An Estimation of the Thermodynamic Properties of Organic Compounds in the Ideal Gas State. I. Acyclic Compounds and Cyclic Compounds with a Ring of Cyclopentane, Cyclohexane, Benzene, or Naphthalene**

Yukio Yoneda
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received October 6, 1978)

A new group-contribution method for estimating the standard enthalpy of formation, the standard absolute entropy, and the standard molar heat of organic compounds in the ideal gas state is proposed with tables of the contribution values. This method (the ABWY method) is a completely revised and enlarged version of the Anderson, Bayer, and Watson method, and it can be used with regard to a more diverse variety of compounds with a higher reliability. The neighboring effects in group-contribution methods are introduced to obtain better estimated values. The substitutions of various functional groups on aromatic rings are discriminated. Type-number corrections of the functional groups and multiple-substitution effects of halogens are also introduced; thus even heterofunctional compounds can be processed. A new concept, the quality of contribution values, is proposed to designate the qualitative reliability of the estimated physical properties. The manual procedures and tables of contribution values are given for estimating the thermodynamic properties of the compounds, as mentioned in the title, composed of C, H, O, halogens, S, and N. This method was critically compared with the Benson method in versatility and reliability.

In spite of the tremendous efforts of many scientists, the *observed* values of the fundamental properties of organic compounds, such as the heat of formation in the ideal gas state, are unexpectedly scarce; only around 1600 are known among several million compounds. As for the observed data of IR, already nearly two hundred thousand spectra have been collected by chemists. If we take into account the difficulty in the measurement of thermochemical and thermodynamic data as compared to that of the IR spectra, *e.g.*, the necessary purity of the specimens and the skill in measurement, one can hardly expect rapid increase of the former data within the next few years.

Thus, many investigators have published various methods of estimating the thermodynamic properties of organic compounds in the ideal gas state.1–2) All of the estimation methods employ the principle of the group contribution; the target molecules are decomposed into atom groups, or functional groups, and the sum of the contributions of these groups makes the estimated values.

Among the group-contribution methods for estimating the standard enthalpy of formation, the standard absolute entropy, and the standard molar heat, the Anderson, Bayer, and Watson method (the ABW method)3) and the Benson method4) have been rated as two of the best.2) The present author has already presented an extended method (the ABWY method)5) modified from the ABW method. In this paper, a further improved version of the ABWY method and updated tables of contribution values will be reported. The functional groups and correlations due to multiple bonds were much diversified in this version; the concept of quality, or reliability, of the contribution values was also introduced.

The present ABWY method was originally intended to be implemented in computer program packages, EMPRIC5) and EROICA,6) the outline of which has been published earlier. These programs permit the CHEMO inputs, *i.e.*, the linear notations of rational formulas also proposed by the present author,5,6) to accept information on organic compounds. The contribution values were statistically selected from the observed properties with the aid of the method of the least squares with a computer program, THEDES.

In this paper the method is presented for estimating acyclic compounds and cyclic compounds that have only one of four ring compounds, cyclopentane, cyclohexane, benzene and naphthalene, both composed of C, H, O, halogens, N, and S. Even the *heterofunctional* compounds, *i.e.*, compounds with plural kinds of functional groups, can be processed, not to mention the *monofunctional* or the *homofunctional* ones. The estimation method for complex compounds, excluded in this report, will be published in forthcoming papers.

This group-contribution method may be applicable in principle even to properties other than those in the ideal gas state if the properties can be so ingeneously converted that the linear additivity holds in them. The methods of estimating the critical properties, the vapor pressure, the heat of vaporization, and the normal boiling point, as well as the thermodynamic properties in the liquid phase, will also be reported in the forthcoming papers.

Theoretical

Since the thermodynamic properties covered in this paper are those of *ideal gas*, intermolecular forces can play no part in their estimation. Also, by the same reasoning, the law of corresponding states, used so widely in the estimation of other properties such as vapor pressure, is inapplicable. All methods of estimating enthalpy, entropy, and molar heat involve some form of group-contribution method based on the structure of the molecule.4)

Benson4) and Benson and Buss7) pointed out a hierarchy of such methods, in the order of the additivi-

---

** CHEMOGRAM, a Computer Program Package for Chemical Logic, Part 3.

ties of (i) atom properties, (ii) bond properties, and (iii) group properties. The present author has described the hierarchy in another way.[5] The most successful method assigns the contribution to common groups, for example, $-CH_3$, $-OH$, or $-COO-$; by simple additivity, one can then estimate the ideal-gas properties from tables of the group-contribution values.

Neighboring Effects in Estimation. Allowance is made at least for the next-nearest neighbors to this group in order to proceed to a more complicated and usually more accurate method. In principle, there is no limit to the extension of the neighborhood-environmental concept, although the effect of neighboring groups separated by more than one atom usually becomes so small as to be insignificant. Some exceptions would be the effects of the *cis-trans* isomerism of olefin and the positional isomerism of polysubstituted ring compounds, and the influence of aromaticity; these effects are due to interaction between groups separated by two or more atoms.

Hence, the following classification and nomenclature of neighboring effects are given:

(1) Nearest-neighboring effect: effect from directly bonded atoms.

(2) Geminal effect: effect from atoms separated by one atom.

(3) Vicinal effect: effect from atoms separated by two atoms.

(4) Global effect: effect from atoms separated by more than two atoms.

Examples of these hierarchial effects will be given later.

Definition of Groups. In the ABWY method, a *group* is defined as follows:

(1) Base groups, *i.e.*, methane and ring compounds such as benzene, cyclohexane or naphthalene. Exceptions are the methyl radical, cation, and anion.

(2) Functional groups including $CH_n (n=0-3)$, but excluding H(hydrogen atom). Functional groups usually consist of an atom or an ensemble of atoms. Even when a complicated functional group could be decomposed into simpler or smaller functional groups, the original one should be adopted as a group when its contribution value is available, because complex groups include neighboring effects of a higher order; for example, the chloroformyl group, $-COCl$, should be adopted instead of carbonyl and chlorine. The only two exceptions to this rule are the formyl group, or aldehyde, $-CHO$, and the carbonyl group, $-CO-$, which should be decomposed into carbon and the oxo group, $=O$, as a heritage from the ABW method. Thus, the ligancy of groups may be from one to four, in contrast to two or more in the case of the Benson method.[4]

Linear Additivity of Thermodynamic Properties. The thermodynamic properties[7a] of organic compounds in the ideal gas state can be empirically represented as the sum of group contributions by virtue of the absence of any intermolecular interaction:

$$\Delta H^\circ_{f,298.15}(g)/\text{kcal mol}^{-1} = \sum_j n_{ij}\Delta(\Delta H)_j \tag{1}$$

$$S^\circ_{298.15}(g)/\text{cal mol}^{-1}\,\text{K}^{-1} = \sum_j n_{ij}\Delta S_j \tag{2}$$

$$C_p^\circ(g,T)/\text{cal mol}^{-1}\,\text{K}^{-1} = a + 10^{-3}bT + 10^{-6}cT^2 \tag{3}$$

$$a = \sum_j n_{ij}\Delta a_j,\ b = \sum_j n_{ij}\Delta b_j,\ \text{and}\ c = \sum_j n_{ij}\Delta c_j \tag{4}$$

where $\Delta(\Delta H)_j$, ΔS_j and Δa_j, Δb_j, and Δc_j are the group-contribution values of the j-th group for the standard enthalpy of formation, the standard absolute entropy, and their coefficients of the three-term molar heat equation respectively, where n_{ij} is the contribution count of the j-th contribution in the i-th compound, and where T is temperature in K.

Thermodynamic Properties of Hydrocarbons. In the ABMY method, molecules with hetero atoms are processed by *replacing* CH_n groups in the chain structure of a parent hydrocarbon with functional groups. Hence, the first step is the estimation of the properties of saturated hydrocarbon skeletons. Each compound is considered to be composed of a base group, *i.e.*, methane, or a cyclic compound, which is modified by the *substitution* of the other groups for the atoms composing it. For example, all paraffinic hydrocarbons are considered to be derived from methane by the successive substitution of CH_3 groups for hydrogen atoms. Similarly, any benzene derivatives are regarded as derived from a base group, benzene.

Primary Methyl Substitution: The contributions resulting from the primary substitution of a methyl group for a hydrogen atom in any one of the base groups are the specified ones for the groups concerned. In the cases of ring compounds as base groups, successive substitutions for the different hydrogen atoms on the ring involve different contributions depending on the number and position owing to geminal, vicinal, or global effects.

Secondary Methyl Substitution: A secondary methyl substitution is the substitution of a methyl group with a hydrogen in the methyl group derived by the primary substitution or in recursively substituted methyl groups. Contributions from the secondary substitution depend empirically on the types of both the nearest-neighboring atom and the geminal atoms. The carbon-atom types are defined, on the basis of the number of non-hydrogen atoms attached, as follows:

Type	
1	$-CH_3$
2	$-\overset{\vert}{C}H_2$
3	$-\overset{\vert}{\underset{\vert}{C}}H$
4	$-\overset{\vert}{\underset{\vert}{C}}-$
9	C atom in aromatic rings.

Branched hydrocarbons are usually more stable than straight-chain isomers, except for highly branched ones, which suffer from steric hindrance. Hence, the contributions of the secondary substitutions are naturally classified according to A, the type number of the carbon atom on which the substitution is made (the nearest-neighboring effect), and B, the highest type number among adjacent atoms (the geminal effect). The type number 9 of an aromatic ring indicates the strongest geminal effect among them. In the present estimation method, an aromatic ring is limited to a benzene ring or one of the benzene rings in fused-ring compounds.

Multiple Bonds and Corrections due to Their Context: After the properties of saturated-hydrocarbon chain-structure are estimated, some of the single bonds may be replaced with multiple bonds, if any. Contributions for this replacement are classified according to the type numbers of the carbon atoms connected by the multiple bonds. Corrections due to conjugated multiple bonds, conjugation with an aromatic ring, and cumulative double bonds may be added.

Replacement of CH_n Groups with Functional Groups. The implementation of functional groups are made by the *replacement* of CH_n groups with functional groups; three kinds of contribution values, *i.e.*, the *fundamental*, *type-number correction*, and *multiple-substitution correction*, will be described below.

Fundamental Contribution : When one of the CH_n groups is replaced, a fundamental contribution is added. Table 1 shows examples of fundamental contributions, where the global effect of the aromaticity is significant. Therefore, the discriminated values must be given to groups directly connected to aromatic rings. The divalent or trivalent functional groups, such as –O–, –NH–, –N<, or –COO–, have different values from those of the monovalent parent groups, like –OH, $-NH_2$, or –COOH.

