc.*, 1951, **73**, 2606.

[24] Ivash, Li, and Pitzer, *J. Chem. Phys.*, 1955, **23**, 1814.

[25] (*a*) Schumann and Aston, *J. Chem. Phys.*, 1938, **6**, 480; (*b*) Aston, *Ind. Eng. Chem.*, 1942, **34**, 514; (*c*) Aston, Szasz, and Isserow, *J. Chem. Phys.*, 1943, **11**, 532; (*d*) Brickwedde, Moskow, and Aston, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 263.

[26] Kelley, *J. Amer. Chem. Soc.*, 1929, **51**, 779.

culated in this way were tabulated.[25d] The agreement with the observed entropy was satisfactory but that of heat capacities was much poorer, the calculated values being too high. Barrow[27] considered the effect of associa-

TABLE 1. *Thermodynamic properties of alcohols, phenols and polyhydric alcohols at 25°C (kcal./mole and cal./deg./mole)*

Alcohol		$-\Delta H_f^\circ$	Ref.	S°	Ref.	$-\Delta G_f^\circ$
Methyl	(l)	57·02 ± 0·05	17	30·3	20	39·73
	(g)	48·08 ± 0·05	17	57·29	24	38·84
Ethyl	(l)	66·36 ± 0·10	17	38·4	26	41·77
	(g)	56·24 ± 0·12	17	67·58	27	40·35
Propyl	(l)	73·20 ± 0·24	28	46·1	33	41·2
	(g)	61·85 ± 0·26	28	76·19	32	39·13
Isopropyl	(l)	76·18	35	43·0	37	43·26
	(g)	65·42	(*a*)	73·92	(*a*)	41·71
Butyl	(l)	79·54 ± 0·10	28	54·5	33	40·33
	(g)	66·92 ± 0·22	28	89·42	32	38·12
Isobutyl	(l)	80·00 ± 0·11	31	—		—
	(g)	67·9 ± 0·25	31	—		—
s-Butyl	(l)	81·88 ± 0·13	31	—		—
	(g)	70·1 ± 0·25	31	—		—
t-Butyl	(l)	85·87 ± 0·10	31	45·3	33	43·92
	(g)	74·9 ± 0·25	31	76·8	(*b*)	42·3
Pentyl	(l)	85·65 ± 0·40	28	60·9	42	38·63
	(g)	71·85 ± 0·47	28	—		—
t-Pentyl	(l)	96·1	13	54·8	42	47·3
Hexyl	(l)	91·75 ± 0·48	28	68·6	26	37·3
	(g)	76·75 ± 0·56	28	—		—
Heptyl	(l)	97·85 ± 0·56	28	77·9	43	36·5
	(g)	81·65 ± 0·66	28	—		—
Hexadecyl	(s)	163·55	35	108·0	43	23·74
	(l)	151·86	43	145·0	43	23·08
Cyclopentyl	(l)	71·77	35	49·3	43	30·6
Cyclohexyl	(l)	83·45	35	47·7	44	32·1
Benzyl	(l)	38·49 ± 0·30	46	51·8	45	6·6
Diphenylmethyl	(s)	25·16 ± 0·50	46	57·3	13	−26·2
Triphenylmethyl	(s)	0·80 ± 0·60	46	78·7	13	−65·2
Phenol	(g)	23·05 ± 0·15	47	75·44	49	7·89
	(s)	39·46 ± 0·08	47	35·71	49	12·45
Ethylene glycol	(l)	108·74	51	39·9	33	77·3
	(g)	95·10	32	77·33	32	74·82
Glycerol	(l)	159·80	51	48·87	53	114·01
Erythritol	(s)	217·61	51	39·9	13	152·71
Mannitol	(s)	319·61	51	57·0	13	225·2
Dulcitol	(s)	321·90	51	56·0	13	227·2

(*a*) See text.
(*b*) Calculated from S° (l), vapour pressure and heat of vaporisation,[40] the effect of gas imperfections being ignored.

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[27] Barrow, *J. Chem. Phys.*, 1952, **20**, 1739.

tion in the vapour by the same method as that used for methyl alcohol[23] and also gave a revised vibrational assignment in terms of which only a symmetrical threefold potential function was required for both the methyl and hydroxyl groups to give good agreement with heat capacities and entropies, as well as measurements of the equilibrium between ethyl alcohol, ethylene, and water. Further calculations giving the functions from 0—1000°K, have been made.[27a]

Data on all other alcohols are more diffuse. The values for heats of formation given in Table 1 for the higher normal aliphatic alcohols are those of a recent revision[28] of the combustion measurements previously considered by Rossini.[29] A fresh choice of "best" selected values within the experimental errors of the results was made but the greatest change is in the values for the heats of vaporisation at 25°C, derived from vapour-pressure measurements. The value given for butyl alcohol is that of Tjebbes[30] but a recent measurement by Skinner and Snelson[31] yielded, at 25°C, ΔH_f° (l) = $-$ 78·49 ± 0·11, ΔH_f° (g) = $-$ 66·1 ± 0·25 kcal./mole.

Values of the entropy, enthalpy, and free-energy functions for propyl and butyl alcohols from 298·16 to 1000°K were calculated by Dyatkina[32] who used a vibrational assignment based on Raman spectra only. The contributions of the possible rotations about the C–C and C–O bonds were allowed for and the barrier heights were assumed to be 3000 and 2100 cal./mole, respectively, but there are insufficient experimental data against which to check the calculations. For propyl alcohol, however, there is satisfactory agreement at 298·16°K between the calculated entropy, 77·25 cal./deg./mole, and the value of 77·1 ± 0·5 cal./deg./mole derivable from the entropy of the liquid,[33] the revised heat of vaporisation[28] and recent vapour-pressure measurements,[34] gas imperfections being ignored.

The two most recent measurements[31,35] of the heat of formation of isopropyl alcohol are in good agreement but the position of the tabulated thermodynamic functions[36] is unsatisfactory. Although reasonably good agreement with the entropy of the vapour, derived[36a] from the value for the liquid,[37] was obtained by Aston and his co-workers using a rather schematic vibrational assignment, the agreement with heat-capacity

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[27a] Green, in preparation.
[28] Green, *Chem. and Ind.*, 1960, 1215.
[29] Rossini, *J. Res. Nat. Bur. Stand.*, 1934, **13**, 189.
[30] Tjebbes, *Acta Chem. Scand.*, 1960, **14**, 180.
[31] Skinner and Snelson, *Trans. Faraday Soc.*, 1960, **56**, 1776.
[32] Dyatkina, *Zhur. fiz. Khim.*, 1954, **28**, 377.
[33] Parks, Kelley, and Huffman, *J. Amer. Chem. Soc.*, 1929, **51**, 1969.
[34] Copp and Findlay, *Trans. Faraday Soc.*, 1960, **56**, 13.
[35] Parks, Mosley, and Paterson, *J. Chem. Phys.*, 1950, **18**, 152.
[36] (*a*) Schumann and Aston, *J. Chem. Phys.*, 1938, **6**, 485; (*b*) Aston, Isserow, Szasz, and Kennedy, *ibid.*, 1944, **12**, 336; (*c*) Kobe, Harrison, and Pennington, *Petroleum Refiner*, 1951, **30**, 119.
[37] (*a*) Kelley, *J. Amer. Chem. Soc.*, 1929, **51**, 1145; (*b*) Ginnings and Corruccini, *Ind. Eng. Chem.*, 1948, **40**, 1990.

measurements[38] was rather poor. A later calculation[36c] of the enthalpy and heat capacity yielded slightly different values from, but no better agreement with, either the earlier or subsequent[39] observations and it is possible that the measured values are in error. The listed heat of formation of isopropyl alcohol of the gas is the mean of the value (65·56 kcal./mole) obtained for the liquid together with the heat of vaporisation,[40] and that deduced from the heat of hydrogenation of acetone discussed later (see p. 139). Similarly, the entropy is the mean of a calculated value[36c] (74·14 cal./deg./mole) and that deduced from measurements of the equilibrium between isopropyl alcohol, hydrogen, and acetone (see p. 139).

For isobutyl, s-butyl, and t-butyl alcohols there is a paucity of data. The heats of combustion are now accurately known for all three compounds[31] but an entropy value is available only for t-butyl alcohol, the listed value for the vapour being calculated from that of the liquid[33] by use of vapour-pressure and heat of vaporisation data,[40] the effect of gas imperfection being ignored. Taft and Riesz[41] studied the equilibrium between isobutene, water, and t-butyl alcohol in dilute acid and obtained results in poor agreement with the earlier[13] values for the alcohol; the agreement is very much improved by the new values and we have, for the reaction at 25°C with the pure liquid, alcohol $\Delta H = -12{\cdot}6$ (obs.), $-13{\cdot}5$ (calc.); $\Delta G = -1{\cdot}3$ (obs.), $-1{\cdot}1$ (calc.) kcal./mole. Measurements of the vapour heat capacities of the butyl alcohols and of pentyl alcohol were made by Sinke and De Vries.[39]

For all other alcohols, entropy measurements at 25°C on the liquids[42–45] are the only data available. Values for hexadecyl alcohol as solid and hypothetical (at 25°C) liquid were given by Parks and his co-workers;[43] the derived heat of formation of the liquid is in satisfactory agreement with the value 152·84 ± 1·3 kcal./mole obtained by extrapolation from the revised values[28] for the lower alcohols.

The listed entropies of diphenylmethyl alcohol and triphenylmethyl alcohol are those given by Parks and Huffman[13] and are based on unpublished measurements by Andrews. The heats of formation of these substances are more reliable and, together with the value for benzyl alcohol, are taken from the work of Parks, Manchester, and Vaughan.[46] However, a comparison of their values for phenol, quinol, and benzoquinone with

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[38] Parks and Shomate, *J. Chem. Phys.*, 1940, **8**, 429.
[39] Sinke and De Vries, *J. Amer. Chem. Soc.*, 1953, **75**, 1815.
[40] Parks and Barton, *J. Amer. Chem. Soc.*, 1928, **50**, 24.
[41] Taft and Riesz, *J. Amer. Chem. Soc.*, 1955, **77**, 902.
[42] Parks, Huffman, and Barmore, *J. Amer. Chem. Soc.*, 1933, **55**, 2733.
[43] Parks, Kennedy, Gates, Mosley, Moore, and Renquist, *J. Amer. Chem. Soc.*, 1956, **78**, 56.
[44] Kelley, *J. Amer. Chem. Soc.*, 1929, **51**, 1400.
[45] Parks, Todd, and Moore, *J. Amer. Chem. Soc.*, 1936, **58**, 398.
[46] Parks, Manchester, and Vaughan, *J. Chem. Phys.*, 1954, **22**, 2089.

later measurements[47,48] suggests that their values of $-\Delta H_f$ may be low by about 0·6—0·8 kcal./mole. For phenol the values listed are therefore preferred. The thermodynamic functions for phenol have been calculated[49] from a complete vibrational assignment together with the barrier height as measured by microwave spectroscopy.[50] These calculations, and accurate vapour-pressure and heat of vaporisation[47] measurements (the correction for gas imperfection is negligible), indicate that the measured value for the entropy of solid phenol[42] is low by 1·6 cal./deg./mole.

The listed value for the heat of formation of ethylene glycol is that of Parks and his co-workers,[51] in preference to that of other workers[52] and a, presumably, averaged value.[17] Calculations of the thermodynamic functions, excluding heat capacity, were made by Dyatkina,[32] using the same procedure and assumptions as for propyl and butyl alcohols. A rather more accurate value[53] of the entropy of glycerol replaces that derived[13] from very early measurements, but no improvement is possible on the previously listed values for erythritol, mannitol, and dulcitol, although the heats of formation have been re-measured.[51] From the heats of solution of erythritol, mannitol, and dulcitol in water[54] the heats of combustion of the hypothetical liquid forms of the substances at 25°c were derived: the corresponding heats of formation are −212·04, −314·22, and −314·81 kcal./mole, respectively. The heats of formation of this series of substances $C_nH_{2n+2}O_n$ are reproduced to within 0·5 kcal./mole by the expression $-\Delta H_f^\circ\,(1, 25^\circ c) = 5{\cdot}82 + 51{\cdot}46n$.

There exist only heats of combustion data for all remaining compounds; heats of formation derived from work not previously summarised are given in Table 2. The values for α- and β-naphthol[55] are rather less accurate than those for the cresols[47] and xylenols;[47] that for cycloheptyl alcohol is from recent work by Skuratov and his co-workers.[56] Values are available for a number of cyclohexyl alcohol derivatives:[57–59] those for the methylcyclohexyl alcohols are due to Skita and Faust[59a] and are listed with the changed assignment of configurations.[60] The values listed for various diols[52a] may be in error by several kcal./mole, to judge by these authors'

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[47] Andon, Biddiscombe, Cox, Handley, Harrop, Herington, and Martin, *J.*, 1960, 5246.

[48] Pilcher and Sutton, *J.*, 1956, 2695.

[49] Green, *J.*, 1961, 2236.

[50] Kojima, *J. Phys. Soc., Japan*, 1960, **15**, 284.

[51] Parks, West, Naylor, Fujii, and McClaine, *J. Amer. Chem. Soc.*, 1946, **68**, 2524.

[52] (*a*) Moureu and Dodé, *Bull. Soc. chim. France*, 1937, **4**, 637; (*b*) Jung and Dahmlos, *Z. phys. Chem.*, 1942, *A*, **190**, 230.

[53] Ahlberg, Blanchard, and Lundberg, *J. Chem. Phys.*, 1937, **5**, 539.

[54] Parks and Manchester, *J. Amer. Chem. Soc.*, 1952, **74**, 3435.

[55] Leman and Lepoutre, *Compt. rend.*, 1948, **226**, 1976.

[56] Skuratov, Kozina, Shtecher, and Varushyenko, *Thermochem. Bull., I.U.P.A.C.*, 1957, No. 3, 25.

[57] Nicholson, *J.*, 1960, 2378.

[58] Landrieu, Baylocq, and Johnson, *Bull. Soc. chim. France*, 1929, **45**, 36.

[59] (*a*) Skita and Faust, *Ber.*, 1931, *B*, **64**, 2878; (*b*) *ibid.*, 1939, *B*, **72**, 1127.

[60] Eliel and Hober, *J. Org. Chem.*, 1958, **23**, 2041.

TABLE 2. *Heats of formation of alcohols, phenols and polyhydric alcohols at* 25°C (*kcal./mole*)

		$-\Delta H_f^\circ$	Ref.
Octyl alcohol	(l)	103·96 ± 0·64	28
	(g)	86·56 ± 0·75	28
Nonyl alcohol	(l)	110·07 ± 0·72	28
	(g)	91·47 ± 0·84	28
Decyl alcohol	(l)	116·18 ± 0·80	28
	(g)	96·36 ± 0·94	28
o-Cresol	(s)	48·91 ± 0·12	47
	(g)	30·74 ± 0·22	47
m-Cresol	(l)	46·38 ± 0·07	47
	(g)	31·63 ± 0·26	47
p-Cresol	(s)	47·64 ± 0·08	47
	(g)	29·97 ± 0·36	47
2,3-Xylenol	(s)	57·67 ± 0.11	47
	(g)	37·59 ± 0·27	47
2,4-Xylenol	(l)	54·69 ± 0·11	47
	(g)	38·95 ± 0·18	47
2,5-Xylenol	(s)	58·96 ± 0·10	47
	(g)	38·65 ± 0·12	47
2,6-Xylenol	(s)	56·75 ± 0·12	47
	(g)	38·68 ± 0·13	47
3,4-Xylenol	(s)	57·93 ± 0·13	47
	(g)	37·44 ± 0·14	47
3,5-Xylenol	(s)	58·43 ± 0·14	47
	(g)	38·63 ± 0·16	47
α-Naphthol	(s)	26·4	55
β-Naphthol	(s)	29·3	55
Cycloheptanol (l)*		94·0	56
3,3,5-Trimethylcyclohexanol (l)		109·2	57
Cyclohexylmethanol		102·0	58

	$-\Delta H_f^\circ$	Ref.
cis-2-Methylcyclohexanol (l)	94·85	59*a*
trans-2-Methylcyclohexanol (l)	100·93	59*a*
cis-3-Methylcyclohexanol (l)	101·02	59*a*
trans-3-Methylcyclohexanol (l)	95·82	59*a*
cis-4-Methylcyclohexanol (l)	100·24	59*a*
trans-4-Methylcyclohexanol (l)	105·07	59*a*
cis-3,*cis*-5-Dimethylcyclohexanol (l)	100·9	59*b*
trans-3,*trans*-5-Dimethyl cyclohexanol (l)	115·4	59*b*
cis-3,*trans*-5-Dimethylcyclohexanol (l)	121·3	59*b*
Diethylene glycol (l)†	149·3	52*a*
Triethylene glycol (l)†	191·0	52*a*
Tetraethylene glycol (l)†	233·1	52*a*
Propane-1,2-diol (l)†	118·9	52*a*
Butane-1,2-diol (l)†	124·4	52*a*
Butane-1,3-diol (l)†	122·3	52*a*
Butane-2,3-diol (l)†	128·7	52*a*
Isobutane-1,2-diol (l)†	128·2	52*a*
2-Ethylhexan-1-ol (l)	103·46	30

* At 20°. † At 17°.

values for ethylene glycol and for ethylene oxide and propylene oxide (see p. 136).

Studies of a number of *cis*- and *trans*-isomers of various diols were made by Verkade, Coops, and their co-workers,[61] and the figures in Table 3 are a revision of their values, converted into heats of formation at 25°C. For cyclopentanediol, more recent work[52b] gives $-\Delta H_f$ (*cis*) $=$ 115·6, (*trans*) $=$ 116·8 kcal./mole. in satisfactory agreement with the listed values.

(*b*) *Ethers, Cyclic Ethers, and Derivatives.*—Thermochemical data on even the simplest aliphatic ethers are extremely scanty and only one modern, accurate value of the heat of formation is available, that for

[61] Verkade, Coops, Maan, and Verkade-Sandbergen, *Annalen*, 1928, **467**, 217.