TABLE 1. GLOBAL EFFECT OF AROMATIC RING ON FUNDAMENTAL CONTRIBUTION VALUES OF FUNCTIONAL GROUPS.

Replacement of CH_3 with functional group	Change by replacement[a]	
	$\Delta H^\circ_{f,298.15}$	$S^\circ_{298.15}$
	kcal mol^{-1}	cal mol^{-1} K^{-1}
$CH_3\text{-}CH_3 \rightarrow CH_3\text{-}NH_2$	14.74	3.13
$C_6H_5\text{-}CH_3 \rightarrow C_6H_5\text{-}NH_2$	8.81	0.36
$CH_3\text{-}CH_3 \rightarrow CH_3\text{-}OH$	−27.84	2.44
$C_6H_5\text{-}CH_3 \rightarrow C_6H_5\text{-}OH$	−34.98	−1.21

a) 1 cal=4.184 J. Data from SWS.[8]

Type-number Correction for Functional Groups : The geminal effect for functional groups generally may be enhanced by the superconjugation between unshared electrons in functional groups and pseudo-π-orbitals in geminal methyl groups. Table 2 shows the reasonings for the type-number correction. Columns 3 and 6 give, respectively, the increases caused by the replacement in the enthalpy of formation and in entropy, both at the standard state. The fundamental contributions being estimated as −0.39 and 1.19 respectively (line 1), deviations solely due to the geminal effect are seen in Columns 4 and 7. On the other hand, t in Column 2, which is equal to (A-1), denotes the number of geminal methyl groups relative to the chloro group; therefore, the type-number corrections for enthalpy and entropy are derived to be −1.18 and 0.69 respectively, on the assumption that the geminal effect is simply additive regardless of the number of geminal atoms. Finally, Columns 5 and 8 show the calculated geminal effects, which are in good agreement with those observed.

Functional groups directly bonded to aromatic rings have no type-number corrections because these fundamental contributions already include the global effect. The groups directly bonded to non-aromatic rings, however, require the appropriate type-number corrections according to the type number of the methyl-substituted carbon atom in the ring; for example, the twofold corrections to chlorocyclohexane are necessary because the type number, A, of the carbon atom in the ring is three.

Multiple-substitution Correction for Functional Groups: The polar groups bonded to one carbon atom may interact with each other, probably because of electrostatic repulsion or steric hindrance. Therefore, the multiple-substitution correction may be added. Table 3 shows an example of this correction. The quantities in Columns 2, 4, and 7 are the same as the corresponding notations in Table 2. Columns 5 and 8 are the remainders of enthalpy and entropy respectively, after type-number correction by the use of t. The notation m in Column 3 implies the number of geminal Cl–C–Cl effects; its sum is ten. By the use of the averaged correction values of 5.04 and −1.66 derived from the totals in Columns 5 and 8 respectively, the values in Columns 6 and 9 are calculated; again, they are in good agreement with the observed values. The mixed substitutions such as F–C–Cl can be corrected similarly.

Preparation of Contribution Values

Sources of Observed Data. The newest observed values of the standard enthalpy of formation, the absolute entropy at 25 °C, and the molar heat at temperatures from 273 to 1000 K were selected from three major sources: SWS,[8] API,[9] and TRC;[10] the estimated, or correlated, values described very often in the sources were carefully excluded. The observed data thus selected (the molar heats were converted into three coefficients of Eq. 3) were stored in a database, the EROICA database,[6] together with their contribution counts, as prepared by a computer program rigorously following the estimation procedures to be described in the next chapter.

Besides these three sources, three other data sources, PRN[11], BCG,[12] and LBT1,[13] were utilized suplementarily in order to obtain the contribution values of functional groups which could not be retrieved from the former three. The PRN, which was recently published, complies the observed data of enthalpy reported up to early 1976, along with their uncertainties, but this is not yet implemented into the EROICA database. In BCG, Benson *et al.*[8] estimated the enthalpies of formation in the gaseous phase of a wide variety of compounds from those in the liquid phase (even in the solid phase in rare cases) by assuming the heat of evaporation.[14] These estimated values were adopted only when unavoidable. The data of molar heats at temperatures were adopted also from LBT1, which is also not implemented.

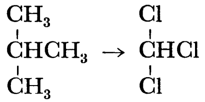
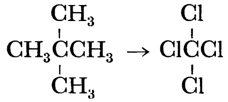
Preparation of Contribution Values from the Database. Most of the contribution values were prepared with the aid of a computer program, THEDES, written in FORTRAN IV, on a HITAC 8800/8700 of the University of Tokyo.

TABLE 2. TYPE-NUMBER CORRECTION FOR REPLACEMENT BY A CHLORO GROUP[a]

Line	(1) Replacement by a chloro group	(2) t[b]	(3) $\Delta(\Delta H^\circ_f)_{obsd}$[c]	(4) $\Delta(\Delta H)_{t,obsd}$	(5) $\Delta(\Delta H)_{t,calcd}$	(6) $\Delta(S^\circ)_{obsd}$[d]	(7) $\Delta(S)_{t,obsd}$	(8) $\Delta(S)_{t,calcd}$
1	$CH_3CH_3 \rightarrow CH_3Cl$	0	−0.39	—	—	1.19[e]	—	—
2	$CH_3CH_2CH_3 \rightarrow CH_3CH_2Cl$	1	−1.88	−1.49	−1.18	1.42	0.23	0.69
3	$CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2Cl$	1	−0.95	−0.56	−1.18	2.15	0.96	0.69
4	$CH_3CH(CH_3)CH_3 \rightarrow CH_3CH(CH_3)Cl$	2	−2.85	−2.46	−2.36	2.28	1.09	1.38
5	$CH_3C(CH_3)_2CH_3 \rightarrow CH_3C(CH_3)_2Cl$	3	−4.13	−3.74	−3.54	3.77	2.58	2.07
6	Total	7	—	−8.25	—	—	4.86	—
7	Mean	—	—	−1.18[e]	—	—	0.69[e]	—

a) 1 cal = 4.184 J. Data from SWS.[8] b) Number of geminal methyl groups. c) Unit in kcal mol^{-1}. d) Unit in cal mol^{-1} K^{-1}. e) These contribution values are different from those listed in Tables A5 and A6 in the Appendex, as the latter values were obtained by employing a wider variety of compounds.

TABLE 3. MULTIPLE SUBSTITUTION CORRECTION OF REPLACEMENT BY A CHLORO GROUP[a]

Line	(1) Replacement by a chloro group	(2) t	(3) m[b]	(4) $\Delta(\Delta H^\circ_f)_{obsd}$[c]	(5) $\Delta(\Delta H)_{m,obsd}$	(6) $\Delta(\Delta H)_{m,calcd}$	(7) $\Delta(S^\circ)_{obsd}$[d]	(8) $\Delta(S)_{m,obsd}$	(9) $\Delta(S)_{m,calcd}$
1	$CH_3CH_3 \rightarrow CH_3Cl$	0	0	−0.39	—	—	1.19	—	—
2	$CH_3CH_2CH_3 \rightarrow ClCH_2Cl$	1×2	1	2.02	4.77	5.04	0.08	−2.49	−1.66
3	 $\underset{CH_3}{\overset{CH_3}{CHCH_3}} \rightarrow \underset{Cl}{\overset{Cl}{CHCl}}$	2×3	3	7.95	15.42	15.12	−0.24	−5.57	−4.98
4	 $CH_3\underset{CH_3}{\overset{CH_3}{C}}CH_3 \rightarrow Cl\underset{Cl}{\overset{Cl}{C}}Cl$	3×4	6	15.67	30.22	30.24	0.89	−8.58	−9.96
5	Total	—	10	—	50.41	—	—	−16.64	—
6	Mean	—	—	—	5.04[e]	—	—	−1.66[e]	—

a) 1 cal = 4.184 J. Data from SWS.[8] b) Number of multiple substitutions. c) Unit in kcal mol^{-1}. d) Unit in cal mol^{-1} K^{-1}. e) See footnote e) in Table 2.

Contribution Values in Tables A1 through A4: Table A1 in the Appendix was prepared from the observed data themselves.

First, all of the paraffins except methane were retrieved from the database, and simultaneous equations of Eqs. 1, 2, and/or 4 were prepared with given contribution counts, n_{ij}'s, as independent variables and observed values minus that of methane as dependent variables; then the parameters, $\Delta(\Delta H)_j$, ΔS_j, and Δa_j, Δb_j, and Δc_j, were calculated by the method of the least squares. The primary substitution to methane in Table A2 and secondary substitutions, except for those related with aromatic rings in Table A3, were thus prepared.

Second, all of the olefins, diolefins and acetylenes were retrieved, and, after the elimination of contributions due to primary and secondary substitutions, multiple-bond contributions and their corrections in acyclic compounds were calculated by the same method; the results are given in Table A4.

Third, all of the hydrocarbon derivatives of cyclopentane and cyclohexane were retrieved, and primary substitutions to these two cycloalkane base groups were estimated; these results are shown in Table A3.

Finally, hydrocarbon derivatives of benzene and naphthalene were processed to estimate the primary substitutions to these two aromatic base groups (Table A2), the secondary substitutions related with the aromatic rings (Table A3), and the conjugation effects of multiple bonds with aromatic rings (Table 4).

Contribution Values in Tables A5 and A6: The fundamental values, type-number corrections, and multiple-substitution corrections were calculated at the same time with the aid of the same procedure, after eliminating the contributions already given in Tables Al through A4. In practice, compounds with hetero atoms derived from methane or the above-mentioned four cyclic base groups were subdivided, so that compounds containing a specified hetero atom besides carbon and hydrogen were processed to calculate the contribution values for functional groups containing the above-mentioned hetero atom. Following this sequence, the majority of the values in Tables A5 and A6 were statistically estimated.

Illustrations for Tables A1 through A8. In Table A2, several primary methyl substitutions are possible for ring compounds, while only one primary substitution is possible for methane. Each line corresponds to one methyl substitution on the base group; hence the primary methyl substitutions to form 1,2,3-trimethylbenzene, for example, are composed of the first primary (line 23) and two of the second primary substitutions, *i.e.*, 1,2 (line 24) and 1,2,3 (line 27). As for the cyclopentane and cyclohexane derivatives, *cis* or *trans* configuration must be discriminated in polymethyl derivatives, although averaged values without the *cis-trans* notation may be used for an equilibrium mixture. The values designated as *unspecified* may be used to form derivatives which require additive substitutions; 1,2,3,4-tetramethylbenzene may be estimated by adding the unspecified values (line 30) to those of 1,2,3-trimethylbenzene.

In Table A4, the unspecified 2=2 contribution implies that of an equilibrium mixture of *cis* and *trans* configurational isomers. An additional correction to multiple-bond arrangements may be present in lines 12 to 17.

The fundamental contributions of the functional group in Table A5 are arranged in the order of O, F, Cl, Br, I, S, and N. Two single bonds and one double bond should be discriminated; the values of –NH–, secondary amine, should not be used instead of those of =NH, imine. The contribution of functional groups directly connected to an aromatic ring (denoted by @) should be discriminated from the others. The observed values of *o*-difluorobenzene deviate slightly from the ordinarily estimated values because of the vicinal effect.

Corrections due to type numbers are given in lines with one functional-group notation in Table A6. Topologically non-symmetric multivalent groups such as –C(=O)–O– should have two kinds of type-number corrections, for which a percent mark(%) is given to indicate the direction of the bonds to be considered. Corrections due to multiple substitutions are given in lines where two functional-group notations are described.

In addition, Table A7 lists simple substances and Table A8 lists inorganic compounds and a few organic compounds whose properties can not be estimated by the present method, for the convenience of users in calculating the change of properties in reaction, *etc*.

Quality of Contribution Values. The reliability of contribution values given in these tables depends on the reliability and plentifulness of the observed thermochemical and thermodynamic data from which the contribution values are derived. Since the compounds in Table A1 are key compounds, the observed values are highly reliable. The contribution values in Tables A2 to A4, which are employed to form various hydrocarbons, are usually of a high quality because the reliable observed data are available for diversified kinds of hydrocarbons; some minor corrections for the context concerned with multiple bonds are, however, less reliable because of the scarcity of observed data of a high quality. The contribution values for some functional groups are less reliable, because often only one set of observed data even with a low accuracy is available. The assumed contribution values, which could not be otherwise determined because of the lack of observed data, may much diversify the range of organic compounds to be handled, but these assumed values are undoubtedly of less reliability.

Thus, the *quality* given in Table 4 was assigned to each of the contribution values in parentheses following values. The qualities in Table 4 range from 1 (the most reliable) to 6. The reliability of a physical property obtained as a sum of the contribution values may be designated by the worst quality of the contributions.

The uncertainty for quality 1 may be evaluated as 0.5 kcal/mol, except for fluorides and chlorides, for the enthalpies of formation judged from the standard deviations discussed in Results and Discussion, while that for quality 4 may be more than 1 kcal/mol; properties with quality 5 or quality 6 must be used at the

TABLE 4. QUALITY OF CONTRIBUTION VALUES

Quality	Remarks
1	Calculated values from reliable observed data
2	Approximated values correlated from very similar contributions
3	(Reserved for observed data)
4	Calculated values from less reliable observed data—in the present version, those from observed data rated 'C' in SWS[8)]
5	Assumed values by correlation with less reliability
6	Assumed values by decomposing functional groups into their fragments

user's risk.

Contribution Values Manually Selected. In Tables A1 through A6 of the Appendix, the values with quality 2 were determined manually, although those from the reliable data in PRN are rated 1; the procedures of estimation are given in the corresponding footnotes of the tables.

As for some primary methyl substitutions (Table A2), the contribution values were assumed from those of the relevant substitutions. The values of the relevant combination of type numbers were also used in place in the secondary methyl substitutions (Table A3). Properties in the gaseous phase were estimated from those in the liquid or even solid phases when the former was unavailable;[12)] these values were rated 5.

Fundamental Contribution Values for Functional Groups : It is surprising that no data are available for the entropy and the molar heat of any aromatic ether, a popular homolog, with which the chemical equilibria of its formation at temperatures may be calculated. The contribution values of aromatic ether (@O–) may be assumed by subtraction : Δ(@OH)+{Δ(–O–)−Δ(–OH)}, where the contributions in the formula stand for phenol, ether, and alcohol, whose values have already been calculated. Supposedly, the entropy and molar heat may be not so seriously affected by the bond to an aromatic ring as enthalpy,[15)] because the former is affected by the curvature of the potential surface, whereas the latter is determined by the bond energy itself. Hence, the application of this method to a fundamental contribution was restricted only for entropy and molar heat, although no data is available to verify the above discussion, even for the latter two properties. These methods may give less reliable values, so they were rated 5.

In the cases where the fundamental values of the functional groups could not be estimated by means of any method given above, some of them were assumed by decomposing a group into small fragments. An example is the entropy and molar heat for –COBr, which was decomposed as consisting of –C(=O)– and Br.[16)] Table 5 shows the effects of decomposing groups whose contribution values were obtained beforehand from observed data. As regards the entropy and molar heat, the estimation by decomposition may not give bad values, although the agreement between values for enthalpy is untolerably poor; hence, a few values only for the former two properties were estimated by this method, and they were rated 6.

Minor Corrections for Functional Groups : As for the minor corrections in Table A6, the subtraction method was employed even for enthalpy because of their small magnitude. In some cases, values were assumed from those of similar functional groups. One example is that the difference between the values for @COF and –COF is assumed to be equal to that between the values for corresponding COCl groups. Assumption that the type correction of %–COO– is equal to that of –COOH is another example. Some type correction values for the entropy and molar heat, which could not be correlated by these methods, were assumed to be zero because they are usually small; they were rated 5.

Sequence of Manual Operations in Estimation

The following features have been changed from the original ABW method : (1) base groups are limited to methane and ring compounds; (2) functional groups substituted to aromatic rings are discriminated from those substituted to non-aromatic fragments; (3) type corrections are given throughout functional groups; (4) multiple-substitution corrections are also given to some of the functional group; (5) corrections due to the context of multiple bonds are expanded, (6) the *quality* of estimated values is made available in order to make it possible to recognize their reliability, and (7) minor corrections due to the chain length as well as the enlargement of the cyclohexane ring are abolished.

Manual Operation. The suggested sequence of operations in estimating the properties of a complex compound is as follows :

Step 1: Select the base group, and determine its properties from Table A1. In an acyclic compound, yan one of the terminal atom groups may be selected

TABLE 5. EFFECTS OF DECOMPOSING FUNCTIONAL GROUPS INTO FRAGMENTS ON THEIR FUNDAMENTAL CONTRIBUTION VALUES

Functional group		Fundamental group-contribution values[a)]				
		$\Delta(\Delta H)$	ΔS	Δa	Δb	Δc
-COCl	from observed data	−38.06	12.89	5.41	−5.63	−0.58
	-CO- and -Cl	−32.58	17.07	5.19	−7.29	1.37
-NHNH$_2$	from observed data	40.64	11.76	—	—	—
	-NH- and NH$_2$	29.13	13.27	—	—	—

a) The units are the same as those given in Table A5.

as the base group. In the case of a cyclic compound, a ring compound should be selected as the base group.

Step 2: Make all the *primary substitutions* before starting the *secondary substitutions*, where *substitution* means an exchange of a hydrogen atom with a methyl group. In the case of methane, only one primary substitution is possible. With ring structures, one primary substitution (the *first* primary substitution) is possible for each hydrogen atom of the base group. If two or more primary substitutions (*second* primary substitutions) are to be made on a base ring, the two substitutions closest together should be made first. If more than one substitution is to be made on a specific carbon atom in the base ring, such additional substitutions are to be treated in the same way. The unspecified contributions may be assigned for substitutions other than those clearly indicated, Table A2 is used to evaluate the group contributions resulting from primary substitutions.

Step 3: Complete the carbon skeleton of the compound by making a series of secondary substitutions, and use Table A3 to obtain the values of group contributions for such substitutions. Each of the multivalent functional groups, *e.g.*, –COO– or $-N<$, should be regarded as a CH_n group of the carbon skeleton. In order to have the results conform with the procedures used in developing the tables, the following rules should be observed, although the deviations are usually small even if they are violated:

(a) The longest straight chain should be fully developed before any side chains are added.

(b) Side chains are added in the order of their length. However, if the carbon atom with the longest side chain is to have a second side chain, this second side chain should be added before additions are made to other carbon atoms of the straight chain.

Step 4: Make additional secondary methyl substitutions for monovalent functional groups. Allowance for such substitution is made from Table A3. For *multibonded* functional groups in Steps 3 and 4, *e.g.*, =O or =N–, *additional* secondary methyl substitutions should be made; *one* additional substitution for *double* bonds and *two* for *triple* bonds.

Step 5: Add multiple bonds and obtain from Table A4 the contributions resulting from such additions. If required, make the additional corrections indicated by Table A4 for correlations between bonds.

Step 6: Replace CH_n groups by the substitution groups listed in Table A5.

(a) First, add the *fundamental* contributions given in Table A5.

(b) Second, check the types of connecting atom groups, and add contributions for the *type-number correction* from Table A6. In counting the type, assume that all of the functional group(s) were replaced *beforehand.*

(c) Third, check the other substituting groups to the group to which the present group is connected (the geminal effect). Add contributions for *multiple-substitution corrections* from Table A6. Repetition from each substituent should be allowed.

Step 7: Find out the maximum of *quality* associated with the contribution values. This gives the user a measure of the reliability of the estimated values.

Examples of Estimation. Four examples will be illustrated in order to make clear the above-mentioned sequence of manual operations.

Example 1. Enthalpy, Entropy, and Molar Heat of 2-Methyl-1,3-butadiene (Isoprene): The replacement of two single bonds with two double bonds in 2-methylbutane makes this compound. Methane is selected as the base group (Step 1); then a hydrogen atom is substituted by a methyl group as the primary methyl substitution to make ethane (Step 2). The carbon skeleton is completed by the successive secondary substitutions, with consideration paid to the type numbers of the atoms concerned (Step 3). Finally the contribution values due to double bonds as well as the correction for the conjugated double bonds are added to make the given compound (Step 5). The numerals will be given below:

	$\Delta(\Delta H)$ kcal mol^{-1}	$\Delta(S)$ cal mol^{-1} K^{-1}
(1) Base group:		
Methane	−17.89(1)[a]	44.50(1)[a]
(2) Primary substitution:		
CH_3CH_3	−2.35(1)	10.35(1)
(3) Secondary substitutions:		
$CH_3CH_2CH_3$ (1,1)[b]	−5.04(1)	10.44(1)
$CH_3CH_2CH_2CH_3$ (1,2)	−4.92(1) (−30.20)[c]	9.29(1) (74.58)[c]
$CH_3CH(CH_3)CH_2CH_3$ (2,2)	−6.35(1)	6.53(1)
(5) Multiple bonds:		
1=3	27.94(1)	0.17(1)
1=2	30.15(1)	−1.43(1)
Conjugated double bonds	−3.66(1)	−4.06(1)
Total	17.88(1)	75.79(1)

where the superscripts a, b, and c indicate the quality, type numbers, and subtotals respectively. The observed values[8)] are 18.10 for $\Delta H^\circ_{f,298.15}$ and 75.44 for $S^\circ_{298.15}$, and the quality of the estimates is 1. The molar heats at 298 K and 1000 K were estimated similarly to be 25.43 cal mol^{-1} and 52.68 respectively, while the observed values[9)] are 25.00 and 52.90. The agreement among these observed and estimated values is surprisingly good in this case.