TABLE 3. *Heats of formation of diols at* 25°C

	$-\Delta H_f^\circ$ (kcal./mole)	
	cis	*trans*
Cyclopentane-1,2-diol (s)	115·2	117·2
1-Methylcyclopentane-1,2-diol (l)	126·0	128·3
1-Phenylcyclopentane-1,2-diol (s)	97·5	—
Indane-1,2-diol (s)	88·7	88·5
1,2,3,4-Tetrahydronaphthalene-1,2-diol (s)	98·5	99·8
1,2,3,4-Tetrahydronaphthalene-2,3-diol (s)	98·5	98·9
Cyclohexane-1,2-diol (s)	131·7	130·7
1-Methylcyclohexane-1,2-diol (s)	143·0	140·5
1-Phenylcyclohexane-1,2-diol (s)	110·6	109·8

diethyl ether, measured by Pilcher,* who finds, by using a flame calorimeter, that ΔH_f°(g, 24°C) = $-60·37 \pm 0·18$ kcal./mole. (The old measurements gave $-57·4$ and, for ethyl methyl ether, $-52·0$ kcal./mole.) The vibrational assignment of dimethyl ether is, however, well established and several calculations of the thermodynamic functions have been made from it,[62] the results of which are in reasonable agreement with one another and with the measured entropy [62a] and heat capacity.[63] The values listed in Table 4 are by Sěha[62c] who tabulated the functions from 298·16—1000°K. Studies of the equilibrium between ethyl alcohol, diethyl ether, and water have been used[64] to derive values for the functions for diethyl ether, but the results are in poor agreement with the meagre data available.

TABLE 4. *Thermodynamic properties of some ethers and cyclic ethers at* 25°C *(kcal./mole and cal./deg./mole)*

	$-\Delta H_f^\circ$	Ref.	S°	Ref.	$-\Delta G_f^\circ$
Dimethyl ether (g)	44·3	62*c*	63·74	62*c*	27·27
Di-isopropyl ether (l)	83·94	65	70·4	42	21·1
Diphenyl ether (s)	7·67	64	55·91	64	34·37
Ethylene oxide (g)	12·19	66	58·13	65*a*	2·79
Propylene oxide (g)	22·02	18*b*	67·15	69	5·60
Trimethylene oxide (g)	—		63·40	69*a*	—
1,4-Dioxan (l)	95·5	71	47·0	70	55·1
1,3-Dioxan (l)	94·5, 92·1*	72, 56	—		—
Furan (l)	14·903	76	42·22	76	−0·050
„ (g)	8·293	76	63·86	76	−0·208
Furfuryl alcohol (l)	66·05	35	51·6	43	36·88

* At 20°.

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* Dr. G. Pilcher, University of Manchester, private communication.

[62] (*a*) Kennedy, Sagenkahn, and Aston, *J. Amer. Chem. Soc.*, 1941, **63**, 2267. (*b*) Hadzi, *Compt. rend.*, 1954, **239**, 349; (*c*) Sěha, *Chem. Listy*, 1955, **49**,1569; (*d*) Taylor and Vidale, *J. Chem. Phys.*, 1957, **26**, 122; (*e*) Mashiko and Pitzer, *J. Phys. Chem.*, 1958, **62**, 367.

[63] Kiastiakowsky and Rice, *J. Chem. Phys.*, 1940, **8**, 610.

[64] Valentin, *J.*, 1950, 498, and references herein.

Values of the entropy[42] and heat of formation[65] of di-isopropyl ether at 25°C are available.

Measurements have been made for diphenyl ether leading to a tabulation of the enthalpy, entropy, and heat capacity in the range 0—570°K, together with the heat of formation.[66]

The heats of formation of a number of cyclic ethers have been measured, and ethylene oxide has been the subject of a number of more complete investigations and calculations which are in satisfactory agreement.[63,67] For the heat of formation we follow an earlier compilation[17] in listing the value obtained by Crog and Hunt;[68] the older work, including that of Moureu and Dodé[52a] gave considerably different results both for this compound and for propylene oxide, for which the value obtained by Stull[18b] is listed in Table 4. The latter value has been used, together with a complete vibrational assignment and the barrier height determined by microwave spectroscopy, to calculate the complete thermodynamic functions for propylene oxide from 0° to 1000°K.[69] Calculated functions for trimethylene oxide are also available[69a] but there is no value for the heat of formation of this compound. A measurement of the entropy[70] of 1,4-dioxan at 25°C is available, but the heat of formation[71] is a rather old one: more recent values exists for 1,3-dioxan,[72] but the difference between them is rather large.

The remaining values are summarised in Table 5. It may be noted that the results due to Badoche[73] for phenol and *m*-cresol agree to within 0·2 kcal./mole with recent measurements.[47] Other values in the Table are due to Springall[74] and Skuratov[56,75] and their co-workers. Their values[74b,56] for the heat of combustion of liquid tetrahydrofuran differ by 0·8 kcal./mole, and the mean value, —598·4 kcal./mole, together with the heat of vaporisation[74b] was used to derive the listed heat of formation. Larger differences exist between the two sets of results for tetrahydropyran, and 1,3-dioxolan both of which are listed.

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[65] Parks and Manchester, *Thermochem. Bull., I.U.P.A.C.*, 1956, No. 2, 8.

[66] Furukawa, Ginnings, McCoskey, and Nelson, *J. Res. Nat. Bur. Stand.*, 1951, **46,** 195.

[67] (*a*) Godnev and Morozov, *Zhur. fiz. Khim.*, 1948, **22,** 801; (*b*) Gordon and Giague, *J. Amer. Chem. Soc.*, 1949, **71,** 2176; (*c*) Arnold, quoted by Kobe and Pennington, *Petroleum Refiner*, 1950, **29,** 135; (*d*) Günthard, Mesikommer, and Kohler, *Helv. Chim. Acta*, 1950, **33,** 1809.

[68] Crog and Hunt, *J. Phys. Chem.*, 1942, **46,** 1162.

[69] Green, *Chem, and Ind.*, 1961, 369.

[69a] Zürcher and Günthard, *Helv. Chim. Acta*, 1955, **38,** 849; 1957, **40,** 89.

[70] Jacobs and Parks, *J. Amer. Chem. Soc.*, 1934, **56,** 1513.

[71] Roth and Meyer, *Z. Elektrochem.*, 1933, **39,** 35.

[72] Fletcher, Mortimer, and Springall, *Bull. Chem. Thermodynamics, I.U.P.A.C.*, 1958, No. 1, A17.

[73] Badoche, *Bull. Soc. Chim. France*, 1941, **8,** 212.

[74] (*a*) Springall, Mortimer, and Fletcher, *Thermochem. Bull., I.U.P.A.C.*, 1957, No. 3, 12; (*b*) Cass, Fletcher, Mortimer, Springall, and White, *J.*, 1958, 1406; (*c*) Cass, Fletcher, Mortimer, Quincey, and Springall, *J.*, 1958, 2595.

[75] Skuratov and Kozina, *Doklady Akad. Nauk S.S.S.R.*, 1958, **122,** 109.

A detailed study of furan has been made[76] and a tabulation given of the complete thermodynamic functions from 273·16° to 1500°K. The subsequent change[77] in the vibrational assignment does not seriously change these values since the original assignment included four frequencies chosen empirically to give the best fit to the measured entropies and heat capacities and at the same time allowed for the contributions of anharmonicity. The latest value for the heat of formation[35] of furfuryl alcohol is in good agreement with an earlier value obtained by Landrieu, Baylocq, and Johnson[58] who also made measurements on some other furan derivatives but unfortunately at an unstated temperature; revised values from their other results are given in Table 5.

TABLE 5. *Heat of formation of some ethers and cyclic ethers at* 25°C *(kcal./mole)*

	$-\Delta H_f{}^\circ$	Ref.		$-\Delta H_f{}^\circ$	Ref.
Methyl phenyl ether (l)	29·61	73	Furylacrylic acid (l)	107·3	58
Ethyl phenyl ether (l)	37·67	73	Tetrahydrofurfuryl alcohol (l)	102·0	58
m-Methoxytoluene (l)	36·69	73	1,3-Dioxolan (l)*	79·5	56
Tetrahydrofuran (l)	51·1	56, 74*b*	,, ,,	80·7	72
,, (g)	43·5	74*b*	4-Methyl-1,3-dioxan (l), 20°	102·0	56
Tetrahydropyran (l)	59·1, 61·33	56, 74*b*	1,3-Dioxepan (l)*	92·5	56
,, (g)	50·7, 53·98	74*b*	1,3-Dioxocan (l)*	90·2	56
			o-Dimethoxybenzene (l)	89·5	74*c*
2-Methoxytetrahydropyran (l)*	104·4	56	1,4-Benzodioxan (l)	61·0	74*c*
			1,3-Benzodioxolan (l)	44·0	74*c*
Dihydropyran (l)	37·6	74*b*	2,3-Benzo-1,4-dioxepan (l)	57·8	74*c*
Dibenzofuran (s)	1·4	74*b*			
Dibenzopyran (s)	15·3	74*b*	Butylene oxide (l)†	39·7	52*a*
5,5′-Spirobis-*m*-dioxan (s)	167·9	74*a*	Furoic acid (l)	119·1	58
Furfuraldehyde (l)	46·4	58	Furylethylene (l)	0·3	58

* At 20°. † At 17°.

(*c*) *Aldehydes.*—The vibrational assignment for formaldehyde is well established[10a] and several calculations of the thermodynamic functions have been made. Dworjanyn[78] tabulated values from 298·16° to 1200°K which were derived by using the most recent determination by microwave spectroscopy of the moments of inertia of the molecule. No very reliable value for the heat of formation is available, however; that listed in Table 6 was derived[17] from rather old work.

[76] Guthrie, Scott, Hubbard, Katz, McCullough, Gross, Williamson, and Waddington, *J. Amer. Chem. Soc.*, 1952, **74**, 4662.