The group contributions by the Benson method are composed of $2\times[(C_d\text{-}(H)_2]+[C_d\text{-}(C_d)_2]+[C_d\text{-}(C_d)(H)]+[C\text{-}(C)(H)_3]$; this gives the estimate of enthalpy of 13.7 in the same unit.

Example 2. Enthalpy and Entropy of 2-Butanone: The replacement of two methyl groups with an oxo-(=O) group will make this compound. First, 2,2-dimethylbutane will be prepared by Steps 1 through 4; second, two methyl groups will be replaced by a substitution group with the twofold type-number corrections, because the 2-carbon atom *after* substitution is tertiary (Step 6).

	$\Delta(\Delta H)$ kcal mol^{-1}	$\Delta(S)$ cal mol^{-1} K^{-1}
(1-3) Methyl substitutions:		
$CH_3CH_2CH_2CH_3$	−30.20(1)	74.58(1)

(4) Additional substitutions for functional groups:		
$CH_3CH(CH_3)CH_2CH_3$ (2,2)	−6.35(1)	6.53(1)
$CH_3C(CH_3)_2CH_2CH_3$ (3,2)	−6.84(1)	4.30(1)
(6) Replacement by functional group:		
$CH_3COCH_2CH_3$		
Fundamental	−7.09(1)	−20.19(1)
Type number	−3.30(1) ×2	7.39(1) ×2
Total	−57.08(1)	80.00(1)

The observed values[9] are −56.97 and 80.81 respectively, whereas the Benson method gives a fairly good value of enthalpy of −56.56.

Example 3. Enthalpy and Entropy of Perfluoroethane: Since fluorine atoms are substituted to ethane by replacing a methyl group for each fluorine atom, the hydrocarbon molecule *before* replacement is 2,2,3,3-tetramethylbutane, as estimated in Steps 1 through 4. In Step 6, the fundamental contributions of fluorine to non-aromatic fragments are added six times at first. As for the type-number correction, threefold corrections for each fluorine atom are necessary because the 2- and 3-carbon atoms are quaternary; hence, altogether 18 corrections are added. Besides, the multiple-substitution corrections must be added six times, because each of the two trifluoromethyl groups has a threefold correction in it.

	$\Delta(\Delta H)$ kcal mol^{-1}	$\Delta(S)$ cal mol^{-1} K^{-1}
(1-4) Methyl substitutions:		
$CH_3C(CH_3)_2$-$C(CH_3)_2CH_3$	−53.99(1)	93.07(1)
(6) Functional groups:		
(a) Fundamental	−221.10(1) (−36.85×6)	−23.82(1) (−3.97×6)
(b) Type number	−26.46(1) (−1.47×3×6)	17.82(1) (0.99×3×6)
(c) Multiple substitution	−22.02(1) (−3.67×3×2)	−5.46(1) (−0.91×3×2)
Total	−323.57	81.61(1)

The agreement between the estimated and observed values,[8] −321.00 and 79.37, shall be rated as excellent in the case of rather large numerals. The estimate of enthalpy by the Benson method is −316.8.

Example 4. Enthalpy and Entropy of 1,2,3,4-Tetramethylbenzene: As a matter of course, benzene is selected as the base group (Step 1). The first- and second-primary substitutions will be processed by exactly following the descriptions in Step 2, as is shown below:

	$\Delta(\Delta H)$ kcal mol^{-1}	$\Delta(S)$ cal mol^{-1} K^{-1}
(1) Base group:		
Benzene	19.82(1)	64.34(1)
(2) Primary substitutions:		
(a) First primary	−8.48(1)	11.45(1)
(b) Second primary		
To make 1,2-	−6.64(1)	8.70(1)
To make 1,2,3-	−7.26(1)	10.24(1)
Unspecified (to make 1,2,3,4-)	−7.61(1)	4.94(1)
Total	−10.17(1)	99.67(1)

The agreement between the estimated and observed values,[9] −10.02 and 99.55, is again excellent. If one employs the second primary substitution to make 1,2,4- instead of the above one to make 1,2,3-, he may obtain the estimates of −10.19 and 99.85, which are slightly poorer values than the above ones, presumably because of less enhancement of the ortho effect among methyl groups. The contributions by the Benson method, composed of $2\times[C_B\text{-}(C)]+4\times[C_B\text{-}(H)]+4\times[C$-

TABLE 6. ERRORS IN THE ESTIMATION OF THERMODYNAMIC PROPERTIES

Line	Compound	$\Delta H^\circ_{f,298.15}$					$S^\circ_{298.15}$				
		N_d[a]	N_c[b]	N_s[c]	e[d]	σ[e]	N_d	N_c	N_s	e[d]	σ[e]
1	Alkanes	51	12	3	0.3	0.4	51	12	3	0.5	0.7
2	Alkenes and alkynes	90	13	3	0.4	0.6	75	13	2	0.5	0.8
3	Cycloalkanes	44	14	12	0.1	0.2	44	14	12	0.1	0.1
4	Aromatics	43	14	4	0.3	0.4	40	13	3	0.3	0.5
5	O[f]	101	34	6	0.9	1.4	49	19	7	1.2	2.0
6	F	30	8	0	2.9	3.5	99	14	1	1.6	2.1
7	Cl	37	5	0	2.2	2.6					
8	Br	21	4	1	0.8	1.1	30	8	0	1.7	2.2
9	I	13	4	1	0.5	0.7					
10	S	49	10	3	0.4	0.6	27	8	2	0.6	1.0
11	N	24	16	7	0.4	0.7	18	12	8	1.3	1.7
	Total/mean	503	134	40	0.8[g]	1.4[g]	433	113	38	0.9[g]	1.5[g]

a) Number of compounds employed in calculation. b) Number of contribution values calculated. c) Number of error$=\sum|\text{obsd}-\text{calcd}|/(N_d-N_s)$; kcal mol^{-1} for H, and percentage error for S and C_p. e) Standard deviation; f) For classification of compounds, see text. g) Mean.

(C)(H)$_3$]+3×[ortho correction], give −10.45.

Results and Discussion

In the evaluation of the estimation methods by the use of the correlation of the physical properties of organic compounds, it may be worthwhile to discuss the following four items.

Accuracy or Reliability of the Estimated Values. Table 6 shows the average errors and the standard deviations derived from the differences between the observed data and the calculated data by the use of contribution values; these tables were prepared during the statistical calculations using the program, THEDES.

The errors as well as the number of compounds, N_d, employed for the calculation, the number of contributions, N_c, whose values were found during the calculation, and the number of compounds which contain the unique contributions, N_s, are given for each classification of compounds.

The degree of freedom used for the calculation of errors should not be the number of samples, N_d, but $N_d - N_s$. Sometimes, it is necessary to determine the value for a specified contribution from one compound, that is, a compound which has a *unique* contribution; for example, the contribution due to the replacement of a single bond in ethane with a triple bond to form acetylene, or $\Delta(1\equiv1)$ in Table A4, is derived solely from the observed value of acetylene. In these cases, the differences between observed and calculated data should be null *by definition*. Hence, the true accuracy must be estimated by excluding the null differences; this consideration suggests the use of $N_d - N_s$, instead of N_d, for the actual degree of freedom. A high accuracy, including many nulls by definition, in the estimation of thermodynamic values has been reported by the use of group-contribution values, supposedly derived not statistically but by the mere subtraction method;[17] nevertheless, such an unthinkably high accuracy can not be expected throughout a wide variety of compounds other than those cited in their report.

The average errors shown in Table 6 are usually small enough for practical purposes. The standard deviations described there give us the statistical reliability of the estimated values; 95% of the population has a deviation not larger than 2σ, 70% of it, one not larger than σ, and 40% of it, one not larger than $\sigma/2$.

During the processing, however, a number of compounds were excluded because of the poor agreement between the estimated and the observed values, although these compounds very often had observed values measured many years ago and, hence, with less reliability.

A certain monograph[18] presents a comparison between the estimated and the observed values of 29 organic compounds obtained by several methods. The average errors in enthalpy are obtained by excluding the compounds which are outside the scope of each method or which have unique contributions; for the Benson and the ABWY methods, the four compounds described in Examples are added. The average errors are :

Benson: 35.70/27=1.3 kcal mol^{-1}; Verma and Doraiswamy:[19] 50.71/19=2.7; Franklin:[20] 42.28/20=2.1; ABW:[3] 82.8/23=3.6; ABWY: 21.06/27=0.8, where the numerator and the denominator are the sum of errors and the degree of freedom defined above respectively. In conclusion, the ABWY method may exceed the existing methods in accuracy or in the reliability of the estimated values.

Every effort should be made to improve further the reliability of the estimated values; one of such effort may be the experimental determination of the properties of the *key* compounds which contain contributions with poor quality in Table A2 through A6. The endeavors of thermochemists are particularly waited for.

Soundness of the Empirical Rules and Formulations. As has been mentioned earlier, it has been empirically guaranteed that the additivity rule holds for the estimation of the thermodynamic properties of organic compounds in the ideal gas state. Therefore, the soundness of the method may be criticized for its way of incorporating a variety of neighboring effects, especially the global effect. In the present method, the geminal effects includes even the multiple-substitution contributions between different halogen atoms, and the type-number corrections are also incorporated as one of the vicinal effects. The contributions of functional groups to aromatic rings are, as a global effect, discriminated from those to non-aromatic fragments.

The *symmetry number* has been taken into account in the Benson method in order to estimate the values of entropy. In our method, the symmetry number due to the three-dimensional geometry of compounds seems to be implicitly incorporated by adopting the secondary methyl substitution, discriminated from the primary one, which produces the propane skeleton with a higher symmetry number from the ethane skeleton. As for the case of more complicated compounds, the rather small correction due to the symmetry or the existence of optical isomers may be negligible as com-

			$C_p°$			
			e[d]		σ[e]	
N_d	N_c	N_s	300 K	700 K	300 K	700 K
28	10	3	0.1	0.0	0.3	0.1
119	28	15	0.9	0.3	1.8	0.6
40	13	3	0.5	0.2	1.0	0.3
40	18	9	0.9	0.4	1.5	0.7
60	15	1	2.9	2.5	4.2	4.0
24	7	1	0.8	0.7	1.3	0.9
9	8	5	0.0	0.7	0.2	1.0
320	99	37	1.5[g]	1.0[g]	2.6[g]	2.2[g]

compounds having a unique contribution. d) Average kcal mol^{-1} for H, and percentage error for S and C_p.

pared with the inevitable errors generally associated with the empirical methods.