[77] Bak, Brodersen, and Hansen, *Acta Chem. Scand.*, 1955, **9**, 749.

[78] Dworjanyn, *Austral. J. Chem.*, 1960, **13**, 175.

TABLE 6. *Thermodynamic properties of some aldehydes and ketones at* 25°C (*kcal./mole and cal./deg./mole*)

	$-\Delta H_f{}^\circ$	Ref.	S°	Ref.	$-\Delta G_f{}^\circ$
Formaldehyde (g)	27·7	17	52·26	78	26·3
Acetaldehyde (g)	39·67	79*b*	63·15	79*b*	31·77
Butyraldehyde (l)	57·2	30,82	59·0	43	28·6
Heptanal (l)	74·5 ± 0·9	82	83·3	43	24·1
Acetone (l)	59·34	84	47·9	84	37·19
„ (g)	51·72	84	70·49	84	36·30
Ethyl methyl ketone (l)	66·68	35	57·71	43	37·73
Benzophenone (s)	8·1	35, 86*a*	58·6	13	−33·5
Dibenzoylethylene (s)	27·55 ± 0·60	46	77·6	87	−26·3
Dibenzoylethane (s)	61·24 ± 0·40	46	76·3	87	− 2·3

Several calculations[79] have also been made for acetaldehyde, that of Pitzer and Weltner[79b] yielding the most reliable values since the parameters were chosen to give agreement with the observed heat capacities[79c] and measurements of the equilibrium between acetaldehyde, ethanol, and hydrogen.[79d] (A revision[80] of the assignment used by these authors is mainly in the region of higher wave-numbers and therefore has a negligible effect on the calculated values.) By using these calculated functions for acetaldehyde, together with those for ethanol[25d] and hydrogen,[17] the listed heat of formation of acetaldehyde can be derived from the heat of hydrogenation, measured by Kistiakowsky and his co-workers.[81]

Recent values for the heat of combustion of butyraldehyde[30,82] and heptanal[82] are available; for the former, the mean of the two values is listed. Tjebbes[30] also gives the heats of formation of the following liquid aldehydes at 25°C: but-2-enal, −34·45 ± 0·09; 2-ethylhexanal, −83·32 ± 0·18, and 2-ethylhex-2-enal, −62·46 ± 0·17.

A heat of combustion of benzaldehyde has been quoted[19] and converted into a heat of formation.[18a] Revision of the original measurements[58] yields $\Delta H_f{}^\circ$ (l) = −17·8 kcal./mole, the temperature not being stated; with the estimated heat of vaporisation this gives $\Delta H_f{}^\circ$ (g) = −6·0 kcal./mole. These values may be subject to fairly large errors, as also may the following values (kcal./mole) for a number of substituted benzaldehydes measured at the temperature stated:[83]

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[79] (*a*) Smith, *Trans. Amer. Inst. Chem. Engineers*, 1946, **42**, 983; (*b*) Pitzer and Weltner, *J. Amer. Chem. Soc.*, 1949, **71**, 2842; (*c*) Coleman and De Vries, *ibid.*, 1949, **71**, 2839; (*d*) Rideal, *Proc. Roy. Soc.*, 1921, *A*, **99**, 153.

[80] Evans and Bernstein, *Canad. J. Chem.*, 1956, **34**, 1083.

[81] Dolliver, Gresham, Kistiakowsky, Smith, and Vaughan, *J. Amer. Chem. Soc.*, 1938, **60**, 440.

[82] Nicholson, *J.*, 1360, 2377.

[83] (*a*) Bonino, Manzoni-Ansidei, and Rolla, *Ricerca sci.*, 1937, **8**, 5; (*b*) Manzoni-Ansidei and Storto, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1940, **1**, 465.

o-hydroxy (20°) −67·0	*o*-methoxy (17°) −62·6
m-hydroxy (20°) −70·3	*m*-methoxy (17°) −64·9
p-hydroxy (20°) −74·3	*p*-methoxy (17°) −62·8

3-hydroxy-4-methoxy (at 17°) −107·3

(*d*) *Ketones.*—A complete tabulation of the thermodynamic functions is available only for acetone. The calculations were based on the heat of formation, entropy measurements of the liquid, heat of vaporisation, and heat-capacity measurements by flow calorimetry of sufficient accuracy to permit evaluation of the contribution of anharmonicity in terms of the vibrational assignment.[84] The resulting values can therefore be regarded as well established.

Several authors have studied the equilibrium between acetone, isopropyl alcohol, and hydrogen,[85] and the early work was discussed by Parks and Huffman,[13] chiefly by using the equilibrium constants measured by Parks and Kelley.[85a] The somewhat different results obtained by later workers were, however, in mutual agreement. Kistiakowsky and his co-workers[81] found the heat of hydrogenation of acetone at 355°K to be 13·407 kcal./mole, with which the value 13·69 kcal./mole found by Kolb and Burwell[85b] from their equilibrium measurements was considered to be in satisfactory agreement. By using the former value, together with heat capacities for acetone,[84] isopropyl alcohol[36c] and hydrogen,[17] we find for isopropyl alcohol $\Delta H_f°$ (g, 25°C) = −65·28 kcal./mole. Similarly, from the equilibrium measurements[85b] we find for isopropyl alcohol, $S°$ (g, 25°C) = 73·71 cal./deg./mole. Vogler and Trumpler[85c] analysed their measurements over the range 277—327°C and 100—400 atm. to obtain fugacities which were in good agreement with those obtained by estimation.

The vapour heat capacities and heats of vaporisation of ethyl methyl ketone and methyl propyl ketone have been measured recently,[86] and the thermodynamic functions tabulated from 0° to 1500°K. From these values, those for the methyl n-alkyl series have been calculated by the method of increments. Values for the entropy[43] and heat of formation[35] of ethyl methyl ketone are also available: the value listed for the latter quantity is preferred to that obtained by Crog and Hunt[68] who burnt the substance as a gas but give the result for the liquid having made an unstated "correction" to this state. Skinner and Snelson,[31] quoting the value[86] of 8·31 kcal./mole for the heat of vaporisation of ethyl methyl ketone at 25°C, find that there is not a very satisfactory consistency between their value for $\Delta H_f°$ (g) of s-butyl alcohol (−70·1 kcal./mole), Crog and Hunt's value of $\Delta H_f°$ (g) of ethyl methyl ketone (−58·9 kcal./mole), and the heat of hydro-

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[84] Pennington and Kobe, *J. Amer. Chem. Soc.*, 1957, **79**, 300.

[85] (*a*) Parks and Kelley, *J. Phys. Chem.*, 1928, **32**, 740; (*b*) Kolb and Burwell, *J. Amer. Chem. Soc.*, 1945, **67**, 1084; (*c*) Vogler and Trumpler, *Helv. Chim. Acta*, 1956, **39**, 757; (*d*) Ciborowski, *Chim. et Ind.*, 1958, **80**, 240.

[86] Nickerson and McKetta, *Bull. Chem. Thermodynamics, I.U.P.A.C.*, 1960, No. 3, 47; Nickerson, Ph.D. thesis, University of Texas, 1960.

genation[80] of the latter substance reduced to 25°C (−12·95 kcal./mole). The agreement is better by 0·45 kcal./mole if the present values are used, but is still not entirely satisfactory.

Two recent measurements of the heat of formation of benzophenone[35,86a] differ by 0·4 kcal./mole; the mean value is listed here, together with the entropy as estimated by Parks and Huffman.[13] For dibenzoylethylene and dibenzoylethane, the entropy measurements are again due to Parks and Huffman;[87] with the modern values[46] for the heats of formation, the sign of $\Delta G_f{}^\circ$ for dibenzoylethane is changed from that given previously.[13] Recent values[88–94] for the heats of formation of a number of ketones are summarised in Table 7. For benzyl methyl ketone, the value listed is that from two measurements[91,92] in good agreement, chosen in preference to a third value[46] of 38·96 kcal./mole. The three recent values for diacetyl

TABLE 7. *Heat of formation of some ketones at* 25°C (*kcal./mole*)

	$-\Delta H_f{}^\circ$	Ref.		$-\Delta H_f{}^\circ$	Ref.
Acetylacetone (l)	101·33	89	2,4,5-Trimethylacetophenone (l)	61·4	93
p-Methylbenzophenone (s)	184·0	86	Cyclopentanone (l)*	57·6	56
p-Ethylbenzophenone (l)	243·0	86	Cyclohexanone (l)*	69·5	56
p-Isopropylbenzophenone (l)	520·5	86	Cycloheptanone (l)*	71·1	56, 90
p-t-Butylbenzophenone (l)	686·7	86	Cyclodecanone (l)*	81·6	90
Methyl phenyl ketone (l)	34·06	88	Dibenzyl ketone (s)	20·3	91
Ethyl phenyl ketone (l)	39·95	88	Benzil (s)	42·7	91
Propyl phenyl ketone (l)	45·13	88	Diacetyl (l)	87·5	46, 91, 92
Isobutyl phenyl ketone (l)	52·62	88	Benzyl methyl ketone (l)	36·4	91, 92
t-Butyl phenyl ketone (l)	49·91	98	Norcamphor (s)	54·4	94
2,4,6-Trimethylacetophenone (l)	65·0	93	*endo*-Ethylenecyclohexanone (s)	15·1	94

* At 20°.

[86a] Colomina, Cambeiro, Perez-Ossorio, and Latore, *Anales real Soc. españ. Fis. Quim.*, 1959, **6**, 509.