Variety of Estimable Compounds. The variety of estimable compounds can be judged by the kinds of fundamental, type-number, and multiple-substitution correction contributions and the combinations of them; the present method exceeds others in this respect, because more recent data have been adopted in this method.

The concepts of both the type number and the multiple substitution have been implicitly incorporated in the Benson method. For example, altogether four kinds of carbon atoms are given in the contribution of bromine, although six kinds are logically necessary to process every variety of bromide derivative of paraffinic compounds. The kind of contribution in their method should, however, be surprisingly increased in order to cover mixed halides such as –CFClBr and haloolefins like =CBr_2 in contrast to the limited kinds of contributions in the present method. It may be additionally remarked that no compound consisting of one carbon such as CFClBrI can, by definition, be treated with the Benson method.

It should be mentioned, however, that hydrogen is not a functional group in the present method, so HCOOH is not derived from =COOH or HCOO–. Also, compounds that are composed only of functional groups can not be treated; thus, for example, the estimation of oxalic acid, HOOC–COOH, by the ABWY method gives an enthalpy of -193.5 kcal mol^{-1} as compared with the observed value of -174.86.[11] The compounds which are otherwise not processed are listed in Table A8 for convenience.

In conclusion, the ABWY method may be evaluated as having a higher potentiality for estimating a much wider variety of compounds than the existing methods.

Applicability for Computation with the Aid of Computers. As was described in the opening paragraphs, the present method has been already implemented in computer programs including the whole logic. The symmetry number, a stereochemical concept, cannot be determined without the knowledge of the whole geometry of a compound, while the geometry can be estimated with only highly sophisticated computer programs such as a program, STERIC,[5] also prepared by the present author. A logic which requires no symmetry number for estimation may be rated higher for implementation into computer programs.

The author's thanks are due to Dr. Makoto Misono for his helpful discussions. A part of the research expenses was defrayed from the Grant-in-Aid for a Special Project Research, "Chemical Research in the Development and Utilization of Nitrogen-Organic Resources," of the Ministry of Education, Science, and Culture. The clerical work of Miss Masako Oya and the technical aid of Mr. Kiyoshi Arai are highly appreciated.

Appendix

Tables of Contribution Values for the Thermodynamic Properties of Organic Compounds in the Ideal Gas State, A1 through A8. Unit of standard enthalpy of formation(H) in kcal mol^{-1}; unit of standard entropy(S) and three coefficients of molar heat (a, b, and c) in cal mol^{-1} K^{-1}. 1 cal=4.184 J. The abbreviations for the contribution values of the functional groups are: Δ_{f}: fundamental; Δ_{t}: type-number correction; Δ_{m}: multiple substitution correction; @: aromatic ring directly connected; %: direction of extending chain in which the type number may be counted. 'Single data source' in the footnotes implies that the contribution value was derived only from a compound (or a pair of compounds for the contribution of functional groups having type-number correction).

The molar heats can be calculated from three coefficients at 273 through 1000 K.

Table A1. Thermodynamic properties of base groups in ideal gas state

Line	Base group	$\Delta H^\circ_{f,298.15}$	$S^\circ_{298.15}$	a	b	c
1	Methane	−17.89(1)	44.50(1)	3.99(1)	15.68	−2.38
2	Cyclopentane	−18.46(1)	70.00(1)	−10.02(1)	113.22	−43.64
3	Cyclohexane	−29.43(1)	71.28(1)	−12.48(1)	143.35	−55.19
4	Benzene	19.82(1)	64.34(1)	−5.38(1)	96.21	−40.97
5	Naphthalene	36.08(1)	80.22(1)	−6.79(1)	148.96	−64.27

Table A2. Contribution of primary methyl substitution for thermodynamic properties in ideal gas state

Line	Base group	$\Delta(\Delta H)$	ΔS	Δa	Δb	Δc
1	Methane	−2.35(1)	10.35(1)	−2.37(1)	24.81	−10.40
	Cyclopentane					
2	(a) First primary substitution	−8.23(1)	11.77(1)	2.09(1)	16.31	−5.54
	(b) Second primary substitution to form					
3	1,1	−6.36(1)[a]	4.10(1)[a]	−1.44(1)[a]	27.81	−13.28
4	1,2(*cis*)	−4.27(1)[a]	5.74(1)[a]	−0.87(1)[a]	26.40	−12.72
5	1,2(*trans*)	−5.98(1)[a]	5.90(1)[a]	−0.59(1)[a]	25.71	−12.46

TABLE A2. (Continued)

Line	Base group	$\Delta(\Delta H)$	ΔS	Δa	Δb	Δc
6	1,2(unspec.)[h]	−5.12(2)[b]	5.82(2)[b]	−0.73(2)[b]	26.05	−12.59
7	1,3(*cis*)	−5.78(1)[a]	5.90(1)[a]	−0.59(1)[a]	25.71	−12.46
8	1,3(*trans*)	−5.24(1)[a]	5.90(1)[a]	−0.59(1)[a]	25.71	−12.46
9	1,3(unspec.)[h]	−5.51(2)[b]	5.90(2)[b]	−0.59(2)[b]	25.71	−12.46
10	Unspecified locant[i]	−5.97(2)[c]	6.55(2)[c]	−0.33(2)[c]	24.61	−11.49
	Cyclohexane					
11	(a) First primary substitution	−8.04(1)	11.07(1)	2.77(1)	19.41	−9.46
	(b) Second primary substitution to form					
12	1,1	−5.79(1)[a]	4.89(1)[a]	−3.23(1)[a]	26.63	−9.80
13	1,2(*cis*)	−3.68(1)[a]	7.16(1)[a]	−1.91(1)[a]	23.90	−9.25
14	1,2(*trans*)	−5.55(1)[a]	6.30(1)[a]	−1.39(1)[a]	24.69	−10.33
15	1,2(unspec.)[h]	−4.61(2)[b]	6.73(2)[b]	−1.65(2)[b]	24.30	−9.79
16	1,3(*cis*)	−6.69(1)[a]	6.19(1)[a]	−1.51(1)[a]	22.74	−7.89
17	1,3(*trans*)	−4.73(1)[a]	7.57(1)[a]	−1.03(1)[a]	21.13	−7.69
18	1,3(unspec.)[h]	−5.71(2)[b]	6.88(2)[b]	−1.27(2)[b]	21.94	−7.79
19	1,4(*cis*)	−4.75(1)[a]	6.19(1)[a]	−1.03(1)[a]	21.13	−7.69
20	1,4(*trans*)	−6.65(1)[a]	4.84(1)[a]	−2.01(1)[a]	25.72	−10.52
21	1,4(unspec.)[h]	−5.70(2)[b]	5.51(2)[b]	−1.52(2)[b]	23.42	−9.10
22	Unspecified locant[i]	−5.73(2)[d]	6.77(2)[d]	−1.17(2)[d]	23.17	−9.08
	Benzene					
23	(a) First primary substitution	−8.48(1)	11.45(1)	1.38(1)	15.40	−4.66
	(b) Second primary substitution to form					
24	1,2	−6.64(1)	8.70(1)	2.98(1)	11.95	−2.86
25	1,3	−6.96(1)	9.95(1)	1.20(1)	15.48	−4.69
26	1,4	−6.86(1)	8.65(1)	1.31(1)	14.41	−3.86
27	1,2,3	−7.26(1)	10.24(1)	3.38(1)	6.99	2.31
28	1,2,4	−8.00(1)	10.42(1)	3.92(1)	4.45	3.88
29	1,3,5	−8.22(1)[a]	6.41(1)[a]	1.48(1)[a]	13.95	−3.52
30	Unspecified locant[i]	−7.61(1)	4.94(1)	1.47(1)	24.17	−13.81
	Naphthalene					
	(a) First primary substitution to form					
31	1	−8.15(1)[a]	9.99(1)[a]	1.52(1)[a]	8.93	−7.67
32	2	−8.33(1)[a]	10.61(1)[a]	2.55(1)[a]	14.76	−4.82
	(b) Second primary substitution to form					
33	1,2	−6.31(2)[e]	7.24(2)[e]	3.12(2)[e]	15.48	−5.87
34	1,3	−6.63(2)[e]	8.50(2)[e]	1.34(2)[e]	19.01	−7.70
35	1,4	−6.53(2)[e]	7.19(2)[e]	1.45(2)[e]	17.94	−6.87
36	2,3	−6.31(2)[g]	7.24(2)[g]	3.12(2)[g]	15.48	−5.87
37	Unspecified locant[i]	−8.24(2)[f]	10.30(2)[f]	2.04(2)[f]	16.84	−6.24

[a] Single data source. [b] Average of *cis* and *trans*. [c] Average of lines 2, 3, 4, 5, 7, and 8. [d] Average of lines 11, 12, 13, 14, 16, 17, 19, and 20. [e] Assumed as (values of the position corresponding to benzene) + {Δ(1-naphthalene) − Δ(1-benzene)}. [f] Average of Δ(1-) and Δ(2-). [g] Assumed to be the same as Δ(1,2-). [h] Equilibrium mixture of *cis*- and *trans*-isomers. [i] For substitution location not mentioned otherwise.

Table A3. Contribution of secondary methyl substitution for thermodynamic properties in ideal gas state

Line	Type number A	Type number B	$\Delta(\Delta H)$	ΔS	Δa	Δb	Δc
1	1	1	−5.04(1)	10.44(1)	−0.88(1)	23.46	−10.10
2	1	2	−4.92(1)	9.29(1)	0.35(1)	19.46	−7.52
3	1	3	−3.67(1)	8.75(1)	−0.23(1)	21.90	−9.31
4	1	4	−3.67(2)	8.75(2)	−0.23(2)	21.90	−9.31
5	1	9	−4.70(1)	10.83(1)	0.37(1)	21.16	−9.00
6	2	1	−6.87(1)	5.13(1)	−0.50(1)	22.87	−9.96
7	2	2	−6.35(1)	6.53(1)	−0.15(1)	21.67	−8.97
8	2	3	−5.31(1)	6.54(1)	−1.17(1) a)	23.33	−9.95
9	2	4	−4.94(1)	6.57(1)	−0.29(1)	22.00	−9.08
10	2	9	−5.82(1)	6.71(1)	−0.76(1)	21.60	−8.68
11	3	1	−7.52(1) a)	2.81(1) a)	−0.66(1) a)	25.74	−11.77
12	3	2	−6.84(1)	4.30(1)	−1.65(1)	26.70	−12.35
13	3	3	−4.96(1) a)	6.20(1) a)	−1.65(2) b)	26.70	−12.36
14	3	4	−5.66(1) a)	1.09(1) a)	−1.00(1) a)	30.96	−15.85
15	3	9	−6.24(1) a)	6.71(2) c)	−0.76(2) c)	21.60	−8.68

a) Single data source. b) Assumed to be the same as $\Delta(3,2)$. c) Assumed to be the same as $\Delta(2,9)$.

Table A4. Multiple-bond contribution replacing single bond for thermodynamic properties in ideal gas state

Line	Type of bond or correction	$\Delta(\Delta H)$	ΔS	Δv	Δb	Δc
1	1=1	32.74(1) a)	−2.40(1) a)	0.12(1)	−7.83	0.89
2	1=2	30.15(1)	−1.43(1)	0.91(1)	−12.17	3.90
3	1=3	27.94(1)	0.17(1)	3.06(1)	−17.06	6.67
4	2=2(unspec.) f)	27.82(2) b)	−2.11(2) b)	0.33(2) b)	−12.55	4.55
5	2=2(*cis*)	28.30(1)	−1.51(1)	−1.53(1)	−8.98	2.70
6	2=2(*trans*)	27.35(1)	−2.72(1)	2.19(1)	−16.14	6.40
7	2=3	27.40(1)	0.14(1)	−0.25(1)	−12.92	5.07
8	3=3	27.70(1) a)	−0.50(1) a)	1.41(1)	−22.91	13.75
9	1≡1	74.43(1) a)	−6.85(1) a)	4.58(1)	−23.60	5.49
10	1≡2	69.50(1)	−4.97(1)	3.95(1)	−27.98	9.73
11	2≡2	65.54(1)	−5.72(1)	3.07(1)	−30.36	12.35
12	Adjacent double bonds	9.89(1)	−3.17(1)	2.33(1)	−1.86	0.51
13	Conjugated double bonds	−3.66(1)	−4.06(1)	−1.60(1)	8.91	−6.57
14	Double bond conjugated with aromatic ring	−1.72(1)	−2.27(1)	1.28(1)	−2.17	1.24
15	Triple bond conjugated with aromatic ring	2.1 (4) a,c)	−4.8 (4) a,c)	−0.9 (4) a,c)	1.1	0.1
16	Conjugated triple bonds	4.2 (4) a,d)	−4.9 (4) a,d)	0.8 (4) a,d)	3.5	−3.5
17	Conjugated double and triple bonds	3.3 (4) a,e)	−1.4 (4) a,e)	3.0 (4) a,e)	5.3	2.3

a) Single data source. b) Average of *cis* and *trans*. c) From $CH{\equiv}CC_6H_5$. d) From $CH{\equiv}CC{\equiv}CH$. e) From $CH_2{=}CHC{\equiv}CH$. f) Equilibrium mixture of *cis*- and *trans*-isomers.

Table A5. Fundamental contribution of functional group replacing CH_n groups for thermodynamic properties in ideal gas state

Line	Functional group	$\Delta(\Delta H)$	ΔS	Δa	Δb	Δc
	Oxygen					
1	=O(aldo)	−2.42(1)	−13.00(1)	4.09(1)	−51.16	20.14
2	=O(keto)	−7.09(1)	−20.19(1)	1.51(1)	−35.49	8.76
3	-OH	−28.44(1)	2.06(1)	1.74(1)	−15.70	5.84
4	@OH	−35.01(1)	−0.30(1)	2.87(1)	−11.90	5.80
5	-O-	−20.43(1)	−1.26(1)	3.17(1)	−20.39(1)	9.22

TABLE A5. (Continued)

Line	Functional group	$\Delta(\Delta H)$	ΔS	Δa	Δb	Δc
6	@O-	−23.37(1)[a,b]	−3.6 (5)[h]	4.3 (5)[h]	−16.6	9.1
7	-OOH	−24.7 (4)[a,b]				
8	-OO-	−5.22(1)				
9	-COOH	−83.69(1)	12.67(1)	1.89(1)[a]	6.98	−6.37
10	@COOH	−80.70(1)[a]	12.40(1)[a]	−1.92(1)[a]	6.02	−1.09
11	-COO-	−73.12(1)[b,g]	13.1 (5)[i]	−4.2 (5)[i]	0.3	1.9
12	@COO-	−75.93(1)[a,b]	13.1 (5)[j]	−4.2 (5)[j]	0.3	1.9
12 a	@OOC-	−74.12(1)[a,b]				
13	-COOCO-	−112.32(1)[a]	27.93(1)[a]	−1.26(1)[a]	29.79	−16.55
14	-COO_2CO-	−93.7 (4)[c,g]				
15	HCOO-	−65.93(1)	17.15(1)[a]	1.89(1)[a]	6.98	−6.37
16	-CO_3-	−117.17(1)[a,b]				
	Fluorine					
17	-F	−36.85(1)	−3.97(1)	1.01(1)	−18.30	5.87
18	@F	−39.49(1)	−4.31(1)	1.55(1)	−14.22	4.39
19	@F(ortho)	−34.24(1)	−3.07(1)	1.41(1)	−18.85	7.75
20	-COF	−84.96(1)[a]	13.7 (6)[k]	3.4 (6)[k]	−4.3	1.1
21	@COF	−84.0 (5)[l]				
	Chlorine					
22	-Cl	0.49(1)	−1.41(1)	1.78(1)	−15.50	3.57
23	@Cl	2.36(1)	−0.95(1)	2.56(1)	−19.92	7.42
24	-COCl	−38.06(1)	12.89(1)	5.41(1)[a]	−5.63	−0.58
25	@COCl	−37.12(1)[a,b]				
	Bromine					
26	-Br	11.84(1)	3.13(1)	2.66(1)	−11.93	3.12
27	@Br	13.76(1)[a]	1.74(1)[a]	2.94(1)[a]	−16.81	6.91
28	-COBr	−25.27(1)[a,b]	16.4 (6)[m]	5.0 (6)[m]	−10.4	2.2
29	@COBr	−23.54(1)[a,b]				
	Iodine					
30	-I	24.17(1)	3.48(1)	2.72(1)	−17.33	4.37
31	@I	27.51(1)[a]	2.1 (5)[n]	3.0 (5)[n]	−22.2	8.2
32	-COI	−9.09(1)[a,b]	21.1 (6)[o]	5.6 (6)[o]	−7.9	2.3
33	@COI	−7.4 (5)[p]				
	Sulfur					
34	-SH	14.42(1)	5.75(1)	3.44(1)	−15.76	6.79
35	@SH	15.32(1)[a]	4.72(1)[a]	2.90(1)[a]	−10.14	4.64
36	-S-	16.64(1)	5.17(1)	4.09(1)	−19.98	11.00
37	@S-	16.96(1)	4.1 (5)[q]	3.6 (5)[q]	−14.4	8.8
38	-SS-	19.08(1)	15.17(1)	8.51(1)	−13.96	4.88
39	-SO-	−10.31(1)				
40	@SO-	−9.5 (5)[r]				
41	-SO_2-	−66.90(1)				
42	@SO_2-	−66.08(1)[a,b]				
43	-SO_3H	−282.7 (5)[s]				
44	-OSO_2-	−90.71(1)				
45	-OSO_3-	−139.38(1)[a,b]				
	Nitrogen					
46	-NH_2	14.69(1)	3.13(1)	1.79(1)	−9.00	3.15
47	@NH_2	9.42(1)[a]	0.49(1)[a]	2.11(1)[a]	−3.44	1.05
48	-NH-	20.78(1)	−0.05(1)[a]	0.33(1)[a]	−5.88	1.85
49	@NH-	13.76(1)	−2.7 (5)[ee]	0.6 (5)[ee]	−0.3	−0.2
50	-N<	26.45(1)	−1.40(1)[a]	0.01(1)[a]	−4.44	1.05
51	@N<	19.28(1)[a]	−4.0 (5)[ff]	0.3 (5)[ff]	1.1	−1.0
52	=N-(keto)	44.7 (5)[c,e,g,t]				

TABLE A5. (Continued)

Line	Functional group	$\Delta(\Delta H)$	ΔS	Δa	Δb	Δc
53	-N=N-	63.6 (5)[a,c,e,u]				
54	-NHNH$_2$	40.64(1)[a]	11.76(1)[a]			
55	@NHNH$_2$	36.69(1)[a,b]				
56	-N(NH$_2$)-	44.87(1)[a,b]	7.53(1)[a]			
57	@N(NH$_2$)-	40.9 (5)[v]				
58	-NHNH-	46.78(1)[a]	9.34(1)			
59	@NHNH-	42.8 (5)[w]				
60	-CN	41.24(1)	1.60(1)	3.42(1)	−12.76	3.51
61	@CN	40.96(1)[a]	0.94(1)[a]	4.25(1)[a]	−11.37	4.82
62	-NC	56.14(1)[a]	4.13(1)[a]	4.2 (5)[x]	−11.4	4.8
63	=NOH	22.0 (4)[c,f,g]				
64	-CONH$_2$	−36.72(1)[b,g]	18.5 (6)[y]	3.6 (6)[y]	5.7	−3.0
65	@CONH$_2$	−33.73(5)[z]				
66	-CONH-	−30.6 (5)[a,b,aa]				
67	@NHCO-	−37.83(1)[a,b]				
68	-CON<	21.00(1)[a,b]				
69	-NO$_2$	2.75(1)	10.88(1)[a]	1.14(1)[a]	1.11	−3.48
70	@NO$_2$	4.30(1)[b,g]	10.9 (5)[bb]	1.1 (5)[bb]	1.1	−3.5
71	-ONO	4.94(1)	13.10(1)[a]	2.47(1)[a]	1.51	−3.84
72	-ONO$_2$	−8.77(1)	17.30(1)	4.12(1)	7.61	−6.96
73	-NCS	56.0 (5)[cc]	14.7 (5)[dd]			