[87] Parks and Huffman, *J. Amer. Chem. Soc.*, 1930, **52**, 4387.

[88] Colomina, Latore, and Perez-Ossorio, *Bull. Chem. Thermodynamics, I.U.P.A.C.*, 1958, No. 1, A19.

[89] Nicholson, *J.*, 1957, 2431.

[90] Skuratov, Kozina, Shtecher, Prevalova, Kamkina, and Zuko, *Bull., Chem. Thermodynamics, I.U.P.A.C.*, 1958, No. 1, A21.

[91] Springall and White, *J.*, 1954, 2764.

[92] Nicholson, Szwarc, and Taylor, *J.*, 1954, 2767; *Thermochem. Bull., I.U.P.A.C.*, 1956 No. 2, 16.

[93] Baker and Tweed, *J.*, 1941 796.

[94] Becker and Roth, *Ber.*, 1934, *B*, **67**, 627.

—87·60,[46] 86·4,[91] 87·35[92]—are in poor agreement, and the choice of 87·5 kcal./mole is listed.

(*e*) *Acids and Anhydrides.*—With the exception of formic, acetic, and benzoic acid the available thermodynamic data on organic acids are incomplete and much is of poor accuracy.

The experimental results for formic acid were reviewed in detail by Waring[95] and subsequent work comprises an accurate measurement by Sinke[96] of the heat of combustion of the liquid substance and a revision[97] of the vibrational assignment leading to a new value for the entropy of the monomer in the ideal gas state at 25°C. The values listed in Table 8 are based on calculations incorporating these new results.[97a] For acetic acid, Weltner[98] made a similar detailed study, treating the effects of dimerisation and giving tabulated values of the thermodynamic functions for

TABLE 8. *Thermodynamic properties of some acids, anhydrides and esters at 25°C (kcal./mole and cal./deg./mole)*

Acid	$-\Delta H_f^\circ$	Ref.	S°	Ref.	$-\Delta G_f^\circ$
Formic (l)	101·52 ± 0·06	96	30·82	95	86·39
Formic, monomer (g)	90·49	97*a*	59·45	97*a*	83·89
Formic, dimer (g)	195·12	97*a*	82·89	97*a*	171·19
Acetic (l)	115·7 ± 0·10	99*b*	38·2	33	93·1
Acetic, monomer (g)	103·8	98	67·5	98	89·9
Acetic, dimer (g)	223·0	98	96·7	98	183·7
Butyric (l)	127·2	101, 102*a*	54·1	33	89·9
Palmitic (s)	211·2	101	104·8	105	75·1
Lactic (s)	165·89 ± 0·11	106	34·0	107	125·0
Lactic (l)	161·1	13	45·9	108	123·7
Benzoic (s)	91·812 ± 0·07	100*d*	40·04	100*d*	59·11
o-Hydroxybenzoic (s)	140·0	16	42·6	110	100·0
m-Hydroxybenzoic (s)	141·1	109	42·3	110	101·0
p-Hydroxybenzoic (s)	142·0	109	42·0	110	101·8
Oxalic (s)	196·7	111	28·7	13	165·9
Fumaric (s)	193·83	117	39·7	87	150·2
Maleic (s)	188·28	117	38·1	87	150·2
Succinic (s)	224·77 ± 0·06	113	42·0	87	178·5
Phthalic (s)	186·88	35	49·7	45	61·30
Phthalic anhydride (s)	110·03	35	42·9	45	79·1
Methyl formate (l)	88·6	126	—		—
Methyl formate (g)	81·0	126	84·6	13	72·0
Ethyl acetate (l)	106·2	102*a*	62·0	42	71·2
Ethyl acetate (g)	103·4	130	90·1	130	76·8

[95] Waring, *Chem. Rev.*, 1952, **51**, 171.
[96] Sinke, *J. Phys. Chem.*, 1959, **63**, 2063.
[97] Mulliken and Pitzer, *J. Chem. Phys.*, 1957, **27**, 1305.
[97a] Green, *J.*, 1961, 2241.
[98] Weltner, *J. Amer. Chem. Soc.*, 1955, **99**, 3941.

both monomer and dimer. A revision of his values is possible to take account of recent measurements[99] of the heat of formation of the liquid; the more accurate value of Evans and Skinner[99b] has been listed.

Benzoic acid has been the subject of considerable study[2,100] and the thermodynamic properties have been tabulated by Goton and Whalley,[100d] whence the listed values are taken.

For the higher aliphatic acids, all the data are old,[101] apart from a few measurements by Schjånberg[102] and by Hancock, Watson, and Gilbey[103] which are not of high accuracy. The values given in the Tables are derived from such revision as is possible of the work cited, with correction to 25°C; they may be in error by several kcal./mole. However, Coops[104] reports that the heats of combustion of the fatty acids from valeric to eicosanoic have been remeasured by Adriaanse and these will no doubt replace all previous values. The listed entropy for palmitic acid (at 298·6°K) is presumably more reliable than the older value[33] of 113·7 cal./deg./mole. For crystalline lactic acid a recent measurement of the heat of combustion is available[106] and a value for the entropy,[107] whilst for the liquid state there are old values for both quantities.[13,108] The values for *m*- and *p*-hydroxybenzoic acids[109,110] are of low accuracy; they have been converted into values for 25°C but the differences between the isomers do not exceed experimental error. For *o*-hydroxybenzoic acid the heat of combustion is rather better established; a summary of the available heats of combustion is given by Timmermans[16] and from these the value −723·31 kcal./mole at 25°C has been selected from which the listed value of the heat of formation is derived.

The heats of combustion of the homologous series of dicarboxylic acids $HO_2C{\cdot}[CH_2]_n{\cdot}CO_2H$ were measured by Verkade, Hartman, and Coops[111] but by modern standards the results are subject to several uncertainties which it is difficult to allow for satisfactorily. Oxalic acid, as was pointed out by Washburn in his classic paper,[112] is subject to an extremely large standard-state correction which he calculated for the

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[99] (*a*) Stull, *Thermochem. Bull., I.U.P.A.C.*, 1956, No. 2, 4; (*b*) Evans and Skinner, *Trans. Faraday Soc.*, 1959, **55**, 260.

[100] (*a*) Jessup, *J. Res. Nat. Bur. Stand.*, 1942, **29**, 247; (*b*) Challoner, Gundry, and Meetham, *Phil. Trans.*, 1955, **247**, 556; (*c*) Ginnings and Furukawa, *J. Amer. Chem. Soc.*, 1953, **75**, 522; (*d*) Goton and Whalley, *Canad. J. Chem.*, 1956, **34**, 1506.

[101] Verkade and Coops, *Rec. Trav. chim.*, 1928, **47**, 608, and references therein.

[102] Schjånberg, *Z. phys. Chem.*, (*a*) 1935, *A*, **172**, 197; (*b*) 1936, *A*, **175**, 342; (*c*) 1937, *A*, **178**, 274; (*d*) 1938, *A*, **181**, 430.

[103] Hancock, Watson, and Gilbey, *J. Phys. Chem.*, 1954, **58**, 127.

[104] Coops, *Bull. Chem. Thermodynamics, I.U.P.A.C.*, 1959, No. 2, 6.

[105] Ward and Singleton, *J. Phys. Chem.*, 1952, **56**, 696.

[106] Saville and Gundry, *Trans. Faraday Soc.*, 1959, **55**, 2036.

[107] Huffman, Ellis, and Borsook, *J. Amer. Chem. Soc.*, 1940, **62**, 297.

[108] Parks, Thomas, and Light, *J. Chem. Phys.*, 1936, **4**, 64.

[109] Keffler and Guthrie, *J. Phys. Chem.*, 1927, **31**, 65.

[110] Parks and Light, *J. Amer. Chem. Soc.*, 1934, **56**, 1511.

[111] Verkade, Hartman, and Coops, *Rec. Trav. chim.*, 1926, **45**, 373.

[112] Washburn, *Bur. Stand. J. Res.*, 1933, **10**, 525.

results of Verkade, Hartman, and Coops. With modern units the heat of combustion becomes −59·7 kcal./mole at 25°c, yielding the listed heat of formation. It may be noted that the value for the entropy of this substance is still that derived from the very old measurements discussed by Parks and Huffman.[13] The heats of formation derived from the older measurements[111] on both succinic and pimelic acids are not in good agreement with more recent values: for succinic acid the listed value is that selected by Pilcher and Sutton[113] after a discussion of their own and other results, whilst for pimelic acid the listed value due to Stull[114] is to be compared with the old value of −240·1 kcal./mole. For malonic acid the listed value is derived from a revision of the old measurements,[111] the standard-state correction being taken as 3·9 cal./g. The homologous series of monoalkylmalonic acids $R{\cdot}CH(CO_2H)_2$, from R = ethyl to n-tetradecyl, was investigated by Verkade and Coops[115] and a more satisfactory revision can be made of this work. Some of the new values thus obtained* are listed. A similar investigation was made by Verkade and Hartman[116] of the heats of combustion of fifteen methyl-, ethyl-, and phenyl-substituted succinic acids and their anhydrides.

For fumaric and maleic acids the values measured by Schwabe and Wagner[117] at 24°c are the most accurate and give a difference of 5·55 ± 0·16 kcal./mole between the two isomers, the earlier value[118] being 5·43 kcal./mole.