a) Single data source. b) Data from PRN.[11] c) Data from BCG.[12] d) Data from LBTl.[13] e) The values of the gaseous state were estimated from those of the liquid phase. f) The values of the gaseous phase were estimated from those of crystal. g) Stasistically calculated with weights reciprocal to errors. h) Assumed as Δ_f(@O-) $=\Delta_f$(@OH) + {Δ_f(-O-) − Δ_f(-OH)}. i) From $CH_3COOC_2H_5$, assuming Δ_f(%-OOC-) $=\Delta_f$(-O-). j) Assnmed as Δ_f(@COO-) $=\Delta_f$(-COO-). k) Assumed to be composed of -CO- and -F. See text. l) Assumed as Δ_f(@COF) $=\Delta_f$(-COF) + {Δ_f(@COCl) − Δ_f(-COCl)}. m) Assumed to be composed of -CO- and -Br. See text. n) Assumed as Δ_f(@I) $=\Delta_f$(-I) + {Δ_f(@Br) − Δ_f(-Br)}. o) Assumed to be composed of -CO- and -I. See text. p) Atsumed as Δ_f(@COI) $=\Delta_f$(-COI) + {Δ_f(@COBr) − Δ_f(-COBr)}. q) Assumed as Δ_f(@S-) $=\Delta_f$(-S-) + {Δ_f(@SH) − Δ_f(-SH)}. r) Assumed as Δ_f(@SO-) $=\Delta_f$(-SO-) + {Δ_f(@SO$_2$-) − Δ_f(-SO$_2$-)}. s) Assumed as Δ_t(-SO$_3$H) $=\Delta_t$(-SO$_3$-). t) Assumed as Δ_t(%=N-) $=\Delta_t$(%=NOH). u) Assumed as Δ_t(-N=N-) $=\Delta_t$(%-N=). v) Assumed as Δ_f(@N(NH$_2$)-) $=\Delta_f$(-N(NH$_2$)-) + {Δ_f(@NHNH$_2$) − Δ_f(-NHNH$_2$)}. w) Assumed as Δ_f(@NHNH-) $=\Delta_f$(-NHNH-) + {Δ_f(@NHNH$_2$) − Δ_f(-NHNH$_2$)}. x) Assumed as Δ_f(-NC) $=\Delta_f$(-CN). y) Assumed to be composed of -CO- and -NH$_2$. See text. z) Assumed as Δ_f(@CONH$_2$) $=\Delta_f$(-CONH$_2$) + {Δ_f(@COOH) − Δ_f(-COOH)}. aa) From $CH_3CONHC_4H_9$, assuming as Δ_t(%-NHCO-) $=\Delta_t$(-NH-). bb) Assumed as Δ_f(@NO$_2$) $=\Delta_f$(-NO$_2$). cc) From CH_2=CHCH$_2$NCS, assuming as Δ_t(-NCS) $=\Delta_t$(%-N=). dd) From the same compound, assuming as Δ_t(-NCS) $=\Delta_t$(-NH$_2$). ee) Assumed as Δ_f(@NH-) $=\Delta_f$(-NH-) + {Δ_f(@NH$_2$) − Δ_f(-NH$_2$)}. ff) Assumed as Δ_f(@N<) $=\Delta_f$(-N<) + {Δ_f(@NH$_2$) − Δ_f(−NH$_2$)}.

TABLE A6. CORRECTIONS DUE TO TYPE NUMBER AND MULTIPLE SUBSTITUTIONS OF FUNCTIONAL GROUPS FOR THERMODYNAMIC PROPERTIES IN IDEAL GAS STATE

Line	Functional group	$\Delta(\Delta H)$	ΔS	Δa	Δb	Δc
	Oxygen					
1	=O(aldo)	−5.42(1)	4.50(1)	−0.86(1)	1.61	−1.15
2	=O(keto)	−3.30(1)	7.39(1)	1.59(1)	−11.30	8.21
3	-OH	−2.65(1)	0.20(1)	0.10(1)	0.00	−0.10
4	-O-	−2.28(1)	−0.55(1)	0.51(1)[a]	−1.20	0.79
5	@O-	−2.81(1)[a,b]	−0.6 (5)[h]	0.5 (5)[h]	−1.2	0.8
6	-OOH	2.0 (4)[a,b]				
7	-OO-	−2.50(1)				
8	-COOH	1.54(1)[a]	8.58(1)[a]	0.0 (5)[i]	0.0	0.0
9	%-COO-	−1.21(1)[b,g]	8.58(5)[j]	0.0 (5)[i]	0.0	0.0
10	%-OOC-	−2.80(1)[b,g]	−0.6 (5)[h]	0.5 (5)[h]	−1.2	0.8
11	@COO-	1.79(1)[b,g]	−0.6 (5)[h]	0.5 (5)[h]	−1.2	0.8
12	-COOCO-	−1.21(1)[a,b]	8.6 (5)[i]	0.0 (5)[i]	0.0	0.0
13	-COO$_2$CO-	−5.1 (4)[c,e,g]				

TABLE A6. (Continued)

Line	Functional group	$\Delta(\Delta H)$	ΔS	Δa	Δb	Δc
14	HCOO-	7.99(1)[a]	−0.6 (5)[m]	0.5 (5)[m]	−1.2	0.8
15	-CO$_3$-	−0.29(1)[a,b]				
	Fluorine					
16	-F	−1.47(1)	0.99(1)	0.38(1)	−0.13	0.38
17	-F, -F	−3.67(1)	−0.91(1)	−0.48(1)	−0.18	−0.42
18	-F, -Cl	2.63(1)	−0.16(1)	1.72(1)[d,g]	−3.34	4.38
19	-F, -Br	4.19(1)	1.63(1)	0.99(1)[d,g]	−4.01	1.05
20	-F, -I	4.12(1)	−0.09(1)	1.68(1)[a,d]	−1.55	1.01
21	-COF	0.4 (5)[n]				
	Chlorine					
22	-Cl	−0.62(1)	1.24(1)	0.90(1)	−3.00	1.92
23	-Cl, -Cl	4.25(1)	−1.49(1)	−0.62(1)	1.55	−0.90
24	-Cl, -Br	5.14(1)	1.48(1)	1.73(1)[d]	−6.95	3.02
25	-Cl, -I	4.9 (5)[o]	1.24(1)[a]	1.68(1)[d]	−6.59	4.52
26	-COCl	0.45(1)				
	Bromine					
27	-Br	−1.73(1)	−1.25(1)	0.39(1)	−6.35	2.31
28	-Br, -Br	4.21(1)	2.37(1)	1.12(1)[d]	−8.59	4.70
29	-Br, -I	4.9 (5)[p]	1.90(1)[a]	−0.38(1)[a,d]	−7.74	3.84
30	-COBr	0.4 (5)[q]				
	Iodine					
31	-I	−1.03(1)	0.94(1)	0.66(1)	−2.42	1.74
32	-I, -I	5.59(1)	−0.73(1)	0.12(1)	0.18	−0.36
33	-COI	0.4 (5)[q]				
	Sulfur					
34	-SH	−0.27(1)	0.38(1)	0.35(1)	−0.29	−0.38
35	-S-	−0.85(1)	−0.04(1)	−0.04(1)	1.08	−0.90
36	@S-	−0.28(1)[a]	−0.1 (5)[r]	−0.1 (5)[r]	1.1	−0.9
37	-SS-	−0.82(1)	0.02(1)	−0.42(1)	2.66	−2.29
38	-SO-	−1.97(1)				
39	@SO-	−2.0 (5)[s]				
40	-SO$_2$-	−0.27(1)				
41	@SO$_2$-	6.18(1)[b,g]				
42	-SO$_3$H	−2.8 (5)[t]				
43	-OSO$_2$-	−2.81(1)[b,g]				
44	-OSO$_3$-	−2.57(1)[b,g]				
	Nitrogen					
45	-NH$_2$	−1.30(1)	−0.34(1)[a]	0.16(1)[a]	0.47	−0.61
46	-NH-	−2.33(1)	−0.3 (5)[u]	0.2 (5)[u]	0.5	−0.6
47	@NH-	−2.08(1)[a]	−0.3 (5)[u]	0.2 (5)[u]	0.5	−0.6
48	-N<	−1.70(1)	−0.3 (5)[u]	0.2 (5)[u]	0.5	−0.6
49	@N<	−1.0 (4)[a,e,v]	−0.3 (5)[u]	0.2 (5)[u]	0.5	−0.6
50	%=N-	0.2 (5)[a,e,w]				
51	%-N=	−0.9 (4)[c,e,g]				
52	-N=N-	−0.9 (5)[x]				
53	-NHNH$_2$	−1.3 (5)[u]	−0.3 (5)[u]			
54	-N(NH$_2$)-	−1.3 (5)[u]	−0.3 (5)[u]			
55	@N(NH$_2$)-	−1.3 (5)[u]				
56	-NHNH-	−1.3 (5)[u]	−0.3 (5)[u]			
57	@NHNH-	−1.3 (5)[cc]				
58	-CN	−3.08(1)	0.56(1)	1.02(1)	−4.88	4.48
59	-NC	−3.1 (5)[y]	0.6 (5)[y]	1.0 (5)[y]	−4.9	4.5
60	=NOH	0.2 (4)[c,f,g]				
61	-CONH$_2$	0.03(1)[b,g]	8.6 (5)[z]	0.0 (5)[i]	0.0	0.0

Table A6. (Continued)

Line	Functional group	$\Delta(\Delta H)$	ΔS	Δa	Δb	Δc
62	%-CONH-	−1.2 (5)[aa]				
63	%-NHCO-	−2.3 (5)[bb]				
64	@NHCO-	−1.2 (5)[aa]				
65	$-NO_2$	−2.26(1)	0.0 (5)[i]	0.0 (5)[i]	0.0	0.0
66	-ONO	−6.34(1)	0.0 (5)[i]	0.0 (5)[i]	0.0	0.0
67	$-ONO_2$	−2.47(1)	0.66(1)[a]	−0.37(1)[a]	0.82	−0.55
68	-NCS	−0.9 (5)[dd]	−0.3 (5)[u]			

a) Single data source. b) Data from PRN.[11] c) Data from BCG.[12] d) Data from LBTl.[13] e) The values of the gaseous phase were estimated from those of the liquid phase. f) The values of the gaseous phase were estimated from those of crystal. g) Statistically calculated with weights reciprocal to errors. h) Assumed to be equal to Δ_t(-O-). i) Assumed as zero. j) Assumed as Δ_t(%-COO-) = Δ_t(-COOH). l) Assumed to be equal to Δ_t(-COOH). m) Assumed as Δ_t(HCOO-) = Δ_t(-O-). n) Assumed as Δ_t(-COF) = Δ_t(-COCl). o) Assumed as Δ_m(-Cl, -I) = {Δ_m(-Cl, -Cl) + Δ_m(-I, -I)}/2. p) Assumed as Δ_m(-Br, -I) = {Δ_m(-Br, -Br) + Δ_m(-I, -I)}/2. q) Assumed to be equal to Δ_t(-COCl). r) Assumed as Δ_t(@S-) = Δ_t(-S-). s) Assumed as Δ_t(@SO-) = Δ_t(-SO-). t) Assumed as Δ_t($-SO_3H$) = Δ_t($-OSO_2-$). u) Assumed to be equal to Δ_t($-NH_2$). v) Data of liquid phase from SWS.[8] w) Assumed as Δ_t(%=N-) = Δ_t(=NOH). x) Assumed as Δ_t(-N=N-) = Δ_t(%-N=). y) Assumed as Δ_t(-NC) = Δ_t(-CN). z) Assumed as Δ_t($-CONH_2$) = Δ_t(-COOH). aa) Assumed as Δ_t(%-CONH-) = Δ_t(%-COO-). bb) Assumed as Δ_t(%-NHCO-) = Δ_t(-NH-). cc) Assumed as Δ_t(@NHNH-) = Δ_t($-NH_2$). dd) Assumed as Δ_t(-NCS) = Δ_t(%-N=).