In Table 9 is summarised the remaining recent work on the heats of formation of organic acids. For the toluic and dimethylbenzoic acids, the listed values are those obtained by Colomina, Perez-Ossorio, and Boned;[119] their value for *o*-toluic acid agrees exactly with that due to Brietenbach and Derkosch,[120] but for *p*-toluic acid the latter authors found −101·0 kcal./mole. The values for three forms of *cis*-cinnamic acid are due to Eisenlohr and Metzer,[121] but the temperature of the measurements was not stated. Large discrepancies exist between the various measurements on (+)-, (−)-, and *meso*-tartaric acids; the listed values are those of Dunken and Wolf[122] but other authors give results differing from these by as much as 5 kcal./mole. The value for citric acid monohydrate is from a recent measurement.[123] The value for crotonic acid,[124] which

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* Calculated by Dr. A. J. Head (private communication).

[113] Pilcher and Sutton, *Phil. Trans.*, 1955, **258**, 23.

[114] Stull, *Bull. Chem. Thermodynamics, I.U.P.A.C.*, 1959, No. 2, 6.

[115] Verkade and Coops, *Rec. Trav. chim.*, 1933, **52**, 747.

[116] Verkade and Hartman, *Rec. Trav. chim.*, 1933, **52**, 945.

[117] Schwabe and Wagner, *Chem. Ber.*, 1958, **91**, 686.

[118] Huffman and Fox, *J. Amer. Chem. Soc.*, 1938, **60**, 1400.

[119] Colomina, Perez-Ossorio, and Boned, *Bull. Chem. Thermodynamics, I.U.P.A.C.*, (*a*) 1959, No. 2, 27; (*b*) 1960, No. 3, 21.

[120] Brietenbach and Derkosch, *Monatsh.*, 1950, **81**, 689; 1951, **82**, 177.

[121] Eisenlohr and Metzer, *Z. phys. Chem.*, 1937, *A*, **178**, 339.

[122] Dunken and Wolf, *Z. phys. Chem.*, 1938, *B*, **38**, 441, and references therein.

[123] Chappel and Hoare, *Trans. Faraday Soc.*, 1958, **54**, 367.

[124] Clopatt, *Soc., Sci. Fennica, Commentations Phys.-Mat.*, 1932, **6**. 1.

TABLE 9. *Heats of formation of some acids and acid anhydrides at 25°C (kcal./mole)*

Acid	$-\Delta H_f^\circ$	Ref.
Propionic (l)	121·3	102*a*
Valeric (l)	133·6	102*c*
Valeric (l)	131·2 ± 1·2	103
α-Methylbutyric (l)	133·1 ± 1·2	103
Isovaleric (l)	134·8 ± 0·8	103
Pivalic (s)	135·5 ± 0·5	103
Malonic (s)	212·7	111
Pimelic (s)	242·75 ± 0·25	114
Ethylmalonic (s)	226·3	115
Propylmalonic (s)	232·1	115
Butylmalonic (s)	239·5	115
Citric monohydrate (s)	439·2	123
(+)-Tartaric (s)	368·7	120
(−)-Tartaric (s)	373·8	120
meso-Tartaric (s)	369·3	120
Crotonic (s)	83	124
Allylacetic (l)	101·8 ± 0·2	102*c*
β-Ethylidenepropionic (l)	102·8 ± 0·2	102*c*
Propylideneacetic (l)	105·6 ± 0·2	102*c*
o-Toluic (s)	99·5 ± 0·22	119*a*
m-Toluic (s)	101·90 ± 0·25	119*a*
p-Toluic (s)	102·58 ± 0·24	119*a*
2,3-Dimethylbenzoic (s)	107·65 ± 0·19	119*b*
2,4-Dimethylbenzoic (s)	109·58 ± 0·20	119*b*
2,5-Dimethylbenzoic	109·02 ± 0·19	119*b*
2,6-Dimethylbenzoic (s)	105·33 ± 0·19	119*b*
3,4-Dimethyl benzoic (s)	112·04 ± 0·25	119*b*
3,5-Dimethylbenzoic (s)	111·48 ± 0·17	119*b*
cis-Cinnamic, m.p. 42° (s)	75·3 ± 0·2	121
cis-Cinnamic, m.p. 58° (s)	73·9 ± 0·2	121
cis-Cinnamic, m.p. 68° (s)	71·5 ± 0·2	124
Acetic anhydride (l)	149·20	127
Maleic anhydride (s)	112·23	35
Succinic anhydride (s)	143·2	116

differs by 20 kcal./mole from that tabulated by Kharasch,[14] is obviously unreliable.

The available data on unsaturated fatty acids are old and satisfactory revision of them is not possible; only the work of Keffler[125] is more recent than that summarised by Kharasch[14] and all the work is discussed by Markley.[126]

Only for phthalic anhydride are there measurements of both the heat of formation[35] and the entropy[45] at 25°C. Values for the heats of formation of some anhydrides can be derived from the heats of hydrolysis measured by Kistiakowsky and his co-workers[127] if the heats of formation of the acids are known; the listed value for acetic anhydride was obtained in this way, the new value[99b] being used for the heat of combustion of acetic

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[125] Keffler, *J. Phys. Chem.*, 1930, **34**, 1319; *Rec. Trav. chim.*, 1933, **52**, 945.
[126] Markley, "Fatty Acids," Interscience Publishers Inc., New York, 1947.
[127] Conn, Kistiakowsky, Roberts, and Smith, *J. Amer. Chem. Soc.*, 1942, **64**, 1747.

acid. For maleic anhydride, the listed heat of formation of the acid being again used, we find ΔH_f° (s) = $-111{\cdot}63$ kcal./mole, in reasonably good agreement with the value of $-112{\cdot}23$ kcal./mole obtained from the heat of combustion of the anhydride. However, for succinic anhydride we find ΔH_f° (s) = $-145{\cdot}25$ kcal./mole compared with the value of $-143{\cdot}2$ kcal./mole derived from a revision of the heat of combustion measured by Verkade and Hartman,[116] and the heats of hydrolysis of the methylsuccinic acids are in rather poor agreement with the differences between the heats of combustion of the acids and the anhydrides measured directly.

(*f*) *Esters.*—Entropy values are available only for methyl formate and ethyl acetate and for the former the value has to be obtained by indirect means. The listed value in Table 8 for methyl formate was derived by a revision of the discussion by Parks and Huffman[13] of the equilibria between methyl alcohol, hydrogen, and methyl formate and between carbon monoxide, methyl alcohol, and methyl formate, the modern value being used (Table 1) for the free energy of formation of gaseous methyl alcohol at 25°C. For the heat of formation of methyl formate, the heats of combustion measured by Roth and Banse[128] have been utilised; they are probably more accurate than the very old measurements used in a previous compilation.[17] The entropy of ethyl acetate was measured by Parks, Huffman, and Barmore,[42] but no reliable value for the heat of formation is available, old sources[14,102a,129] yielding results differing by 2 kcal./mole. A study[130] of the equilibrium between ethyl acetate, hydrogen, and ethyl alcohol at two temperatures (181° and 201·5°C) gave for the ester the listed values for the gaseous state, but these are not in good agreement with those which can be derived from the liquid-state values and heat of vaporisation and vapour-pressure data cited by the authors.

The heats of formation of numerous fatty acid esters are available from the work of Schjånberg,[102] and the values for the liquid substances, corrected to modern units at 25°C, are listed in Table 10. Values for the heats of vaporisation, partly from old work,[131] were also given by Schjånberg. Also included in Table 10 are revised values for esters of oleic and elaidic acid from measurements by Keffler.[132] Other recent measurements of the heats of combustion of esters are as follows: dimethyl tartrate and dimethoxysuccinate,[122] α- and β-naphthyl acetates and β-naphthyl benzoate,[55] the four ethyl pentynoates,[102d] and methyl α-t-butylacrylate and α-t-butylpropionate.[132a]

(*g*) *Peroxides and Miscellaneous Compounds.*—Heats of combustion of peroxides are inevitably difficult to measure accurately; the available

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[128] Roth and Banse, quoted in Landolt-Börnstein, II Eng. Bd., 1931, p. 1644.
[129] Berenger-Calvet, *J. Chim. phys.*, 1927, **24**, 325.
[130] Vredensky, Ivannikov, and Nekrasova, *Zhur. obshchei Khim.*, 1949, **19**, 1094
[131] Brown, *J.*, 1903, 987.
[132] Keffler, *J. Phys. Chem.*, 1937, **41**, 715
[132a] Crawford and Swift, *J.*, 1952, 7220.

TABLE 10. *Heats of formation* ($-\Delta H_f^\circ$) *of liquid esters* R′·CO$_2$R″ *at* 25°C (*kcal./mole*)

R′ …… R″	Me	Et	Pr^n	Bu^n	C_2H_5^{a}	C_4H_7^{b}	C_4H_7^{c}	C_4H_7^{d}	$C_{17}H_{33}$^{e}	$C_{17}H_{33}$^{f}
Me	106·2	111·6	117·2	—	90·6	—	—	—	173·7	175·3
Et	113·9	119·9	126·3	130·8	99·1	102·0	103·2	105·4	184·7	184·1
Pr^n	119·3	124·9	132·1	137·3	104·6	105·4	107·1	109·5	188·5	190·0
Pr^i	122·0	128·2	133·9	140·0	107·8	109·2	111·5	113·9	—	—
Bu^n	125·5	130·1	138·1	145·1	110·2	113·8	114·3	116·3	194·3	196·2
Bu^i	127·5	133·7	139·8	147·2	112·7	114·8	116·8	119·2	—	—
Bu^s	—	—	136·0	148·3	112·9	116·8	118·2	120·1	—	—
C_5H_{11}^{n}	—	—	—	—	—	—	—	—	—	202·4
C_5H_{11}^{i}	133·6	139·0	146·0	—	117·6	—	—	—	—	—

(*a*) Me·CH=CH; (*b*) CH$_2$=CH·CH$_2$·CH$_2$; (*c*) Me·CH=CH·CH$_2$; (*d*) Me·CH$_2$·CH=CH; (*e*) *cis*-Me·[CH$_2$]$_7$·CH=CH·[CH$_2$]$_7$; (*f*) *trans*-Me·[CH$_2$]$_7$·CH=CH·[CH$_2$]$_7$.

TABLE 11. *Heats of formation of liquid peroxides and hydroperoxides* (*kcal./mole*)

	$-\Delta H_f^\circ$	Ref.		$-\Delta H_f^\circ$	Ref.
Ethyl peroxide	55·6	133	Ethyl hydroperoxide	58 ± 12	134
Propyl peroxide	76 ± 15	134	t-Butyl peroxide	94·0	136
t-Butyl hydroperoxide	63·8 ± 0·3	137	Acetyl peroxide	127·9 ± 2·4	135
Propionyl peroxide	148·2 ± 1·6	135	Butyryl peroxide	161·0 ± 1·1	135
Benzoyl peroxide	93·5	120	Cinnamoyl peroxide	84·7	120
o-Toluoyl peroxide	119·4	120	Decalin hydroperoxide	83·2	120
p-Toluoyl peroxide	107·7	120	Tetralin hydroperoxide	44·6	120

heats of formation so obtained[133–137] are summarised in Table 11. For ethyl peroxide the value obtained by Zihlman is more reliable than the older value[134] but these old values are the only ones available for ethyl and propyl hydroperoxides.

The quinol-*p*-benzoquinone system was studied by Pilcher and Sutton[48] who give the following values for the solid substances at 25°C (kcal./mole and cal./deg./mole):

$$Q \quad -\Delta H_f^\circ = 44{\cdot}65 \pm 0{\cdot}17;\ S^\circ = 38{\cdot}55;\ -\Delta G_f^\circ = 20{\cdot}49$$
$$QH_2 \quad -\Delta H_f^\circ = 87{\cdot}51 \pm 0{\cdot}28;\ S^\circ = 32{\cdot}77;\ -\Delta G_f^\circ = 52{\cdot}32$$

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[133] Zihlman, quoted by Rabbert and Laidler, *J. Chem. Phys.*, 1952, **20**, 574.

[134] (*a*) Stathis and Egerton, *Trans. Faraday Soc.*, 1940, **36**, 606; (*b*) Harris, *Proc. Roy. Soc.*, 1939, *A*, **173**, 126.

[135] Jaffe, Prosen, and Szwarc, *J. Chem. Phys.*, 1957, **27**, 416.

[136] Rayley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88.

[137] Bell, Dickley, Rayley, Rust, and Vaughan, *Ind. Eng. Chem.*, 1949, **41**, 2597.

and the thermodynamic properties for the oxidation–reduction process in the solid, solution, and gaseous states. Rather different values for the heats of combustion were reported by Magnus[138] who also gives values for a number of other quinones.

Heats of combustion have been reported for paraldehyde,[141] and for the condensation product of ethylene glycol with acetone and of *cis*-cyclopentane-1,2-diol with acetone.[52b]

Regularities and Estimation Methods

Regularities in the thermodynamic data for related compounds and homologous series form the basis of the numerous methods of estimation that have been proposed. Since the previous review,[10b] the important work of Benson and Buss[142] has provided a unification of procedures involving additivity of atomic values, bond values, and group values. However, the paucity of reliable information on oxygen compounds still prevents the establishment of accurate methods for the estimation of their thermodynamic properties. A survey of the simpler and less accurate methods for estimating heats of combustion should be noted.[143]

Several empirical correlations between various groups of compounds were pointed out by Parks and Huffman,[13] and further observations made in the light of more recent data.[43] Similarly, a constancy was claimed for the difference between the heats of combustion of furan and benzene, and of a number of their derivatives with the same substituent;[58] whilst Badoche[73] reported regularities in the heats of combustion of benzene derivatives on substitution with methyl and methoxyl groups. More accurate work reveals that such observations are only first approximations, however. Empirical equations, involving structural parameters only, have been developed to express the isomeric variation of the thermodynamic properties of hydrocarbons and applied to some physical properties of the saturated aliphatic alcohols.[144]

An alternative approach makes use of comparisons with the comprehensive and accurate information available for the hydrocarbons. For example, increments in the entropies[43] and heat capacities[39] of normal alcohols have been compared with the corresponding increments for the paraffins. It is now well established that the increment for the methylene group for the normal paraffins, mono-olefins, normal alkylbenzenes, normal alkylcyclopentanes, and normal alkylcyclohexanes is —4·926 kcal./mole in the heat of formation, or —157·44 ± 0·05 kcal./mole in the

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[138] Magnus, *Z. phys. Chem. (Frankfurt)*, 1956, **9**, 141.
[139] Hubbard, Katz, Guthrie, and Waddington, *J. Amer. Chem. Soc.*, 1952, **74**, 4456.
[140] Tonaka and Watase, *Technol. Reports Osaka Univ.*, 1956, **6**, 367.
[141] (*a*) Cass, Springall, and White, *Chem. and Ind.*, 1955, 387; (*b*) Delépine and Badoche, *Compt. rend.*, 1942, **214**, 777.
[142] Benson and Buss, *J. Chem. Phys.*, 1958, **29**, 546.
[143] Handrick, *Ind. Eng. Chem.*, 1956, **48**, 1366.
[144] Greenshields and Rossini, *J. Phys. Chem.*, 1958, **62**, 271.

heat of combustion, in the gaseous state, provided the number of carbon atoms in the chain is greater than five.[10b] For the normal paraffins the increment per methylene group is 1·18 kcal./mole in the heat of vaporisation at 25°c. So the increment becomes −156·26 ± 0·05 kcal./mole in the heat of combustion for the liquid state. It is noteworthy that a very similar increment is established for the higher members of a number of homologous series of oxygen compounds:

	Increments per methylene group in $-\Delta H_c^\circ$ (l, 25°c) (kcal./mole)
Normal alcohols[28]	156·26
Fatty acids (C_5–C_9)[104]	156·26 ± 0·17
Methyl esters of fatty acids (C_5–C_{15})[104]	156·26 ± 0·10
Dimethyl esters of oxalic acid series (20°c)[145]	156·3
Esters of oleic and elaidic acid	156·2
Esters of fatty acids (C_2–C_4)	156·3 ± 1·0

The identity of the increments for the higher fatty acids and their methyl esters is particularly important in showing that the degree of association of all members of the series, in the liquid state at 25°c, is the same. For the solid state the increment is more variable, as would be expected: thus, for the alkylmalonic acids it is 155·2 ± 0·4 kcal./mole (data[115] revised to basis of 25°c), whilst for the oxalic acid series[111] there is an alternation between the values 158·3 ± 0·2 and 155·1 ± 0·4 kcal./mole.

An expression relating the heat of combustion of alcohols to the number of carbon atoms present has been derived by Maslov.[146a] The increment is given as −156·246 kcal./mole but the values for individual alcohols are all numerically higher than those recently quoted.[28] The same author has also given[146b] expressions for the vapour heat capacities of a number of oxygen compounds which can be written as

$$C_p^\circ = a + bT + cT^2 + dT^3 + nC_2(T) + \mathrm{f}(n, m)\exp(-0{\cdot}007T)$$

where n and m are the total number of carbon and hydrogen atoms, respectively, and $C_2(T)$ is the increment per methylene group given by

$$C_2(T) = 0{\cdot}1203 + 21{\cdot}3 \times 10^{-3}T - 116{\cdot}33 \times 10^{-7}T^2 + 2{\cdot}502 \times 10^{-9}T^3$$

The values for the constants a, b, c, and d, and for the function $\mathrm{f}(n,m)$ were given as:

	a	10^3b	10^7c	10^9d	$\mathrm{f}(n,m)$
Alcohols	−6·602	17·8	139·85	−12·51	$242{\cdot}2m$
Aldehydes	−6·882	5·98	211·88	−15·01	$215(n^2+m)$
Acids	−5·692	18·2	122·48	−15·012	$127{\cdot}56\,n^{-1}m^{-1}$
Esters	−14·54	24·2	275·8	−25·02	$14(10-z)$

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[145] Verkade, Coops, and Hartman, *Rec. Trav. chim.*, 1926, **45**, 585.

[146] Maslov, (*a*) *Zhur. fiz. Khim.*, 1955, **29**, 718, (*b*) *Zhur. priklad. Khim.*, 1957, **30**, 736.

In the last expression for f(n,m), z is the number of methylene groups. According to Maslov, the differences between the calculated and observed values for the first three members of these series may be about 7%, but decrease rapidly with increase of n; it is not clear, however, on what experimental data these statements are based.