Table A7. Thermodynamic properties of simple substances in standard states[a]

Line	Simple Substance	$\Delta H^\circ_{f,298.15}$	$S^\circ_{298.15}$	a	b	c
1	Br_2(g)[b]	7.47	58.63	8.90	0.14	0
2	Br_2(l)[b]	0	36.80	17.10	0	0
3	C(graphite)	0	1.36	0.33	7.13	−2.19
4	C(diamond)	0.45	0.58	0.01	8.09	−2.45
5	Cl_2(g)	0	53.29	7.59	2.31	−0.89
6	F_2(g)	0	46.80	6.50	1.00	0
7	H_2(g)	0	31.21	6.62	0.81	0
8	I_2(g)[c]	14.88	62.28	9.00	0	0
9	I_2(s)[c]	0	27.90	41.58	−191.00	321.00
10	N_2(g)	0	45.77	6.50	1.00	0
11	O_2(g)	0	49.00	5.21	5.52	−2.26
12	O_3(g)	34.00	57.05	5.68	14.70	−7.42
13	P(yellow)	0	10.60	3.41	7.18	0
14	S(rhombic)[d]	0	7.62	3.63	6.40	0
15	S(monoclinic)[d]	0.07	7.78	4.38	4.40	0

a) Arrangement in alphabetical order. The properties of gases are in the ideal state, regardless of the most stable modifications at 298.15 K. Data are cited from Ref. 5. b) Liquid from 298 K to 332.62 K; ideal diatomic gas state from 332.62 K. c) Crystal from 298 K to 386.75 K; ideal diatomic gas state from 458.39 K. d) Rhombic crystal from 298 K to 368.46 K; monoclinic crystal from 368.46 K to 388.36 K. For those needing more accurate data on liquid and gas states, see W. H. Evans and D. D. Wagman, *J. Res. Natl. Bur. Std.*, **55**, 147 (1955), and D. R, Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," Advances in Chemistry Series No. 18, American Chemical Society, Washington, D. C. (1956).

Table A8. Thermodynamic properties of inorganic compounds and a few organic compounds in standard states[a]

Line	Compound	$\Delta H^\circ_{f,298.15}$	$S^\circ_{298.15}$	a	b	c
1	HBr(aq, $600H_2O$)	−28.78				
2	HBr(g)	−8.66	47.44	7.01	−0.53	1.22
3	HCl(aq, $600H_2O$)	−39.89				
4	HCl(g)	−22.06	44.64	7.05	−0.66	1.19
5	NOCl(g)	12.57	62.53	8.62	7.95	−3.33
6	NO_2Cl(g)	3.12	65.01	7.54	20.51	−9.94
7	SO_2Cl(g)	−50.60	73.23	12.34	14.43	−7.69

Table A8. (Continued)

Line	Compound	$\Delta H^\circ_{f,298.15}$	$S^\circ_{298.15}$	a	b	c
8	$SO_2Cl_2(g)$	−85.40	74.37	13.14	21.38	−11.69
9	$S_2Cl_2(g)$	−4.66	76.35	14.71	11.30	−6.52
10	$HF(aq, 50H_2O)$	−77.03				
11	$HF(g)$	−64.80	41.51	7.06	−0.52	0.66
12	$NOF(g)$	−15.70	59.27	7.34	9.98	−4.59
13	$NOF_2(g)$	−19.00	62.24	6.22	22.62	−10.97
14	$SF_4(g)$	−174.10	69.58	8.74	34.86	−19.26
15	$HI(g)$	6.30	49.35	6.82	0.14	0.99
16	$NH_3(g)$	−10.92	46.03	5.95	8.91	−1.37
17	$N_2H_4(g)$	22.75	57.41	4.91	29.91	−12.67
18	$HNO_3(g)$	−32.02	63.68	4.70	31.90	−14.77
19	$H_2O(g)$	−57.80	45.11	7.56	1.21	1.10
20	$H_2O(l)$	−68.31	16.72	18.00	0	0
21	$H_2O_2(g)$	−32.53	55.66	6.10	16.61	−7.78
22	$H_2SO_4(aq, 115H_2O)$	−212.20				
23	$H_2SO_4(l)$	−194.45	37.49	19.37	58.34	−39.25
24	$H_2S(g)$	−4.82	49.18	7.06	3.53	0.40
25	$NO(g)$	21.60	50.35	6.85	0.66	0.66
26	$NO_2(g)$	8.09	57.35	5.92	11.16	−4.44
27	$N_2O(g)$	19.49	52.56	6.04	12.43	−5.40
28	$SO_2(g)$	−70.95	59.30	6.41	12.16	−5.59
29	$SO_3(g)$	−94.47	61.19	5.34	26.49	−12.19
30	$CNBr(g)$	43.35	59.07	8.98	8.51	−3.90
31	$CNCl(g)$	31.60	56.28	8.82	7.65	−3.10
32	$CNI(g)$	53.80	61.33	9.81	6.84	−2.97
33	$CO(g)$	−26.42	47.30	6.76	0.38	0.82
34	$COCl_2(g)$	−52.80	67.82	9.13	18.77	−9.53
35	$COF_2(g)$	−153.00	61.84	5.23	24.01	−11.56
36	$COS(g)$	−33.08	55.32	6.65	12.94	−6.04
37	$CO_2(g)$	−94.05	51.07	5.54	12.89	−5.51
38	$CS_2(g)$	27.98	56.83	7.83	12.17	−6.04
39	$HCN(g)$	31.20	48.21	6.09	9.56	−3.51
40	$HCOOH(g)$	−90.49	59.49	3.37	28.50	−12.00
41	$(CN)_2(g)$	73.84	57.90	9.96	14.21	−5.98
42	$(COOH)_2(g)^{b)}$	−174.86				
43	$(COOH)_2(s)$	−198.36	28.70			
44	$C_3O_2(g)$	−22.38	66.05	9.95	23.66	−10.30

a) Data from Ref. 5 unless otherwise mentioned. b) Data from PRN.[11]

References

1) R. C. Reid and T. K. Sherwood, "The Properties of Gases and Liquids: Their Estimation and Correlation," 2nd ed, McGraw-Hill Book Co., New York (1966).

2) R. C. Reid, J. M. Prausnitz and T. K. Sherwood, "The Properties of Gases and Liquids," 3rd ed, McGraw-Hill Book Co., New York (1977).

3) J. W. Anderson, G. H. Beyer and K. M. Watson, *Natl. Pet. News Tech. Sec.*, **36**, R475 (July 5, 1944).

3a) Also cited in O. A. Hougen, K. M. Watson and R. A. Ragatz, "Chemical Process Principles," 2nd ed, Part II, "Thermodynamics," John Wiley, New York (1959), and Refs. 1 and 2.

4) S. W. Benson, "Thermochemical Kinetics," 2nd ed, John Wiley, New York (1967).

5) Y. Yoneda, "Kemoguramu (CHEMOGRAM)," Maruzen, Tokyo (1972), Vol. 1.

6) Y. Yoneda, "Information Chemistry. Computer Assisted Chemical Research Design," ed by S. Fujiwara and H. B. Mark, Jr., University of Tokyo Press, Tokyo (1975), p. 239.

7) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).

7a) Units of thermodynamic properties in cal or kcal were adopted because they are still prevalent in industrial chemistry; the units can be converted into the SI system using the factor described in each table.

8) SWS: D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," John Wiley, New York (1969).

9) API: B. J. Zwolinski *et al.*, "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Thermodynamics Research Center, Texas A & M University, College Station, Texas.

10) TRC: B. J. Zwolinski *et al.*, "Selected Values of Properties of Chemical Compounds," Thermodynamics Research Center Data Project, Thermodynamics Research Center, Texas A&M University, College Station, Texas.

11) PRN: J. B. Pedley and J. Rylance, "Sussex-N.P.L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds," University of Sussex (1977).

12) BCG: S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

13) LBT1: "Landolt-Börnstein Tabellen," 6 Aufl., II Band, 4 Teil, "Zahlen und Funktionen," Springer-Verlag, Berlin (1961).

14) Benson *et at.*[12] assumed that the heat of evaporation was given by the equation:

$\Delta H_{\mathrm{v},298}=S_{\mathrm{T}}[(1.76\times 10^{-3})t_{\mathrm{bp}}+0.253]$ (kcal mol^{-1}),

where S_{T} is the Trouton constant, usually 22 kcal mol^{-1} K^{-1} (in original paper, 22 cal mol^{-1} K^{-1}) and t_{bp}, the normal boiling point in °C.

15) The differences in contribution values for enthalpy between aliphatic and aromatic amines, which reflect the global effect of aromaticity, 5.27 kcal mol^{-1} K^{-1} (primary), 7.22 (secondary), and 7.31 (tertiary), show a fairly good agreement among themselves, whereas those between aliphatic and aromatic hydroxyl, 6.57 for –OH and 2.94 for –O–, may suggest that a subtraction method like this may give a poor estimate of the enthalpy.

16) The values of CH_3COBr are derived from the observed value of CH_3COCH_3 by replacing a methyl group with –Br, with consideration taken of a twofold-type number correction. The subtraction of ethane from acetyl bromide gives the fundamental values for –COBr.

17) T. P. Thinh and T. K. Trong, *Can. J. Chem. Eng.*, **54**, 344 (1976).

18) Tables 7—8 in Ref. 2.

19) K. K. Verma and L. K. Doraiswamy, *Ind. Eng. Chem. Fundam.*, **4**, 389 (1965).

20) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949); *J. Chem. Phys.*, **21**, 2029 (1953).