A partial application of the method of group equations to organic oxygen compounds was made by Van Krevelen and Chermin[147] but it can be noted that some of the results are in less satisfactory agreement with more recent experimental data, notably for acetone. From the appropriate group equations it would be expected that the differences in the heats of formation of the pairs (butane–isobutane), (pentane–isopentane), (butane-1-thiol–butane-2-thiol), (propane-1-thiol–propane-2-thiol) and (propyl alcohol–isopropyl alcohol) would be equal. For the first four pairs the values[148] are 2·00 ± 0·10 kcal./mole, but for (propyl alcohol–isopropyl alcohol) and (butyl alcohol–s-butyl alcohol) are 3·71 and 3·2 kcal./mole, respectively, the data of Table 1 being used. This increase, which has been related to the electronegativity of the substituent,[148] indicates an important limitation in the application of the method of group equations.

Lovering and Laidler[149] have recently given a scheme of thermochemical bond energies for organic oxygen compounds: bond contributions to heats of atomisation, formation, and combustion were obtained for the gas at 25°c. The contributions to the heats of formation for C–C and for primary, secondary, and tertiary C–H bonds, −0·45, 3·45, 2·63, and 1·78 kcal./mole, respectively, were taken as those previously found for hydrocarbons. (These are equivalent to an increment per methylene group in the heat of combustion of 157·56 kcal./mole for the gas, or 156·40 kcal./mole for the liquid.) It was assumed that the attachment of an oxygen atom to carbon affects the bond strength of hydrogen bound to that carbon atom. Such C–H bonds can be primary, secondary, or tertiary and make the following contributions to the heat of formation: 1·22, 0·40, and −0·48 kcal./mole, respectively. The C–O bond is assumed to have no effect on other C–H bonds; its own contribution to the heat of formation is 18·48 kcal./mole, that of the O–H bond is 28·12 kcal./mole, and that of the O–O bond in peroxides, −11·44 kcal./mole. These values reproduce the heats of formation of the compounds from which they were derived to 1 kcal./mole or better, but it may be noted that the "observed" values utilised differ in some cases from those tabulated here.

Applications of Thermochemical Data

The most obvious practical application of thermodynamic data is to the calculation of the equilibrium constants for known or hypothetical

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[147] Van Krevelen and Chermin, *Chem. Eng. Sci.*, 1951, **1**, 66.
[148] Hubbard and Waddington, *Rec. Trav. chim.*, 1954, **73**, 910.
[149] Lovering and Laidler, *Canad. J. Chem.*, 1960, **38**, 2367.

reactions, and the estimation of the feasibility of a given process. An example is the calculation by Mazurek[150] of the equilibrium constants for numerous reactions involving ethyl alcohol, acetic acid, and ethyl acetate, and for the formation of acetone from these compounds, leading to the conclusion that the ketonisation of ethyl alcohol at 250—450° is essentially irreversible. Two other important applications are the calculation of bond energy terms, and the determination of barriers to free internal rotation.

Bond Energy Terms.—Prediction of heats of combustion and formation can be made by using a self-consistent scheme of thermochemical bond energies. The latter quantities are also important in obtaining values for the resonance energy of substances by comparing the observed heat of formation with that computed for the individual valency bond structures. Springall and his co-workers have recently used such an approach in studying a number of ketones[91] and cyclic ethers,[74] obtaining quantitative expression for the molecular stabilisation or strain.

The significance of the concept of bond energy has been reviewed by Cottrell[3] who lists values for several bond-energy terms; these may be revised slightly in terms of the data presented in this paper. For the heats of the gaseous atoms from the elements in their standard states at 25°c we use the values[3]: C (graphite), 170·9; $\frac{1}{2}H_2$(g), 52·09; $\frac{1}{2}O_2$ (g), 59·54 kcal./mole. The value of the bond energy term *E*(O–H) deduced from these values and the heat of formation of gaseous water[17] at 25°c (−57·80 kcal./mole) is then 110·76 kcal./mole. Following Coates and Sutton,[151] the values for *E*(C–C) and *E*(C–H) are obtained from the constant increment in the heat of formation of the higher paraffins, and are 82·60 kcal./mole and 98·70 kcal./mole respectively. Using the new values[28] for the heats of formation of the gaseous alcohols we now find *E*(C–O)is 80·01 in methyl alcohol, 83·25 in ethyl alcohol, 83·95 in propyl alcohol, and thereafter constant at 84·1 kcal./mole up to decyl alcohol. In some acetals the value of *E*(C–O) is slightly higher, being 86·1 in formaldehyde dimethyl acetal, 86·5 in formaldehyde diethyl acetal, and 86·0 in acetaldehyde dimethyl acetal, but the heats of combustion[14,19] are rather unreliable. It is likewise difficult to establish accurate values for *E*(C–O) in ethers owing to the absence of reliable values for their heats of combustion. For dimethyl ether, ethyl methyl ether, and diethyl ether *E*(C–O) is about 84 kcal./mole [actually, 84·8 in diethyl ether, the new value (p. 135) being used for the heat of formation]. In tetrahydrofuran we find *E*(C–O) = 84·1 kcal./mole from the heat of combustion obtained by Springall[74b] or 85·2 kcal./mole from the value given by Skuratov.[75] Cottrell has pointed out that *E*(C=O) is more variable, being 164·9 kcal./mole in formaldehyde, 172 kcal./mole in acetaldehyde, 179·1 in acetone, and very slightly higher in some other ketones.[91] From the heat of combustion of diethyl

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[150] Mazurek, *Zhur. obschei Khim.*, 1952, **22**, 1324.

[151] Coates and Sutton, *J.*, 1948, 1187.

peroxide[133] E(O–O) is found to be 50·9 kcal./mole, E(C–O) being assumed to be 84·1 kcal./mole in this compound.

A rather different approach is adopted by Allen[152] in recent work since the carbon–hydrogen bond energy has been taken as 99·29 kcal./mole and assumed constant throughout a range of hydrocarbons. The same author has also given a method for including the effects of next-nearest neighbour interactions. Mention must also be made of the work of Glockler[153] who has established empirical relations between bond energies and bond lengths and extended this to carbon–oxygen bonds.

Barrier Heights to Internal Rotation.—It is well known that one of the oldest and most successful methods for determining barrier heights to internal rotation is by a comparison of calculated and observed heat capacities and entropies, and the results obtained by this method have been reviewed.[10b,154] In recent years microwave spectroscopy has provided two new methods,[155] one of which, the frequency method, is capable of giving results which are usually more accurate than those obtained from thermodynamics, whilst the other, the intensity method, gives results of accuracy comparable to those obtained from thermodynamics. The thermodynamic procedure involves the difference between two relatively large quantities and so it is very sensitive to errors in both of them—that is, in the vibrational assignment and in the measured quantities. It is important,

TABLE 12. *Barrier heights to internal rotation (cal./mole) obtained by thermodynamic and microwave methods*

	Thermodynamic	Ref.	Microwave	Ref.
Ethane	2875 ± 125	154*a*	2875 ± 125	156
Propane	3400	154*a*	—	
Isobutane	3620	154*a*	3900	157
Neopentane	4300	154*a*	—	
Propene	1950	154*a*	1978 ± 17	158
Methyl alcohol	1070	24	1070	24
Ethyl alcohol	3300, 800	27	—	
Phenol	—		3140	50
Dimethyl ether	2700	154*b*	2720	159
Propylene oxide	—		2560 ± 70	160
Acetaldehyde	1000	79*b*	1150 ± 30; 1103 ± 60	161
Acetone	1000	84	760	162
Acetic acid	2500 ± 700	98	483	163
Methyl formate	—		1190 ± 40	164

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[152] Allen, *J. Chem. Phys.*, 1959, **31**, 1039.

[153] Glockler, *J. Phys. Chem.*, 1958, **62**, 1049, and references therein.

[154] (*a*) Pitzer, *Discuss. Faraday Soc.*, 1951, **10**, 66; (*b*) Aston, *ibid.*, p. 73.

[155] (*a*) Lin and Swalen, *Rev. Mod. Phys.*, 1959, **31**, 841; (*b*) Wilson, "Advances in Chemical Physics," Interscience Publishers Inc., New York, 1959, Vol. II, p. 367; (*c*) *Proc. Nat. Acad., Sci. U.S.A.*, 1957, **43**, 816; (*d*) Pauling, *ibid.*, 1958, **44**, 211.

therefore, to compare the final values obtained and these[156-164] are summarised in Table 12, for some hydrocarbons and all organic oxygen compounds for which data are available.

For methyl alcohol the agreement is exact since the results of several detailed studies by the microwave method were used to obtain calculated thermodynamic functions in agreement with observation.[45] On the other hand, the values for acetic acid are considerably different and further investigation is required.

[156] Lide, *J. Chem. Phys.*, 1958, **29**, 1426.

[157] Lide and Mann, *J. Chem. Phys.*, 1958, **28**, 914.

[158] Lide and Mann, *J. Chem. Phys.*, 1957, **27**, 868.

[159] Kasai and Myers, *J. Chem. Phys.*, 1959, **30**, 1096.

[160] Herschbach and Swalen, *J. Chem. Phys.*, 1958, **29**, 761.

[161] Kilb, Lin, and Wilson, *J. Chem. Phys.*, 1957, **26**, 1695; Verdier and Wilson, *ibid.*, 1958, **29**, 340.

[162] Swalen and Costain, *J. Chem. Phys.*, 1959, **31**, 1562.

[163] Tabor, *J. Chem. Phys.*, 1957, **27**, 974.

[164] Curl, *J. Chem. Phys.*, 1959, **30**, 1529.